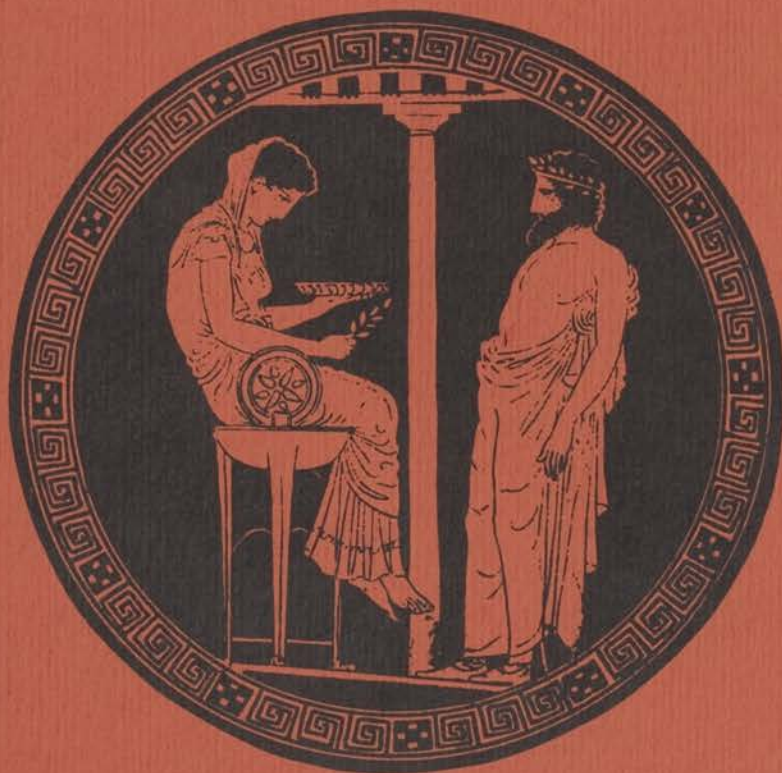


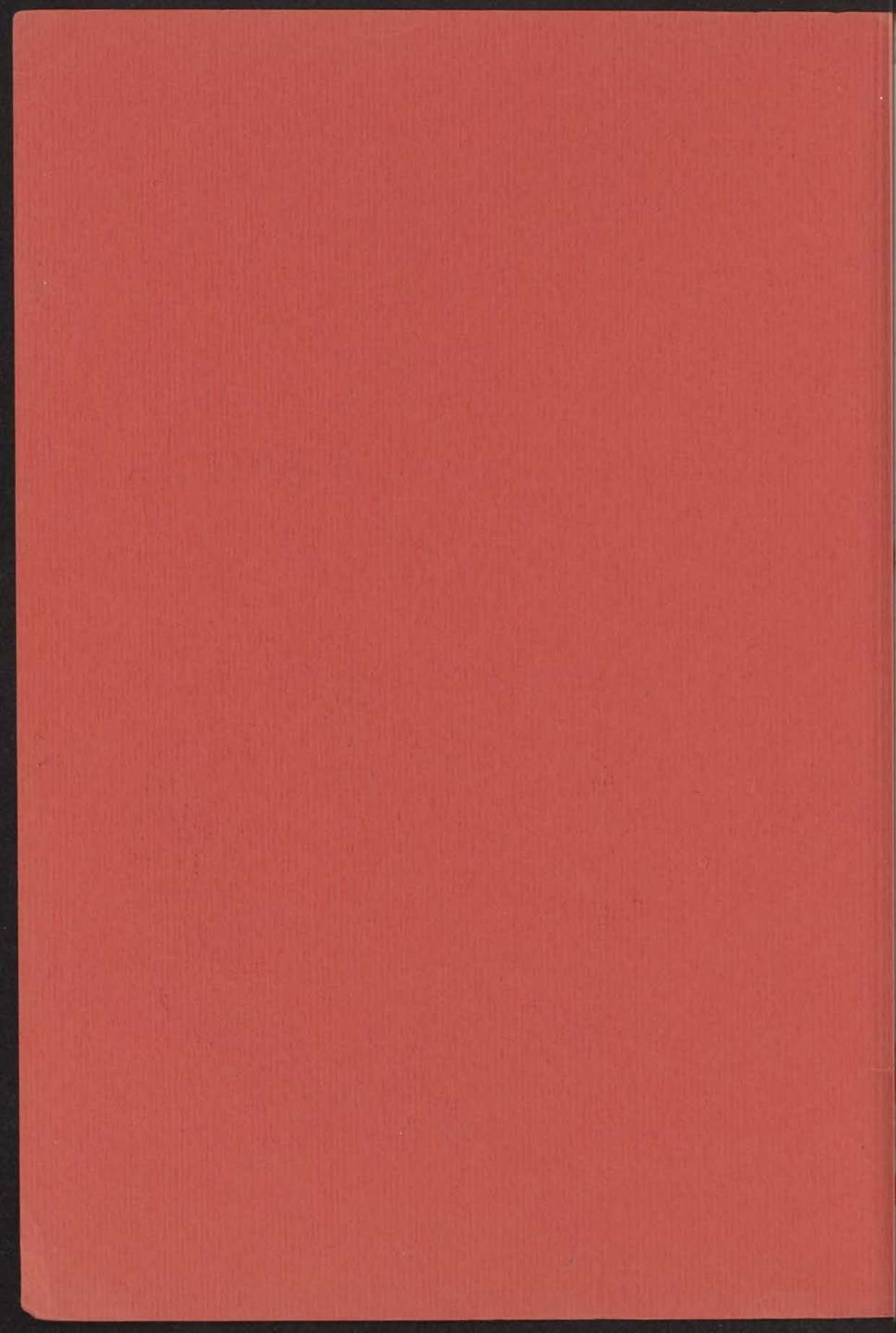
21 JUNI 1973

INTJESST-LORENTZ
voor theoretische natuurkunde
Wiskunde - Natuur - Geneeskunde
Wiskunde - Natuur - Geneeskunde

SPIN DYNAMICS



P.W. VERBEEK



21 MAART 1973

Corrected by the author
19-9-73 PM

SPIN DYNAMICS

THEORY AND SOME TYPICAL EXPERIMENTS

PROEFSCHRIFT

ter verkrijging van de graad van Doctor in
de Wiskunde en Natuurwetenschappen aan de
Rijksuniversiteit te Leiden, op gezag van de
Rector Magnificus Dr. A.E. Cohen, Hoogleraar
in de Faculteit der Letteren, volgens
besluit van het college van Dekanen te
verdedigen op woensdag 28 maart 1973
te klokke 16.15 uur.

door

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PROMOTOREN: PROF.DR. C.J. GORTER
PROF.DR. W.J. CASPERS

Dit proefschrift is tot stand gekomen onder
kritische begeleiding van Dr. J.C. Verstelle.

STELLINGEN

1. In paramagnetische stoffen waarin de wisselwerking voornamelijk uit isotrope antiferromagnetische exchange bestaat geeft bestudering van spin-spin-relaxatietijden in afwezigheid van een constant magneetveld een duidelijker inzicht in het kritisch gedrag boven het Néelpunt dan de bepaling van paramagnetische resonantie lijnbreedtes in velden die klein zijn ten opzichte van de interactie.

Dit proefschrift, hoofdstuk 7

- 2a. De breedte van de verboden resonantielijnen, die worden gemeten in de configuratie waarbij een sterk constant veld evenwijdig aan het wisselveld is aangebracht, in stoffen waarin de wisselwerking niet voornamelijk seculair is, wordt door het seculaire deel van de wisselwerking bepaald.

Dit proefschrift, § 6.36.

- 2b. De huidige beschrijving van Kronig-Bouwkamp relaxatie in het in stelling 2a aangeduide geval laat geen zinvolle confrontatie met het experiment toe.

Dit proefschrift, appendix K.

3. Bij de beschrijving van paramagnetische relaxatie in stoffen met voornamelijk seculaire wisselwerking kunnen veronderstellingen omtrent de vorm van de lijnen, waaruit het geheugen-spectrum is opgebouwd, in vele gevallen worden vermeden.

Dit proefschrift, hoofdstuk 8.

4. De bewering van Mori, dat de geheugenfunctie (integraalkern, "damping function") in tegenstelling tot de relaxatiefunctie, geen bijdrage van een langzaam proces bevat, is in haar algemeenheid onjuist.

Mori, H., Prog.Th.Phys. 33 (1965) 423

Dit proefschrift, § 3.3 Second example.

(hierin dient de laatste formule te luiden: $\frac{1}{\tau} \equiv \frac{1-\alpha}{\tau_1} + \frac{\alpha}{\tau_2}$.)

5. Het gebruik van het sprongpunt van lood als ijktemperatuur verdient groter bekendheid onder experimentatoren die werkzaam zijn in het temperatuur interval 4 K tot 14 K.

N.B.S. Special Publication 260-44.

6. Het valt te verwachten, dat de spin-spin absorptie behorende bij enkelvoudige relaxatie in stoffen met voornamelijk seculaire wisselwerking, voor frequenties ver beneden de omgekeerde relaxatietijd, in goede benadering evenredig is met χ_{ad}^2 . Ter aanvulling van de tweede stelling uit Locher's ^{ad} proefschrift kan derhalve worden opgemerkt, dat Shaposhnikov's formule voor een grote klasse van stoffen wel degelijk voor de bepaling van de grootheid

$$b/C = H^2 (\chi_o \chi_{ad}^{-1} - 1)^{-1}$$

mag worden gebruikt.

Shaposhnikov, I.G., Zh. eksp. teor. Fiz. (U.S.S.R.) 18 (1948) 533

7. Ten minste één der benaderende uitdrukkingen, die Strombotne en Hahn geven voor de sporen K_3 , K_1 (2) en K_0 (3), is onbetrouwbaar.

Strombotne, R.L. en Hahn, E.L., Phys. Rev. 133A (1964) 1629.

8. Ten onrechte passen Fulinski en Kramarczyk de middelwaardestelling toe op een tetraede (d.i. een $n \times n \times n \times n$ matrix).

Fulinski, A. en Kramarczyk, W.J., Physica 39 (1968) 575.

9. Ter berekening van $\text{Tr}(S_z)^n = \sum_{k=0}^{2S} (k - S)^n$ voor één ion met spin S kan men gebruik maken van de recursieformule

$$(n+1) \sum_{k=0}^N (k+a)^n = (N+1+a)^{n+1} - a^{n+1} - \sum_{q=0}^{n-1} \binom{n+1}{q} \sum_{k=0}^N (k+a)^q,$$

waarin $0^0 \equiv 1$, a reëel is en k, q, n en N geheel zijn.

10. De wijze, waarop in dit proefschrift de figuren ten opzichte van de tekst zijn geplaatst heeft onmiskenbare voordelen.

Bradshaw, J. et al., New Scientist 54 (1972) 628.

11. De standaardinrichting van kabels, bestemd voor signaaluitwisseling met een bandopname-apparaat voor huiselijk gebruik, houdt een nodeloze beperking in van hun toepassingsmogelijkheden.

DIN 41524.

12. De op asfaltwegen gebruikelijke wijze van liniëring, uitsluitend door middel van kleurverschil van het wegdek, is niet doelmatig.
13. De derde geldstroom, ten behoeve van wetenschappelijk onderzoek in Nederland, zou moeten vloeien via het Ministerie van Cultuur, Recreatie en Maatschappelijk Werk, en niet via dat van Sociale Zaken en Volksgezondheid.

Stellingen behorende bij het proefschrift van P.W. Verbeek,
Leiden, 1973.

"It seems a shame", the Walrus said,
"To play them such a trick,
After we've brought them out so far,
And made them trot so quick!"
The Carpenter said nothing but
"The butter's spread too thick!"

The Walrus and the Carpenter
L. Carroll, Through the Looking Glass.

Ter herinnering aan mijn moeder.

Aan mijn vader.

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*In all ages man has sought ways to predict a time development.
The cover shows a most classical method: Aegeus, king of Athens,
inquires at the Delphi oracle about his future.*

SURVEY

The dynamics of a quantummechanical many body system, complicated as it may be, satisfies Schrödinger's equation. At first sight this is a simple statement, but as the equation is governed by the hamiltonian of the system, which contains all information about its interactions, internal or with the outer world, it is nearly all that can or needs to be said. Such compact statements are characteristic for the work to be given here.

Only few specifications of the hamiltonian will be made, the most important one being: that it depends on an external vector parameter \vec{H} . For the magnetic systems to be studied \vec{H} stands for the magnetic field.

The reason for choosing magnetic systems as a subject is primarily that in many magnetic systems all interactions are believed to be known. They therefore provide a nearly ideal testcase for quantum-statistical theory, such as the Kubo formalism and its extensions.

For a confrontation of theory and experiment in such systems the frequency spectrum of linear response to variations of \vec{H} constitutes a convenient and commonly used feature. Experimentally this spectrum can be determined through a measurement of energy absorption in oscillating magnetic fields of various frequencies. Theoretically it is seen to correspond to the spectrum of a certain correlation function.

Although this spectrum is generally too complicated to admit a full numerical evaluation, some characteristic values such as moments or relaxation times may be calculated and compared with experimental results. When even such a calculation proves too troublesome, one may look for theoretically predicted relations between the experimental data.

The present investigations are an extension of Locher's work on spin-spin effects in the paramagnetic susceptibility of powdered samples at frequencies around 1 GHz²⁶). As his experimental set-up has not essentially been altered before the end of the measurements described here, the reader will find no chapter on the

experimental method used. Ref. 26 is a sufficient source of information.

The most important extension made is the decrease of temperature to the region of critical phenomena (MnF_2 , chapter 7). This implied the need for a theoretical description of relaxation in which the usual high-temperature approximation plays no role. A review of the theoretical tools available is given in the chapters 1 to 4.

A second extension is the exclusive use of single crystals as a measuring sample. Hence the anisotropy of the g-tensor is of more importance than it is in powders. The necessary adaptations for the decomposition of the hamiltonian are given in chapter 5.

Chapter 6 can be considered to contain the most direct continuation of Locher's work. The copper Tutton salts which have relatively small exchange interaction are discussed. The main novelty in the theoretical approach of this case is the rule that the width of the forbidden resonances in parallel fields is almost exclusively determined by the so-called secular part of the interaction. Experimental results are given. The moments and intensities obtained (both in zero and in high field) are confronted with theoretical values.

Critical phenomena have been observed in MnF_2 . The results are discussed in Chapter 7. Based on an analysis by Tjon a relation is derived between low-field resonance absorption and zero field relaxation in compounds with strong exchange interaction. This relation can be specialized to give a translation rule between EPR linewidths and zero field relaxation-times, that stays valid down to temperatures near the transition point in antiferromagnetic compounds.

Experimentally this theory is confirmed by the present work. For the first time in MnF_2 an enormous anisotropy has been directly observed, as high-frequency susceptibility with alternating field parallel to the easy axis shows hardly any critical behaviour. No theoretical explanation is given for this anisotropy. Some measurements have been made in the antiferromagnetic temperature region.

Chapter 8 is devoted to the most frequently investigated aspect of spin-spin relaxation being the parallel-field dependence at high temperature of the relaxation time in compounds with relatively strong exchange interaction. The usual assumption of Gaussian lineshapes for the integral kernel of the relaxation description is experimentally found to be wrong in the copper alkali halides. The theory given has been put so as to avoid this assumption. The confrontation between theory and experiment has been focused on intensities and moments of the observed curves rather than on relaxation times.

Moreover it is shown that assuming the occurrence of antisymmetric exchange in copper alkali halides, one can give a reasonable description of experimental results.

The relation between EPR widths and zero field relaxation times derived in chapter 7 is confirmed. Their temperature dependence, although not understood, may thus be given a unified description.

Hobbits delighted in such things, if they were accurate: they liked to have books filled with things that they already knew, set out fair and square with no contradictions.

J.R.R. Tolkien, The Lord of the Rings, Allen & Unwin, London 1968, p. 20.

CHAPTER 1

LINEAR RESPONSE THEORY

1.1

If a sample of magnetic material lies in a homogeneous, oscillating field (cf. appendix A)

$$\vec{H}_1(t) = \text{Re } e^{i\omega t} \vec{H}_1(0) = (e^{i\omega t} + e^{-i\omega t}) \frac{\vec{H}_1(0)}{2} \quad 1.01$$

the corresponding variation of magnetisation can commonly be described by

$$\begin{aligned} \vec{M}_1(t) &= \bar{\chi}'(\omega) v \text{Re } e^{i\omega t} \vec{H}_1(0) + \bar{\chi}''(\omega) v \text{Im } e^{i\omega t} \vec{H}_1(0) \\ &= \text{Re } (\bar{\chi}'(\omega) - i\bar{\chi}''(\omega)) v e^{i\omega t} \vec{H}_1(0) \\ &\equiv \text{Re } \bar{\chi}(\omega) v e^{i\omega t} \vec{H}_1(0) \\ &= (e^{i\omega t} v \bar{\chi}(\omega) + e^{-i\omega t} v \bar{\chi}^*(\omega)) \cdot \frac{\vec{H}_1(0)}{2} \end{aligned} \quad 1.02$$

where $\bar{\chi}(\omega)$ is a complex tensor of second order, called frequency dependent susceptibility tensor, and v is the volume of the sample. $\bar{\chi}'(\omega)$ and $\bar{\chi}''(\omega)$ are real tensors. The work done by the oscillating field during one period equals

$$- \mu_0 \int_{t=0}^{t=2\pi/\omega} \vec{M}_1(t) \cdot d\vec{H}_1(t) = 2\pi v \frac{\mu_0}{2} \vec{H}_1(0) \cdot \bar{\chi}''(\omega) \cdot \vec{H}_1(0) \quad 1.03$$

which may be compared with the energy stored in the sample volume $v \frac{\mu_0}{2} \vec{H}_1(0) \cdot \vec{H}_1(0)$.

$\bar{\chi}(\omega)$ will generally depend on more parameters than frequency alone. Apart from the oscillating field there may be a static field \vec{H} .

This description excludes non-linear effects, and $\vec{H}_1(0)$ is supposed to be so small as to make a linear approximation realistic. (Van Vianen and Tjon¹) have indicated that this may be a rather strong condition in the neighbourhood of a phase transition.)

1.2

In experimental situations it is not possible to have an oscillating field as given by 1.01, as this would be everlasting. Instead one has an oscillating field $\Delta\vec{H}(t)$ of variable amplitude, the field being turned on at t_p and off at $t_f > t_p$. It is therefore allowed to write

$$\Delta\vec{H}(t) = 0 \text{ for } t < t_p \text{ and } t > t_f > t_p \quad 1.04$$

$$|\Delta\vec{H}(t)| < H_{\max} \text{ for certain } H_{\max} \text{ and all } t \quad 1.05$$

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \Delta\vec{H}(t) dt \equiv \vec{H}(\omega) = \vec{H}^*(-\omega) \quad 1.06$$

$$\int_{-\infty}^{+\infty} e^{i\omega t} \vec{H}(\omega) d\omega = \Delta\vec{H}(t) = \Delta\vec{H}^*(t). \quad 1.07$$

According to Kubo²) and Siskens and Mazur³) *, the variation of magnetisation, which is measured as the response to an arbitrary field variation $\Delta\vec{H}(t)$, is in linear approximation described by

$$\begin{aligned} \Delta\vec{M}(t) &= - \int_{-\infty}^t \dot{\vec{\phi}}(t - \tau, \vec{H}) \cdot \Delta\vec{H}(\tau) d\tau + v \bar{\chi}_{\infty}(\vec{H}) \cdot \Delta\vec{H}(t) \\ &= - \int_0^{\infty} \dot{\vec{\phi}}(\tau, \vec{H}) \cdot \Delta\vec{H}(t - \tau) d\tau + v \bar{\chi}_{\infty}(\vec{H}) \cdot \Delta\vec{H}(t) \end{aligned} \quad 1.08$$

*) Siskens and Mazur have pointed out that a (real) term $v \bar{\chi}_{\infty}(\vec{H}) \cdot \Delta\vec{H}(t)$ should be added in order to account for diamagnetic effects (cf. section 3.1).

where $\bar{\phi}(\tau, \vec{H})$ and $\bar{\chi}_{\infty}(\vec{H})$ are second order tensors, to be defined in section 3 (3.05 and 3.06) for the case of a sample in very weak contact with a bath of constant temperature; $\bar{\phi}(\tau, \vec{H}) \equiv \frac{\partial}{\partial \alpha} \bar{\phi}(\alpha, \vec{H})$ for $\alpha = \tau$.

The first integration in 1.08 is not performed beyond t , and all information from $\Delta \vec{H}(\tau)$ for $\tau > t$ is discarded; this reflects the principle of causality, which excludes corresponding contributions to $\Delta \vec{M}(t)$. As is well known and easily verified, a tensor element $\phi_{ij}(t, \vec{H})$ may for $t \geq 0$ - apart from constant factors and terms and the 'diamagnetic' term $v \chi_{\infty ij}(\vec{H}) \Delta H_j(t)$ - be visualized as the response $\Delta M_i(t)$ to a stepwise field variation, $\Delta H_j(t) = \Delta H_j(0)$ for $t \leq 0$ and $\Delta H_j(t) = 0$ for $t > 0$ (i and j indicate components in a fixed xyz frame; confusion with $i = \sqrt{-1}$ is not to be expected). This type of field variation does not fulfill 1.04, 1.06 and 1.07 and will therefore not be used.

1.3

In the sections 2 and 3 the tensor elements $\phi_{ij}(t, \vec{H})$ are shown to be continuous, real, bounded functions of t , with continuous t derivatives of arbitrary order. Furthermore, due to a slightly generalized form of the Wiener-Khinchin theorem, they are seen to be the Fourier transform of 'spectral density functions' $s_{ij}(\omega, \vec{H})$

$$\phi_{ij}(t, \vec{H}) = \int_{-\infty}^{+\infty} e^{i\omega t} s_{ij}(\omega, \vec{H}) d\omega. \quad 1.09$$

As $\phi_{ij}(t, \vec{H})$ is real, one has

$$s_{ij}(\omega, \vec{H}) = s_{ij}^*(-\omega, \vec{H}). \quad 1.10$$

The inverse transformation should formally yield

$$s_{ij}(\omega, \vec{H}) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \phi_{ij}(t, \vec{H}) dt \quad 1.11$$

but one cannot be sure as to the convergence of this integral and use of 1.11 should be avoided. The time average of $\phi_{ij}(t, \vec{H})$ is well defined (cf. 2.37)

$$\bar{\phi}_{ij}(\vec{H}) \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \phi_{ij}(t, \vec{H}) dt. \quad 1.12$$

If $\bar{\phi}_{ij}(\vec{H}) \neq 0$, $s_{ij}(\omega, \vec{H})$ contains a δ -distribution at $\omega = 0$, with intensity $\bar{\phi}_{ij}(\vec{H})$. It is useful to define

$$\phi_{ij}(t, \vec{H}) \equiv \phi_{ij}(t, \vec{H}) - \bar{\phi}_{ij}(\vec{H}) \quad 1.13$$

$$s_{ij}(\omega, \vec{H}) \equiv s_{ij}(\omega, \vec{H}) - \bar{\phi}_{ij}(\vec{H})\delta(\omega) \quad 1.14$$

which are like $\Delta\vec{M}(t)$, independent of a possible additive constant in $\phi_{ij}(t, \vec{H})$. The functions $\phi_{ij}(t, \vec{H})$ are bounded and $\lim_{t \rightarrow \infty} \Delta\vec{H}(t) = 0$; therefore partial integration of 1.08 is allowed and yields

$$\Delta\vec{M}(t) = (\bar{\phi}(0, \vec{H}) + v \bar{\chi}_{\infty}(\vec{H})) \cdot \Delta\vec{H}(t) - \int_0^{\infty} \bar{\phi}(\tau, \vec{H}) \cdot \dot{\Delta\vec{H}}(t - \tau) d\tau \quad 1.15$$

or

$$\Delta\vec{M}(t) = (\bar{\phi}(0, \vec{H}) + v \bar{\chi}_{\infty}(\vec{H})) \cdot \Delta\vec{H}(t) - \int_0^{\infty} \bar{\phi}(\tau, \vec{H}) \cdot \dot{\Delta\vec{H}}(t - \tau) d\tau. \quad 1.16$$

Under certain conditions (cf. section 1.4) this can also be written as

$$\Delta\vec{M}(t) = \int_{-\infty}^{+\infty} e^{i\omega t} v \bar{\chi}(\omega, \vec{H}) \cdot \vec{H}(\omega) d\omega \quad 1.17$$

with $v \bar{\chi}(\omega, \vec{H}) = v \bar{\chi}_{\infty}(\vec{H}) + \bar{\phi}(0, \vec{H}) - i\omega \int_0^{\infty} e^{-i\omega\tau} \bar{\phi}(\tau, \vec{H}) d\tau. \quad 1.18$

As $\bar{\phi}(\tau, \vec{H})$ is real, splitting 1.18 into real and imaginary parts yields

$$v \bar{\chi}'(\omega, \vec{H}) = v \bar{\chi}_{\infty}(\vec{H}) + \bar{\phi}(0, \vec{H}) - \omega \int_0^{\infty} \sin \omega\tau \bar{\phi}(\tau, \vec{H}) d\tau \quad 1.19$$

$$v \bar{\chi}''(\omega, \vec{H}) = \omega \int_0^{\infty} \cos \omega\tau \bar{\phi}(\tau, \vec{H}) d\tau. \quad 1.20$$

Moreover, as $\Delta\vec{M}(t)$ is real, 1.17 implies

$$\bar{\chi}(\omega, \vec{H}) = \bar{\chi}^*(-\omega, \vec{H}). \quad 1.21$$

1.4 A more detailed account of frequency dependent susceptibility.

It follows from the theory given in section 2 that the spectral density function $s_{ij}(\omega, \vec{H})$ generally contains a countable number of δ -distributions (further to be called δ -functions).

$$s_{ij}(\omega, \vec{H}) = S_{ij}(\omega, \vec{H}) + \bar{\phi}_{ij}(\vec{H})\delta(\omega) = s_{ij}^R(\omega, \vec{H}) + \Sigma' \phi_{ij}^k(\vec{H})\delta(\omega - \omega_k) + \bar{\phi}_{ij}(\vec{H})\delta(\omega) \quad 1.22$$

where $s_{ij}^R(\omega, \vec{H})$ contains no δ -functions; Σ' indicates summation over k , omitting $\omega_k = 0$; and $\omega_k = \omega_k(\vec{H})$. The δ -function at $\omega = 0$ was already seen to correspond to the time average of $\phi_{ij}(t, \vec{H})$ whereas the δ -functions at $\omega \neq 0$ (which, due to 1.10 occur in pairs of opposite frequency and complex conjugate intensity) correspond to undamped oscillations in $\phi_{ij}(t, \vec{H})$. The Fourier transform of 1.22 reads

$$\phi_{ij}(t, \vec{H}) = \Phi_{ij}(t, \vec{H}) + \bar{\phi}_{ij}(\vec{H}) = \phi_{ij}^R(t, \vec{H}) + \Sigma' \phi_{ij}^k(\vec{H})e^{i\omega_k t} + \bar{\phi}_{ij}(\vec{H}). \quad 1.23$$

Inserting this into 1.16 one gets

$$\begin{aligned} \Delta \vec{H}(t) = & (\bar{\Phi}(0, \vec{H}) + v \bar{\chi}_{\infty}(\vec{H})) \cdot \Delta \vec{H}(t) - \int_{-\infty}^{+\infty} \bar{\Phi}^R(\tau, \vec{H}) U(\tau) \cdot \Delta \vec{H}(t - \tau) d\tau \\ & - \int_0^{\infty} \Sigma' \bar{\Phi}^k(\vec{H}) e^{i\omega_k \tau} \cdot \Delta \vec{H}(t - \tau) d\tau \end{aligned} \quad 1.24$$

where $U(\tau)$ is the Heaviside unit step function and

$$\Delta \vec{H}(t - \tau) = \int_{-\infty}^{+\infty} e^{i\omega(t-\tau)} i\omega \vec{H}(\omega) d\omega. \quad 1.25$$

One may show that $\bar{\Phi}(\tau, \vec{H}) U(\tau)$ is Kubo's relaxation tensor ²⁾, the elements of which are called relaxation functions (cf. 2.40). The first integral in 1.24 has been written in the form of a convolution integral, and one is tempted to apply the convolution theorem to it. However, it should be remarked that $\phi_{ij}^R(\tau, \vec{H}) U(\tau)$ cannot generally be proven to be square integrable over τ , which implies that its Fourier transform need not exist and that the convolution theorem need not hold.

Nevertheless one may formally proceed and derive some expressions, the general validity of which must be considered afterwards. It will be seen that only for equations 1.18, 1.19 and 1.20 the condition of square integrability is essential. No such difficulties arise with respect to the second integral in 1.24 which can be calculated according to

$$\begin{aligned} & \frac{1}{2\pi} \int_0^{\infty} e^{i\omega_k \tau} \int_{-\infty}^{+\infty} e^{i\omega(t-\tau)} i\omega \vec{H}(\omega) d\omega d\tau \\ &= \int_{-\infty}^{+\infty} \frac{1}{2\pi} \int_0^{\infty} e^{i(\omega_k - \omega)\tau} d\tau e^{i\omega t} i\omega \vec{H}(\omega) d\omega \\ &= \int_{-\infty}^{+\infty} \left\{ \frac{1}{2} \delta(\omega - \omega_k) + \frac{P}{2\pi i(\omega - \omega_k)} \right\} e^{i\omega t} i\omega \vec{H}(\omega) d\omega \end{aligned} \quad 1.26$$

where P indicates a principle value integral for ω . Hence one may write 1.24 in the generalized form of 1.02

$$\Delta \vec{M}(t) = \int_{-\infty}^{+\infty} e^{i\omega t} v \vec{\chi}(\omega, \vec{H}) \cdot \vec{H}(\omega) d\omega \quad 1.17$$

with

$$\begin{aligned} v \vec{\chi}(\omega, \vec{H}) &= v \vec{\chi}_{\infty}(\vec{H}) + \vec{\Phi}(0, \vec{H}) - i\omega \int_{-\infty}^{+\infty} e^{-i\omega\tau} \phi_{ij}^R(\tau, \vec{H}) U(\tau) d\tau \\ &\quad - 2\pi i \omega \Sigma' \vec{\Phi}^k(\vec{H}) \left\{ \frac{1}{2} \delta(\omega - \omega_k) + \frac{P}{2\pi i(\omega - \omega_k)} \right\}. \end{aligned} \quad 1.27$$

If no undamped oscillations occur, this implies 1.18, 1.19 and 1.20. Formally again, one can calculate the Fourier transform of $\phi_{ij}^R(\tau, \vec{H}) U(\tau)$ in a way analogous to 1.26 and insert it into 1.27; in appendix B the result is shown to be approximately valid in experimental circumstances regardless of square integrability

$$\begin{aligned} v \vec{\chi}(\omega, \vec{H}) &= v \vec{\chi}_{\infty}(\vec{H}) + \vec{\Phi}(0, \vec{H}) - 2\pi i \omega \int_{-\infty}^{+\infty} \left\{ \frac{1}{2} \delta(\omega - \omega_k) + \frac{P}{2\pi i(\omega - \omega_k)} \right\} \vec{s}^R(\omega_1, \vec{H}) d\omega_1 \\ &\quad - 2\pi i \omega \Sigma' \vec{\Phi}^k(\vec{H}) \left\{ \frac{1}{2} \delta(\omega - \omega_k) + \frac{P}{2\pi i(\omega - \omega_k)} \right\} \end{aligned} \quad 1.28$$

or

$$v \bar{\chi}(\omega, \vec{H}) = v \bar{\chi}_{\infty}(\vec{H}) + \bar{\Phi}(0, \vec{H}) - \pi i \omega (\bar{s}^R(\omega, \vec{H}) + \Sigma' \bar{\Phi}^k(\vec{H}) \delta(\omega - \omega_k)) - \omega \left(\int_{-\infty}^{+\infty} \frac{P}{\omega - \omega_1} \bar{s}^R(\omega_1, \vec{H}) d\omega_1 + \Sigma' \bar{\Phi}^k(\vec{H}) \frac{P}{\omega - \omega_k} \right). \quad 1.29$$

Inserting (cf. 1.23, 1.13)

$$\bar{\Phi}(0, \vec{H}) = \int_{-\infty}^{+\infty} \bar{s}^R(\omega, \vec{H}) d\omega + \Sigma' \bar{\Phi}^k(\vec{H}) \quad 1.30$$

into 1.29 one gets

$$v \bar{\chi}(\omega, \vec{H}) = v \bar{\chi}_{\infty}(\vec{H}) - \pi i \omega (\bar{s}^R(\omega, \vec{H}) + \Sigma' \bar{\Phi}^k(\vec{H}) \delta(\omega - \omega_k)) - \left(\int_{-\infty}^{+\infty} P \frac{\omega_1}{\omega - \omega_1} \bar{s}^R(\omega_1, \vec{H}) d\omega_1 + \Sigma' \omega_k \bar{\Phi}^k(\vec{H}) \frac{P}{\omega - \omega_k} \right). \quad 1.31$$

In terms of the Hilbert transform, defined by

$$\text{Hil}_{\omega} f(\omega') \equiv \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{P}{\omega' - \omega} f(\omega') d\omega' \equiv \frac{1}{\pi} \lim_{\epsilon \rightarrow 0} \int_{\epsilon}^{\infty} \frac{f(\omega + \omega') - f(\omega - \omega')}{\omega'} d\omega' \quad 1.32$$

with ⁴⁾ $\text{Hil}_{\omega} \delta(\omega') \equiv - \frac{P}{\pi \omega} \quad 1.33$

and the properties

$$\text{Hil}_{\omega} f(-\omega') = - \text{Hil}_{-\omega} f(\omega') \quad 1.34$$

and $\text{Hil}_{\omega} \omega' \delta(\omega' - \omega_k) = \text{Hil}_{\omega} \omega_k \delta(\omega' - \omega_k) = - P \frac{\omega_k}{\pi(\omega - \omega_k)} \quad 1.35$

the equations 1.29 and 1.31 take the simple form

$$v \bar{\chi}(\omega, \vec{H}) - v \bar{\chi}_{\infty}(\vec{H}) - \bar{\Phi}(0, \vec{H}) = \pi \omega (-i \bar{s}(\omega, \vec{H}) + \text{Hil}_{\omega} \bar{s}(\omega', \vec{H})) \quad 1.36$$

$$v \bar{\chi}(\omega, \vec{H}) - v \bar{\chi}_{\infty}(\vec{H}) = \pi (-i \omega \bar{s}(\omega, \vec{H}) + \text{Hil}_{\omega} \omega' \bar{s}(\omega', \vec{H})). \quad 1.37$$

It may be reassuring to know, that the existence of these Hilbert transforms follows straightaway from a property of $\bar{S}^R(\omega, \vec{H})$ (cf. 2.28).

Some remarks concerning undamped oscillations.

Generally the $\bar{\phi}^k(\vec{H})$ are relatively small in the limit of an infinite system. Moreover, when $\vec{H}(\omega)$ consists of narrow lines, there is not much chance for a contribution from $\Sigma' \bar{\phi}^k(\vec{H}) \delta(\omega - \omega_k)$. Usually the $\bar{\phi}^k(\vec{H})$ are therefore excluded from theoretical considerations as corresponding to uninteresting reversible processes⁵⁾. Nevertheless the $\bar{\phi}^k(\vec{H})$ are here taken into account at little extra cost, in order that the cases of broadband $\vec{H}(\omega)$, such as for pulse-like $\Delta \vec{H}(t)$, and of a finite system, where $\Sigma' \bar{\phi}^k(\vec{H}) \delta(\omega - \omega_k)$ can be shown to be the only contribution, are included as well. For broadband $\vec{H}(\omega)$ appendix B need not apply.

1.5 Diagonal tensor elements.

For diagonal tensor elements one has (as $\phi_{ii}(t, \vec{H})$ is real and even in time, cf. section 3.6) $S_{ii}(\omega, \vec{H}) = S_{ii}^*(\omega, \vec{H})$, which means that in the right hand side of 1.29 the third term is the only imaginary one. Therefore

$$\frac{v \chi_{ii}''(\omega, \vec{H})}{\pi \omega} = S_{ii}(\omega, \vec{H}) \quad 1.38$$

and
$$\phi_{ii}(t, \vec{H}) = \int_{-\infty}^{+\infty} e^{i\omega t} \frac{v \chi_{ii}''(\omega, \vec{H})}{\pi \omega} d\omega. \quad 1.39$$

The zeroth moment or total intensity of $\frac{v \chi_{ii}''(\omega, \vec{H})}{\pi \omega}$ is found by taking $t = 0$ in 1.39

$$\phi_{ii}(0, \vec{H}) = \int_{-\infty}^{+\infty} \frac{v \chi_{ii}''(\omega, \vec{H})}{\pi \omega} d\omega. \quad 1.40$$

If $\frac{\partial}{\partial t}$ and $\int d\omega$ may be interchanged

$$\left. \frac{\partial^n}{\partial t^n} \phi_{ii}(t, \vec{H}) \right|_{t=0} = \int_{-\infty}^{+\infty} (i\omega)^n \frac{v \chi_{ii}''(\omega, \vec{H})}{\pi \omega} d\omega, \quad n=1,2,3,\dots \quad 1.41$$

yields the higher moments with respect to $\omega = 0$. ($S_{ii}(\omega, \vec{H})$ is even in ω (2.52), therefore odd moments are zero). Inserting 1.38 into 1.37 one gets (cf. 1.32)

$$\chi'_{ii}(\omega, \vec{H}) - \chi_{\infty ii}(\vec{H}) = \text{Hil}_{\omega} \chi''_{ii}(\omega', \vec{H}) \quad 1.42$$

one of the Kramers-Kronig relations.

These are usually derived from a set equations like 1.19, 1.20 while some assumption of square integrability plays an essential role⁶). With the aid of appendix B, 1.28 and consequently 1.42 can be derived without such assumptions. This cannot be done for the inverse relation, as one cannot be sure as to the existence of $\text{Hil}_{\omega} \text{Hil}_{\omega'} \chi''_{ii}(\omega'', \vec{H})$.

Due to the symmetry relation $S_{ij}(\omega, \vec{H}) = S_{ji}(-\omega, \vec{H})$ (cf. 3.6) $\chi'_{ii}(\omega, \vec{H})$ is an odd function of ω , and, as $S_{ii}(\omega, \vec{H})$ contains neither a δ -function nor a step, at $\omega = 0$, 1.42 may be written as

$$\chi'_{ii}(\omega, \vec{H}) - \chi_{\infty ii}(\vec{H}) = \frac{2}{\pi} \int_0^{\infty} P \frac{\omega_1^2}{\omega_1^2 - \omega^2} \frac{\chi''_{ii}(\omega_1, \vec{H})}{\omega_1} d\omega_1 \quad 1.43$$

which for very smooth $\chi''_{ii}(\omega, \vec{H})/\omega$ may be roughly approximated by the thumb rule

$$\chi'_{ii}(\omega, \vec{H}) - \chi_{\infty ii}(\vec{H}) \sim \frac{2}{\pi} \int \frac{\chi''_{ii}(\omega_1, \vec{H})}{\omega_1} d\omega_1. \quad 1.44$$

On the other hand one may see from 1.43, that a step in $\chi''_{ii}(\omega, \vec{H})/\omega$, at $\omega \neq 0$, which is not at all excluded by the results of section 2, gives rise to a singularity in $\chi'_{ii}(\omega, \vec{H})$ at the same frequency.

Moreover, 1.42 shows the way to a formal phenomenological interpretation of $\bar{\chi}_{\infty}(\vec{H})$. As Hilbert transformation is linear and never results in a constant, $\chi_{\infty ii}(\vec{H})$ is uniquely defined by $\chi'_{ii}(\omega, \vec{H})$ and 1.42: $\chi_{\infty ii}(\vec{H})$ is the constant value, which must be subtracted from $\chi'_{ii}(\omega, \vec{H})$ in order to make the difference a Hilbert transform. As no necessary and only few sufficient conditions for a function to be a Hilbert transform are known, the experimental value of $\chi_{\infty ii}(\vec{H})$ can only be determined from the measured $\chi'_{ii}(\omega, \vec{H})$, if this function can be made to meet such a known condition by subtraction of a constant. (e.g. if $\chi'_{ii}(\omega, \vec{H})$ converges for $\omega \rightarrow \infty$ to a constant, faster than $\sim \omega^{-\frac{1}{2}-\epsilon}$, $\epsilon > 0$, then $\chi_{\infty ii}(\vec{H})$ equals this constant, the corresponding sufficient condition being square integrability; in other words, then $\lim_{\omega \rightarrow \infty} \chi'_{ii}(\omega, \vec{H}) = \chi_{\infty ii}(\vec{H})$). In principle this method is unambiguous and valid without restrictions (the xyz-frame may always be chosen so as to diagonalize $\bar{\chi}_{\infty}(\vec{H})$) but practical applicability is less general than one would wish it to be.

1.6 Static measurements.

In the case of a static measurement, $\vec{H}(\omega)$ consists of one narrow line, around $\omega = 0$. In theoretical calculations this line is often taken Lorentzian with vanishing width ⁷⁾⁸⁾. The corresponding zero frequency susceptibility, also called isolated susc. or Kubo-susc. can be found by inspection of 1.65 and 1.67 (appendix B), realizing, that $S_{ij}(\omega, \vec{H})$ contains no δ -function at $\omega = 0$

$$\bar{\chi}(0, \vec{H}) = \bar{\chi}_{\infty}(\vec{H}) + v^{-1} \bar{\Phi}(0, \vec{H}) \equiv \bar{\chi}_{is}(\vec{H}). \quad 1.45^*)$$

This may also be seen from 1.38, 1.40 and the Kramers Kronig relation 1.42 (based on 1.65 and 1.67 etc.); combining 1.40 and 1.42 one gets

$$\chi'_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}) = \frac{1}{\pi} \int_{-\infty}^{+\infty} P \frac{\chi''_{ii}(\omega, \vec{H})}{\omega} d\omega = \int_{-\infty}^{+\infty} \frac{\chi''_{ii}(\omega, \vec{H})}{\pi\omega} d\omega = v^{-1} \phi_{ii}(0, \vec{H}) \quad 1.46$$

and using 1.38

$$\chi''_{ii}(0, \vec{H}) = v^{-1} \pi \omega S_{ii}(\omega, \vec{H}) \Big|_{\omega=0} = 0 \quad 1.47$$

($S_{ij}(\omega, \vec{H})$ contains no δ -function or step at $\omega = 0$ and - due to its integrability, cf. sections 2,3 - cannot be $O(\omega^{-1})$ for $\omega \rightarrow 0$ or $\omega \rightarrow \infty$). Due to the freedom of choice of the xyz-frame one may apply 1.46 to a frame which diagonalizes $\bar{\chi}'(0, \vec{H}) - \bar{\chi}_{\infty}(\vec{H}) - v^{-1} \bar{\Phi}(0, \vec{H})$, and 1.47 to a frame, in which $\bar{\chi}''(0, \vec{H})$ is diagonal. This results in the equalities (equivalent to 1.45)

$$\bar{\chi}'(0, \vec{H}) = \bar{\chi}_{\infty}(\vec{H}) + v^{-1} \bar{\Phi}(0, \vec{H}) \equiv \bar{\chi}_{is}(\vec{H}) \quad 1.48$$

$$\bar{\chi}''(0, \vec{H}) = 0. \quad 1.49$$

~~With the aid of 1.45 the expression 1.36 can be given a simpler shape still:~~

*) It should be remarked that the width of the $H(\omega)$ line required for a measurement of $\bar{\chi}_{is}(\vec{H})$, might be so narrow as to correspond to an unpractically long measuring time.

With the aid of 1.45 the expression 1.36 can be given a simpler shape still

$$\frac{\bar{\chi}(\omega, \vec{H}) - \bar{\chi}(0, \vec{H})}{\pi\omega v^{-1}} = -i\bar{S}(\omega, \vec{H}) + \text{Hi} \int_{\omega} \bar{S}(\omega', \vec{H}) \cdot \quad 1.50$$

1.7 Absorbed energy.

The total amount of work done by the varying field, or 'the energy absorbed by the sample' in the course of the measurement, equals

$$\Delta E = -\mu_0 \int_{t=t_p}^{t=t_f} \vec{\Delta M}(t) \cdot d\vec{\Delta H}(t) = -\mu_0 \int_{t_p}^{t_f} \vec{\Delta M}(t) \cdot \dot{\vec{\Delta H}}(t) dt \quad 1.51$$

(constant terms in the magnetisation do not contribute, as $\vec{\Delta H}(t \leq t_p) = \vec{\Delta H}(t \geq t_f) = 0$). When the xyz-frame is chosen in such a way, that $\vec{\Delta H}(t)$ is oriented along the i-direction ($i = x, y$ or z), if $\vec{\Delta H}(t)$ satisfies 1.04 through 1.07, if $\frac{\partial^n}{\partial t^n} \Delta H_i(t)$ is continuous for any $n \geq 0$ and if $\Delta H_i(t)$ is either an even or an odd function of time, then the absorbed energy can - without further assumptions or approximations - exactly be expressed in terms of the spectral density function $S_{ii}(\omega, \vec{H})$ (cf. app. B)

$$\Delta E = \mu_0 \int_{-\infty}^{+\infty} S_{ii}(\omega, \vec{H}) \frac{1}{2} \omega^2 |2\pi H_i(\omega)|^2 d\omega. \quad 1.52$$

A different aspect of $\vec{\Phi}(t, \vec{H})$ and $\bar{S}(\omega, \vec{H})$ - not to be emphasized here - is their use in the description of fluctuations of magnetisation in absence of a varying field. 1.52 may be seen as a link between these fluctuations and energy absorption and constitutes a representation of the fluctuation - dissipation - theorem. If - due to 1.27 or to 1.66 - $\bar{\chi}(\omega, \vec{H})$ is properly defined, one may insert 1.38 and get

$$\Delta E = 2\pi\mu_0 \int_{-\infty}^{+\infty} v \chi''_{ii}(\omega, \vec{H}) \omega |H_i(\omega)|^2 d\omega. \quad 1.53$$

The relation with 1.03 is given at the end of appendix B.

The appendices are dedicated to Dr. H.P. Wijnen, surgeon, who removing the author's one just in time, made a decisive contribution to this thesis.

Appendix A.

The term 'magnetic field' and the symbol \vec{H} are used throughout to indicate the magnetic field strength in absence of, or just outside the sample. To put it more accurately: $\vec{H} \equiv \vec{B}/\mu_0$ where \vec{B} is the magnetic induction in the sample and μ_0 is the permeability of the vacuum. The change of sample energy at an infinitesimal field variation defines the magnetisation \vec{M} and equals per definitionem

$$-\vec{M} \cdot \Delta \vec{B} = -\mu_0 \vec{M} \cdot \Delta \vec{H}. \quad 1.54$$

The magnetic susceptibility is defined through relations of the form

$$\Delta \vec{M}/v \equiv \bar{\chi} \cdot \Delta \vec{H} \equiv \bar{\chi} \cdot \Delta \vec{B}/\mu_0 \quad 1.55$$

(in a rationalized system of units; v is the sample volume). Conventionally the symbol \vec{H} is used to indicate the magnetic field strength in the sample

$$\vec{H}_{\text{conv}} \equiv \vec{B}/\mu_0 - \vec{M}/v \quad 1.56$$

$$\text{implying: } \Delta \vec{H}_{\text{conv}} = (1 - \bar{\chi}) \cdot \Delta \vec{H}. \quad 1.57$$

According to the historical definition of susceptibility

$$\Delta \vec{M}/v \equiv \bar{\chi}_{\text{hist}} \cdot \Delta \vec{H}_{\text{conv}} \quad 1.58$$

$$\text{implying: } \bar{\chi} = \bar{\chi}_{\text{hist}} \cdot (1 - \bar{\chi}). \quad 1.59$$

As in most problems of interest $1 - \bar{\chi} \approx 1$ (this may fail in case of ferromagnetic ordering) there is in practice only slight difference between \vec{H} and \vec{H}_{conv} and between $\bar{\chi}$ and $\bar{\chi}_{\text{hist}}$. Thus, thanks to the unconventional use of the symbol \vec{H} for \vec{B}/μ_0 , the expressions are practically compatible with those in older literature.

Appendix B

By the following argument the assumptions about the square integrability of $\phi_{ij}^R(\tau, \vec{H})U(\tau)$ and the validity of the formal calculation of its Fourier transform can be replaced by experimental considerations: some conditions imposed on the varying field. (These however, are of no help in proving the existence of the transforms in 1.18, 1.27, 1.19 and 1.20). Let apart from having the features 1.04 through 1.07, $\vec{H}(t)$ be such, that for any positive integer n , $\frac{\partial^n}{\partial t^n} \Delta H_i(t)$ is continuous ($i = x, y$ or z). (An example of such a function is $\vec{H}(t) = \vec{H}(0)(\exp(1 + (t^2 \tau_0^{-2} - 1)^{-1})) \cos \omega_0 t$ for $-\tau_0 < t < \tau_0$, $\vec{H}(t) = 0$ elsewhere). Then for any t , the function $f(\tau) \equiv \phi_{ij}(\tau, \vec{H}) \Delta \dot{H}_j(t - \tau)$ satisfies (as $\frac{\partial^n}{\partial \tau^n} \phi_{ij}(\tau, \vec{H})$ is continuous for all $n \geq 0$)

$$f(\tau) = 0 \text{ for } t - \tau < t_p \text{ and } t - \tau > t_f,$$

$$\frac{\partial^n}{\partial \tau^n} f(\tau) \text{ is continuous for all } n \geq 0.$$

According to Gel'fand and Schilow⁹⁾ $f(\tau)$ is therefore a test function and combined with $U(\tau)$ the Parseval theorem for generalized functions applies

$$\int_0^\infty f(\tau) d\tau = \int_{-\infty}^{+\infty} U(\tau) f(\tau) d\tau = \int_{-\infty}^{+\infty} (\frac{1}{2} \delta(\omega) + \frac{P}{2\pi i \omega}) \int_{-\infty}^{+\infty} e^{i\omega\tau} f(\tau) d\tau d\omega. \quad 1.60$$

As $\Delta \dot{H}_j(t - \tau)$ is square integrable over τ , so is its Fourier transform

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega\tau} \Delta \dot{H}_j(t - \tau) d\tau = e^{-i\omega t} (-i\omega) H_j(-\omega). \quad 1.61$$

Furthermore $s_{ij}^R(\omega, \vec{H})$ is absolutely integrable (cf. 2.32) therefore theorem 65 of Titchmarsh¹⁰⁾ states that

$$2\pi \int_{-\infty}^{+\infty} s_{ij}^R(-\omega - \omega_1) e^{-i\omega_1 t} (-i\omega_1) H_j(-\omega_1) d\omega_1 = \int_{-\infty}^{+\infty} e^{i\omega\tau} \phi_{ij}^R(\tau) \Delta \dot{H}_j(t - \tau) d\tau. \quad 1.62$$

The analogue of this formula for $\phi_{ij}^k(\vec{H}) \delta(\omega - \omega_k)$ is straightforwardly derived

$$2\pi \int_{-\infty}^{+\infty} \phi_{ij}^k(\vec{H}) \delta(-\omega - \omega_1 - \omega_k) e^{-i\omega_1 t} (-i\omega_1) H_j(-\omega_1) d\omega_1 =$$

$$\int_{-\infty}^{+\infty} e^{i\omega \tau} \phi_{ij}^k(\vec{H}) e^{i\omega_k \tau} \Delta \dot{H}_j(t - \tau) d\tau. \quad 1.63$$

After construction of the Fourier transform of $\phi_{ij}^k(\tau, \vec{H}) \Delta \dot{H}_j(t - \tau)$ from 1.62 and 1.63 the expression 1.24 can be written as

$$\Delta \vec{H}(t) = (\vec{\Phi}(0, \vec{H}) + v \vec{\chi}_{\infty}(\vec{H})) \cdot \Delta \vec{H}(t)$$

$$- \int_{-\infty}^{+\infty} \left(\frac{1}{2} \delta(\omega) + \frac{P}{2\pi i \omega} \right) 2\pi \int_{-\infty}^{+\infty} \vec{S}(\omega_1 - \omega, \vec{H}) \cdot e^{i\omega_1 t} i\omega_1 \vec{H}(\omega_1) d\omega_1 d\omega \quad 1.64$$

or

$$\Delta \vec{H}(t) = (\vec{\Phi}(0, \vec{H}) + v \vec{\chi}_{\infty}(\vec{H})) \cdot \Delta \vec{H}(t) - i\pi \int_{-\infty}^{+\infty} \omega_1 \vec{S}(\omega_1, \vec{H}) \cdot e^{i\omega_1 t} \vec{H}(\omega_1) d\omega_1$$

$$- \int_{-\infty}^{+\infty} \frac{P}{\omega} \int_{-\infty}^{+\infty} \omega_1 \vec{S}(\omega_1 - \omega, \vec{H}) \cdot e^{i\omega_1 t} \vec{H}(\omega_1) d\omega_1 d\omega. \quad 1.65$$

This is equivalent to 1.17 and 1.28, 1.29, 1.31, 1.36 or 1.37, if the following equality holds.

$$\int_{-\infty}^{+\infty} \frac{P}{\omega} \left\{ \int_{-\infty}^{+\infty} \omega_1 \vec{S}^R(\omega_1 - \omega, \vec{H}) \cdot e^{i\omega_1 t} \vec{H}(\omega_1) d\omega_1 \right\} d\omega =$$

$$\int_{-\infty}^{+\infty} \omega_1 \left\{ \int_{-\infty}^{+\infty} \frac{P}{\omega} \vec{S}^R(\omega_1 - \omega, \vec{H}) d\omega \right\} \cdot e^{i\omega_1 t} \vec{H}(\omega_1) d\omega_1. \quad 1.66$$

It will now be shown, that some additional conditions for $\Delta \vec{H}(t)$, quite natural from an experimental point of view (except for broad band $\vec{H}(\omega)$), make 1.66 hold in good approximation. In experimental situations the measuring time $t_f - t_p$ should - in order to get sufficient resolution - be chosen much longer than the characteristic times of $\vec{\Phi}^R(t, \vec{H})$. Then the corresponding widths of the components of $\vec{H}(\omega)$ are small

compared to the structural detail in $\overline{s}^R(\omega, \vec{H})$ *) and one may approximate the left hand side of 1.66 by

$$\sum_m \int_{-\infty}^{+\infty} \frac{P}{\omega} \omega_m \overline{s}^R(\omega_m - \omega, \vec{H}) d\omega \cdot e^{i\omega_m t} \vec{H}^m = -\pi \sum_m \omega_m \text{Hil}_{\omega_m} \overline{s}^R(\omega, \vec{H}) \cdot e^{i\omega_m t} \vec{H}^m \quad 1.67$$

where \vec{H}^m is the intensity of the m'th line in $\vec{H}(\omega)$, and $\text{Hil}_{\omega_m} \overline{s}^R(\omega, \vec{H})$ is - according to 2.32 - almost everywhere well defined.

In principle one may thus obtain information about the structural detail of $\text{Hil}_{\omega} \overline{s}^R(\omega', \vec{H})$ through inspection of the experimental result for $\Delta \vec{H}(t) - (\vec{\Phi}(0, \vec{H}) + v \vec{\chi}_{\infty}(\vec{H})) \cdot \Delta \vec{H}(t)$. When the linewidths in $\vec{H}(\omega)$ are found to be narrow compared to the detail in $\text{Hil}_{\omega} \overline{s}^R(\omega', \vec{H})$ *) as well, one may also approximate the right hand side of 1.66 by 1.67 (if necessary a longer measuring time may be chosen to achieve this). Therefore 1.66 holds in good approximation for sufficiently narrow $\vec{H}(\omega)$ lines.

Absorbed energy. Under some other conditions for $\Delta \vec{H}(t)$ one can show that the absorbed energy ΔE (cf. 1.7) can be expressed in a spectral density function $S_{ij}(\omega, \vec{H})$ without making use of the square integrability of $\phi_{ij}^R(\tau, \vec{H}) U(\tau)$ or the existence of its Fourier transform. Let $\Delta \vec{H}(t)$ be oriented along the i-direction and let $\Delta H_i(t)$ be an even (or odd) function of time. ΔE will then contain no contribution from the off-diagonal elements of $\overline{s}(\omega, \vec{H})$ or of that part of $\Delta \vec{H}(t)$, which is even (odd) in time (cf. 1.65)

$$\begin{aligned} \Delta E &= -\mu_0 \int_{-\infty}^{+\infty} \Delta M_i(t) \Delta H_i(t) dt = \\ &= -\mu_0 \int_{-\infty}^{+\infty} \left\{ -i\pi \int_{-\infty}^{+\infty} \omega_1 S_{ii}(\omega_1, \vec{H}) e^{i\omega_1 t} H_i(\omega_1) d\omega_1 \right\} \Delta H_i(t) dt \\ &= \mu_0 \int_{-\infty}^{+\infty} S_{ii}(\omega, \vec{H}) \frac{1}{2} \omega^2 |2\pi H_i(\omega)|^2 d\omega. \end{aligned} \quad 1.52$$

*) Singularities in $s_{ij}^R(\omega, \vec{H})$ and $\text{Hil}_{\omega} s_{ij}^R(\omega', \vec{H})$ at $\omega = \omega_m$ might complicate matters and are assumed absent. Such singularities could be of the form $|\omega - \omega_m|^{-\frac{1}{2}}$ within an interval around ω_m (which would not spoil the integrability of $s_{ij}^R(\omega, \vec{H})$) or of the type induced in $\text{Hil}_{\omega} s_{ij}^R(\omega', \vec{H})$ by a step in $s_{ij}^R(\omega, \vec{H})$. The absence of singularities at the measuring frequencies does not imply square integrability.

The last equality is mainly due to Titchmarsh¹⁰⁾ theorem 35, realizing that $s_{ii}^R(\omega, \vec{H})$ is absolutely integrable; $\Delta \vec{H}_i(t)$ is continuous and zero outside the finite interval (t_p, t_f) ; hence $\Delta \vec{H}_i(t)$ and its Fourier transform $i\omega H_i(\omega)$ are bounded and $i\omega s_{ii}^R(\omega, \vec{H}) H_i(\omega)$ is absolutely integrable, just like $\Delta \vec{H}_i(t)$. The contribution from the $\phi_{ii}^k(\vec{H})$ terms is found through a simple δ -function argument.

When $H_i(\omega)$ consists of lines, narrow compared to the structure of $s_{ii}^R(\omega, \vec{H})$, the right hand side of 1.52 may be approximated by

$$\Delta E \approx \mu_0 \sum_m s_{ii}^R(\omega_m, \vec{H}) \frac{1}{2} \omega_m^2 \int_{-\infty}^{+\infty} |2\pi H_i^m(\omega)|^2 d\omega + \mu_0 \sum' \phi_{ii}^k(\vec{H}) \frac{1}{2} \omega_k^2 |2\pi H_i(\omega_k)|^2 \quad 1.68$$

where $H_i^m(\omega)$ is the m 'th line of $H_i(\omega)$ and ω_m its center frequency. For such a $\vec{H}(\omega)$ equation 1.66 holds, so that 1.38 may be applied

$$\Delta E = 2\pi\mu_0 \int_{-\infty}^{+\infty} v\chi_{ii}''(\omega, \vec{H}) \omega |H_i(\omega)|^2 d\omega. \quad 1.53$$

The relation with 1.03. In the usual measuring situation $H_i(\omega)$ consists of two lines

$$\Delta H_i(t) = \Delta H_i^a(t) \cos \omega_0 t \quad 1.69$$

$$2H_i(\omega) = H_i^a(\omega - \omega_0) + H_i^a(\omega + \omega_0) \quad 1.70$$

where $H_i^a(\omega)$, the Fourier transform of the slow amplitude variation $\Delta H_i^a(t)$, is a very narrow line around $\omega = 0$. Furthermore, $\phi_{ii}^k(\vec{H})$ and $H_i(\omega_k)$ being small ($\omega_k \ll \omega_0$) in an "infinite" system and $s_{ii}^R(\omega, \vec{H})$ being even in ω , the right hand side of 1.68 can be approximated by

$$\Delta E \approx \chi_{ii}''(\omega_0, \vec{H}) \pi \omega_0 v \mu_0 \int_{-\infty}^{+\infty} |H_i^a(\omega)|^2 d\omega = \chi_{ii}''(\omega_0, \vec{H}) \frac{1}{2} \omega_0 v \mu_0 \int_{-\infty}^{+\infty} \Delta H_i^a{}^2(t) dt. \quad 1.71$$

During an average period the oscillating field does an amount of work

$$\frac{2\pi}{\omega_0(t_f - t_p)} \Delta E \approx 2\pi \chi''_{11}(\omega_0, \vec{H}) \frac{v}{t_f - t_p} \int_{t_p}^{t_f} \frac{\mu_0}{2} \Delta H_1^2(t) dt \quad 1.72$$

or $2\pi \chi''_{11}(\omega_0, \vec{H})$ times the average magnetic energy of the oscillating field stored within the sample volume (cf. 1.03).

Die Physik ist ja für die Physiker viel zu schwer.

D. Hilbert

CHAPTER 2

OPERATOR SPACE

2.1

For a finite system with a discrete eigenvalue spectrum for every relevant observable, the linear operators - working in the Hilbert space of state vectors of the system - themselves constitute a linear space under the commonly defined operator addition and multiplication by a scalar factor. All features of this space, to be defined or derived in this section, are assumed to remain valid in the limit of an infinite system with pseudocontinuous eigenvalue spectra. In this space henceforth to be called 'operator space', one may define a unitary scalar product (A, B) , with

$$(A, B) = (B, A)^* \quad 2.00$$

$$(A, A) \geq 0 \quad 2.01$$

$$(A, A) = 0 \text{ if and only if } A = 0\text{-operator} \quad 2.02$$

$$(A, \lambda B) = \lambda(A, B) \quad 2.03$$

and corresponding projection (super)operators P

$$P_A B \equiv \frac{(A, B)}{(A, A)} A. \quad 2.04$$

One thus has $P_A^2 B \equiv P_A P_A B = P_A B \quad 2.05$

$$\text{and } (B_1, B_2) = (P_A B_1, P_A B_2) + ((1 - P_A) B_1, (1 - P_A) B_2). \quad 2.06$$

If the scalar product is zero one may speak of 'orthogonal' operators'. Furthermore as $((1 - P_A) B, (1 - P_A) B) \geq 0$ (cf. 2.01, 2.06 and ¹¹), the scalar product obeys Schwarz's inequality:

$$|(A, B)|^2 \leq (A, A)(B, B). \quad 2.07$$

It should be noted that the common operator product of A and B, which yields a new product operator AB, will play no particular role in operator space. Any linear mapping of the operator space in itself may be called a linear superoperator working in operator space. Analogously to the situation in the common space of state vectors a hermitean adjoint, hermiticity and unitarity can be defined by means of the scalar product.

2.2

Choosing the Heisenberg picture one has operators that develop in time according to

$$\frac{d}{dt} A(t) = \frac{i}{\hbar} (\mathcal{K}A(t) - A(t)\mathcal{K}) \equiv \frac{i}{\hbar} [\mathcal{K}, A(t)] \equiv iLA(t) \quad 2.08$$

where \mathcal{K} is the Hamiltonian of the system. Like any operator in section 2, \mathcal{K} is assumed not to be explicitly time dependent. The Liouville operator L, transforming each operator into its time derivative (multiplied by 1/i), is an example of a superoperator. The scalar product is assumed to grant hermiticity to this Liouville operator

$$(A(t_1), LB(t_2)) \equiv (L^\dagger A(t_1), B(t_2)) = (LA(t_1), B(t_2)). \quad 2.09$$

Then the corresponding exponential superoperator e^{iLt}

$$e^{iLt} A(t_1) = e^{\frac{it_1\mathcal{K}}{\hbar}} A(t_1) e^{-\frac{it_1\mathcal{K}}{\hbar}} = A(t_1 + t) \quad 2.10$$

shifting every operator in time over the interval t, is unitary under the same scalar product definition

$$(A(t_1), e^{iLt} B(t_2)) \equiv ((e^{iLt})^\dagger A(t_1), B(t_2)) = (e^{-iLt} A(t_1), B(t_2)) \quad 2.11$$

the inverse of e^{iLt} being e^{-iLt} . Consequently one has for any t, introducing the notation $A(0) \equiv A$, $B(0) \equiv B$

$$(e^{iLt} A, e^{iL(t+t_1)} B) = (A, e^{-iLt} e^{iL(t+t_1)} B) = (A, e^{iLt_1} B) \quad 2.12$$

which proves (e^{iLt_1A}, e^{iLt_2B}) to be a stationary function of t_1 and t_2 , further to be called correlation function. By analogy (e^{iLt_1A}, e^{iLt_2A}) is an autocorrelation function. Without loss of generality these functions can and will be studied in the form (A, e^{iLt_B}) . Time derivatives are calculated according to

$$\frac{\partial^n}{\partial t^n} (A, e^{iLt_B}) = (A, (iL)^k e^{iLt} (iL)^{n-k} B), \quad \begin{matrix} k = 0, 1, 2, \dots, n \\ n = 1, 2, 3, \dots \end{matrix} \quad 2.13$$

According to the definition of L both (A, e^{iLt_B}) and its time derivatives are continuous functions of t . This may be seen from the inequality

$$|(A, e^{iL(t+\Delta t)B}) - (A, e^{iLt_B})|^2 \leq 2(A, A) \operatorname{Re}\{(B, B) - (B, e^{iL\Delta t}B)\} \quad 2.14$$

From 2.00 and 2.11 follows the symmetry relation

$$(A, e^{iLt_B}) = (e^{iLt_B, A})^* = (B, e^{-iLt_A})^* \quad 2.15$$

Due to 2.07 one has the bounds

$$\left| \frac{\partial^n}{\partial t^n} (A, e^{iLt_B}) \right| \leq (L^k A, L^k A)^{\frac{1}{2}} (L^{n-k} B, L^{n-k} B)^{\frac{1}{2}}, \quad \begin{matrix} k = 0, 1, 2, \dots, n \\ n = 0, 1, 2, \dots \end{matrix} \quad 2.16$$

in particular for $n = 0$

$$|(A, e^{iLt_B})| \leq (A, A)^{\frac{1}{2}} (B, B)^{\frac{1}{2}} \quad 2.17$$

2.3 Autocorrelation functions.

Autocorrelation functions of the type mentioned satisfy the relations 2.12 through 2.17. As moreover for each function $f(t)$ that is continuous in a bounded interval (a, b)

$$\begin{aligned} 0 &\leq \left(\left(\int_a^b f(t) e^{iLt} dt \right), \left(\int_a^b f(t) e^{iLt} dt \right) \right) = \\ &= \iint_{aa}^{bb} f^*(t_1) f(t_2) (e^{iLt_1A}, e^{iLt_2A}) dt_1 dt_2 = \\ &= \iint_{aa}^{bb} f^*(t_1) f(t_2) (A, e^{iL(t_2-t_1)A}) dt_1 dt_2 \end{aligned} \quad 2.18$$

one can write ¹²⁾

$$(A, e^{iLt_A}) = \int_{-\infty}^{+\infty} e^{i\omega t} dF_{AA}(\omega) \quad 2.19$$

$$F_{AA}(\omega) - F_{AA}(0) = \lim_{\Omega \rightarrow \infty} \frac{1}{2\pi} \int_{-\Omega}^{\Omega} (A, e^{iLt_A}) \frac{e^{-i\omega t} - 1}{-it} dt \quad 2.20$$

where $F_{AA}(\omega)$ is a real monotonic non-decreasing function of bounded variation called the spectrum (Fourier-Stieltjes transform) of (A, e^{iLt_A}) . In terms of the more commonly used Fourier transform this reads

$$(A, e^{iLt_A}) = \int_{-\infty}^{+\infty} e^{i\omega t} s_{AA}(\omega) d\omega \quad 2.21$$

where $s_{AA}(\omega)$ may contain δ -functions and is called spectral density function. Further following reference ¹²⁾ one may divide the Fourier-Stieltjes transform $F_{AA}(\omega)$ into a continuous part $F_{AA}^R(\omega)$ and a countable sum of stepfunctions

$$F_{AA}(\omega) = F_{AA}^R(\omega) + \sum_{k=1,2,\dots} \phi_{AA}^k U(\omega - \omega_k) \quad 2.22$$

$F_{AA}^R(\omega)$ has the same features as $F_{AA}(\omega)$ and is moreover continuous, whereas for all k

$$\phi_{AA}^{k*} = \phi_{AA}^k \geq 0 \quad 2.23$$

Correspondingly the spectral density function $s_{AA}(\omega)$ can be written as

$$s_{AA}(\omega) = s_{AA}^R(\omega) + \sum_{k=1,2,\dots} \phi_{AA}^k \delta(\omega - \omega_k) \quad 2.24$$

The first term $s_{AA}^R(\omega)$ (possibly containing stepfunctions) satisfies

$$s_{AA}^R(\omega) = s_{AA}^{R*}(\omega) \quad 2.25$$

$$s_{AA}^R(\omega) \geq 0 \quad 2.26$$

and
$$\int_{-\infty}^{+\infty} |s_{AA}^R(\omega)| d\omega < \infty \quad 2.27$$

as
$$\int_{-\infty}^{+\infty} |s_{AA}^R(\omega)| d\omega = \int_{-\infty}^{+\infty} s_{AA}^R(\omega) d\omega = \int_{-\infty}^{+\infty} dF_{AA}^R(\omega) = \lim_{\omega \rightarrow \infty} (F_{AA}^R(\omega) - F_{AA}^R(-\omega)). \quad 2.28$$

The existence of this limit follows from the fact that $F_{AA}^R(\omega)$, like $F_{AA}(\omega)$ is monotonic and of bounded variation. The Hilbert transform $\text{Hil}_{\omega} s_{AA}^R(\omega')$ is therefore almost everywhere ^{*}) well-defined (cf. theorem 100 of ref. ¹⁰) and so is $\text{Hil}_{\omega} s_{AA}(\omega')$ (cf. 1.33).

Thus for an autocorrelation function of the type

$$(e^{iLt_1 A}, e^{iLt_2 A}) = \int_{-\infty}^{+\infty} e^{i\omega(t_2 - t_1)} s_{AA}(\omega) d\omega \quad 2.29$$

the spectral density function $s_{AA}(\omega)$, apart from δ -functions of real non-negative intensity, which it may contain, is a real positive non-definite function of ω . It should be remarked, that proving this generalized form of the Wiener-Khinchin theorem (and the inequality 2.34 a to be derived from it) no use is made of hermiticity of the linear operator A . The crucial feature is rather the unitarity of the scalar product

$$(A, B) = (B, A)^* \quad 2.00$$

Using a proof of Khinchin ¹³) one can derive from 2.19 that the following time average exists (cf. appendix C)

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt A}) dt = \lim_{\epsilon \rightarrow 0} (F_{AA}(\epsilon) - F_{AA}(-\epsilon)) = \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} s_{AA}(\omega) d\omega \geq 0 \quad 2.30$$

being equal to the intensity of the δ -function at $\omega = 0$.

^{*}) A step in $s_{AA}^R(\omega)$ at ω_1 i.e. a corner in $F_{AA}^R(\omega)$ implies that $\text{Hil}_{\omega_1} s_{AA}^R(\omega')$ is undefined.

2.4 Correlation functions.

As any correlation function of the type $(e^{iLt_1 A}, e^{iLt_2 B})$ may be written as a linear combination of autocorrelation functions according to

$$(A, e^{iLt_B}) = \frac{1}{2} \{ ((A+B), e^{iLt_{(A+B)}}) - (A, e^{iLt_A}) - (B, e^{iLt_B}) \} - \frac{i}{2} \{ ((A+iB), e^{iLt_{(A+iB)}}) - (A, e^{iLt_A}) - (B, e^{iLt_B}) \} \quad 2.31$$

one may define the spectral density function

$$s_{AB}(\omega) \equiv \frac{1}{2} s_{A+B \ A+B}(\omega) - \frac{i}{2} s_{A+iB \ A+iB}(\omega) - \left(\frac{1}{2} - \frac{i}{2}\right) (s_{AA}(\omega) + s_{BB}(\omega)). \quad 2.32$$

This is a complex function of ω , for which

$$\int_{-\infty}^{+\infty} |s_{AB}(\omega)| d\omega < \infty \quad 2.33$$

$$(A, e^{iLt_B}) = \int_{-\infty}^{+\infty} e^{i\omega t} s_{AB}(\omega) d\omega \quad 2.34$$

$$s_{BA}^*(\omega) = s_{AB}(\omega) \quad 2.35$$

and

$$\text{Hil}_{\omega} s_{AB}(\omega') \equiv \int_{-\infty}^{+\infty} \mathcal{P} \frac{s_{AB}(\omega')}{\omega - \omega'} d\omega' \text{ is almost everywhere well defined.} \quad 2.36$$

Again the time average exists ^{*}) and is equal to the intensity of the δ -peak at $\omega = 0$

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt_B}) dt = \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{+\epsilon} s_{AB}(\omega) d\omega \quad 2.37$$

which according to a lemma about Cesaro limits ¹⁴⁾, implies the following limits to exist and to have the same values as 2.37

^{*}) For the existence of the time average of a function of t , it is not sufficient that it be bounded, as the counterexample $\cos \log(1 + |t| \tau_0^{-1})$ illustrates.

$$\lim_{\epsilon \rightarrow 0} \epsilon \int_0^{\infty} (A, e^{iLt} B) e^{-\epsilon t} dt \quad 2.38$$

and
$$\lim_{\epsilon \rightarrow 0} \epsilon \int_t^{\infty} (A, e^{iL\tau} B) e^{-\epsilon \tau} d\tau = (A, e^{iLt} B) + \lim_{\epsilon \rightarrow 0} \int_t^{\infty} e^{-\epsilon \tau} d(A, e^{iL\tau} B) \quad 2.39$$

implying
$$(A, e^{iLt} B) - \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iL\tau} B) d\tau = - \lim_{\epsilon \rightarrow 0} \int_t^{\infty} e^{-\epsilon \tau} d(A, e^{iL\tau} B) \quad 2.40$$

an expression, which for $t > 0$ coincides with Kubo's definition of the relaxation function ²⁾. Furthermore one can derive from 2.37 that

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iL\tau} B) d\tau = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T}^0 (A, e^{iL\tau} B) dt \quad 2.41$$

and from 2.15 a series of related expressions for the time averages. Due to 2.17 the time average is bounded according to

$$\left| \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iL\tau} B) d\tau \right| \leq (A, A)^{\frac{1}{2}} (B, B)^{\frac{1}{2}} \quad 2.42$$

Furthermore it satisfies an inequality similar to 2.07

$$\left| \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iL\tau} B) d\tau \right|^2 \leq \left(\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, -e^{iL\tau} A) d\tau \right) \left(\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (B, e^{iL\tau} B) d\tau \right) \quad 2.43$$

This is proven by defining the auxiliary scalar product $\{A, B\} \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iL\tau} B) d\tau$ for which the analogon of 2.01, $\{A, A\} \geq 0$ holds (cf. 2.30) together with relations similar to 2.00 and thus also Schwarz's inequality.

Due to 2.26 one has for $C = \alpha A + e^{-i\phi} B$, with $\alpha = \alpha^*$ and $e^{i\phi} = s_{AB}^R(\omega) |s_{AB}^R(\omega)|^{-1}$

$$0 \leq s_{CC}^R(\omega) = \alpha^2 s_{AA}^R(\omega) + 2\alpha \operatorname{Re}(e^{-i\phi} s_{AB}^R(\omega)) + s_{BB}^R(\omega) \quad 2.44$$

and consequently the Schwarz inequality for spectral density functions

$$|s_{AB}^R(\omega)| \leq (s_{AA}^R(\omega) s_{BB}^R(\omega))^{1/2}. \quad 2.45$$

2.5 The scalar product of (anti)hermitian operators.

At this stage it is useful to make a specification concerning the scalar product of linear operators A^\dagger and B^\dagger , which (according to the scalar product in the Hilbert space of statevectors) are hermitean adjoint to the operators A and B respectively. It will henceforth be assumed that the scalar product satisfies

$$(A^\dagger, B^\dagger) = (A, B)^* \quad 2.46$$

As $\mathcal{K}^\dagger = \mathcal{K}$ one has

$$(LA(t))^\dagger = -LA^\dagger(t) \quad 2.47$$

$$(e^{iLt}A)^\dagger = e^{iLt}A^\dagger \quad 2.48$$

$$\text{implying } (A^\dagger, e^{iLt}B^\dagger) = (A^\dagger, (e^{iLt}B)^\dagger) = (A, e^{iLt}B)^* \quad 2.49$$

Particularly for pairs of (anti)hermitean operators $A^\dagger = \pm A$, $B^\dagger = \pm B$, one has

$$(A, B) = (A, B)^* \quad 2.50$$

$$\text{from which } (A, e^{iLt}B) = (A, e^{iLt}B)^* = (B, e^{-iLt}A) \quad 2.51$$

$$\text{implying } s_{AB}(\omega) = s_{AB}^*(-\omega) = s_{BA}(-\omega). \quad 2.52$$

It follows that $s_{AA}(\omega)$ has zero odd moments, if A is (anti)hermitian.

2.6 The integro-differential equality. Memory function and memory spectrum.

Following Mori's method ¹⁶⁾ one can derive the following equality for an autocorrelation function $(A, e^{iLt}A)$ (cf. appendix D):

$$\frac{d}{dt} e^{-i\bar{\omega}t} (A, e^{iLt} A) = - \int_0^t e^{-i\bar{\omega}(t-\tau)} \frac{((1-P_A)LA, e^{i(1-P_A)L(t-\tau)} (1-P_A)LA)}{(A, A)} e^{-i\bar{\omega}\tau} (A, e^{iL\tau} A) d\tau \quad 2.53$$

with
$$\bar{\omega} \equiv \int_{-\infty}^{+\infty} \omega s_{AA}(\omega) d\omega / \int_{-\infty}^{+\infty} s_{AA}(\omega) d\omega = \left. \frac{d}{dt} (A, e^{iLt} A) \right|_{t=0} (A, A)^{-1} = (A, LA) (A, A)^{-1} \quad 2.54$$

(the first moment of $s_{AA}(\omega)$, which equals zero for (anti)hermitean A , cf. 2.51, 2.52). Within the subspace of operators orthogonal to A the superoperator $e^{i(1-P_A)Lt}$ is unitary and thus $(e^{i(1-P_A)Lt} B_1, e^{i(1-P_A)Lt} B_2)$ (with $(A, B_1) = (A, B_2) = 0$) is a stationary correlation function based on an unusual (cf. 2.10) rule of time development. Particularly the kernel $((1-P_A)LA, e^{i(1-P_A)Lt} (1-P_A)LA)$ sometimes called "memory function" is seen to be an autocorrelation function of that kind. It should be noted, that all features of the functions $(A, e^{iLt} A)$ as listed in 2.3 have their counterparts for the memory function. One may even extend the analogy so far as to derive another integro-differential equality. The procedure can be repeated which yields a hierarchy of equalities and corresponding, increasingly complicated autocorrelation functions. As far as the Laplace transforms exist, they are given by

$$l(z) \equiv \int_0^{\infty} e^{-zt} (A, e^{iLt} A) dt \quad 2.55$$

$$l'(z) \equiv \int_0^{\infty} e^{-zt} (A', e^{iL't} A') dt \quad 2.56$$

$$A' \equiv (1 - P_A)LA, \quad L' \equiv (1 - P_A)L \quad 2.57$$

$$l''(z) \equiv \int_0^{\infty} e^{-zt} (A'', e^{iL''t} A'') dt \quad 2.58$$

$$A'' \equiv (1 - P_{A'})L'A', \quad L'' \equiv (1 - P_{A'})L' \quad 2.59$$

The Laplace transforms $l(z)$, $l'(z)$, ... are related by

$$l(z) = \frac{(A,A)}{z - i\bar{\omega} + l'(z)(A,A)^{-1}}, \quad \bar{\omega} \equiv (A,LA)(A,A)^{-1} \quad 2.60$$

$$l'(z) = \frac{(A',A')}{z - i\bar{\omega}' + l''(z)(A',A')^{-1}}, \quad \bar{\omega}' \equiv (A',L'A')(A',A')^{-1} \quad 2.61$$

The hierarchy of equalities thus results in a continued fraction of the form

$$l(z) = (A,A)/z - i\bar{\omega} + (A',A')(A,A)^{-1}/z - i\bar{\omega}' + (A'',A'')(A',A')^{-1}/z - i\bar{\omega}'' + \dots \quad 2.62$$

(For (anti)hermitean A one may show $0 = \bar{\omega} = \bar{\omega}' = \bar{\omega}'' = \dots$ (cf. appendix D))

The counterparts of 2.15 and 2.21 read

$$(A', e^{iL't_{A'}}) = (A', e^{-iL't_{A'}})^* \quad 2.63$$

and
$$(A', e^{iL't_{A'}}) = \int_{-\infty}^{+\infty} e^{i\omega t} s'_{A',A'}(\omega) d\omega \quad 2.64$$

It is perhaps useful to denote the spectral density function $s'_{A',A'}(\omega)$ of the memory function by the short name "memory spectrum". If $l(i\omega)$ and $l'(i\omega)$ exist, one has for the spectral density functions of the original autocorrelation function and its memory function respectively

$$\pi s_{AA}(\omega) = \text{Re } l(i\omega) \quad 2.65$$

and
$$\pi s'_{A',A'}(\omega) = \text{Re } l'(i\omega) \quad 2.66$$

such that 2.60 implies that

$$l'(z)(A,A)^{-1} = \frac{(A,A)}{l(z)} - z + i\bar{\omega} \quad 2.67$$

$$\text{Re } l'(i\omega)(A,A)^{-1} = \frac{\text{Re } l(i\omega)(A,A)}{|l(i\omega)|^2} \quad 2.68$$

$$\text{Im } l'(i\omega)(A,A)^{-1} = \frac{\text{Im } l(i\omega)(A,A)}{|l(i\omega)|^2} - \omega + \bar{\omega} \quad . \quad 2.69$$

Consequently the memory spectrum can be written as

$$s'_{A'A'}(\omega) = \frac{s_{AA}(\omega)}{|l(i\omega)|^2} (A,A)^2 \quad . \quad 2.70$$

In some cases the memory spectrum offers an easier confrontation between experimental results and theoretical analysis (cf. 3.3) than $s_{AA}(\omega)$ would do.

It follows from 2.53 through repeated differentiation that for (anti)hermitean A the moments of $s_{AA}(\omega)$ and of $s'_{A'A'}(\omega)$ are related by

$$\int_{-\infty}^{+\infty} \omega^{2n+2} s_{AA}(\omega) d\omega = \sum_{l=0}^n (A,A)^{-1} \int_{-\infty}^{+\infty} \omega^{2l} s'_{A'A'}(\omega) d\omega \int_{-\infty}^{+\infty} \omega^{2n-2l} s_{AA}(\omega) d\omega \quad . \quad 2.71$$

2.7 Invariant operators.

Operators C describing a constant of motion have a zero time derivative and thus lie in the kernel of the Liouville operator L. This kernel constitutes a linear subspace of operator space: the subspace of invariant operators. As every invariant operator commutes with \mathcal{K} , there will always be a representation in which that particular operator and \mathcal{K} both are diagonal. In case of degeneracy of energy levels, this does not imply that a representation exists that diagonalizes all invariant operators including \mathcal{K} . Therefore the adjective "invariant" is used rather than "diagonal". Projection on a linear subspace can be done by projecting on an orthogonal basis spanning the subspace. It is assumed that an, at most countable infinite, number of basis vectors spans the subspace; this is reasonable if a finite system is looked into in the limit of an infinite system (e.g. a system of N particles with k states per particle corresponding with k^N states; the number of independent operators in operatorspace is $(k^N)^2 = (k^2)^N$ and it might be counted (on base k^2) by a number of N digits.) The projection superoperator D will denote the projection on the subspace of invariant operators:

$$DA \equiv \sum_k P_C A \quad . \quad 2.72$$

where $\{C_k\}$ is an orthogonal basis in that subspace. Due to 2.46 one can always choose $\{C_k\}$ so that $C_k^\dagger = C_k$ for all k (cf. appendix E). Let this be the case and let

$$C_0 \equiv I \equiv \text{the identity operator} \quad 2.73$$

$$C_1 \equiv \mathcal{K} - P_1 \mathcal{K} \equiv \mathcal{K}' \quad 2.74$$

In cases where all invariant operators are diagonal in one representation, D may be called extractor of the diagonal part in that representation¹⁵). In analogy with 2.05 and 2.06 one has

$$D^2 B \equiv DDB = DB \quad 2.75$$

$$(B_1, B_2) = (DB_1, DB_2) + ((1-D)B_1, (1-D)B_2) \quad 2.76$$

Moreover, as $LC_k = 0$

$$LDB = 0 \quad 2.77$$

and, as $C_k^\dagger = C_k$,

$$(DB)^\dagger = DB^\dagger \text{ and } ((1-D)B)^\dagger = (1-D)B^\dagger \quad 2.78$$

(this stays - of course - valid for a different choice of $\{C_k\}$, even not Hermitean.)

2.8 Application of D to correlation functions.

With the aid of the projection superoperator D a correlation function may be split into two contributions: one from the invariant components of the operators and the other from the remaining time dependent parts

$$\begin{aligned} (A, e^{iLt} B) &= (DA, De^{iLt} B) + ((1-D)A, (1-D)e^{iLt} B) = \\ &= (DA, DB) + ((1-D)A, e^{iLt} (1-D)B) \end{aligned} \quad 2.79$$

Applying 2.17 to the last term yields narrower bounds for $(A, e^{iLt} B)$:

$$|(A, e^{iLt}B) - (DA, DB)| \leq ((1-D)A, (1-D)A)^{\frac{1}{2}} ((1-D)B, (1-D)B)^{\frac{1}{2}} \quad 2.80$$

Due to 2.72 the invariant term in 2.79 may further be split

$$\begin{aligned} (A, e^{iLt}B) &= (P_I A, P_I B) + (P_{\mathcal{J}C} A, P_{\mathcal{J}C} B) + \\ &+ \sum_{k=2,3,\dots} (P_{C_k} A, P_{C_k} B) + ((1-D)A, e^{iLt}(1-D)B) \quad 2.81 \end{aligned}$$

Taking the time average one gets

$$\begin{aligned} \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt}B) dt &= (P_I A, P_I B) + (P_{\mathcal{J}C} A, P_{\mathcal{J}C} B) + \sum_{k=2,3,\dots} (P_{C_k} A, P_{C_k} B) + \\ &+ \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T ((1-D)A, e^{iLt}(1-D)B) dt \quad 2.82 \end{aligned}$$

In particular for an autocorrelation function this reads

$$\begin{aligned} \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt}A) dt &= (P_I A, P_I A) + (P_{\mathcal{J}C} A, P_{\mathcal{J}C} A) + \sum_{k=2,3,\dots} (P_{C_k} A, P_{C_k} A) + \\ &+ \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T ((1-D)A, e^{iLt}(1-D)A) dt \quad 2.83 \end{aligned}$$

From 2.01 and 2.30 it follows that all terms in 2.83 are real non-negative, yielding the lower bound for the time average of an autocorrelation function

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt}A) dt \geq (P_I A, P_I A) + (P_{\mathcal{J}C} A, P_{\mathcal{J}C} A) + \sum_{k=2,3,\dots} (P_{C_k} A, P_{C_k} A) \quad 2.84$$

This inequality remains valid, if not all invariants are included in the summation²⁰⁾.

In section 3.3 one special case will be seen to be of particular practical interest. It is characterized by the following property: ^{One of the} ~~Both~~ operators A and B in the correlation function $(A, e^{iLt}B)$ satisfy:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt} A) dt = (P_1 A, P_1 A) + (P_{\mathcal{H}'} A, P_{\mathcal{H}'} A) \quad 2.85$$

This occurs if A ^{or} ~~and~~ B correspond to ergodic observables ^{*}). Then 2.84 implies

$$(P_{C_k} A, P_{C_k} A) = 0, \quad k=2,3,\dots \quad 2.86$$

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T ((1-D)A, e^{iLt} (1-D)A) dt = 0 \quad 2.87$$

^{or} ~~and~~ the same for B . Applying 2.07 to 2.86 and 2.43 to 2.87 one finds

$$(P_{C_k} A, P_{C_k} B) = 0, \quad k=2,3,\dots \quad 2.88$$

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T ((1-D)A, e^{iLt} (1-D)B) dt = 0 \quad 2.89$$

by which (cf. 2.81) the equations 2.85 ^s have been proven to imply ^{its} ~~their~~ analogon

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt} B) dt = (P_1 A, P_1 B) + (P_{\mathcal{H}'} A, P_{\mathcal{H}'} B) \quad 2.90$$

Moreover it is seen that

$$(A, e^{iLt} B) - \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt} B) dt = ((1-P_1 - P_{\mathcal{H}'})A, e^{iLt} (1-P_1 - P_{\mathcal{H}'})B) \quad 2.91$$

equals a stationary correlation function and has all its features (cf. section 2.4).

^{*}) For a more detailed discussion of ergodic observables see sections 4.1 and 4.2.

Appendix C.

Inserting 2.19 the time average of $(A, e^{iLt}A)$ can be written as

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt}A) dt = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \int_{-\infty}^{+\infty} e^{i\omega t} dF_{AA}(\omega) dt.$$

For further progress the following lemma is proven (In the remaining part of app. C $F_{AA}(\omega)$ is written as $F(\omega)$.)

lemma $\lim_{k \rightarrow \infty} \int_{-k}^k e^{i\omega t} dF(\omega)$ converges uniformly on the interval $t \in (-\infty, +\infty)$.

proof $\left| \int_a^b e^{i\omega t} dF(\omega) \right| \leq \int_a^b \left| e^{i\omega t} \right| \left| \frac{d}{d\omega} F(\omega) \right| d\omega = \int_a^b \frac{d}{d\omega} F(\omega) = F(b) - F(a)$, as $F(\omega)$

is real and monotonous non-decreasing, and therefore

$$\left| \int_{-\infty}^{+\infty} e^{i\omega t} dF(\omega) - \int_{-k}^k e^{i\omega t} dF(\omega) \right| \leq \left| \int_{-\infty}^{-k} \right| + \left| \int_k^{+\infty} \right| \leq (F(-k) - F(-\infty)) + (F(\infty) - F(k))$$

which does not depend on t and converges to zero for $k \rightarrow \infty$. q.e.d.

Due to this uniform convergence the integrals over $F(\omega)$ and t may be interchanged

$$\begin{aligned} \int_0^T \int_{-\infty}^{+\infty} e^{i\omega t} dF(\omega) dt &= \int_{-\infty}^{+\infty} \int_0^T e^{i\omega t} dt dF(\omega) = \int_{-\infty}^{+\infty} \frac{e^{i\omega T} - 1}{i\omega} dF(\omega) = \\ &= \int_{-\infty}^{+\infty} \frac{\sin \omega T}{\omega} dF(\omega) - i \int_{-\infty}^{+\infty} \frac{\cos \omega T - 1}{\omega} dF(\omega). \end{aligned}$$

According to a lemma by Khinchin ¹³⁾ taking the limit $T \rightarrow \infty$ one gets

$$\begin{aligned} \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \int_{-\infty}^{+\infty} e^{i\omega t} dF(\omega) dt &= \lim_{T \rightarrow \infty} \int_{-\infty}^{+\infty} \frac{\sin \omega T}{\omega T} dF(\omega) - i \lim_{T \rightarrow \infty} \int_{-\infty}^{+\infty} \frac{\cos \omega T - 1}{\omega T} dF(\omega) = \\ &= \lim_{\omega \rightarrow 0} \frac{\sin \omega T}{\omega T} (F(\omega) - F(-\omega)) - i \lim_{\omega \rightarrow 0} \frac{\cos \omega T - 1}{\omega T} (F(\omega) - F(-\omega)) = \\ &= \lim_{\omega \rightarrow 0} (F(\omega) - F(-\omega)) - 0. \quad \text{This proves 2.30.} \end{aligned}$$

Appendix D.

One may split

$$\frac{d}{dt} P_A e^{iLt} B = iP_A L P_A e^{iLt} B + iP_A L (1 - P_A) e^{iLt} B \quad 2.92$$

An expression for the last term can be found through

$$\frac{d}{dt} (1 - P_A) e^{iLt} B = i(1 - P_A) L P_A e^{iLt} B + i(1 - P_A) L (1 - P_A) e^{iLt} B \quad 2.93$$

which yields

$$(1 - P_A) e^{iLt} B = e^{i(1 - P_A)Lt} (1 - P_A) B + i \int_0^t e^{i(1 - P_A)L(t-\tau)} (1 - P_A) L P_A e^{iL\tau} B d\tau \quad 2.94$$

Hence 2.92 takes the form

$$\begin{aligned} \frac{d}{dt} P_A e^{iLt} B &= iP_A L P_A e^{iLt} B + \\ &+ iP_A L e^{i(1 - P_A)Lt} (1 - P_A) B - \int_0^t P_A L e^{i(1 - P_A)L(t-\tau)} (1 - P_A) L P_A e^{iL\tau} B d\tau \end{aligned} \quad 2.95$$

from which for $B = A$ the equality 2.53 may be derived.

For $(A, B_1) = (A, B_2) = 0$ one has ¹⁶⁾

$$(B_1, (1 - P_A) L B_2) = (B_1, L B_2) = (L B_1, B_2) = ((1 - P_A) L B_1, B_2) \quad 2.96$$

and thus

$$(B_1, e^{i(1 - P_A)Lt} B_2) = (e^{-i(1 - P_A)Lt} B_1, B_2) \quad 2.97$$

or in words: within the subspace of operators orthogonal to A , the superoperator $(1 - P_A)L$ is Hermitean and $e^{i(1 - P_A)Lt}$ is unitary.

Due to 2.46 $A^\dagger = \pm A$ implies $(P_A B)^\dagger = P_A B^\dagger$, thus if $A, A', A'', \dots, A^{(n)}$ (anti) hermitean then $(L^{(n)} B)^\dagger = -L^{(n)} B^\dagger$ (cf. 2.36) and $A^{(n)\dagger} = \pm A^{(n)}$. Hence all $A^{(n)}$ are (anti)hermitean, all $(A^{(n)}, e^{iL^{(n)}t} A^{(n)}) = (A^{(n)}, e^{-iL^{(n)}t} A^{(n)})$ and all $\bar{\omega}^{(n)} \sim \frac{d}{dt} (A^{(n)}, e^{iL^{(n)}t} A^{(n)}) \Big|_{t=0} = 0$

Appendix E.

Let $\{K_k\}$ be a basis in the subspace of invariant operators. Out of $\{K_k\}$ a basis of hermitean operators can be constructed. (I)

This basis can be orthogonalized by Schmidt's procedure; the resulting orthogonal basis is still hermitean. (II).

Proof of I: Let $K_k^\dagger = K_k$ if $k \leq h$. $K_{h+1}^\dagger = \mathcal{K}$, hence $LK_{h+1}^\dagger = LK_{h+1} = 0$ and K_{h+1}^\dagger is an element of the subspace and can be expressed in the basis $\{K_k\}$; $K_{h+1}^\dagger = \sum_{k=1,2,3,\dots} c_k K_k$. Therefore one may define

$$\text{if } c_{h+1} \neq -1 \quad K'_{h+1} \equiv K_{h+1} + K_{h+1}^\dagger = (c_{h+1} + 1) K_{h+1} + \sum_{k \neq h+1} c_k K_k$$

$$\text{if } c_{h+1} = -1 \quad K'_{h+1} \equiv i(-K_{h+1} + K_{h+1}^\dagger) = i(c_{h+1} - 1) K_{h+1} + i \sum_{k \neq h+1} c_k K_k$$

In both cases K'_{h+1} is hermitean and allowed to replace K_{h+1} as a basis member. After the replacement the new set satisfies: $K_k^\dagger = K_k$ if $k \leq h+1$. In this way all non hermitean operators can be replaced and a hermitean basis constructed.

Proof of II: Schmidt's orthogonalization procedure does not introduce non-hermitean operators: Let $\{K_k\}$ be a basis of hermitean operators. Schmidt's method yields

$$K''_1 \equiv K_1, \quad K''_2 \equiv (1 - P_{K''_1})K_2, \quad K''_k \equiv K_k - \sum_{\kappa=1}^{k-1} P_{K''_\kappa} K_k \quad 2.98$$

In order to prove the hermiticity of $\{K''_k\}$ it is sufficient to show that, if $K''_k^\dagger = K''_k$ for $k \leq h$, then $K''_{h+1}^\dagger = K''_{h+1}$. And indeed, due to 2.46

$$K''_{h+1}^\dagger = K_{h+1}^\dagger - \sum_{\kappa=1}^h \frac{(K''_\kappa, K_{h+1})^*}{(K''_\kappa, K''_\kappa)} K''_\kappa^\dagger = K_{h+1}^\dagger - \sum_{\kappa=1}^h \frac{(K''_\kappa, K_{h+1})}{(K''_\kappa, K''_\kappa)} K''_\kappa = K''_{h+1} \quad 2.99$$

Μαγνήτων δ' ἤρχε Πρόθοος,

Homer, Iliad, Second Book, verse 756, Greece, ca - 800 .

The oldest description of an externally driven magnetic assembly in a field (And Forerunner commanded the Magnetes, ...).

CHAPTER 3

FORM AND PROPERTIES OF $\phi_{ij}(t, \vec{H})$

3.1 Expressions for $\phi_{ij}(t, \vec{H})$ and $\chi_{\infty ij}(\vec{H})$.

A system with magnetic properties is characterized by the fact that its Hamiltonian is field dependent

$$\mathcal{K} = \mathcal{K}(\vec{H}) \quad 3.00$$

The operator of the component of magnetization in the i -direction is defined by

$$M_i(\vec{H}) \equiv -\frac{1}{\mu_0} \frac{\partial}{\partial H_i} \mathcal{K}(\vec{H}), \quad i = x, y \text{ or } z \quad 3.01$$

In appendix F it is shown, that this definition yields the macroscopic expression 1.51. As \mathcal{K} is hermitean the same is true for M_i . Provided that a Taylor expansion of $\mathcal{K}(\vec{H})$ is allowed, an increment $\Delta\vec{H}$ can be accounted for in the following way

$$\mathcal{K}(\vec{H} + \Delta\vec{H}) = \mathcal{K}(\vec{H}) + \sum_i \frac{\partial \mathcal{K}(\vec{H})}{\partial H_i} \Delta H_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 \mathcal{K}(\vec{H})}{\partial H_i \partial H_j} \Delta H_i \Delta H_j + \dots \quad 3.02$$

As

$$M_i(\vec{H} + \Delta\vec{H}) = -\frac{1}{\mu_0} \frac{\partial \mathcal{K}(\vec{H} + \Delta\vec{H})}{\partial (H_i + \Delta H_i)} = -\frac{1}{\mu_0} \frac{\partial \mathcal{K}(\vec{H} + \Delta\vec{H})}{\partial \Delta H_i} \quad 3.03$$

one gets from 3.02 (if term by term differentiation is permitted) the expansion

$$M_i(\vec{H} + \Delta\vec{H}) = -\frac{1}{\mu_0} \frac{\partial \mathcal{K}(\vec{H})}{\partial H_i} - \frac{1}{\mu_0} \sum_j \left\{ \frac{\partial^2 \mathcal{K}(\vec{H})}{\partial H_i \partial H_j} + \frac{\partial^2 \mathcal{K}(\vec{H})}{\partial H_j \partial H_i} \right\} \Delta H_j + \dots \quad 3.04$$

An additional problem is the differentiation of an operator in the limit of an infinite system. However, most often the Hamiltonian is a polynomial in H_x, H_y, H_z and for this case the method given is rigorous.

When \vec{H} is a function of time $\vec{H}(t)$ (like in chapter 1) not only the Hamiltonian but also the magnetization operator is explicitly time-dependent (cf. 3.04). This implies that the Kubo formalism should be rederived with some care. Doing so (Appendix F) one obtains in linear approximation (cf. section 1.1)

$$\Delta \vec{M}(t) = - \int_0^t \dot{\vec{\phi}}(\tau, \vec{H}) \cdot \Delta \vec{H}(t-\tau) d\tau + \vec{\chi}_{\infty}(\vec{H}) \cdot \Delta \vec{H}(t) \quad 1.08$$

where

$$\phi_{ij}(t, \vec{H}) \equiv (\text{Tr} e^{-\beta \mathcal{H}(\vec{H})})^{-1} \mu_0 \int_0^{\beta} \text{Tr} e^{-(\beta-\lambda) \mathcal{H}(\vec{H})} M_j(\vec{H}) e^{-\lambda \mathcal{H}(\vec{H})} \frac{it}{\hbar} \mathcal{H}(\vec{H}) M_i(\vec{H}) e^{-\frac{it}{\hbar} \mathcal{H}(\vec{H})} d\lambda \quad 3.05$$

and

$$\chi_{\infty ij}(\vec{H}) \equiv - \frac{1}{\mu_0} (\text{Tr} e^{-\beta \mathcal{H}(\vec{H})})^{-1} \text{Tr} (e^{-\beta \mathcal{H}(\vec{H})} \{ \frac{\partial^2 \mathcal{H}(\vec{H})}{\partial H_i \partial H_j} + \frac{\partial^2 \mathcal{H}(\vec{H})}{\partial H_j \partial H_i} \}) \quad 3.06$$

For $t \geq 0$ the function $-\frac{\partial}{\partial t} \phi_{ij}(t, \vec{H})$ equals Kubo's Response- or After-effect function. As \mathcal{H} is hermitean $\chi_{\infty ij}(\vec{H})$ is real; moreover $\chi_{\infty ij}(\vec{H}) = \chi_{\infty ji}(\vec{H})$. The $\vec{\chi}_{\infty}(\vec{H})$ tensor, which is particularly important in diamagnetic systems, is seen to occur whenever the hamiltonian contains terms which are non-linear in \vec{H} . Higher derivatives in \vec{H} should not be expected to contribute to the magnetization variations, as far as the linear approximation is concerned. Both in 3.05 and 3.06 none of the operators is explicitly time-dependent; the symbol β has been used: $\beta^{-1} \equiv kT_b$, k being Boltzmann's constant, and T_b the temperature of a bath with which the system has a very weak thermal contact (cf. section 4.7).

3.2 Choice of a scalar product.

Defining the scalar product in operator space by ^{18) 7) 19)}

$$(A, B) \equiv (\beta \text{Tr} e^{-\beta \mathcal{H}(\vec{H})})^{-1} \int_0^{\beta} \text{Tr} e^{-(\beta-\lambda) \mathcal{H}(\vec{H})} A^{\dagger} e^{-\lambda \mathcal{H}(\vec{H})} B d\lambda \quad 3.07$$

which meets all requirements of chapter 2 (cf. 2.01, 2.02, 2.03, 2.09, 2.46) one may conveniently write 3.05 as

$$\phi_{ij}(t, \vec{H}) = \beta \mu_0 (M_j(\vec{H}), e^{iL(\vec{H})t} M_i(\vec{H})) \quad 3.08$$

(The \vec{H} dependence of M_j, M_i and L will henceforth be omitted from the notation.) Thus $\phi_{ij}(t, \vec{H})$ equals a stationary correlation function of the type $(e^{iLt_1 A}, e^{iLt_2 B})$, it is continuous and has continuous time derivatives of arbitrary order (cf. 2.14, 2.31). Due to Schwarz's inequality (2.07) it is bounded (cf. 2.80) and, $M_i(\vec{H})$ and $M_j(\vec{H})$ being

hermitean, it is real (cf. 2.51).

Eqs. 2.51 and 2.11 imply

$$\phi_{ji}(t, \vec{H}) = \phi_{ij}(-t, \vec{H}) \quad 3.09$$

Furthermore the spectral density function $s_{ij}(\omega, \vec{H}) = \beta \nu_0 s_{M_j M_i}(\omega)$, its Hilbert transform, and the time average of $\phi_{ij}(t, \vec{H})$ are well defined (2.34, 2.36, 2.37). In particular the diagonal tensor elements $\phi_{ii}(t, \vec{H})$ equal autocorrelation functions, have real, positive non-definite spectral density functions (cf. 2.25, 2.26, 2.27) and satisfy 2.53 and resulting equations.

3.3 Memory spectrum and susceptibility.

If 2.85 is satisfied by M_i and M_j (i.e. if these are ergodic observables), one has (1.13, 2.91)

$$\phi_{ij}(t, \vec{H}) \equiv \phi_{ij}(t, \vec{H}) - \bar{\phi}_{ij}(\vec{H}) = \beta \nu_0 ((1 - P_i - P_{\mathcal{H}'}), M_j, e^{iLt} (1 - P_i - P_{\mathcal{H}'}) M_i) \quad 3.10$$

which has a form analogous to 3.08*). Consequently $\phi_{ij}(t, \vec{H})$ has all the features of $\phi_{ij}(t, \vec{H})$ listed above. E.g. taking $A = (1 - P_i - P_{\mathcal{H}'}) M_i$, 2.53 implies (as $A' \equiv (1 - P_A) LA = LM_i$)

$$\frac{d}{dt} \phi_{ii}(t, \vec{H}) = - \int_0^t \frac{(LM_i, e^{i(1-P_A)L(t-\tau)} LM_i)}{(M_i, M_i) - (1, M_i)^2 - (\mathcal{H}', M_i)^2 (\mathcal{H}', \mathcal{H}')^{-1}} \phi_{ii}(\tau, \vec{H}) d\tau \quad 3.11$$

and the relation between memory function and memory spectrum (2.64) reads in this

case

$$(LM_i, e^{i(1-P_A)Lt} LM_i) = \int_{-\infty}^{+\infty} e^{i\omega t} s_{LM_i LM_i}(\omega, \vec{H}) d\omega \quad 3.12$$

If $\phi_{ii}^R(t, \vec{H}) U(t)$ is square integrable, such that 1.18 holds, if no undamped oscillations (i.e. δ - and P -functions at $\omega \neq 0$) occur, such that $\phi_{ii}^R(t, \vec{H}) = \phi_{ii}(t, \vec{H})$ **) and if the

*) One could - at the cost of a non-unitary scalar product - choose the definition of Nakano²¹⁾ and Mori¹⁶⁾ for that and - in analogy to Terwiel and Mazur¹⁷⁾ - avoid the ergodicity condition forcing $\phi_{ij}(t, \vec{H})$ into the shape of 3.08 rightaway. The resulting increase of generality being of little practical interest, this method has not been followed here.

**) It is clear that the same argument cannot be given for $\phi_{ii}(t, \vec{H})$ instead of $\phi_{ii}^R(t, \vec{H})$, as $\phi_{ii}^R(t, \vec{H}) = \phi_{ii}(t, \vec{H})$ would demand $\bar{\phi}_{ii}(\vec{H}) = 0$.

Laplace transforms used exist, then 1.18, 1.48 and 2.55 imply that

$$l(i\omega)(A, A)^{-1} = \frac{\chi_{ii}(\omega, \vec{H}) - \chi_{ii}(0, \vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} (-i\omega)^{-1} \quad 3.12a$$

Inserting this into 2.70 one obtains for the memory spectrum

$$\pi s'_{LM_i, LM_i}(\omega, \vec{H})(A, A)^{-1} = \frac{\omega \chi''_{ii}(\omega, \vec{H})(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))}{(\chi'_{ii}(\omega, \vec{H}) - \chi'_{ii}(0, \vec{H}))^2 + (\chi''_{ii}(\omega, \vec{H}))^2} \quad 3.13$$

As $\beta \nu_{0AA} s(\omega) = S_{ii}(\omega, H) = \frac{\nu \chi''_{ii}(\omega, \vec{H})}{\pi \omega}$, 2.71 takes the form

$$\pi \int_{-\infty}^{+\infty} \omega^{2n+2} \chi''(\omega, \vec{H}) \omega^{-1} d\omega = \sum_{l=0}^n \int_{-\infty}^{+\infty} \pi s'_{LM_i, LM_i}(\omega, \vec{H})(A, A)^{-1} \omega^{2l} d\omega \int_{-\infty}^{+\infty} \omega^{2n-2l} \chi''_{ii}(\omega, \vec{H}) \omega^{-1} d\omega \quad 3.13a$$

Using 2.60 one gets ($\bar{\omega} = 0$)

$$\frac{\chi_{ii}(\omega, \vec{H}) - \chi_{ii}(0, \vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} (-i\omega)^{-1} = \frac{1}{i\omega + l'(i\omega)(A, A)^{-1}} \quad 3.14$$

which implies

$$\frac{\chi'_{ii}(\omega, \vec{H}) - \chi'_{ii}(0, \vec{H})}{-\omega(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))} = \frac{\omega + \text{Im } l'(i\omega)(A, A)^{-1}}{(\omega + \text{Im } l'(i\omega)(A, A)^{-1})^2 + (\text{Re } l'(i\omega)(A, A)^{-1})^2} \quad 3.15$$

and

$$\frac{\chi''_{ii}(\omega, \vec{H})}{\omega(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))} = \frac{\text{Re } l'(i\omega)(A, A)^{-1}}{(\omega + \text{Im } l'(i\omega)(A, A)^{-1})^2 + (\text{Re } l'(i\omega)(A, A)^{-1})^2} \quad 3.16$$

First example: resonance and single relaxation.

If an absorption spectrum is known to consist (approximately or within a certain frequency interval) of two Lorentz lines at center frequencies $\pm \omega_0$ with equal intensities $I_+ = I_- = \frac{\alpha}{2} (\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))\pi$ such that

$$\frac{\chi''_{ii}(\omega, \vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} = \frac{\alpha \omega \tau}{2} ((1 + (\omega - \omega_0)^2 \tau^2)^{-1} + (1 + (\omega + \omega_0)^2 \tau^2)^{-1}) \quad 3.17$$

and if the dispersion satisfies similarly the corresponding relation

$$\frac{\chi'_{ii}(\omega, \vec{H}) - \chi'_{ii}(0, \vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} = -\frac{\alpha \omega \tau}{2} ((\omega - \omega_0)_{\tau} (1 + (\omega - \omega_0)^2 \tau^2)^{-1} + (\omega + \omega_0)_{\tau} (1 + (\omega + \omega_0)^2 \tau^2)^{-1}) \quad 3.18$$

then the memory spectrum is given by

$$\pi s'_{LM_i, LM_i}(\omega, \vec{H})(A, A)^{-1} = \frac{1}{\alpha\tau} + \omega_0^2 \frac{\tau/\alpha}{1 + \omega^2\tau^2} \quad 3.19$$

If $\omega_0 = 0$ the two lines coincide and constitute a Debye line at $\omega = 0$ to which a frequency independent $s'_{LM_i, LM_i}(\omega, \vec{H})$ is seen to correspond. This holds within any interval around $\omega = 0$ in which absorption is purely Debye-like. Conversely, using 3.16 Mazur and Terwiel²⁸) have shown that a memory spectrum $s'_{LM_i, LM_i}(\omega, \vec{H})$, that is frequency independent in a large interval around $\omega = 0$ implies such a Debye line (in other words a single relaxation in the time domain).

Second example: double relaxation.

If an absorption spectrum is known to equal (within a frequency interval around $\omega = 0$) the sum of two Debye lines with relaxation times τ_1 and τ_2 and intensities $I_1 = \alpha(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))\pi, I_1/I_2 = \alpha/(1-\alpha)$ such that

$$\frac{\chi'_{ii}(\omega, \vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} = \alpha\omega\tau_1(1 + \omega^2\tau_1^2)^{-1} + (1 - \alpha)\omega\tau_2(1 + \omega^2\tau_2^2)^{-1} \quad 3.20$$

and if the dispersion similarly satisfies

$$\frac{\chi''_{ii}(\omega, \vec{H}) - \chi''_{ii}(0, \vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} = -\alpha\omega^2\tau_1^2(1 + \omega^2\tau_1^2)^{-1} - (1 - \alpha)\omega^2\tau_2^2(1 + \omega^2\tau_2^2)^{-1} \quad 3.21$$

then the memory spectrum is given by

$$\pi s'_{LM_i, LM_i}(\omega, \vec{H})(A, A)^{-1} = \frac{\alpha}{\tau_1} + \frac{1-\alpha}{\tau_2} - \alpha(1 - \alpha)\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right)^2 \frac{\tau}{1 + \omega^2\tau^2} \quad 3.22$$

where

$$1/\tau \equiv \frac{1-\alpha}{\tau_1} + \frac{\alpha}{\tau_2}$$

Like the resonance case the double relaxation is seen to give a Lorentz shaped contribution at $\omega = 0$ in the memory spectrum. Here however the contribution is negative.

3.4 The scalar product of some special operators.

$$(I, I) = 1 \quad 3.23$$

$$(DB, A) = (\text{Tr } e^{-\beta\mathcal{H}})^{-1} \text{Tr } e^{-\beta\mathcal{H}}(DB^\dagger)A = (I, (DB^\dagger)A) = (I, A(DB^\dagger)) \quad 3.24$$

$$(I, A) = (\text{Tr } e^{-\beta\mathcal{H}})^{-1} \text{Tr } e^{-\beta\mathcal{H}}A \quad 3.25$$

$$\langle \mathcal{K}, A \rangle = \langle 1, A \mathcal{K} \rangle = \langle 1, A \rangle \langle 1, \mathcal{K} \rangle + kT_b^2 \frac{\partial}{\partial T_b} \langle 1, A \rangle \quad 3.26$$

$$\lim_{\beta \rightarrow 0} \langle A, B \rangle = \text{Tr} A^\dagger B / \text{Tr} 1 \quad 3.27$$

$$\langle A, LB \rangle = \beta^{-1} \hbar^{-1} \langle 1, [A^\dagger, B] \rangle \quad 3.28$$

$$\langle A, A \rangle \leq \langle 1, \frac{AA^\dagger + A^\dagger A}{2} \rangle \quad 3.29$$

which may be combined with 2.80 to give a bound for $\langle A, e^{iL t B} \rangle$, or with 2.07 to yield Bogoliubov's inequality

$$\langle 1, \frac{AA^\dagger + A^\dagger A}{2} \rangle - \langle DA, DA \rangle \geq \frac{| \langle (1 - D)A, LB \rangle |^2}{\langle LB, LB \rangle} = \beta^{-1} \hbar^{-1} \frac{| \langle 1, [A^\dagger, B] \rangle |^2}{\langle 1, [-LB^\dagger, B] \rangle} \quad 3.30$$

3.5 Inversion of the static field.

For electromagnetic interactions the q - (place, angle) - representation $\mathcal{K}_q(\vec{H})$ of the hamiltonian $\mathcal{K}(\vec{H})$ obeys

$$\mathcal{K}_q(-\vec{H}) f(q) = (\mathcal{K}_q(\vec{H}) f^*(q))^* \quad 3.31$$

for any square integrable $f(q)$.

Let $A(\vec{H})$ be an observable, of which the operator in q -representation $A_q(\vec{H})$ obeys

$$A_q(-\vec{H}) f(q) = \alpha_A (A_q(\vec{H}) f^*(q))^* \quad 3.32$$

for similar $f(q)$.

It is shown in appendix G that if $B_q(\vec{H})$ satisfies a similar relation, the scalar product obeys

$$\langle A(\vec{H}), e^{iL(\vec{H})t} B(\vec{H}) \rangle = (\alpha_A A(-\vec{H}), e^{-iL(-\vec{H})t} \alpha_B B(-\vec{H}))^* \quad 3.33$$

$$\text{implying } \phi_{ij}(t, \vec{H}) = \phi_{ij}^*(-t, -\vec{H}) \quad 3.34$$

$$\text{and } \chi_{\infty ij}(\vec{H}) = \chi_{\infty ij}(\vec{H}) \quad 3.35$$

As the relations 3.31 and 3.32 are not independent of representation, this type of symmetry cannot be derived within the framework of chapter 2.

One implication of 3.34 is the invariance of $\chi_{11}(\omega, \vec{H})$ and all related expressions 3.12a to 3.22 with respect to inversion of the static field.

3.6 Symmetries.

The symmetries that have been found may be listed as follows

M operators hermitean (cf. 2.52)

$$\begin{aligned}
 \phi_{ij}(t, \vec{H}) &= \phi_{ij}^*(t, \vec{H}) & s_{ij}(\omega, \vec{H}) &= s_{ij}^*(-\omega, \vec{H}) \\
 \bar{\phi}_{ij}(\vec{H}) &= \bar{\phi}_{ij}^*(\vec{H}) & \bar{\phi}_{ij}(\vec{H})\delta(\omega) &= \bar{\phi}_{ij}^*(\vec{H})\delta(-\omega) \\
 \phi_{ij}(t, \vec{H}) &= \phi_{ij}^*(t, \vec{H}) & S_{ij}(\omega, \vec{H}) &= S_{ij}^*(-\omega, \vec{H}) \\
 \nu(\chi_{ij}(\omega, \vec{H}) - \chi_{\infty ij}(\vec{H})) &= \nu(\chi_{ij}(-\omega, \vec{H}) - \chi_{\infty ij}(\vec{H}))^* & \chi_{ij}(\omega, \vec{H}) &= \chi_{ij}^*(-\omega, \vec{H}) \\
 \chi_{\infty ij}(\vec{H}) &= \chi_{\infty ij}^*(\vec{H}) \text{ cf. 3.06}
 \end{aligned}$$

Correlation functions stationary (cf. 2.15, 2.35)

$$\begin{aligned}
 \phi_{ij}(t, \vec{H}) &= \phi_{ji}^*(-t, \vec{H}) = \phi_{ji}(-t, \vec{H}) & s_{ij}(\omega, \vec{H}) &= s_{ji}^*(\omega, \vec{H}) = s_{ji}(-\omega, \vec{H}) \\
 \bar{\phi}_{ij}(\vec{H}) &= \bar{\phi}_{ji}^*(\vec{H}) = \bar{\phi}_{ji}(\vec{H}) & \bar{\phi}_{ij}(\vec{H})\delta(\omega) &= \bar{\phi}_{ji}^*(\vec{H})\delta(\omega) = \bar{\phi}_{ji}(\vec{H})\delta(-\omega) \\
 \phi_{ij}(t, \vec{H}) &= \phi_{ji}^*(t, \vec{H}) = \phi_{ji}(t, \vec{H}) & S_{ij}(\omega, \vec{H}) &= S_{ji}^*(\omega, \vec{H}) = S_{ji}(-\omega, \vec{H})
 \end{aligned}$$

Inversion of the static field (cf. 3.34)

$$\begin{aligned}
 \phi_{ij}(t, \vec{H}) &= \phi_{ij}(-t, -\vec{H}) = \phi_{ji}(t, -\vec{H}) & s_{ij}(\omega, \vec{H}) &= s_{ij}(-\omega, -\vec{H}) = s_{ji}(\omega, -\vec{H}) \\
 \bar{\phi}_{ij}(\vec{H}) &= \bar{\phi}_{ij}(-\vec{H}) = \bar{\phi}_{ji}(-\vec{H}) & \bar{\phi}_{ij}(\vec{H})\delta(\omega) &= \bar{\phi}_{ij}(-\vec{H})\delta(-\omega) = \bar{\phi}_{ji}(-\vec{H})\delta(\omega) \\
 \phi_{ij}(t, \vec{H}) &= \phi_{ij}(-t, -\vec{H}) = \phi_{ji}(t, -\vec{H}) & S_{ij}(\omega, \vec{H}) &= S_{ij}(-\omega, -\vec{H}) = S_{ji}(\omega, -\vec{H}) \\
 \nu(\chi_{ij}(\omega, \vec{H}) - \chi_{\infty ij}(\vec{H})) &= \nu(\chi_{ji}(\omega, -\vec{H}) - \chi_{\infty ji}(-\vec{H})) & \chi_{ij}(\omega, \vec{H}) &= \chi_{ji}(\omega, -\vec{H}) \\
 \chi_{\infty ij}(\vec{H}) &= \chi_{\infty ij}(-\vec{H}) = \chi_{\infty ji}(-\vec{H}) \text{ cf. 3.35}
 \end{aligned}$$

Appendix F.

Using the standard method of quantum statistical mechanics one has - due to the Schrödinger equation - the following equation of motion for the time dependent density operator $\rho(t)$ (Schrödinger picture)

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar}[\mathcal{H}_t, \rho(t)], \quad \mathcal{H}_t \equiv \mathcal{H}(\vec{H} + \Delta\vec{H}(t)) \quad 3.36$$

If before the start of the measurement, at time t_p , a description by a stationary density operator is adequate

$$\rho(t < t_p) = \rho(t_p), \mathcal{K}_{t < t_p} = \mathcal{K}_{t_p} = \mathcal{K}(\vec{H}), [\mathcal{K}_{t_p}, \rho(t_p)] = 0 \quad 3.37$$

then $\rho(t)$ satisfies the identity

$$\rho(t) = \rho(t_p) - \frac{i}{\hbar} \int_{t_p}^t e^{-iL(t-\tau)} [\mathcal{K}_\tau - \mathcal{K}_{t_p}, \rho(\tau)] d\tau, LA \equiv \hbar^{-1} [\mathcal{K}_{t_p}, A] \quad 3.38$$

For the explicitly time dependent operator $M_i(\vec{H} + \Delta\vec{H}(t))$ the statistical average equals

$$\begin{aligned} & \text{Tr } M_i(\vec{H} + \Delta\vec{H}(t))\rho(t) = \\ & = \text{Tr } M_i(\vec{H} + \Delta\vec{H}(t))\rho(t_p) - \frac{i}{\hbar} \int_{t_p}^t \text{Tr } M_i(\vec{H} + \Delta\vec{H}(t)) e^{-iL(t-\tau)} [\mathcal{K}_\tau - \mathcal{K}_{t_p}, \rho(\tau)] d\tau = \\ & \approx \text{Tr } M_i(\vec{H})\rho(t_p) - \frac{1}{\mu_0} \text{Tr} \sum_j \left(\frac{\partial^2 \mathcal{K}(\vec{H})}{\partial H_i \partial H_j} + \frac{\partial^2 \mathcal{K}(\vec{H})}{\partial H_j \partial H_i} \right) \Delta\vec{H}_j(t) \rho(t_p) \\ & \quad - \frac{i}{\hbar} \int_{t_p}^t \text{Tr } M_i(\vec{H}) e^{-iL(t-\tau)} \sum_j -\mu_0 [M_j(\vec{H}), \rho(t_p)] \Delta\vec{H}_j(\tau) d\tau \quad 3.39 \end{aligned}$$

(linear approximation in $\Delta\vec{H}$). The first term is the average magnetization before the measurement, the second is the contribution to the magnetization variation from the non-linearity of $\mathcal{K}(\vec{H})$ (to be comprehended in $\overline{\chi_\infty}$) and the third term is the well-known Kubo response. For a canonical density operator (cf. section 4.7)

$$\rho(t_p) = (\text{Tr } e^{-\beta \mathcal{K}(t_p)})^{-1} e^{-\beta \mathcal{K}(t_p)} \quad 3.40$$

the expression 1.08, together with 3.05 and 3.06, is found after some algebra, where use is made of

$$\Delta M_i(t) \equiv \text{Tr } M_i(\vec{H} + \Delta\vec{H}(t))\rho(t) - \text{Tr } M_i(\vec{H})\rho(t_p) \quad 3.41$$

In order to derive 1.51 it is again convenient to use the statistical density operator method in the Schrödinger picture. The derivative of the statistical average for the explicitly time dependent operator $\mathcal{K}(\vec{H} + \Delta\vec{H}(t))$ equals

$$\begin{aligned} \frac{d}{dt} \text{Tr} \mathcal{K}(\vec{H} + \Delta\vec{H}(t))\rho(t) &= \text{Tr} \left(\sum_i \frac{\partial (\mathcal{K}(\vec{H}) + \Delta\mathcal{K}(\vec{H}))}{\partial H_i + \Delta H_i(t)} \frac{d\Delta H_i(t)}{dt} \right) \rho(t) + \text{Tr} \mathcal{K}(\vec{H} + \Delta\vec{H}(t)) \frac{d}{dt} \rho(t) = \\ &= -\mu_0 \text{Tr} \left(\sum_i M_i(\vec{H} + \Delta\vec{H}(t)) \Delta\dot{H}_i(t) \right) \rho(t) - \frac{i}{\hbar} \text{Tr} \mathcal{K}(\vec{H} + \Delta\vec{H}(t)) [\mathcal{K}(\vec{H} + \Delta\vec{H}(t)), \rho(t)] = \\ &= -\mu_0 \left(\sum_i \text{Tr } M_i(\vec{H} + \Delta\vec{H}(t))\rho(t) \right) \Delta\dot{H}_i(t) \quad 3.42 \end{aligned}$$

Integration yields, as $\Delta H_i(t_p) = \Delta H_i(t_f) = 0$, eq. 1.51

$$\begin{aligned} \Delta E &= \int_{t_p}^{t_f} \frac{d}{dt} \text{Tr} \mathcal{K}(\vec{H} + \Delta \vec{H}(t)) \rho(t) dt = -\mu_0 \int_{t_p}^{t_f} \sum_i \Delta M_i(t) \Delta \dot{H}_i(t) dt = -\mu_0 \sum_i \text{Tr} M_i(\vec{H}) \rho(t_p) \int_{t_p}^{t_f} \Delta \dot{H}_i(t) dt \\ &= -\mu_0 \int_{t_p}^{t_f} \Delta \vec{H}(t) \cdot \dot{\Delta \vec{H}}(t) dt . \end{aligned} \quad 1.51 \approx 3.43$$

Appendix G. Inversion of the static field.

For electromagnetic interactions the q-(place, angle)-representation $\mathcal{K}_q(\vec{H})$ of the hamiltonian $\mathcal{K}(\vec{H})$ obeys

$$\mathcal{K}_q(-\vec{H}) f(q) = (\mathcal{K}_q(\vec{H}) f^*(q))^* \quad 3.31$$

for any square integrable $f(q)$, this implies

$$\begin{aligned} M_{i,q}(-\vec{H}) f(q) &= -\frac{1}{\mu_0} \frac{\partial}{\partial h_i} \mathcal{K}_q(\vec{H}) \Big|_{\vec{h}=-\vec{H}} f(q) = \\ &= \frac{1}{\mu_0} \frac{\partial}{\partial h_i} \mathcal{K}_q(-\vec{H}) \Big|_{\vec{h}=\vec{H}} f(q) = \frac{1}{\mu_0} \frac{\partial}{\partial h_i} (\mathcal{K}_q(\vec{H}) f^*(q))^* \Big|_{\vec{h}=\vec{H}} = -(M_{i,q}(\vec{H}) f^*(q))^* \end{aligned} \quad 3.44$$

and

$$\begin{aligned} \frac{\partial^2 \mathcal{K}_q(\vec{H})}{\partial h_i \partial h_j} \Big|_{\vec{h}=-\vec{H}} f(q) &= \frac{\partial^2 \mathcal{K}_q(-\vec{H})}{\partial h_i \partial h_j} \Big|_{\vec{h}=\vec{H}} f(q) = \\ &= \frac{\partial^2}{\partial h_i \partial h_j} (\mathcal{K}_q(\vec{H}) f^*(q))^* \Big|_{\vec{h}=\vec{H}} = \left(\frac{\partial^2 \mathcal{K}_q(\vec{H})}{\partial h_i \partial h_j} \Big|_{\vec{h}=\vec{H}} f^*(q) \right)^* . \end{aligned} \quad 3.45$$

Let $\psi(q;t)$ denote the q-representation of a state vector $\Psi(t)$ which under the hamiltonian $\mathcal{K}(\vec{H})$ evolves according to

$$\frac{\partial}{\partial t} \psi(t) = -\frac{i}{\hbar} \mathcal{K}(\vec{H}) \psi(t) \Rightarrow \frac{\partial}{\partial t} \psi(q;t) = -\frac{i}{\hbar} \mathcal{K}_q(\vec{H}) \psi(q;t) \quad 3.46$$

then

$$\frac{\partial}{\partial t} \psi^*(q;t) = \frac{i}{\hbar} (\mathcal{K}_q(\vec{H}) \psi(q;t))^* \Rightarrow \frac{\partial}{\partial t} \psi^*(q;-t) = -\frac{i}{\hbar} \mathcal{K}_q(-\vec{H}) \psi^*(q;-t) \quad 3.47$$

Apparently $\psi^*(q;-t)$ is the q-representation of some state vector $\phi(t)$, which under $\mathcal{K}(-\vec{H})$ evolves according to

$$\frac{\partial}{\partial t} \phi(t) = -\frac{i}{\hbar} \mathcal{K}(-\vec{H}) \phi(t) \quad 3.48$$

In this way every $\Psi(t)$ has its counterpart $\Phi(t)$. This relation constitutes ^{an anti-}linear mapping of $\{\Psi(t)\}$ on $\{\Phi(t)\}$ often called the antilinear unitary operator of time reversal, K : $K\Psi(t) = \Phi(t)$.

It should be noted that this operator K is as tightly bound to q -representation as is 3.32 on which it is based. Starting from different representations corresponding, different types of time reversal may be constructed which may differ from one's "common sense" notion of time reversal which is based on q -representation. Therefore it is suggested that more stress could be given to the particularity of the K -operator e.g. by fixing an index: K_q . Here the K -operator will not be used at all.

Let $A(\vec{H})$ be an observable, of which the operator in q -representation $A_q(\vec{H})$ obeys

$$A_q(-\vec{H})f(q) = \alpha_A (A_q(\vec{H})f^*(q))^* \quad 3.32$$

for any square integrable $f(q)$. The expectation value of such an observable in the field \vec{H} , for the state $\Psi(t)$ equals

$$\langle \Psi(t) | A(\vec{H}) | \Psi(t) \rangle = \int \Psi^*(q;t) A_q(\vec{H}) \Psi(q;t) dq \quad 3.49$$

In the field $-\vec{H}$, and in the state $\Phi(t)$ this is

$$\begin{aligned} \langle \Phi(t) | A(-\vec{H}) | \Phi(t) \rangle &= \int \Psi(q;-t) A_q(-\vec{H}) \Psi^*(q;-t) dq \\ &= \int \Psi^*(q;-t) \alpha_A A_q(\vec{H}) \Psi(q;-t) dq^* \\ &= \langle \Psi(-t) | \alpha_A A(\vec{H}) | \Psi(-t) \rangle^* \end{aligned} \quad 3.50$$

The scalar product definition 3.07 may be given in the form

$$\begin{aligned} (A, e^{iL(\vec{H})t} B) &= (\beta \sum_n \langle n | e^{-\beta \mathcal{H}(\vec{H})} | n \rangle)^{-1} \int_0^\beta \sum_{k, l, m, n} \langle k | e^{-(\beta-\lambda)\mathcal{H}(\vec{H})} | l \rangle \\ &\langle l | A^\dagger | m \rangle \langle m | e^{-\lambda \mathcal{H}(\vec{H})} | n \rangle \langle n | e^{i\mathcal{H}(\vec{H})t/\hbar} B e^{-i\mathcal{H}(\vec{H})t/\hbar} | k \rangle d\lambda \end{aligned} \quad 3.51$$

where $\{|n\rangle\}$ is some basis in the Hilbert space of state vectors. A set of energy eigenvectors may be chosen as a basis. Let $\Psi_n(t)$ be the n 'th eigenvector of $\mathcal{H}(\vec{H})$ and E_n the corresponding eigenvalue, and let there be no degeneracy. Then the set $\{\Psi_n(0)\}$ is such a basis and

$$\begin{aligned} (A, e^{iL(\vec{H})t} B) &= \\ &= (\beta \sum_n e^{-\beta E_n})^{-1} \int_0^\beta \sum_{k, m} e^{-(\beta-\lambda)E_k} \langle \Psi_k(0) | A^\dagger | \Psi_m(0) \rangle e^{-\lambda E_m} \\ &\langle \Psi_m(0) | e^{i\mathcal{H}(\vec{H})t/\hbar} B e^{-i\mathcal{H}(\vec{H})t/\hbar} | \Psi_k(0) \rangle d\lambda. \end{aligned} \quad 3.52$$

The last factor in the integrand equals $\langle \psi_m(t) | B | \psi_k(t) \rangle$.

For the opposite field direction the hamiltonian is $\mathcal{H}(-\vec{H})$ having a different set of eigenvectors. As $\mathcal{H}(\vec{H})\psi_n(t) = E_n\psi_n(t) \Rightarrow \mathcal{H}_q(\vec{H})\psi_n(q;t) = E_n\psi_n(q;t) \Rightarrow \mathcal{H}_q(-\vec{H})\psi_n^*(q;t) = E_n^*\psi_n^*(q;t)$ (\mathcal{H}_q does not interfere with the t-dependence of $\psi(q;t)$) $\Rightarrow \mathcal{H}_q(-\vec{H})\psi_n^*(q;-t) = E_n^*\psi_n^*(q;-t) \Rightarrow \mathcal{H}(-\vec{H})\phi_n(t) = E_n^*\phi_n(t)$, the counterpart $\phi_n(t)$ of $\psi_n(t)$ is seen to be an eigenvector of $\mathcal{H}(-\vec{H})$ with eigenvalue E_n^* . If there is no degeneracy the set of counterparts is a complete set of eigenvectors and $\{\phi_n(0)\}$ is a basis. Thus not only

$$(A(\vec{H}), e^{iL(\vec{H})t} B(\vec{H})) = (\beta \sum_n e^{-\beta E_n})^{-1} \sum_{k,m} \int_0^\beta e^{-(\beta-\lambda)E_k} \langle \psi_k(0) | A^\dagger(\vec{H}) | \psi_m(0) \rangle e^{-\lambda E_m} \langle \psi_m(t) | B(\vec{H}) | \psi_k(t) \rangle d\lambda \quad 3.53$$

but also

$$(A(-\vec{H}), e^{iL(-\vec{H})t} B(-\vec{H})) = (\beta \sum_n e^{-\beta E_n^*})^{-1} \sum_{k,m} \int_0^\beta e^{-(\beta-\lambda)E_k^*} \langle \phi_k(0) | A^\dagger(-\vec{H}) | \phi_m(0) \rangle e^{-\lambda E_m^*} \langle \phi_m(t) | B(-\vec{H}) | \phi_k(t) \rangle d\lambda \quad 3.54$$

If $A(\vec{H})$ and $B(\vec{H})$ obey 3.32, one gets for the scalar product the relation

$$(A(\vec{H}), e^{iL(\vec{H})t} B(\vec{H})) = (\alpha_A A(-\vec{H}), e^{-iL(-\vec{H})t} \alpha_B B(-\vec{H}))^* \quad 3.33$$

and especially for the magnetization operators ($\alpha_{M_i} = \alpha_{M_j} = -1$, cf. 3.44)

$$(M_j(\vec{H}), e^{iL(\vec{H})t} M_i(\vec{H})) = (M_j(-\vec{H}), e^{-iL(-\vec{H})t} M_i(-\vec{H}))^* \quad 3.55$$

implying

$$\phi_{ij}(t, \vec{H}) = \phi_{ij}^*(-t, -\vec{H}) \quad 3.34$$

As the relations 3.31 and 3.32 are not independent of representation, this type of symmetry cannot be derived within the framework of chapter 2. Analogously one derives (as $\alpha_1 = \alpha_{\partial^2 \mathcal{H}} = 1$, cf. 3.45)

$$v_{\chi_{\infty ij}}(\vec{H}) = -\frac{1}{\mu_0} (1, \partial^2 \mathcal{H}(\vec{H})) = -\frac{1}{\mu_0} (\alpha_1, \alpha_{\partial^2 \mathcal{H}} \partial^2 \mathcal{H}(-\vec{H})) = v_{\chi_{\infty ij}}(-\vec{H}) \quad 3.35$$

with

$$\partial^2 \mathcal{H}(\vec{H}) \equiv \frac{\partial^2 \mathcal{H}(\vec{h})}{\partial h_i \partial h_j} \Big|_{\vec{h}=\vec{H}} + \frac{\partial^2 \mathcal{H}(\vec{h})}{\partial h_j \partial h_i} \Big|_{\vec{h}=-\vec{H}} \quad .$$

Re ipsa autem cum ad idem, unde semel profecta sunt, cuncta astra redierint eandemque totius caeli descriptionem longis intervallis rettulerint, tum ille vere vertens annus appellari potest.

M.T. Cicero. *De Re Publica*, VII, 16 (*Somnium Scipionis*), Rome, - 53. An early appearance of the Poincaré cycle.

(In fact, however, when all stars will have returned to the same position, from which they once started, and will have restored the state of the whole heaven in long time intervals, then that can be really called a year going by).

CHAPTER 4

STATIC SUSCEPTIBILITY

In absence of a varying contribution to the magnetic field the hamiltonian of the system is not explicitly time dependent and in the limit of an infinite system a large set of theoretical tools becomes available: the concept of ergodicity, of system temperature and the theory of equilibrium thermodynamics including specific heat, adiabatic and isothermal susceptibility etc..

4.1. Ergodicity.

An observable A is said to be an ergodic observable of the system, if, for almost every initial state, the time average of the expectation value of A is very near the expectation value of A averaged over the set of energy eigenstates with eigenvalues near the energy expectation value E of the initial state. Such a set is called a microcanonical ensemble, the average over this set is notated as $\langle A \rangle_E$.

4.2. Time average of the autocorrelation function of an ergodic observable.

Mazur²⁰⁾ has shown, that the time average of the autocorrelation function of an ergodic variable A satisfies

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt} A) dt = (P_1 A, P_1 A) + ({}^m A, {}^m A) \quad 4.01$$

with

$${}^m A_{\alpha\beta} \equiv \delta_{\alpha\beta} \langle (1 - P_1) A \rangle_{E_\alpha}, \quad E_\alpha \equiv \mathcal{H}_{\alpha\alpha} \quad 4.02$$

in a representation which diagonalizes \mathcal{H} ; for reasons of simple notation both observable and operator are designated with A . According to Tjon²²⁾ and Mazur²⁰⁾

one moreover has

$$(\overset{m}{A}, \overset{m}{A}) = (P_{\mathcal{H}^1, A}, P_{\mathcal{H}^1, A}) \quad 4.03$$

These relations hold for sufficiently large systems and under conditions, which, at least if one excepts phase transition points, are believed to be fulfilled in the underlying situations ²⁰⁾. Combination of 4.01 and 4.03 shows an ergodic observable A to satisfy 2.85. If ^{one of} the observables A and B ^{is} ~~are~~ both ergodic, their operators obey

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T (A, e^{iLt} B) dt = (P_I A, P_I B) + (P_{\mathcal{H}^1, A}, P_{\mathcal{H}^1, B}) \quad 2.90$$

Thus if M_i and M_j are ergodic observables of the system without field variations, the zero frequency susceptibility as measured through a very slow field variation (isolated susceptibility) equals (cf. 1.45)

$$\chi_{ij}(0, \vec{H}) = \chi_{\infty ij}(\vec{H}) + \frac{\beta \mu_0}{v} \{ (M_j, M_i) - (P_I M_j, P_I M_i) - (P_{\mathcal{H}^1, M_j}, P_{\mathcal{H}^1, M_i}) \} \quad 4.04$$

an expression to be called adiabatic susceptibility (cf. 4.4).

4.3 Canonical ensemble.

When all relevant observables of a system are ergodic the system may be called ergodic and microcanonical averages may replace time averages throughout. Using standard arguments the microcanonical ensemble on its turn can - in the limit of an infinite system - be replaced by a canonical ensemble, i.e. a set of states, which yields the same average expectation values as does a set of energy eigenstates when weighed by the Boltzmann distribution function for a certain temperature T_b . The description by a canonical ensemble was used by Wilcox ⁷⁾ to derive expressions for the adiabatic and isothermal static susceptibility.

4.4 Adiabatic susceptibility.

In thermodynamics the adiabatic susceptibility of a system is defined as the derivative of (the expression for the canonically averaged expectation value of) the magnetization, under the condition that the average energy interchange between the system and the bath to which it is coupled be zero. According to this definition Wilcox ⁷⁾ has derived an expression which after correction for diamagnetism ³⁾ may be written as

$$\chi_{\text{adij}}(\vec{H}) = \chi_{\infty ij}(\vec{H}) + \frac{\beta \mu_0}{v} \{ (M_j, M_i) - (P_j M_j, P_i M_i) - (P_{jC} M_j, P_{iC} M_i) \} \quad 4.05$$

One might wonder if such an approach in which time plays no role is so realistic as to describe an actual experiment in which the field variation however slow is essentially a function of time. But comparing 4.05 with 4.04 it becomes clear that there is no reason for such doubt: the adiabatic susceptibility is seen to equal the zero frequency susceptibility found in 4.2 for a system in very weak (cf. 4.7) contact with a bath (isolated s.) in case M_j and M_i are ergodic (cf. 4.04). If M_j and M_i are non-ergodic or if the system is too small, no such experimental interpretation of 4.05 can be given. Still 4.05 keeps a formal validity and the expression keeps the name "adiabatic susceptibility". Mazur has pointed out that a discrepancy between this formal adiabatic s. and the isolated s. proves the non-ergodicity of the magnetization in the system - provided that it is large and not in a phase transition.

4.5 Isothermal susceptibility.

In thermodynamics the isothermal susceptibility is defined in a way similar to the adiabatic one i.e. as a field derivative of the average magnetization, but under the condition of constant temperature. Again one may ask for the experimental situation in which the quantity can be measured. The isothermal s. may be written as

$$\chi_{0ij}(\vec{H}) = \chi_{\infty ij}(\vec{H}) + \frac{\beta \mu_0}{v} \{ (M_j, M_i) - (P_j M_j, P_i M_i) \} \quad 4.06$$

an expression in terms of the scalar product 3.07 and corresponding projection operators, which contain only the system hamiltonian (in absence of field variations). Although in any measuring situation the condition of constant temperature implies that the system has a good contact with a thermostat, the hamiltonian of the latter or the interaction, do not appear explicitly in 4.06; the only parameter in 4.06 pertaining to the thermostat is the temperature T_b . This is inherent to the canonical description.

It is instructive to see, how 4.06 can be derived from 4.04. Consider the system, interaction and thermostat as a new system, which may also be supposed ergodic. It makes no difference to assume the new system in very weak contact with a bath of the same temperature as the thermostat. Therefore 4.04 holds for the new system, but M_j, M_i , the scalar product and the projection operators now belong to the new system. If the extra terms in the hamiltonian are field independent, 3.01 and 3.06 yield essentially the same magnetization operators and χ_{∞} -tensor as for the original system such that (M_j, M_i) and $(P_j M_j, P_i M_i)$ stay practically unaltered. The character of

$P_{\mathcal{K}'}^i$ shows an important change: the new \mathcal{K}' contains a contribution from the big non-magnetic thermostat. Therefore $P_{\mathcal{K}'}^i M_i$ is expected to be very small and 4.04 for the new system implies 4.06 for the original one. Indeed the isothermal susceptibility of a system equals a measurable quantity: its zero-frequency susceptibility if it is strongly coupled to a non-magnetic thermostat. Again even when this experimental interpretation cannot be given, 4.06 keeps its formal validity and the expression keeps the name "isothermal susceptibility".

4.6 Specific heats.

The canonical description used in the definitions of $\overline{\chi}_{ad}(\vec{H})$ and $\overline{\chi}_O(\vec{H})$ can be identified with equilibrium thermodynamics. Using this older language the difference between $\chi_{O_{ii}}(\vec{H})$ and $\chi_{ad_{ii}}(\vec{H})$ can be expressed in terms of the specific heats $C_{H,i}$ and $C_{M,i}$

$$(\chi_{O_{ii}}(\vec{H}) - \chi_{ad_{ii}}(\vec{H})) / \chi_{O_{ii}}(\vec{H}) = (C_{H,i} - C_{M,i}) / C_{H,i} \quad 4.07$$

where $C_{H,i}(C_{M,i})$ is the specific heat at constant field (magnetization) and constant magnetization- (field-) components in other directions than i . The extension with a non-magnetic thermostat as used in 4.5 does not affect the numerator while enhancing the denominator, which illustrates the relative weakness of the $P_{\mathcal{K}'}^i M_i$ contribution in another way.

4.7 The canonical average in the Kubo formalism.

Kubo ²⁾ justifies his use of canonical averages in the derivation of 3.05 through the assumption that the actual system may be divided into a great number of identical systems, which develop independently in time and are sufficiently large on their own, and that - before starting the measurement - this set of systems constitutes a realistic canonical ensemble. (This explains the Boltzmann-like factors in 3.05.) To this end the system was assumed to have a very weak contact with a bath of temperature T_b . Very weak means thus that the contact is good enough to warrant the Boltzmann distribution at the start of the measurement. It should however be so weak that it may be neglected in the description of the measurement. The expression 3.05 describes the time dependence of the measured magnetization in presence of time dependent field variations, whereas the canonical ensemble averages introduced in 4.3 essentially stand for time averages in absence of such field variations.

Obviously Kubo's justification does not rest on ergodicity of observables (in the course of the measurement, when the coupling to the bath is neglected) and in this

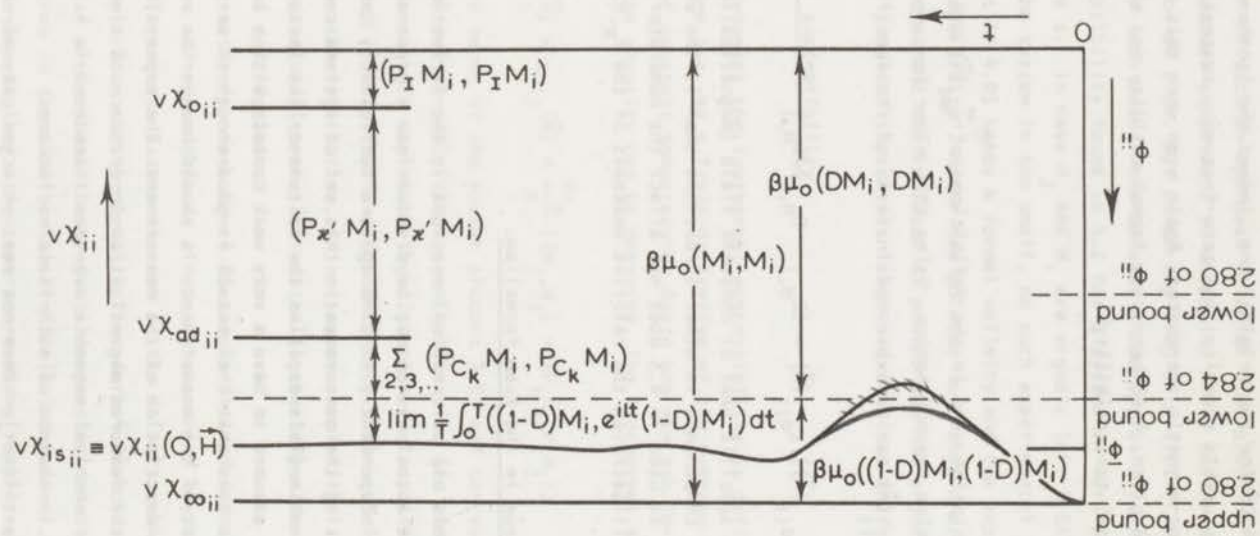


Fig. 4.01 Diagonal elements of static susceptibilities and bounds for $\phi_{ii}(t, \vec{H})$.

sense non-ergodic observables can be handled. The following argument does give a justification based on ergodicity. The experimental fact, that measuring results are - within the accuracy asked from the description - independent from the time at which the measurement is started, implies that a theory describing an average over starting times would be sufficient. But the states in which the systems would be at those starting times are the states through which the system evolves when not starting the measurement at all, that is the set of states involved in taking a time average in absence of field variations. Indeed it was seen, that this set can be replaced by a canonical ensemble as far as averages over ergodic observables are concerned. However, the observable wanted ergodic here is not just magnetization but magnetization at a certain time after having started the measurement (in presence of a time dependent field). Though a formal unification has thus been achieved, Kubo's argument has a more general validity and is based on less complicated assumptions.

4.8 Extremely high temperature.

In the limit of infinite temperature ($\beta \rightarrow 0$) the term $(P_I M_j, P_I M_i)$ vanishes, if in the same limit the canonical average of energy $(1, \mathcal{K})$ (cf. 3.11) is independent of the field (i.e. if $\frac{\partial}{\partial H_i} \lim_{\beta \rightarrow 0} (1, \mathcal{K}) = \frac{\partial}{\partial H_i} \text{Tr } \mathcal{K} / \text{Tr } 1 = 0$)

$$\begin{aligned} \lim_{\beta \rightarrow 0} (P_I M_j, P_I M_i) &= (\text{Tr } 1)^{-2} \text{Tr } M_j \text{Tr } M_i = (\text{Tr } 1)^{-2} \text{Tr } \frac{\partial \mathcal{K}}{\partial H_j} \text{Tr } \frac{\partial \mathcal{K}}{\partial H_i} = \\ &= \left(\frac{\partial}{\partial H_j} \frac{\text{Tr } \mathcal{K}}{\text{Tr } 1} \right) \left(\frac{\partial}{\partial H_i} \frac{\text{Tr } \mathcal{K}}{\text{Tr } 1} \right) = \left(\frac{\partial}{\partial H_j} \lim_{\beta \rightarrow 0} (1, \mathcal{K}) \right) \left(\frac{\partial}{\partial H_i} \lim_{\beta \rightarrow 0} (1, \mathcal{K}) \right) = 0. \end{aligned} \quad 4.08$$

4.9 Short survey of static susceptibilities.

Equality 1.45 states

$$\overline{\chi}_{ij}(\vec{H}) \equiv \overline{\chi}(0, \vec{H}) = \overline{\chi}_{\infty}(\vec{H}) + v^{-1} \overline{\phi}(0, \vec{H}) = \overline{\chi}_{\infty}(\vec{H}) + v^{-1} (\overline{\phi}(0, \vec{H}) - \overline{\phi}(\vec{H})) \quad . \quad 1.45$$

According to 2.82

$$\begin{aligned} \beta^{-1} \mu_0^{-1} \overline{\phi}_{ij}(\vec{H}) &= (P_I M_j, P_I M_i) + (P_{\mathcal{K}'} M_j, P_{\mathcal{K}'} M_i) + \sum_{k=2,3,\dots}^{\infty} (P_{C_k} M_j, P_{C_k} M_i) + \\ &+ \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T ((1-D) M_j, e^{iLt} (1-D) M_i) dt \quad . \quad 4.09 \end{aligned}$$

Insertion into 1.45 and comparison with the various definitions given in the sections 4.4 and 4.5 yields

$$\begin{aligned}
 \chi_{is_{ij}}(\vec{H}) &\equiv \chi_{ij}(0, \vec{H}) = \underbrace{\chi_{\infty ij}(\vec{H}) + \beta \mu_0 v^{-1} \{ (M_j, M_i) - (P_1 M_j, P_1 M_i) - (P_{\mathcal{K}'} M_j, P_{\mathcal{K}'} M_i) \}}_{= \chi_{0ij}(\vec{H})} \\
 &= \underbrace{\chi_{ad ij}(\vec{H})}_{= \chi_{ad ij}(\vec{H})} \\
 &- \sum_{k=2,3,\dots} (P_{C_k} M_j, P_{C_k} M_i) - \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T ((1-D)M_j, e^{iLt}(1-D)M_i) dt. \quad 4.10
 \end{aligned}$$

About this sum the following remarks can be made

- $\chi_{\infty}(\vec{H}) = 0$, if \mathcal{K} is linearly dependent on \vec{H} .
- $(P_1 M_j, P_1 M_i) = 0$, if the temperature is extremely high.
- $(P_{\mathcal{K}'} M_j, P_{\mathcal{K}'} M_i) = 0$, if the system contains a thermostat.

Last "two" terms = 0, if the system is not in a phase transition and the magnetization components are ergodic observables of the system.

Last term = 0, if the Hilbert space of state vectors has a finite dimension.

Finally some inequalities for the diagonal tensor elements will be given.

Due to 2.30 and 2.42 one has the relation

$$0 \leq \bar{\phi}_{ii}(\vec{H}) \leq \phi_{ii}(0, \vec{H}) \quad 4.11$$

from which (cf. 1.45)

$$\chi_{is_{ii}}(\vec{H}) \equiv \chi_{ii}(0, \vec{H}) \geq \chi_{\infty ii}(\vec{H}) \quad 4.12$$

Furthermore, for $i = j$, all terms in the right hand side of 4.09 are non-negative; therefore one gets (also using 4.12) the inequality

$$\chi_{0ii}(\vec{H}) \geq \chi_{ad ii}(\vec{H}) \geq \chi_{is_{ii}}(\vec{H}) \geq \chi_{\infty ii}(\vec{H}) \quad 4.13$$

This is valid for any choice of the xyz-frame. The differences between the various tensors are thus positive non-definite tensors. The inequality 4.13 is illustrated in figure 4.01, where also the bounds and values of $\phi_{ii}(\vec{H}, t)$ and $\bar{\phi}_{ii}(\vec{H})$ are indicated, together with a possible specimen of $\phi_{ii}(\vec{H}, t)$ vs. t (to be read upside down).

Appendix H. Illustration to the proof of $\chi_{adj} = \chi_{isij}$ for an ergodic system.

Here an illustration will be given to the proof of $\chi_{adj} = \chi_{isij}$. This equality the proof of which in 4.2 was based directly on the perhaps rather abstract concept of ergodicity, will here be made plausible by an argument depending on ergodicity in the more common way through canonical statistics and thermodynamics.

The invariant operators.

Let the system, just for this illustration, be large but finite and have a discrete spectrum of L , non-degenerate, energy levels. Any operator D , which is invariant in time (commuting with \mathcal{H} ; diagonal in \mathcal{H} -representation, a meaningful concept here) then is a linear combination of powers of \mathcal{H}

$$D = \sum_{k=0}^{L-1} a_k \mathcal{H}^k \quad \text{with } \mathcal{H}^0 \equiv 1 \quad . \quad 4.14$$

One might call the set $\{\mathcal{H}^k\}$ a basis in the subspace of invariant operators. In section 2.7 use has been made of an orthogonal basis of hermitean operators in this subspace. By means of Schmidt's orthogonalization process such a basis is easily acquired here

$$C_0 \equiv 1, C_1 \equiv \mathcal{H} - (1 - P_1)\mathcal{H}, C_k = \mathcal{H}^k - \sum_{\kappa=0}^{k-1} P_{C_\kappa} \mathcal{H}^k \quad . \quad 4.15$$

The difference between χ_{adj} and χ_{isij} was seen to be

$$\chi_{adj}(\vec{H}) - \chi_{isij}(\vec{H}) = \frac{\mu_0 \beta}{v} \sum_{k=2}^{L-1} (P_{C_k} M_j, P_{C_k} M_i) + \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \frac{\mu_0 \beta}{v} ((1-D)M_j, e^{iLt}(1-D)M_i) dt \quad . \quad 4.16$$

According to Wilcox the last term vanishes under the circumstances assumed above. Furthermore

$$\chi_{oij}(\vec{H}) - \chi_{adj}(\vec{H}) = \frac{\mu_0 \beta}{v} (P_{\mathcal{H}'} M_j, P_{\mathcal{H}'} M_i) \quad . \quad 4.17$$

Translation into equilibrium quantities.

The illustration consists of an explicit translation of the first terms of 4.09 into (optionally thermodynamical) quantities of the system in canonical equilibrium, from which their order of magnitude may be estimated. The system has already been assumed to be sufficiently large, in which large means: consisting of a large number (N) of interacting subsystems. If the system is also able to, and indeed does, develop in time through a series of states, such that the time averages of relevant observables are equal to the corresponding canonical ensemble averages, - no matter

how this has been achieved*) - equilibrium thermodynamics are expected to apply **). In that case the value a , measured - without disturbing the canonical equilibrium - for a quantity A , is predicted to be

$$a = \frac{\text{Tr } e^{-\beta \mathcal{C}} A}{\text{Tr } e^{-\beta \mathcal{C}}} = (1, A) \quad 4.18$$

Thus

$$m_i \equiv (1, M_i) \quad 4.19$$

$$u \equiv (1, \mathcal{C}) \quad 4.20$$

and

$$(1, \mathcal{C}) = (1, A)(1, \mathcal{C}) + kT_b^2 \frac{\partial}{\partial T} (1, A) \quad 3.26$$

Introducing the abbreviation

$$\dot{a} \equiv k^{-1} \frac{\partial a}{\partial T} \quad 4.21$$

one may now write

$$(P_{1M_j}, P_{1M_i}) = \dot{m}_i \dot{m}_j \quad 4.22$$

$$(P_{\mathcal{C}M_j}, P_{\mathcal{C}M_i}) = \frac{\dot{m}_i \dot{m}_j}{\beta^2 \dot{u}} \quad 4.23$$

$$(P_{C_2 M_j}, P_{C_2 M_i}) = \frac{(\dot{m}_i \dot{u} - \dot{m}_i \ddot{u})(\dot{m}_j \dot{u} - \dot{m}_j \ddot{u})}{2\beta^4 (\dot{u})^4 + \beta^2 \ddot{u} (\dot{u})^2 + 2\beta^3 \ddot{u} (\dot{u})^2 + 2\beta^4 (\dot{u})^3 - \beta^2 (\ddot{u})^2 \dot{u}} \quad 4.24$$

From thermodynamics one knows m_i, m_j and u together with their temperature derivatives to be extensive parameters, that is to be of the order N (all in the limit of very large N). In this way

$$(P_{1M_j}, P_{1M_i}) = \dot{m}_i \dot{m}_j \sim N^2 \quad 4.25$$

$$(P_{\mathcal{C}M_j}, P_{\mathcal{C}M_i}) = \frac{\dot{m}_i \dot{m}_j}{\beta^2 \dot{u}} \sim N^1 \quad 4.26$$

*) It is not necessary that the system automatically acquires such a type of time development after a very long time or in other words "tends to equilibrium".

***) In section 4.2 only the M_i have been assumed ergodic. This is more subtle than to suppose the system (i.e. all relevant observables) to be ergodic, which warrants the existence of such a time development.

Retaining terms of highest order in N one may further approximate

$$(P_{C_2 M_j}, P_{C_2 M_i}) \approx \frac{(\ddot{m}_i \dot{u} - \dot{m}_i \ddot{u})(\ddot{m}_j \dot{u} - \dot{m}_j \ddot{u})}{2\beta^4 (\dot{u})^4} \sim N^0 \quad 4.27$$

$$(P_{C_3 M_j}, P_{C_3 M_i}) \approx \frac{(\ddot{m}_i (\dot{u})^2 - 3\dot{m}_i \ddot{u} \dot{u} - 3\dot{m}_i (\ddot{u})^2 - \dot{m}_i \dot{u} \ddot{u}) (\text{idem for } j)}{6\beta^6 (\dot{u})^7} \sim N^{-1} \quad 4.28$$

Though higher terms have not been checked, it is tempting to approximate

$$\begin{aligned} x_{adij}(\ddot{H}) - x_{isij}(\ddot{H}) &= \mu_0 \beta v^{-1} \sum_{k=2}^{Z-1} (P_{C_k M_j}, P_{C_k M_i}) = \mu_0 \beta v^{-1} (P_{C_2 M_j}, P_{C_2 M_i}) \ll \\ &\ll \mu_0 \beta v^{-1} (P_{\mathcal{H} C M_j}, P_{\mathcal{H} C M_i}) = x_{oij}(\ddot{H}) - x_{adij}(\ddot{H}) \end{aligned} \quad 4.29$$

Conversely Caspers et al. ²³⁾ have made an analysis of expansion 4.16 in order to study ergodicity in systems, of which the hamiltonian shows a certain type of structure encountered in most models and realistic systems.

Link with thermodynamics for $i = j$.

The equality

$$\mu_0 \beta v^{-1} (P_{\mathcal{H} C M_i}, P_{\mathcal{H} C M_i}) = x_{oii}(\ddot{H}) - x_{adii}(\ddot{H}) = \frac{C_{H,i} - C_{M,i}}{C_{H,i}} x_{oii}(\ddot{H}) \quad 4.30$$

was already discussed in 4.6. The next term may be written as

$$\begin{aligned} \mu_0 \beta v^{-1} (P_{C_2 M_i}, P_{C_2 M_i}) &= \frac{1}{2\beta} \left\{ T_b \frac{\partial}{\partial T_b} \left(\frac{C_{H,i} - C_{M,i}}{T_b C_{H,i}^2} x_{oii}(\ddot{H}) \right)^2 \right. \\ &\quad \left. \left[1 + \frac{k}{C_{H,i}} + \frac{k}{2C_{H,i}} \frac{\partial}{\partial T_b} \left(\frac{T_b^2}{C_{H,i}} \frac{\partial C_{H,i}}{\partial T_b} \right) \right]^{-1} \right\} \end{aligned} \quad 4.31$$

such that in the same approximation as in 4.29

$$x_{adii}(\ddot{H}) - x_{isii}(\ddot{H}) = \frac{1}{2\beta} \left\{ T_b \frac{\partial}{\partial T_b} \left(\frac{C_{H,i} - C_{M,i}}{T_b C_{H,i}^2} x_{oii}(\ddot{H}) \right)^2 \right\} \quad 4.32$$

which indicates that difficulties may arise if strong temperature dependences occur in specific heat, as may be the case at phase transition points, where the argument of 4.2 may not apply. Even if the approximation in 4.29 and 4.32 is not valid, the expression 4.31 constitutes a lower bound for $x_{adii}(\ddot{H}) - x_{isii}(\ddot{H})$.

Conclusion.

In a system with non-degenerate energy levels one has for large N, at least if one excepts phase transition points

$$\chi_{ad_{ii}}(\vec{H}) = \chi_{is_{ii}}(\vec{H})$$

4.04

if the system can be in canonical equilibrium (there may be ergodicity to warrant this). It should be emphasized that, although the difference between $\chi_{ad_{ii}}(\vec{H})$ and $\chi_{is_{ii}}(\vec{H})$ has been expressed in terms of the system in canonical equilibrium, this does not imply that $\chi_{is_{ii}}(\vec{H})$ can be directly measured in that state.

Energy and Work, in the old English meaning, are things not unfamiliar to me. But I have only the dimmest views of the modern meanings attached to those terms.

W.R. Hamilton writing to P.G. Tait, 1862.

CHAPTER 5

THE HAMILTONIAN OF A SPIN SYSTEM.

5.1

Up to here only few specifications have been made about the kind of system to be investigated: it should be magnetic, i.e. have a field dependent hamiltonian (3.00) and for a given value of the field this hamiltonian should have a discrete spectrum of energy eigenvalues, most often becoming quasi continuous in the limit of an infinite system. (In fact the theoretical argument given has a wider validity still, as only small modifications would be needed to describe systems, the hamiltonian of which depends on some other external quantity than the magnetic field).

Henceforth the rather general theory will be further evaluated for a special class of magnetic systems: crystals containing ions with incomplete electron shells ('magnetic ions'); in particular those ions of which the single ion hamiltonian can, in good approximation be replaced by an expression written in terms of (effective) spin operators $(S_n)_x$, $(S_n)_y$ and $(S_n)_z$. Such an expression is called a spin hamiltonian²⁴). Usually the electrostatic interaction between the magnetic ions and the non-magnetic ions surrounding them is included in the single ion hamiltonians.

The hamiltonian of a crystal may then be divided into four parts:

- I The sum of spin hamiltonians $(\sum_n \dots)$.
- II The interaction between magnetic ions $(\sum_{m < n} \dots)$.
- III The hamiltonian of lattice vibrations and of non-magnetic ions.
- IV The interaction between magnetic ions and lattice vibrations and the modulation of II by these vibrations.

In principle one may apply the general theory to this total hamiltonian and get a description of the magnetic behaviour, where effects due to lattice vibrations, called spin-lattice-relaxation effects, are included²⁵).

If, as is often found, these effects are mainly restricted to relatively low frequencies, the faster processes due to interactions between the magnetic ions, then called spin-spin relaxation, can be described by a model, in which the hamiltonian consists of part I and part II. This model may also be characterized as a crystal without lattice vibrations or as an assembly of magnetic ions situated at fixed places in fixed electrostatic fields. Leaving out the constant terms in its hamiltonian one obtains a reduced model: the spin system.

The hamiltonian of the spin system reads

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{el} + \mathcal{H}_{hfs} + \mathcal{H}_{ex} + \mathcal{H}_d \quad 5.01$$

Here part I contributes

the Zeeman energy, the potential energy of the magnetic ion in the external magnetic field

$$\mathcal{H}_z = \mu_0 \vec{H} \cdot \mu_B \sum_n \vec{g}_n \cdot \vec{S}_n \quad 5.02$$

the electric field splitting

$$\mathcal{H}_{el} = \sum_n D_n \{ (S_n)_z^2, -\frac{1}{3} |\vec{S}_n|^2 \} + E_n \{ (S_n)_x^2, - (S_n)_y^2 \} + \dots \quad 5.03$$

and the hyperfine interaction, characteristic for the coupling with the nuclear spin \vec{I}_n

$$\mathcal{H}_{hfs} = \sum_n \vec{I}_n \cdot \vec{A}_n \cdot \vec{S}_n \quad 5.04$$

Part II contributes in the first place

the exchange interaction, which represents the effect of spurious covalent bonding between the ions on their magnetic behaviour,

$$\mathcal{H}_{ex} = 2 \sum_{m < n} \vec{S}_m \cdot \vec{J}_{mn} \cdot \vec{S}_n \quad 5.05$$

The \vec{J}_{mn} tensor can be split into an antisymmetric (Dzialoshinsky-Moriya) part, a traceless symmetric part and a scalar (Heisenberg) part

$$\vec{J}_{mn} = (\frac{1}{2} \vec{J}_{mn} - \frac{1}{2} \tilde{\vec{J}}_{mn}) + (\frac{1}{2} \vec{J}_{mn} + \frac{1}{2} \tilde{\vec{J}}_{mn} - \frac{1}{3} (\text{Tr } \vec{J}_{mn}) \vec{U}) + \frac{1}{3} (\text{Tr } \vec{J}_{mn}) \vec{U} \quad 5.06$$

The isotropic Heisenberg exchange often yields a satisfying description

$$\mathcal{H}_{\text{ex}} = 2 \sum_{m < n} J_{mn} \vec{S}_m \cdot \vec{S}_n, \quad J_{mn} \equiv \frac{1}{3} \text{Tr } \bar{J}_{mn} \quad 5.07$$

The summation over pairs may often be restricted to nearest neighbours (and next nearest neighbours).

Moreover part II contributes

the magnetic dipole-dipole interaction

$$\begin{aligned} \mathcal{H}_d = \mu_o \mu_B^2 \sum_{m < n} \{ & |\vec{r}_{mn}|^{-3} (\vec{g}_m \cdot \vec{S}_m) \cdot (\vec{g}_n \cdot \vec{S}_n) \\ & - 3 |\vec{r}_{mn}|^{-5} (\vec{r}_{mn} \cdot \vec{g}_m \cdot \vec{S}_m) (\vec{r}_{mn} \cdot \vec{g}_n \cdot \vec{S}_n) \} \end{aligned} \quad 5.08$$

where \vec{r}_{mn} is the vector connecting the sites of ions m and n . Just like in the Zeeman term, the so called g -tensor gives the connection between (effective) spin \vec{S}^* and magnetic moment $-\mu_B \vec{g} \cdot \vec{S}$ of the ion. μ_B is the Bohr magneton, μ_o the permeability of vacuum (cf. appendix A). Expressing the Zeeman energy one often uses the g -value, defined by

$$g_n |\vec{H}| \equiv |\vec{H} \cdot \vec{g}_n| \quad 5.09$$

and sometimes the effective field at ion n (which brings about the quantisation of spin \vec{S}_n if $\mathcal{H} = \mathcal{H}_Z$)

$$\vec{H}_{\text{eff},n} \equiv \vec{H} \cdot \vec{g}_n \quad 5.10$$

Neither of these are of use in writing \mathcal{H}_d .

It may be remarked that the spin hamiltonian given here lacks a term proportional to the square of the magnetic field and consequently cannot be used for the description of diamagnetic effects ($\chi_{\infty}(\vec{H})=0$).

* The symbols \vec{S} and \vec{I} and the word "spin" are (to be) used here for dimensionless operators representing the angular momentum divided by \hbar .

5.2 The decomposition of \mathcal{K}_{hfs} , \mathcal{K}_{ex} and \mathcal{K}_{d} into eigenoperators of L_z .

In the chapters 6 and 8 the decomposition of \mathcal{K}_{hfs} , \mathcal{K}_{ex} and \mathcal{K}_{d} into eigenoperators of the superoperator L_z , the Liouville operator which corresponds to the Zeeman term \mathcal{K}_z , will be used (cf. 6.08). In this section the way will be shown to achieve such a decomposition in the general case of an anisotropic g-tensor.

5.21 Eigenoperators of L_z .

Combining eqs. 5.02 and 5.10 one can write

$$\mathcal{K}_z = \mu_o \mu_B \sum_n \vec{H}_{\text{eff},n} \cdot \vec{S}_n \quad . \quad 5.11$$

In the case $\mathcal{K} = \mathcal{K}_z$ (zero interaction) $\vec{H}_{\text{eff},n}$ gives the quantization axis for the ion n. It is therefore convenient to give each ion its own coordinate system, with orthonormal basis vectors \vec{e}_{xn} , \vec{e}_{yn} , \vec{e}_{zn} , where $\vec{e}_{zn} // \vec{H}_{\text{eff},n}$ and \vec{e}_{xn} , \vec{e}_{yn} arbitrary. Consequently

$$\mathcal{K}_z = \mu_o \mu_B \sum_n |\vec{H}_{\text{eff},n}| S_n^O \quad 5.12$$

with

$$S_n^O \equiv (S_n)_{zn} \quad .$$

Looking for eigenoperators of L_z , i.e. operators A that satisfy the equation

$$L_z A \equiv \hbar^{-1} [\mathcal{K}_z, A] = \lambda A \quad 5.13$$

for some scalar λ , one finds as simple examples the single-spin operators S_n^O and $S_n^{\pm 1} \equiv (S_n)_{xn} \pm i(S_n)_{yn}$. One has

$$L_z S_n^\alpha = \alpha \omega_{Ln} S_n^\alpha \quad , \quad \alpha = -1, 0, +1 \quad 5.14$$

where

$$\omega_{Ln} \equiv \mu_o \mu_B \hbar^{-1} |\vec{H}_{\text{eff},n}| \quad 5.15$$

is the Larmor frequency of ion n.

More complicated eigenoperators of L_z are the two-spin operators $S_m^\alpha S_n^\beta$, $m \neq n$, $\alpha, \beta = -1, 0, +1$, with

$$L_z S_m^\alpha S_n^\beta = (\alpha \omega_{Lm} + \beta \omega_{Ln}) S_m^\alpha S_n^\beta \quad 5.16$$

One may define subsystems of ions (numbered $u, v = I, II, \dots$) demanding that members of one subsystem (u) have the same g -tensor (\vec{g}_u), hence the same effective field ($|\vec{H}_{eff,n}|$) and the same Larmor frequency (ω_{Lu}). This leads to two classes of eigenoperators of L_z

$$\mathcal{K}_u^\alpha \equiv \sum_{n \in u} C_n^\alpha S_n^\alpha \quad 5.17$$

and

$$u, v = I, II, \dots; \alpha, \beta = -1, 0, +1$$

$$\mathcal{K}_{uv}^{\alpha\beta} \equiv \sum_{\substack{m < n \\ m \in u, n \in v}} C_{mn}^{\alpha\beta} S_m^\alpha S_n^\beta \quad 5.18$$

where $C_n^\alpha, C_{mn}^{\alpha\beta}$ are arbitrary constants (or operators that commute with all S_n^α operators). They are eigenoperators of L_z due to

$$L_z \mathcal{K}_u^\alpha = \alpha \omega_{Lu} \mathcal{K}_u^\alpha \quad 5.19$$

and

$$u, v = I, II, \dots; \alpha, \beta = -1, 0, +1$$

$$L_z \mathcal{K}_{uv}^{\alpha\beta} = (\alpha \omega_{Lu} + \beta \omega_{Lv}) \mathcal{K}_{uv}^{\alpha\beta} \quad 5.20$$

It will be shown in section 5.22 that $\mathcal{K}_{hfs}, \mathcal{K}_{ex}$ and \mathcal{K}_d can be written as a sum of operators of the \mathcal{K}_u^α and $\mathcal{K}_{uv}^{\alpha\beta}$ types.

5.22 Decomposition of $\mathcal{K}_{hfs}, \mathcal{K}_{ex}$ and \mathcal{K}_d into \mathcal{K}_u^α and $\mathcal{K}_{uv}^{\alpha\beta}$ operators.

According to 5.04, 5.05 and 5.08, the operators $\mathcal{K}_{hfs}, \mathcal{K}_{ex}$ and \mathcal{K}_d are conveniently expressed in terms of \vec{S}_m and \vec{S}_n . In order to translate them into operators of the \mathcal{K}_u^α and $\mathcal{K}_{uv}^{\alpha\beta}$ types, defined by 5.17 and 5.18, the relation between \vec{S}_n and the S_n^α operators must be used. One has

$$\vec{S}_n = \sum_{\alpha=-1,0,+1} S_n^\alpha \vec{c}_n^\alpha \quad 5.21$$

$$\text{with } 2\vec{c}_n^{+1} \equiv \vec{e}_{xn} + i \vec{e}_{yn}, \quad \vec{c}_n^0 \equiv \vec{e}_{zn} \quad 5.22$$

Inserting this into 5.04, 5.05 and 5.08 one obtains

$$\mathcal{H}_{hfs}^c = \sum_n \sum_\alpha k_n^{\alpha\alpha} S_n^\alpha \quad 5.23$$

with $k_n^\alpha \equiv \vec{T}_n \cdot \vec{A}_n \cdot \vec{c}_n^\alpha \quad 5.24$

and $\mathcal{H}_{ex}^c + \mathcal{H}_d^c = \sum_{m < n} \sum_{\alpha, \beta} k_{mn}^{\alpha\beta} S_m^\alpha S_n^\beta \quad 5.25$

with $k_{mn}^{\alpha\beta} \equiv \vec{c}_m^\alpha \cdot 2\vec{J}_{mn} \cdot \vec{c}_n^\beta$

$$+ \mu_o \mu_B^2 |\vec{r}_{mn}|^{-3} (\vec{g}_m \cdot \vec{c}_m^\alpha) \cdot (\vec{g}_n \cdot \vec{c}_n^\beta)$$

$$- 3\mu_o \mu_B^2 |\vec{r}_{mn}|^{-5} (\vec{r}_{mn} \cdot \vec{g}_m \cdot \vec{c}_m^\alpha) (\vec{r}_{mn} \cdot \vec{g}_n \cdot \vec{c}_n^\beta) \quad 5.26$$

Using the notion of subsystems of similar ions one may write this in the required form (cf. 5.17, 5.18) ($\vec{c}_u^\alpha \equiv \vec{c}_n^\alpha, n \in u$)

$$\mathcal{H}_{hfs}^c = \sum_u \sum_\alpha \mathcal{H}_u^\alpha \quad 5.27$$

with $c_n^\alpha \equiv \vec{T}_n \cdot \vec{A}_n \cdot \vec{c}_u^\alpha, n \in u \quad 5.28$

(if the ions are also similar in \vec{A} one may replace \vec{A}_n by \vec{A}_u)

and $\mathcal{H}_{ex}^c + \mathcal{H}_d^c = \sum_{u, v} \sum_{\alpha, \beta} \mathcal{H}_{uv}^{\alpha\beta} \quad 5.29$

with $c_{mn}^{\alpha\beta} \equiv \vec{c}_u^\alpha \cdot 2\vec{J}_{mn} \cdot \vec{c}_v^\beta$

$$+ \mu_o \mu_B^2 |\vec{r}_{mn}|^{-3} (\vec{g}_u \cdot \vec{c}_u^\alpha) \cdot (\vec{g}_v \cdot \vec{c}_v^\beta)$$

$$- 3\mu_o \mu_B^2 |\vec{r}_{mn}|^{-5} (\vec{r}_{mn} \cdot \vec{g}_u \cdot \vec{c}_u^\alpha) (\vec{r}_{mn} \cdot \vec{g}_v \cdot \vec{c}_v^\beta), m \in u, n \in v \quad 5.30$$

5.23 Secular and non-secular operators.

Operators that commute with \mathcal{H}_Z^0 are usually called secular. Hence \mathcal{H}_u^0 and $\mathcal{H}_{uv}^{\alpha\beta}$ with $\alpha\omega_{Lu} + \beta\omega_{Lv} = 0$ are secular. The secular parts of \mathcal{H}_{hfs}^c and $\mathcal{H}_{ex}^c + \mathcal{H}_d^c$ are defined by

$$\mathcal{H}_{hfs}^0 \equiv \sum_u \mathcal{H}_u^0, \text{ with 5.17, 5.28} \quad 5.31$$

and $\mathcal{H}_{ex}^0 + \mathcal{H}_d^0 \equiv \sum_{u, v} \sum_{\alpha\omega_{Lu} + \beta\omega_{Lv} = 0} \mathcal{H}_{uv}^{\alpha\beta}, \text{ with 5.18, 5.30} \quad 5.32$

The other parts are called non-secular.

Tutton on his salts:

It was this discovery of these two important series which has rendered the many years of work possible which the author has devoted to their study and very detailed measurement.

*A.E.H. Tutton, Crystallography II
Macmillan London (1922) p. 1223.*

CHAPTER 6

MEASUREMENTS ON COPPER TUTTON SALTS.

6.1 Introductory remarks.

6.11 Introduction.

The investigation of the high-frequency magnetic susceptibility in a static field parallel to the alternating field was started by Locher and Gorter²⁶). In compounds where magnetic dipole-dipole interaction is not relatively weak compared to exchange interaction they found 'forbidden resonances' at the Larmor frequency and at twice this frequency.

A theoretical description of these resonances was given by Caspers²⁷), Tjon²²) and extended by Mazur and Terwiel²⁸). A further improvement will be given here.

The samples Locher used were powdered concentrated copper Tutton salts, which indeed have some drawbacks: two magnetically different ions in the unit cell, a somewhat anisotropic g-tensor, the occurrence of hyperfine interaction. The drawbacks are balanced

- by the simple single-ion energy spectrum (spin $\frac{1}{2}$), in which no near higher levels occur and in which electrostatic fields are of no direct importance,
- by the fact that spin-lattice relaxation is so slow as not to obscure the spin-spin effects²⁹)
- and by the large distances between the magnetic ions, even in the concentrated compound, which are a reason for the moderate role of exchange interaction.

In order to overcome the complications in powdered samples due to g-anisotropy Locher suggested to study single crystals. The underlying work gives the outcome of his suggestion.

6.12 Choice of sample material.

In spite of a long search no series of compounds has been found which have ^{more of} the following desired properties than the copper Tutton salts have.

- 1) Slow spin-lattice relaxation.
- 2) Spin one half; if this is not a property an equivalent situation may sometimes be achieved through cooling down until all single-ion spin levels except the lowest doublet are depopulated. The method may cause serious paramagnetic saturation and does not apply if a singlet lies lowest.
- 3) Small exchange, at most one order larger than the dipole-dipole interaction.
- 4) Nearly isotropic g-tensor.
- 5) Magnetically identical ions.
- 6) Availability of single crystals.
- 7) Absence of hyperfine interaction.

Some examples. Cu silico fluoride violates 5, Cu benzene sulfonate lacks property 7 and, more or less, 5; the acetyl acetonates, the ethyl sulphates and the lanthanum magnesium nitrate family accomodate 3+ ions, which either miss 2 or 7. The same holds for alums and moreover these miss 5. The Ti^{3+} ion looks attractive but there 6 is the problem, or even 1. The La Mg nitrate type may also be used in 'in the 2+ mode', but then 5 can cause trouble. Rare earth ions often disobey 1 or 4.

Recent computational work of Hillaert (cf. 6.4) has overcome 4 and greatly mitigated the need for 5 or 7.

Four copper Tutton salts, all sulphates, $(Cu M_2 (SO_4)_2 \cdot 6H_2O)$ have been studied with Cs, Rb, K and NH_4 as monovalent ion M. They constitute a series with increasing exchange interaction and nearly constant dipole-dipole and hyperfine interaction.

6.13 Crystal structure and hamiltonian.

The magnetic ions in copper Tutton salts are situated in a monoclinic lattice with axes $a : b : c \approx 3 : 4 : 2$ where the angles (b,a) and (b,c) are 90° and the angle (a,c) is $105^\circ 30'$. Half of the ions occupy $(0, 0, 0)$, the other half $(\frac{1}{2}, \frac{1}{2}, 0)$ sites. These two groups also differ in the orientation of the g-tensor, which has the approximately tetragonal symmetry of the electrostatic field generated by the stretched water octahedron around each Cu^{2+} ion. Both tetragonal axes that occur make an angle $(90^\circ - \alpha)$ of about 50° with the b-axis, but on opposite sides.

The magnetic principle axes (those of the static susceptibility tensor) are called k_1, k_2 and k_3 . The k_3 axis coincides with the b-axis, the k_2 axis is

perpendicular to both tetragonal axes and lies in the a-c-plane, together with k₁. Both the k₂-k₁-plane and the k₂-k₃-plane thus make equal angles with both types of tetragonal axis.

The angle ψ_1 between k₁ and c depends on the monovalent + ion (cf. table 6.1). ψ_1 is defined in such a way that for k₁ = a, $\psi_1 = 105^\circ$.

Table 6.1 ³⁰⁾

Monovalent + ion	α	ψ_1	$\frac{a}{3} \approx \frac{b}{4} \approx \frac{c}{2}$	g_1	$g_2 = g_{\perp}$	g_3	$g_{//}$
Cs	40	114	3.15 Å	2.28	2.06	2.22	2.43
Rb	40	105	3.12 Å	2.29 ₅	2.07	2.23	2.45
K	42	105	3.04 ₅ Å	2.26	2.05	2.22 ₅	2.43
NH ₄	39	77	3.08 ₅ Å	2.27	2.06	2.20	2.40

g_1, g_2 and g_3 are the values for $g_i = g_{1i}$ when $\vec{e}_i // k_1, k_2$ and k_3 respectively (cf. section 6.42).

The hamiltonian of the spin system in a sample of copper Tutton salt can be written as

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_d + \mathcal{H}_{hfs} + \mathcal{H}_{ex} \equiv \mathcal{H}_z + \mathcal{H}_{int} \quad (\text{cf. 5.01}) \quad 6.00$$

where $\mathcal{H}_z, \mathcal{H}_d, \mathcal{H}_{hfs}$ and \mathcal{H}_{ex} are the hamiltonian terms defined in 5.02, 5.08, 5.04 and 5.05.

The exchange interaction is assumed isotropic (scalar, cf. 5.07). No information is available about antisymmetric or anisotropic exchange in these compounds, but in view of the experimental results there is no need for a more complicated description.

The dependence of J_{mn} on the distance between the ions m and n constitutes a second problem. One could try to derive these values from experiment, but for a first estimate it is convenient if one takes the range of exchange interaction restricted to the (0, 0, ± 1) and ($\pm \frac{1}{2}, \pm \frac{1}{2}, 0$) neighbours attributing equal values (J) to them all.

For the compounds used the elements of g- and A-tensor, the corresponding values for $N^{-1}h^{-2}\text{Tr } \mathcal{H}_d^2/\text{Tr } I$ and $N^{-1}h^{-2}\text{Tr } \mathcal{H}_{hfs}^2/\text{Tr } I$, the values for $N^{-1}h^{-2}\text{Tr } \mathcal{H}_{int}^2/\text{Tr } I$ (from specific heat measurements in the T⁻² region ³¹⁾) and the resulting values for $N^{-1}h^{-2}\text{Tr } \mathcal{H}_{ex}^2/\text{Tr } I$, $N^{-1}h^{-2}\text{Tr } \mathcal{H}_d \mathcal{H}_{ex}/\text{Tr } I$ and Jh^{-1} are listed in table 6.2 As the A-tensor has approximately the same tetragonal symmetry and principle axes as the

g-tensor, it is sufficient to give $A_{//}$ and A_{\perp} where // and \perp refer to the tetragonal axis of the ion.

Table 6.2

+ion	$g_{//}$	g_{\perp}	$A_{//}h^{-1}$ (GHz)	$A_{\perp}h^{-1}$ (GHz)	$\frac{\text{Tr } \mathcal{K}_d^2}{N h^2 \text{Tr } I}$ (GHz ²)	$\frac{\text{Tr } \mathcal{K}_{hfs}^2}{N h^2 \text{Tr } I}$ (GHz ²)	$\frac{\text{Tr } \mathcal{K}_{int}^2}{N h^2 \text{Tr } I}$ (GHz ²)	$\frac{\text{Tr } \mathcal{K}_{ex}^2}{N h^2 \text{Tr } I}$ (GHz ²)	$\frac{2\text{Tr } \mathcal{K}_d \mathcal{K}_{ex}}{N h^2 \text{Tr } I}$ (GHz ²)	$\frac{J}{h}$ (GHz)
Cs	2.43	2.06	0.36	0.09	0.048 ₁	0.045 ₅	0.10 ₉	0.015 ₅	- 0.0007	0.083
								0.014 ₀	+ 0.0007	-0.079
Rb	2.45	2.07	0.34 ₈	0.09 ₀	0.051 ₉	0.042 ₉	0.13 ₉	0.046	- 0.00 ₂	0.14 ₃
								0.042 ₅	+ 0.00 ₂	-0.13 ₇
K	2.43	2.05	0.30 ₉	0.10 ₂	0.058 ₀	0.036 ₃	0.24 ₇	0.15 ₇	- 0.00 ₄	0.26 ₄
								0.15 ₀	+ 0.00 ₄	-0.25 ₈
NH ₄	2.40	2.06	0.39 ₀	0.09	0.053 ₂	0.052 ₆	0.35 ₆	0.25 ₇	- 0.00 ₆	0.33 ₈
								0.24 ₅	+ 0.00 ₆	-0.33 ₀

The following remarks can be made.

One has
$$\frac{\text{Tr } \mathcal{K}_{hfs}^2}{N h^2 \text{Tr } I} = \frac{5}{16} (A_{//}^2 h^{-2} + 2A_{\perp}^2 h^{-2})$$

and
$$\frac{\text{Tr } \mathcal{K}_{ex}^2}{N h^2 \text{Tr } I} = \frac{9}{4} \frac{J^2}{h^2}$$

The $A_{//}$ and A_{\perp} values for the Cs-compound are estimations on the basis of assumed analogy with the other salts.

Assuming an isotropic g-tensor Locher calculated $N^{-1} h^{-2} \text{Tr } \mathcal{K}_d^2 / \text{Tr } I$ to be 0.050₄ GHz² in the Cs- and 0.056₂ GHz² in the NH₄-compound. The deviations are totally due to the assumption made.

The sign of J does not follow from the data given. Both possibilities have been investigated (cf. table 6.2). The resulting absolute value of J is found to differ but little for both cases. The positive value has been adopted for further use.

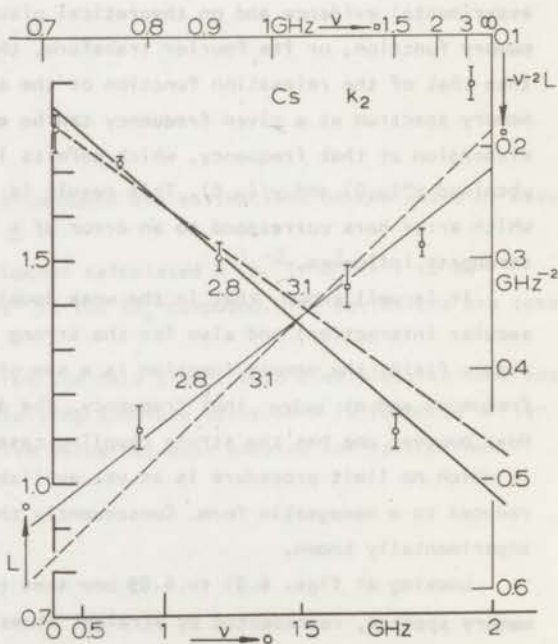
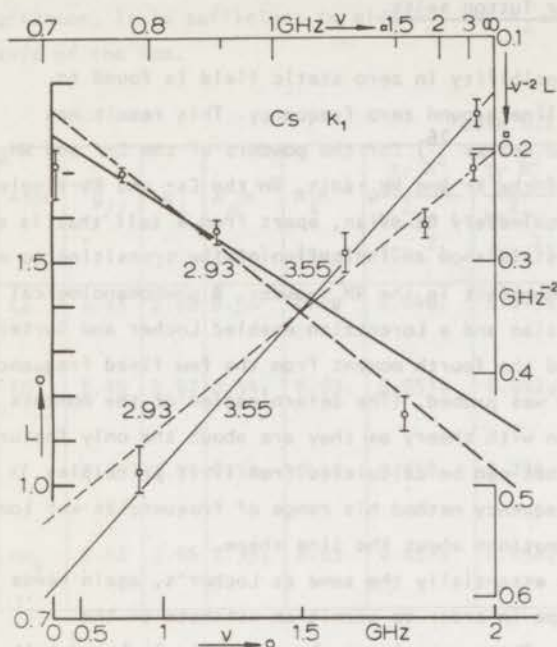
6.2 Zero field behaviour of copper Tutton salts.

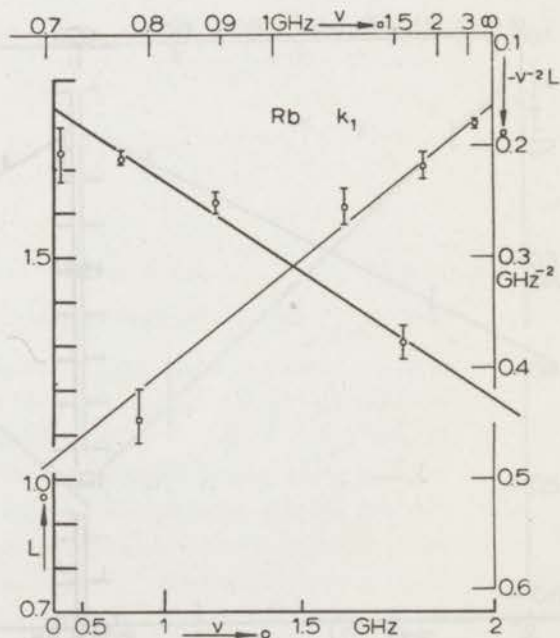
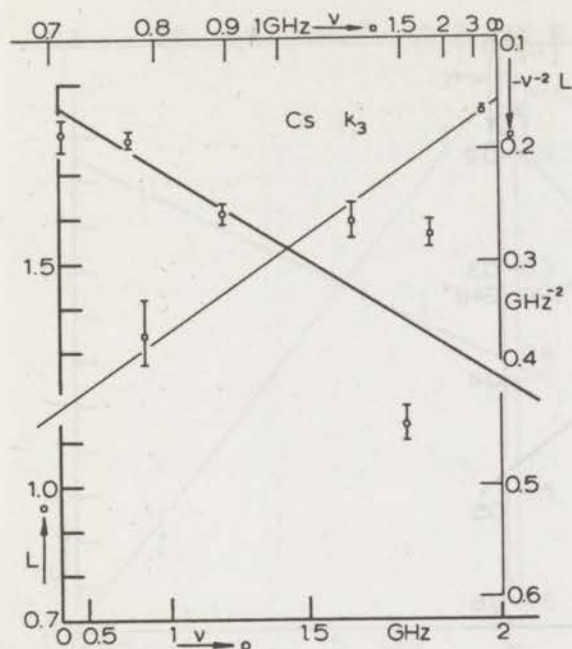
The frequency dependent susceptibility in zero static field is found to correspond to a single absorption line around zero frequency. This result has already been obtained by Locher and Gorter²⁶⁾ for the powders of the Cs- and NH₄-salt and by Pickar³²⁾ for those of the K- and NH₄-salt. In the Cs- and Rb-single-crystals the line shapes look approximately Gaussian, apart from a tail that is distinctly too high. The K-single-crystals show an indication of the transition to more Lorentz like line forms, which is manifest in the NH₄-powder. A phenomenological description by a product of a Gaussian and a Lorentzian enabled Locher and Gorter to derive values for the second and the fourth moment from the few fixed frequency measurements by which the spectrum was probed. (The determination of the moments is an essential means of confrontation with theory as they are about the only features of the spectral density function that can be calculated from first principles.) Although Pickar used a variable frequency method his range of frequencies was too limited to do without similar assumptions about the line shape.

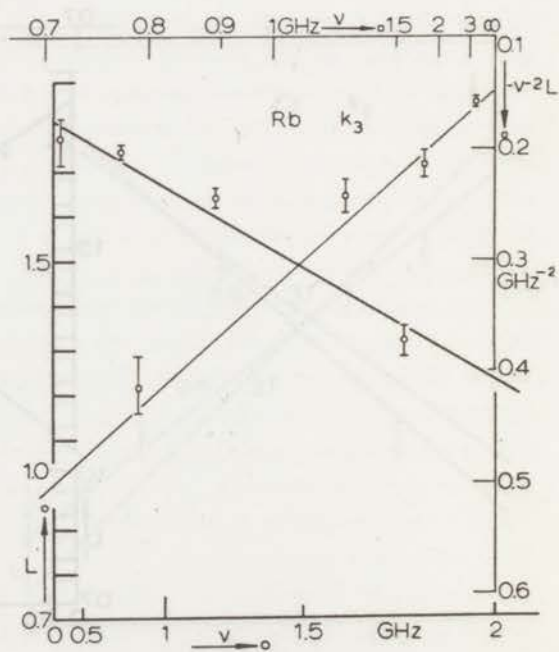
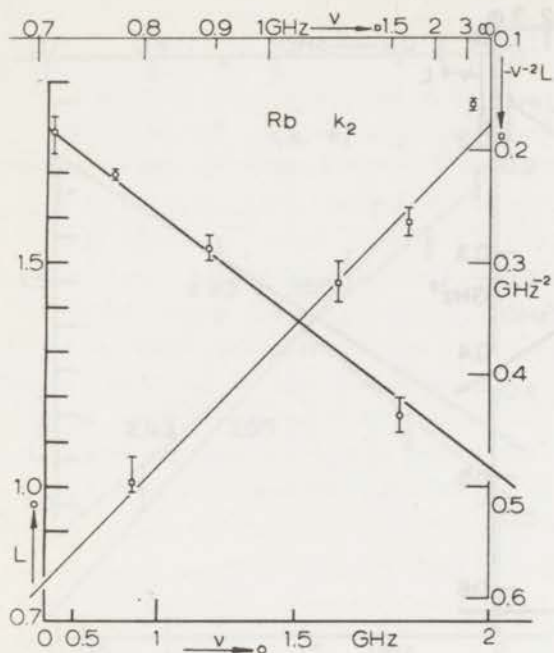
The present experiment, being essentially the same as Locher's, again needs some assumption concerning the line shape in order to permit an estimate of the experimental values of the moments. The assumption to be made here is based both on experimental evidence and on theoretical plausibility. It concerns the shape of the memory function, or its Fourier transform, the memory spectrum (cf. 2.64), rather than that of the relaxation function or the absorption line. According to 3.13 the memory spectrum at a given frequency can be expressed in the absorption and dispersion $\chi''(\omega, 0)$ and $\chi'(\omega, 0)$. This result is plotted in figs. 6.01 to 6.09, in which error bars correspond to an error of $\pm 10\%$ in χ'' or χ' , whichever has the strongest influence.

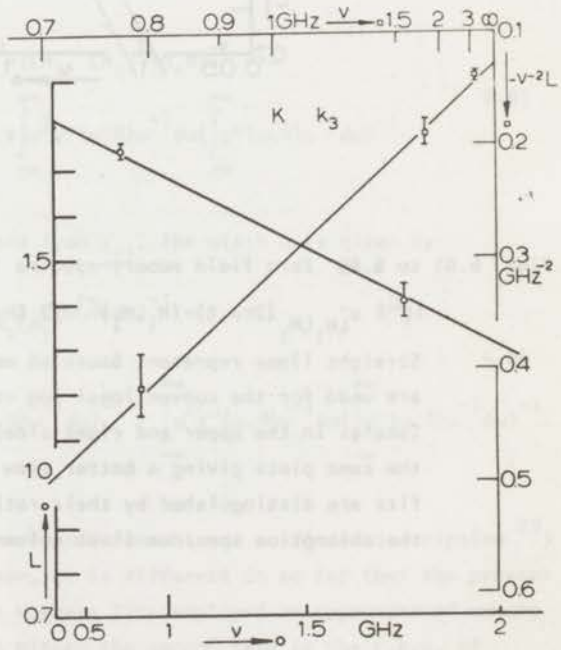
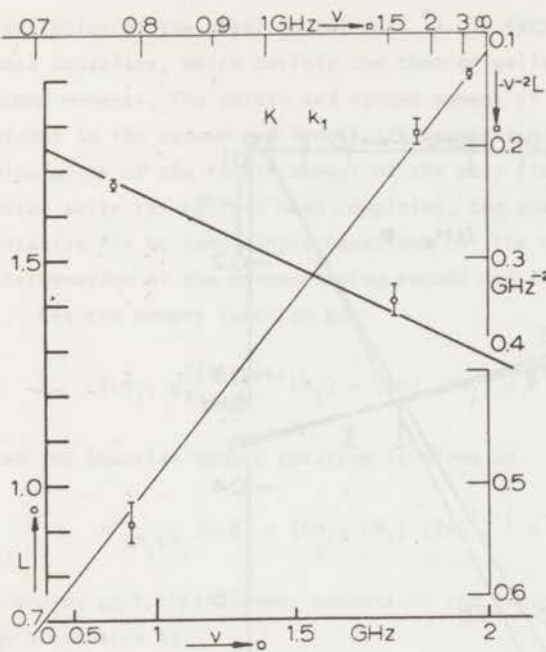
It is well known, that in the weak coupling limit (i.e. for relatively weak non-secular interaction) and also for the strong coupling case in the limit of high static field, the memory function is a sum of two damped oscillations at the Larmor frequency and at twice that frequency. The damping is usually assumed Gaussian. Here, however, one has the strong coupling case with zero static field, a situation in which no limit procedure is as yet available by which the memory function can be reduced to a manageable form. Consequently the shape of the memory spectrum is only experimentally known.

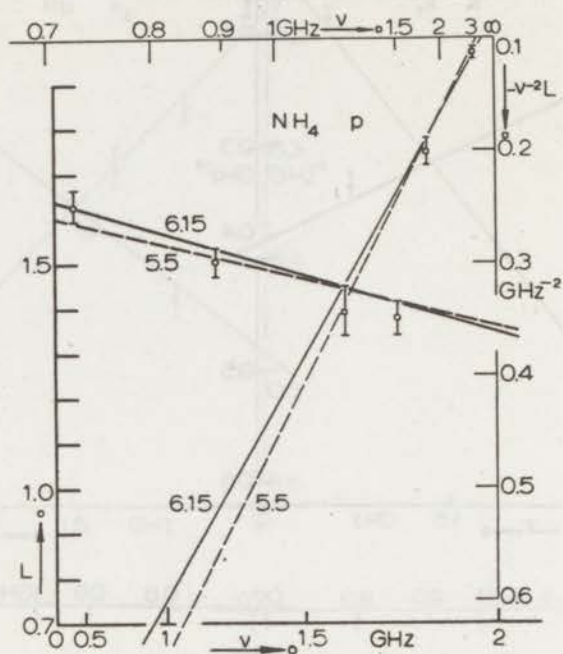
Looking at figs. 6.01 to 6.09 one sees that, apart from some deviations, Gaussian memory spectra, represented by straight lines, can give a reasonable











Figs. 6.01 to 6.09 Zero field memory-spectra in Cu Tutton salts.

$$10^4 \equiv s_{LM_i, LM_i}^1(2\pi\nu, 0) (M_i, M_i)^{-1} (2 \text{ GHz})^{-1}$$

Straight lines represent Gaussian memory spectra. Circles and thick lines are used for the conventional log vs. square plots. Squares and thin lines (scales in the upper and right side) show the perspective transform of the same plots giving a better view of the high frequencies. Alternative fits are distinguished by their ratio 4th moment to square 2^d moment of the absorption spectrum (last column of table 6.3).

description of the experimental data ^{*}). In fact one should confront these data with those Gaussians, which satisfy the theoretically known values with their zeroth and second moments. The zeroth and second moment of the memory spectrum are simply related to the second and fourth of the absorption spectrum (cf. 2.71). As the calculation of the fourth moment of the zero field absorption spectrum in the copper Tutton salts has not yet been completed, the analysis has been restricted to a tentative fit by some single Gaussians for the memory spectrum and to the determination of the corresponding second and fourth moment of the absorption line.

Let the memory function be

$$(LM_i, e^{i(1-P_A)Lt} LM_i) = (LM_i, LM_i) e^{-\frac{1}{2}\Delta^2 t^2} \quad 6.01$$

then the Gaussian memory spectrum is given by

$$s'_{LM_i, LM_i}(\omega, 0) = (LM_i, LM_i) (2\pi\Delta^2)^{-\frac{1}{2}} e^{-\frac{1}{2}\omega^2 \Delta^{-2}} \quad 6.02$$

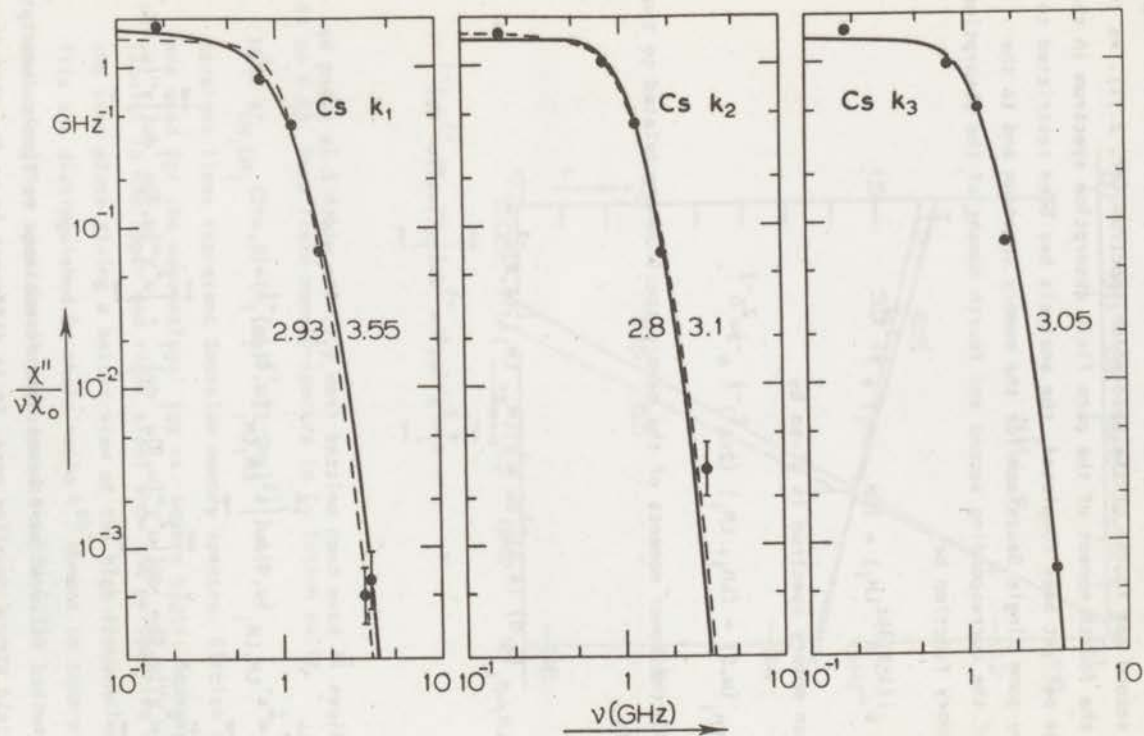
According to 3,13a the lower moments of the memory spectrum are related to those of the absorption by

$$\begin{aligned} \int_{-\infty}^{+\infty} \pi s'_{LM_i, LM_i}(\omega, 0) (A, A)^{-1} d\omega &= \pi (LM_i, LM_i) (A, A)^{-1} = \\ &= \pi \int_{-\infty}^{+\infty} \omega^2 \chi''(\omega, 0) \omega^{-1} d\omega \left\{ \int_{-\infty}^{+\infty} \chi''(\omega, 0) \omega^{-1} d\omega \right\}^{-1} \end{aligned} \quad 6.03$$

in which the indices *ii* have been omitted from χ_{ii} . The width Δ is given by

$$\begin{aligned} \Delta^2 &= \int_{-\infty}^{+\infty} \omega^2 s'_{LM_i, LM_i}(\omega, 0) d\omega \left\{ \int_{-\infty}^{+\infty} s'_{LM_i, LM_i}(\omega, 0) d\omega \right\}^{-1} = \\ &= \int_{-\infty}^{+\infty} \omega^4 \chi''(\omega, 0) \omega^{-1} d\omega \left\{ \int_{-\infty}^{+\infty} \omega^2 \chi''(\omega, 0) \omega^{-1} d\omega \right\}^{-1} - \int_{-\infty}^{+\infty} \omega^2 \chi''(\omega, 0) \omega^{-1} d\omega \left\{ \int_{-\infty}^{+\infty} \chi''(\omega, 0) \omega^{-1} d\omega \right\}^{-1}. \end{aligned} \quad 6.04$$

^{*}) Although the method followed here bears some resemblance to Tjon's description ²²⁾ of the zero field strong coupling case, it is different in so far that the present work uses the exact memory functions whereas Tjon employed an approximated memory function. A consequence is that Tjon misses the second term in the r.h.s. of equation 6.04.



Figs. 6.10 to 6.12 $\text{CuCs}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$; $\chi''_{11}(2\pi\nu, 0)$ as derived from the fitted Gaussian memory spectra, and experimental results. The 4th to $(2^d)^2$ ratio is indicated.

The results of the fit for the second and fourth moment of the absorption $\chi''(\omega,0)\omega^{-1}$ are given in table 6.3.

Table 6.3

type of Cu Tutton salt	direction k	$\frac{1}{2\pi} \left(\int \omega^2 \chi''(\omega)^{-1} d\omega \right)^{\frac{1}{2}} \left\{ \int \chi''(\omega)^{-1} d\omega \right\}^{-\frac{1}{2}}$		$\int \omega^4 \chi''(\omega)^{-1} d\omega \int \chi''(\omega)^{-1} d\omega \left\{ \int \omega^2 \chi''(\omega)^{-1} d\omega \right\}^{-2}$
		exp. (GHz)	theor.	
Cs	1	0.75 _s	0.684 ₃	3.3 ± 0.3
Cs	2	0.74 _s	0.702 ₁	2.95 0.2
Cs	3	0.82 _e	0.718 ₉	3.05 0.2
Rb	1	0.79 _e	0.716 ₇	3.1 0.1
Rb	2	0.74	0.699 ₄	3.3 0.2
Rb	3	0.80	0.737 ₄	3.3 0.1
K	1	0.78 ₂	0.752 ₅	4.05 0.15
K	3	0.82 _e	0.759 ₁	3.5 0.1
NH ₄	powder	0.77 _e		5.8 0.4

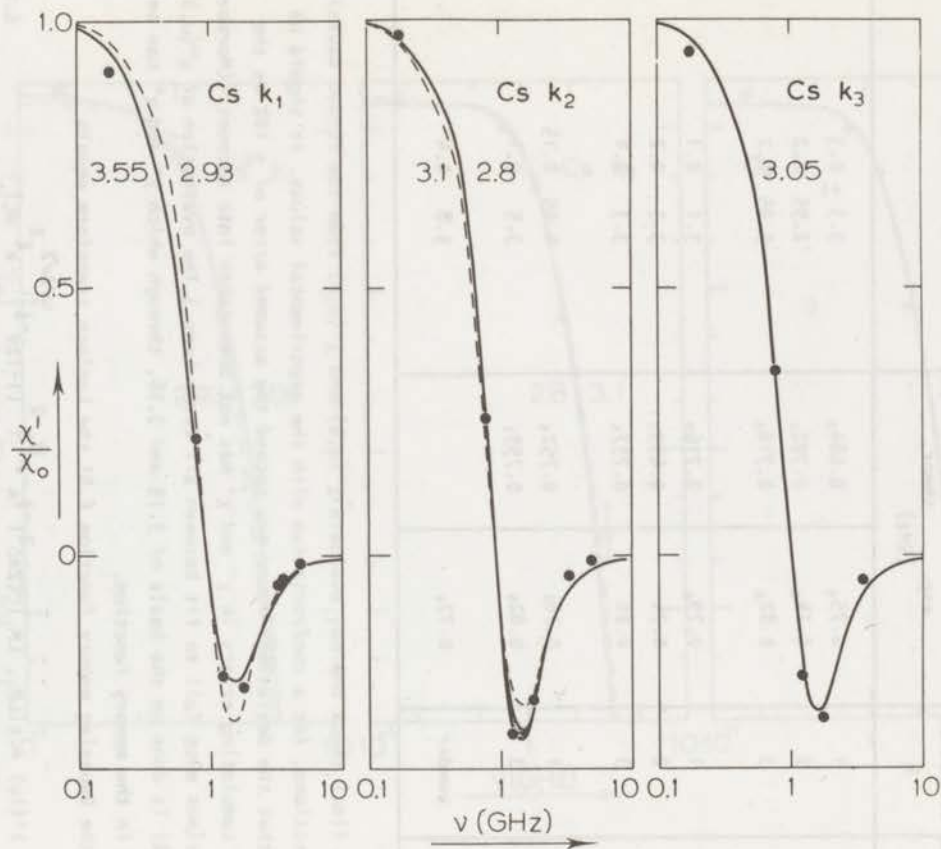
As a final check one may evaluate $\chi''(\omega,0)$ and $\chi'(\omega,0)$ from the fitted Gaussian memory functions, for a confrontation with the experimental values. It should be remarked that the deviations found may exceed the assumed error of $\pm 10\%$ as the effect of cumulating errors in χ'' and χ' has not been taken into account. (Moreover, some Gaussians even fail to fit between all error bars.) The evaluation of $\chi''(\omega,0)$ and $\chi'(\omega,0)$ is done on the basis of 3.15 and 3.16, through which χ' and χ'' can be expressed in the memory function.

For the Gaussian memory function 6.01 the Laplace transform equals

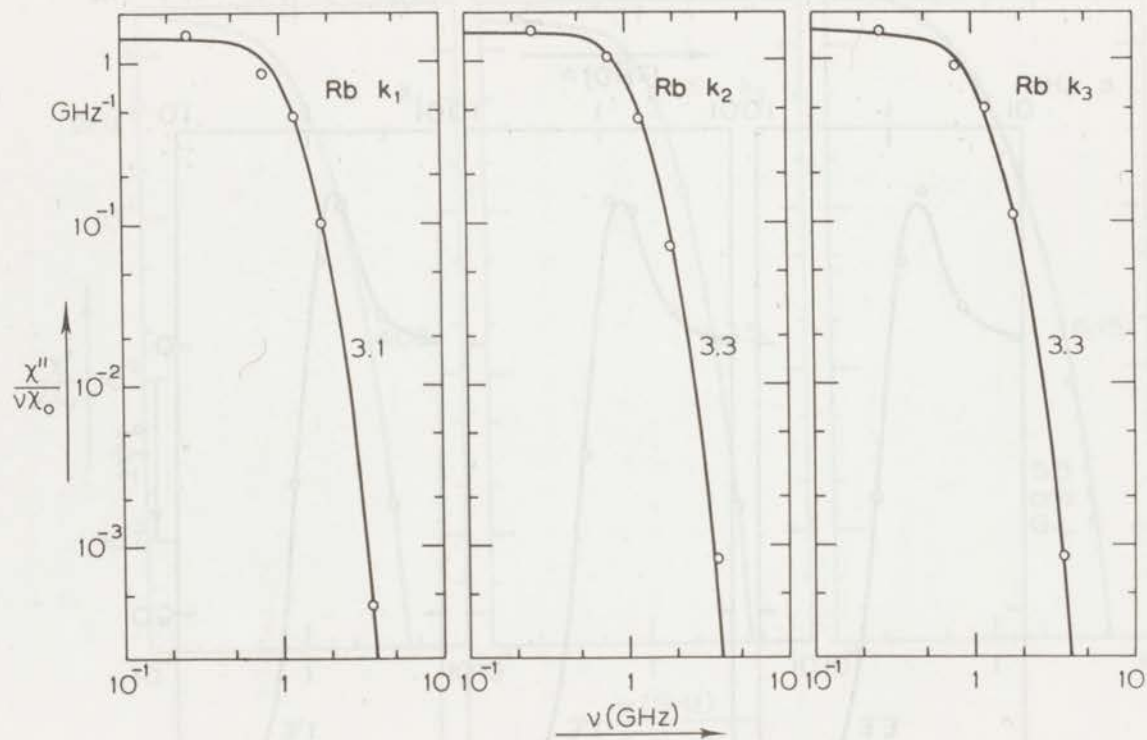
$$l'(i\omega) = \pi(LM_1, LM_1) (2\pi\Delta^2)^{-\frac{1}{2}} e^{-\frac{1}{2}\omega^2\Delta^2} \{1 - i2\pi^{-\frac{1}{2}} \int_0^{\omega/\Delta\sqrt{2}} e^{-\xi^2} d\xi\} \quad 6.05$$

and consequently χ' and χ'' can be found from:

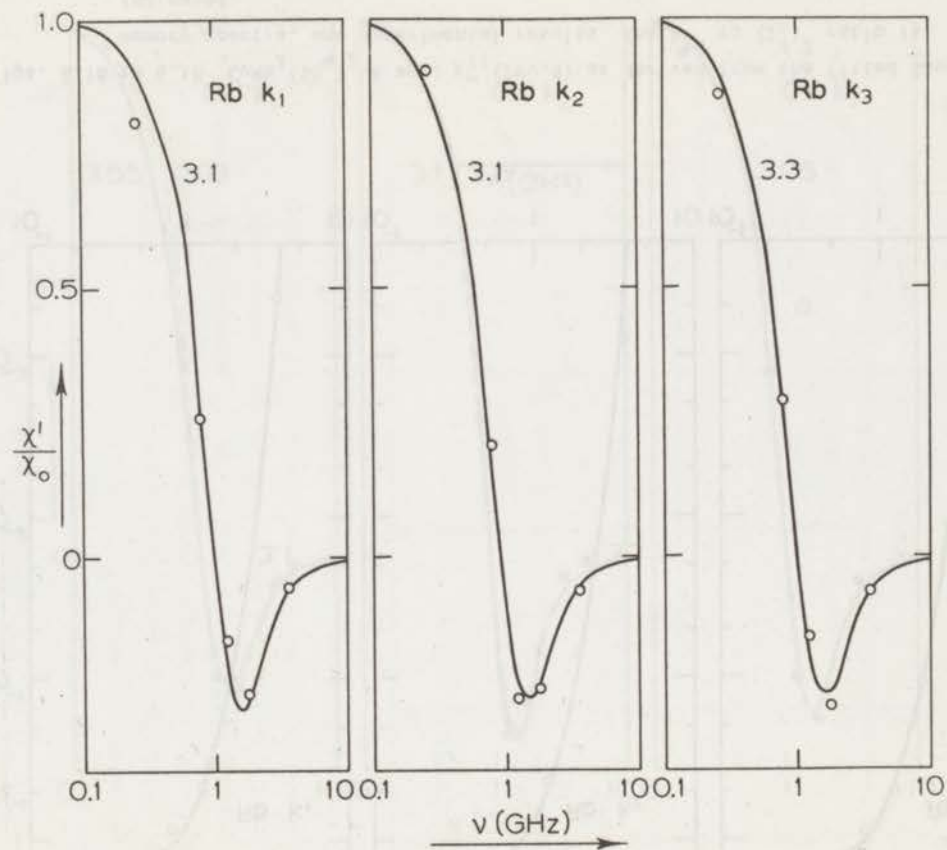
$$1 - \frac{\chi'(\omega,0) - \chi_\infty(0)}{\chi(0,0) - \chi_\infty(0)} = \omega \frac{\omega + im}{(\omega + im)^2 + Re^2} \quad 6.06$$



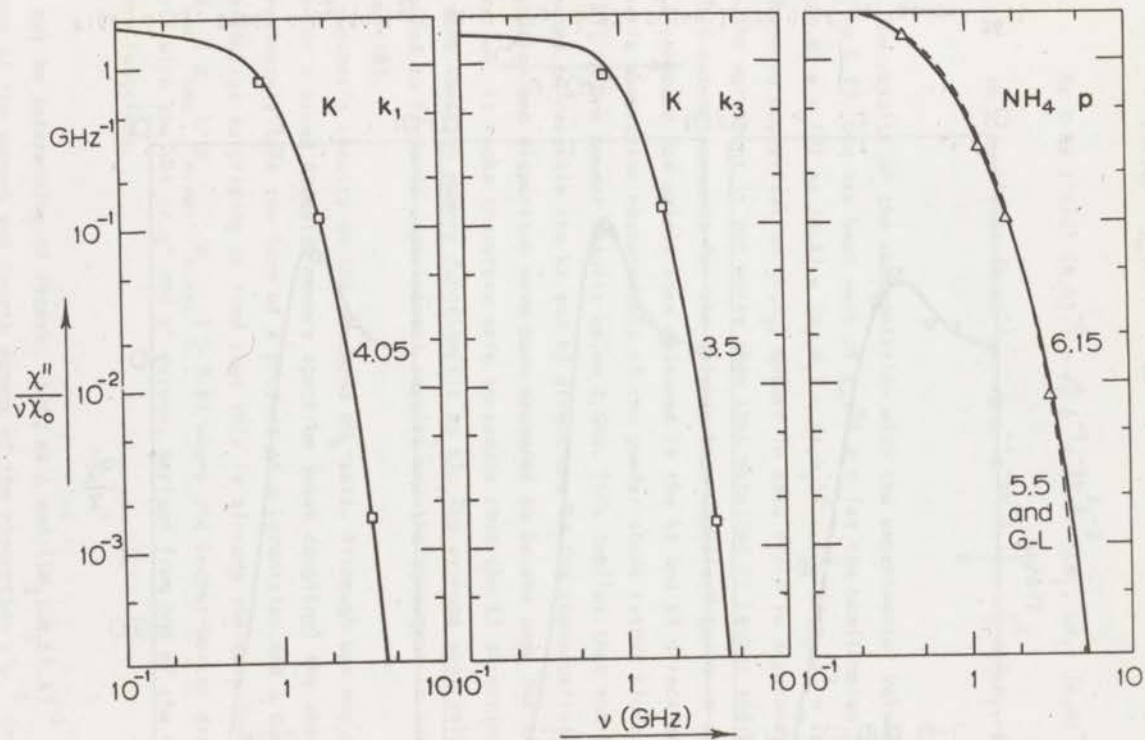
Figs. 6.13 to 6.15 $\text{CuCs}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$; $\chi''_{ii}(2\pi\nu, 0)$ as derived from the fitted Gaussian memory spectra, and experimental results. The 4th to $(2^d)^2$ ratio is indicated.



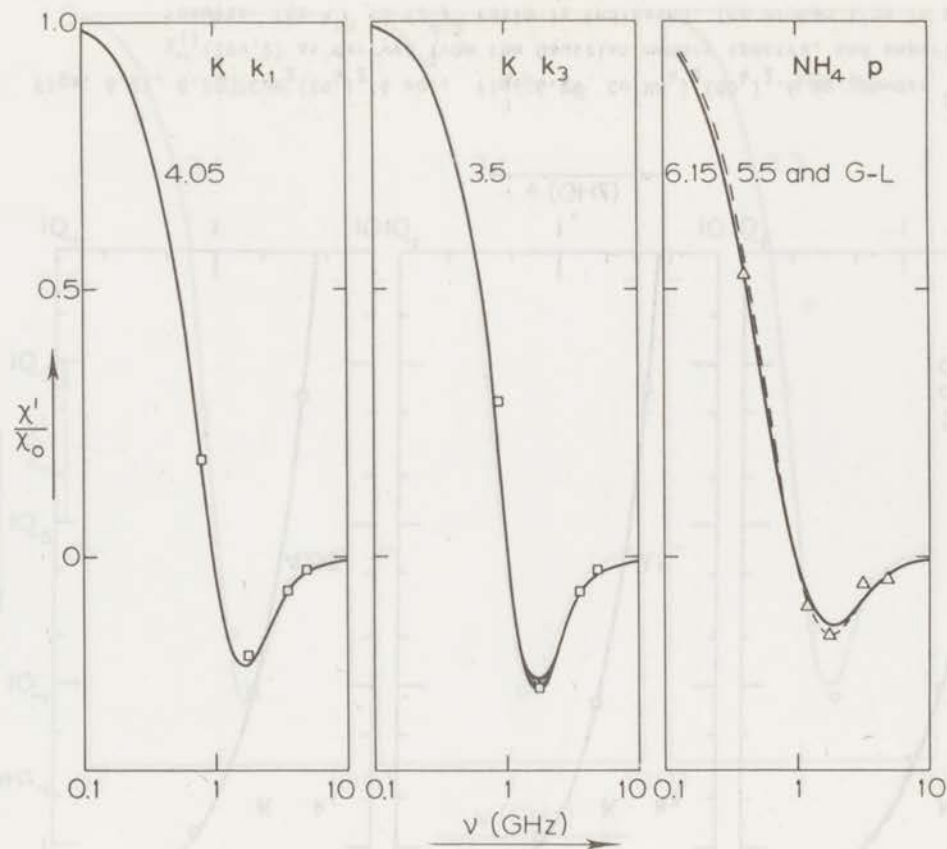
Figs. 6.16 to 6.18 $\text{CuRb}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$; $\chi''_{11}(2\pi\nu, 0)$ as derived from the fitted Gaussian memory spectra, and experimental results. The 4^{th} to $(2^d)^2$ ratio is indicated.



Figs. 6.19 to 6.21 $\text{CuRb}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$; $\chi''_{ij}(2\pi\nu, 0)$ as derived from the fitted Gaussian memory spectra, and experimental results. The 4^{th} to $(2^{\text{d}})^2$ ratio is indicated.



Figs. 6.22, 6.23 $CuK_2(SO_4)_2 \cdot 6$ aq.; fig. 6.24 $Cu(NH_4)_2(SO_4)_2 \cdot 6$ aq. powder²⁶;
 $\chi''_{11}(2\pi\nu, 0)$ as derived from the Gaussian memory spectra, and experimental
 results. The 4th to $(2^d)^2$ ratio is indicated. The broken line is also
 a good representation of the mixed Gauss-Lorentz (G-L) shape.



Figs. 6.25, 6.26 $\text{CuK}_2(\text{SO}_4)_2 \cdot 6$ aq.; fig. 6.27 $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6$ aq. powder²⁶;
 $\chi''_{11}(2\pi\nu, 0)$ as derived from the Gaussian memory spectra, and experimental
 results. The 4th to $(2^d)^2$ ratio is indicated. The broken line is also
 a good representation of the mixed Gauss-Lorentz (G-L) model.

$$\frac{\chi''(\omega, 0)}{\chi(0, 0) - \chi_\infty(0)} = \omega \frac{\text{Re}}{(\omega + i\text{Im})^2 + \text{Re}^2} \quad 6.07^*)$$

$$\begin{aligned} \text{with } \text{Re} &\equiv \text{Re } l'(i\omega) (A, A)^{-1} = \sqrt{\frac{\pi}{2}} \Delta^{-1} e^{-\frac{1}{2}\omega^2 \Delta^{-2}} (LM_i, LM_i) (A, A)^{-1} \\ \text{Im} &\equiv \text{Im } l'(i\omega) (A, A)^{-1} = -\sqrt{2} \Delta^{-1} e^{-\frac{1}{2}\omega^2 \Delta^{-2}} \int_0^{\omega/\Delta\sqrt{2}} e^{\xi^2} d\xi (LM_i, LM_i) (A, A)^{-1} . \end{aligned}$$

The results of the confrontation with the experimental values are shown in figs. 6.10 to 6.27. Use has been made of $\chi_\infty(\vec{H}) = 0$ (as the hamiltonian is linear in \vec{H}) and of $\chi(0, 0) = \chi_0(0)$ as $(A, A) = (M_i, M_i) - (I, M_i)^2 - \left(\frac{\partial}{\partial \beta} (I, M_i)\right)^2 = (M_i, M_i)$ (as no spontaneous magnetisation (I, M_i) occurs in zero field in a paramagnet). It appears that the agreement is not worse than that obtained by Locher and Gorter, and to a certain extent accounts for the "higher than Gaussian" tails in the Cs- and Rb-salts. The K-compound has mainly been measured in the k1 and k3 directions. Comparison with Pickar's absorption measurements of the powder shows rather close agreement between the k1, k3 and powder results below 2 GHz. This implies that the k2 direction may be expected to resemble the k1 and k3 directions in its characteristics. At 3.6 GHz absorption and dispersion have been measured to be the same for the k2 and k3 direction. It looks therefore safe to assume that the k2 direction would yield about the same Gaussian memory function fit as k3. The average absorption fit may be compared to Pickar's experimental results and the agreement is satisfactory (cf. fig. 6.28).

Locher's results on the powdered NH_4 -salt. Although one may expect from 3.16 that for a broad Gaussian memory spectrum (weak coupling) the absorption will approximately take the form of a product of a Lorentzian and a Gaussian, it is nevertheless surprising to find that this is already the case for the NH_4 -salt $(\mathcal{K}_{\text{sec}}, \mathcal{K}_{\text{sec}})/(\mathcal{K}_{\text{n.sec}}, \mathcal{K}_{\text{n.sec}}) \approx 3.5$ where the Locher-Gorter description coincides nicely with the set of χ'' and χ' curves, derived from one of the fitted Gaussian memory functions.

*) It may be interesting to remark, that, as Δ and $(LM_i, LM_i X A, A)^{-1}$ can be written in terms of the second and fourth moment of the absorption $\chi'' \omega^{-1}$ (cf. 6.04), eq. 6.07 embodies an expression of the absorption in its second and fourth moment, which constitutes a probably more realistic model than that of miss Wright³³).

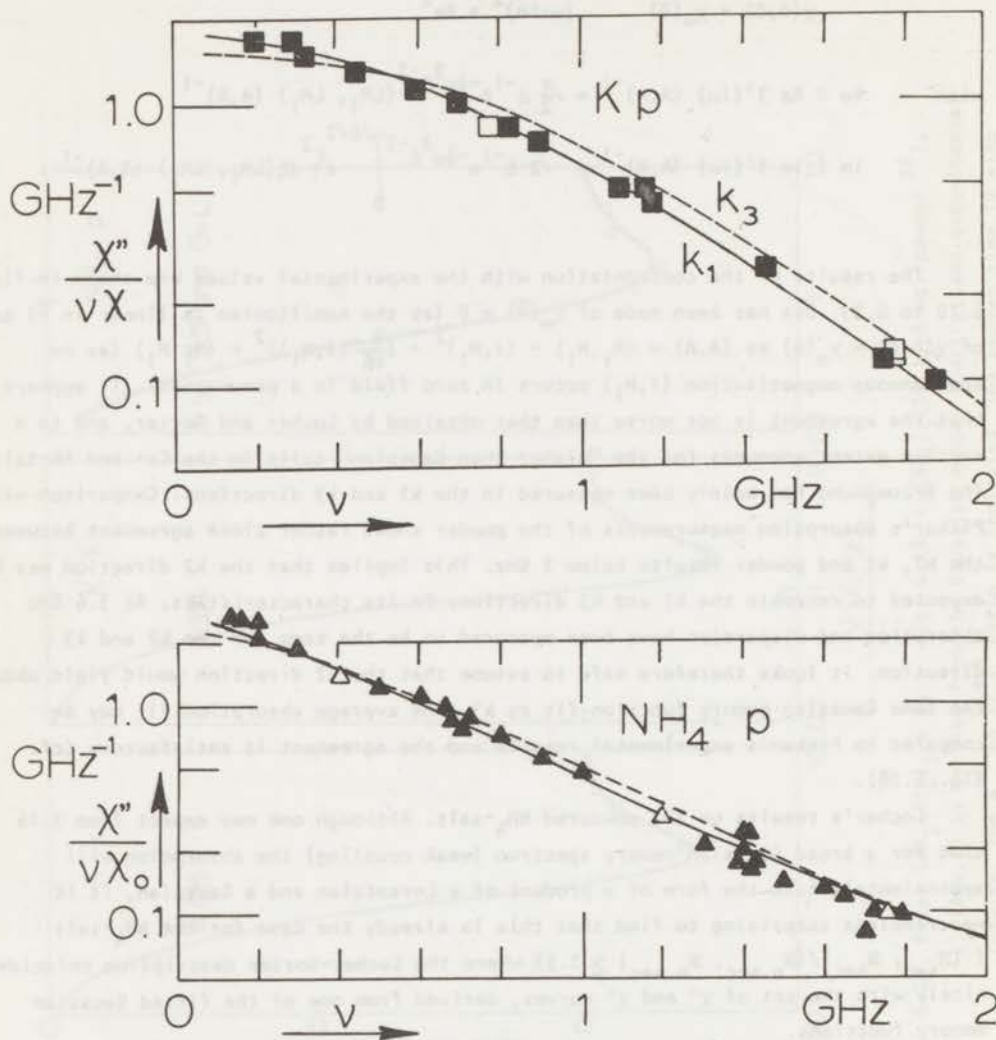


Fig. 6.28 $\text{CuK}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$; fig. 6.29 $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$

Absorption.

Powder measurements of ref. 32 (full points).

Powder measurements of ref. 26 and single crystal results from the present work are indicated by open points (cf. figs. 6.22 to 6.24).

It is however questionable if the method used may indeed be applied to powdered samples. If 1, 2 and 3 are the principle axes of $\bar{\chi}(\omega, 0)$ and if the memory functions corresponding to $\chi_{11}(\omega, 0)$, $\chi_{22}(\omega, 0)$ and $\chi_{33}(\omega, 0)$ are Gaussian and different, then the powder average $1/3(\chi_{11}(\omega, 0) + \chi_{22}(\omega, 0) + \chi_{33}(\omega, 0))$ will not correspond to an exactly Gaussian memory function, as the relation 3.11 between relaxation function and memory function is non-linear. For a not too anisotropic $\bar{\chi}(\omega, 0)$ the method might keep its significance and hence it has been applied to the results of the powdered NH_4 -salt.

The fit thus made to Locher's few single-frequency measurements on the NH_4 compound also gives a reasonable description of Pickar's multi-frequency results (cf. fig. 6.29).

6.3 Theory of strong parallel field behaviour at high frequencies.

6.31 Strong field and zero interaction.

The high-frequency susceptibility of compounds with relatively weak exchange interaction (strong coupling) in a strong static field parallel to the alternating field has been studied theoretically by Caspers²⁷⁾, Tjon²²⁾ and Mazur and Terwiel²⁸⁾. All have used the high-temperature approximation as a starting point. Here such an approximation will be postponed to the calculation of time independent quantities.

The essential point in assuming a strong static field is the hope that the interaction term \mathcal{H}_{int} in the hamiltonian may be handled as a small correction to the large Zeeman term \mathcal{H}_Z . The latter has such a simple structure that eigenoperators \mathcal{H}_p of the corresponding Liouville (super) operator L_Z can be given explicitly and that the interaction term \mathcal{H}_{int} can be expressed in such eigenoperators (cf. sec. 5.22)

$$L_Z \mathcal{H}_p = \omega_p \mathcal{H}_p \quad 6.08$$

which implies $\omega_p \sim H$ for $\vec{H} = H\vec{e}_i$ leading to $\omega_p \equiv \gamma_p H$

$$L_Z \mathcal{H}_p^\dagger = -\omega_p \mathcal{H}_p^\dagger \quad \text{allowing} \quad \mathcal{H}_p \equiv \mathcal{H}_{-p}^\dagger \quad \text{and} \quad \omega_p \equiv -\omega_{-p}$$

$$e^{iL_Z t} \mathcal{H}_p = e^{i\omega_p t} \mathcal{H}_p \quad \text{and} \quad L_Z [\mathcal{H}_p, \mathcal{H}_q] = (\omega_p + \omega_q) [\mathcal{H}_p, \mathcal{H}_q]$$

Let the numbers $0, \pm 1, \dots, \pm n$ be reserved for the components of \mathcal{H}_{int} , then

$$\mathcal{H}_{int} = \sum_{p=0, \pm 1, \dots, \pm n} \mathcal{H}_p$$

with different ω_p 's for different \mathcal{K}_p 's. \mathcal{K}_0 is called the secular part of the interaction, $L_z \mathcal{K}_0 = 0$. Thus, in order to make a rough analysis of the absorption spectrum it is attractive to study the approximation in which \mathcal{K} is replaced by \mathcal{K}_z .

This approximation will here be called the limit of zero interaction. It should be noted that this excludes the description of low-temperature effects in the sense of (anti)ferromagnetic transitions. The only low-temperature feature preliminarily admitted is paramagnetic saturation by the strong static field.

One may give a more experimental interpretation of the zero interaction limit. The only expressions of interest where \mathcal{K} is replaced by \mathcal{K}_z are of the type $\beta\mathcal{K}$ and $\mathcal{K}t$ with $\mathcal{K} = \mathcal{K}_{int} + \mathcal{K}_z = \mathcal{K}_{int} - \mu_0 H M_1$. Consequently the limit $H \rightarrow \infty$, βH , tH constant, is fully equivalent with $\mathcal{K} \rightarrow \mathcal{K}_z$. In a sense this limit is a high-temperature limit ($\beta \rightarrow 0$) but as it is accompanied by $H \rightarrow \infty$ it retains the non-zero value of the average magnetization, (I, M_1) . The other implication ($t \rightarrow 0$) leaves $\omega_p t$ constant, such that one stays within the range of experimental interest.

6.32 The absorption spectrum.

According to 1.39 one has

$$\phi_{11}(t, \vec{H}_e) = \int_{-\infty}^{+\infty} e^{i\omega t} \frac{v}{\pi} \chi''_{11}(\omega, \vec{H}_e) \omega^{-1} d\omega \quad 1.39$$

which, due to 3.10 equals

$$\begin{aligned} \phi_{11}(t, \vec{H}_e) &= \beta \mu_0 ((1 - P_{1-P_{\mathcal{K}}}) M_1, e^{iLt} (1 - P_{1-P_{\mathcal{K}}}) M_1) = \\ &= \beta \mu_0^{-1} H^{-2} ((1 - P_{1-P_{\mathcal{K}}}) \mathcal{K}_{int}, e^{iLt} (1 - P_{1-P_{\mathcal{K}}}) \mathcal{K}_{int}) \end{aligned} \quad 6.09$$

Anticipating the zero interaction limit one may split \mathcal{K}_{int}

$$\phi_{11}(t, \vec{H}_e) = \beta \mu_0^{-1} H^{-2} \sum_{p, q=0, \pm 1, \dots, \pm n} (P, e^{iLt} Q) \quad 6.10$$

$$\frac{v}{\pi} \chi''_{11}(\omega, \vec{H}_e) = \beta \mu_0^{-1} H^{-2} \sum_{p, q=0, \pm 1, \dots, \pm n} S_{pQ}(\omega, \vec{H}_e) \quad 6.11$$

with $Q \equiv (1 - P_1 - P_2) \mathcal{K}_Q$, $P \equiv (\dots) \mathcal{K}_P$ and $0 \equiv (\dots) \mathcal{K}_0$

$$\text{and } (P, e^{iLt} Q) \equiv \int_{-\infty}^{+\infty} e^{i\omega t} S_{PQ}(\omega, H\vec{e}_1) d\omega \quad 6.12$$

6.33 The absorption spectrum in zero interaction limit.

For $\mathcal{K} \rightarrow \mathcal{K}_Z$ not only the usual relation $(A, LB) = (LA, B)$ but also $(A, L_Z B)_{\mathcal{K}_Z} \rightarrow (L_Z A, B)_{\mathcal{K}_Z}$ holds ^{*}, L_Z becomes Hermitean (for $\beta \neq 0$ this is not a trivial point). Consequently the eigenoperators $1, \mathcal{K}'$ and \mathcal{K}_0 with eigenvalue 0 become orthogonal to those (\mathcal{K}_p) with eigenvalue $\omega_p \neq 0$ and the latter become mutually orthogonal if their eigenvalues are different. Hence $P \rightarrow \mathcal{K}_p$ if $\omega_p \neq 0$. The autocorrelation terms in $\Phi_{ij}(t, H\vec{e}_1)$ become undamped oscillations

$$\beta \mu_0^{-1} H^{-2} (P, e^{iLt} P) \rightarrow \beta \mu_0^{-1} H^{-2} (\mathcal{K}_p, \mathcal{K}_p)_{\mathcal{K}_Z} e^{i\omega_p t}, \quad \omega_p \neq 0.$$

The term $(0, e^{iLt} 0)$ must be handled separately. Other terms vanish due to the orthogonality. The oscillations having an intensity proportional to H^{-2} could be called "forbidden resonances". In the absorption spectrum they yield δ -lines at frequencies ω_p . In the term $(0, e^{iLt} 0)$ the replacement of \mathcal{K} by \mathcal{K}_Z would cause a fundamental change. The term would become a constant and this would lead to a non zero time average of $\Phi_{ij}(t, H\vec{e}_1)$, contrary to 1.23. Instead one may study its character through its second time derivative $-(L_{int} \mathcal{K}_0, e^{iLt} L_{int} \mathcal{K}_0)$. For $t = 0$ one gets the second moment of the contribution to the absorption spectrum

$$(L_{int} \mathcal{K}_0, L_{int} \mathcal{K}_0) (0, 0)^{-1}$$

An estimate of its order of magnitude shows that the bulk of intensity of this contribution must be confined to a frequency interval around $\omega = 0$, which has a width, at most of the order of $\hbar^{-1} (\mathcal{K}_{int}, \mathcal{K}_{int})^{\frac{1}{2}}$. This rough analysis yields the following picture: For $\mathcal{K} \rightarrow \mathcal{K}_Z$ the absorption spectrum consists of very narrow lines at frequencies ω_p including zero frequency.

^{*}) The index \mathcal{K}_Z has been added in order to stress the change of character in the scalar product definition, where \mathcal{K} has been replaced by \mathcal{K}_Z as well.

6.34 The absorption spectrum for finite interaction strength.

In the preceding section it was seen that the autocorrelation terms play the main role, if $\mathcal{K} \rightarrow \mathcal{K}'_z$. One may hope that this will already be the case for a small but finite interaction strength. Mazur and Terwiel²⁸⁾ *) have shown the way to an upper bound for the cross terms ($P, e^{iLt}Q$). Their result follows immediately from the Schwarz inequality for spectral density functions 2.45.

Assuming that $\phi_{ii}(t, \vec{H}e_i) = \phi_{ii}^R(t, \vec{H}e_i)$ (i.e. that for finite interaction it is free from undamped oscillations), and consequently $S_{ii}(\omega, \vec{H}e_i) = s_{ii}^R(\omega, \vec{H}e_i)$, one may identify $S_{PQ}(\omega, \vec{H}e_i) = s_{PQ}^R(\omega, \vec{H}e_i)$, such that 2.45 implies

$$|S_{PQ}(\omega, \vec{H}e_i)| \leq (S_{PP}(\omega, \vec{H}e_i) S_{QQ}(\omega, \vec{H}e_i))^{\frac{1}{2}} \quad 6.13$$

This inequality gives an impression of the way in which the various terms in 6.11 develop as the interaction strength is reduced. The main terms $S_{PP}(\omega, \vec{H}e_i)$ gradually concentrate their intensity around ω_p . Consequently the overlap between them, characterized by the product $S_{PP}(\omega, \vec{H}e_i) S_{QQ}(\omega, \vec{H}e_i)$, vanishes and so do the cross terms $S_{PQ}(\omega, \vec{H}e_i)$ due to 6.13.

It is however hard to tell from experimental results to what extent a situation has been reached, in which the cross terms may be neglected. When one finds a set of well-resolved absorption lines at the expected frequencies ω_p then there is no a priori reason why these lines could be described by the terms $S_{PP}(\omega, \vec{H}e_i)$. One should realize that a line at ω_p may still contain contributions (e.g. satellite lines) from other main terms than $S_{PP}(\omega, \vec{H}e_i)$ (and hence perhaps from cross terms $S_{PQ}(\omega, \vec{H}e_i)$ as well), which will only vanish through a further reduction of interaction strength.

Even if the experimental shape and intensity of the lines are not essentially altered by an enhancement of field, temperature and measuring frequency (the experimental equivalent of reduction of interaction strength) one can only hope that the main terms have at last mainly withdrawn to their own frequency domains becoming approximately equal to the measured lines:

*) These authors made a slip of the pen in stating that the inequality 6.13 is based on the fact that the spectrum of a real autocorrelation function of the form $\text{Tr}(A^\dagger e^{iLt} A) + \text{Tr}(A e^{iLt} A^\dagger)$ is real and positive semi-definite. This should read: the spectrum of an autocorrelation function of the form $\text{Tr} A^\dagger e^{iLt} A$ is real and positive semi-definite.

$$\frac{v}{\pi} \chi_{ij}''(\omega, H\vec{e}_i) \omega^{-1} \approx \beta \mu_0^{-1} H^{-2} S_{pp}(\omega, H\vec{e}_i), \quad \omega_p - \delta < \omega < \omega_p + \delta \quad 6.14$$

It will henceforth be assumed that this hope is actually fulfilled, such that not only the experimental lines but also the theoretical terms are well resolved. In that case one may try to determine the intensity and second moment of the measured lines and confront these values with those calculated for the corresponding terms $S_{pp}(\omega, H\vec{e}_i)$. A closer estimate of the importance of the cross terms will be given in appendix I.

6.35 Intensity.

For the intensity of the line at ω_p one simply has

$$I_p \equiv \int_{\omega_p - \delta}^{\omega_p + \delta} \frac{v}{\pi} \chi_{ij}''(\omega, H\vec{e}_i) \omega^{-1} d\omega \approx \beta \mu_0^{-1} H^{-2} \int_{-\infty}^{+\infty} S_{pp}(\omega, H\vec{e}_i) d\omega = \beta \mu_0^{-1} H^{-2} (P, P) \quad 6.15$$

where $\omega_p - \delta$ to $\omega_p + \delta$ indicates the frequency domain of the line, also used for the experimental determination of the intensity.

As $(P, P) = (\mathcal{H}_p, \mathcal{H}_p) - (1, \mathcal{H}_p)^2 - (\mathcal{H}_p, \mathcal{H}_p)^2 (\mathcal{H}_p, \mathcal{H}_p)^{-1}$, where $(1, \mathcal{H}_p) = (\text{Tr } e^{-\beta \mathcal{H}_p})^{-1} \text{Tr } e^{-\beta \mathcal{H}_p}$ and $(\mathcal{H}_p, \mathcal{H}_p) = -\frac{\partial}{\partial \beta} (1, \mathcal{H}_p)$ are both of second order ($p \neq 0$) in the interaction strength, one has up to third order $(P, P) \approx (\mathcal{H}_p, \mathcal{H}_p)$. But due to cross terms the approximation $I_p \approx \beta \mu_0^{-1} H^{-2} (P, P)$ is not even better than second order (cf. appendix I). In the same approximation one may write $(\mathcal{H}_p, \mathcal{H}_p) \approx (\mathcal{H}_p, \mathcal{H}_p) \mathcal{H}_p^{-1}$. Hence the intensity of the line at $\omega_p \neq 0$ is in second and lowest order given by

$$I_p \beta^{-1} \mu_0 H^2 \approx (\mathcal{H}_p, \mathcal{H}_p) \mathcal{H}_p^{-1} = (\beta \hbar \omega_p)^{-1} (1 - e^{-\beta \hbar \omega_p}) (\text{Tr } e^{-\beta \mathcal{H}_p})^{-1} \text{Tr } e^{-\beta \mathcal{H}_p} \mathcal{H}_p^{-1} \mathcal{H}_p.$$

For two-particle interaction $\mathcal{H}_p = \sum_{m < n} \mathcal{H}_{p, mn}$ one may write, dividing the Zeeman energy into its single particle contributions $\mathcal{H}_z = \sum_n \mathcal{H}_{z, n}$ (with $[\mathcal{H}_{z, m}, \mathcal{H}_{z, n}] = 0$):

$$I_p \beta^{-1} \mu_0 H^2 \approx (\beta \hbar \omega_p)^{-1} (1 - e^{-\beta \hbar \omega_p}) \sum_{k < l} \text{Tr } e^{-\beta (\mathcal{H}_{z, k} + \mathcal{H}_{z, l} + \mathcal{H}_{z, m} + \mathcal{H}_{z, n})} \text{Tr } e^{-\beta (\mathcal{H}_{z, k} + \mathcal{H}_{z, l} + \mathcal{H}_{z, m} + \mathcal{H}_{z, n})} \mathcal{H}_{p, kl} \mathcal{H}_{p, mn} \quad 6.16$$

In most cases these four particle terms reduce to expressions, in which only two

particles occur. It can be seen from 6.16 that for temperatures so high as to make β negligible compared to $(\hbar\omega_p)^{-1}$ and to the single-particle Zeeman energy one may approximate

$$I_p \beta^{-1} \mu_0 H^2 \approx (\mathcal{H}_p, \mathcal{H}_p) \mathcal{H}_z \approx (\text{Tr } 1)^{-1} \text{Tr } \mathcal{H}_p^\dagger \mathcal{H}_p. \quad 6.17$$

6.36 Second moment.

Within the frequency interval $\omega_p - \delta$ to $\omega_p + \delta$ the absorption is supposed to be reasonably described by $S_{pp}(\omega, \vec{H}_i)$. Other terms are of minor importance

$$S_{pp}(\omega, \vec{H}_i) \gg S_{qq}(\omega, \vec{H}_i) \text{ and } |S_{pq}(\omega, \vec{H}_i)| \leq (S_{pp}(\omega, \vec{H}_i) S_{qq}(\omega, \vec{H}_i))^{\frac{1}{2}}.$$

Consequently one also has

$$(\omega - \omega_p)^2 S_{pp}(\omega, \vec{H}_i) \gg (\omega - \omega_p)^2 S_{qq}(\omega, \vec{H}_i)$$

$$\text{and } |(\omega - \omega_p)^2 S_{pq}(\omega, \vec{H}_i)| \leq ((\omega - \omega_p)^2 S_{pp}(\omega, \vec{H}_i) (\omega - \omega_p)^2 S_{qq}(\omega, \vec{H}_i))^{\frac{1}{2}}.$$

The second moment $\langle \omega^2 \rangle_p$ of the line at ω_p with respect to its centre can thus be calculated from

$$\langle \omega^2 \rangle_p I_p \equiv \int_{\omega_p - \delta}^{\omega_p + \delta} (\omega - \omega_p)^2 \frac{v}{\pi} \chi''_{ii}(\omega, \vec{H}_i) \omega^{-1} d\omega \approx \beta \mu_0^{-1} H^{-2} \int_{\omega_p - \delta}^{\omega_p + \delta} (\omega - \omega_p)^2 S_{pp}(\omega, \vec{H}_i) d\omega \quad 6.18$$

which holds in lowest order in interaction strength. This expression is further evaluated with the aid of the relation (proven in appendix J)

$$(\omega - \omega_p) (\omega - \omega_q) S_{pq}(\omega, \vec{H}_i) = \sum_{k, l=0, \pm 1, \dots, \pm n} S_{pkql}(\omega, \vec{H}_i) \quad 6.19$$

where $Q_j \equiv \hbar^{-1} (1 - P_{1j} - P_{j1}) [\mathcal{H}_1, \mathcal{H}_j]$.

For $p = q$ it follows that

$$(\omega - \omega_p)^2 S_{pp}(\omega, \vec{H}_i) = \sum S_{pkpl}(\omega, \vec{H}_i).$$

At this stage one may again distinguish main terms $S_{pkpk}(\omega, \vec{H}_i)$ and cross terms $S_{pkpl}(\omega, \vec{H}_i)$, for which the inequality 6.13 holds:

$$|S_{PkP1}(\omega, \vec{H}\vec{e}_i)| \leq (S_{PkPk}(\omega, \vec{H}\vec{e}_i) S_{P1P1}(\omega, \vec{H}\vec{e}_i))^{\frac{1}{2}} \dots$$

Again one may get a rough impression of the features of $(\omega - \omega_p)^2 S_{pp}(\omega, \vec{H}\vec{e}_i)$ replacing \mathcal{K} by \mathcal{K}_z . For the main terms one gets

$$S_{PkPk}(\omega, \vec{H}\vec{e}_i) \rightarrow h^{-2} ([\mathcal{K}_k, \mathcal{K}_p], [\mathcal{K}_k, \mathcal{K}_p]) \mathcal{K}_z \delta(\omega - \omega_k - \omega_p)$$

where again the low frequency terms $S_{p-p-p}(\omega, \vec{H}\vec{e}_i)$ should be given some extra care. The situation is fully equivalent to that of section 6.34. Again one may hope that the main terms alone will give a reasonable description, such that in lowest order approximation

$$(\omega - \omega_p)^2 S_{pp}(\omega, \vec{H}\vec{e}_i) \sim \sum_{k=0, \pm 1, \dots, \pm n} S_{PkPk}(\omega, \vec{H}\vec{e}_i)$$

a sum of main terms, which concentrate around frequencies $\omega_p + \omega_k$.

Inserting this into 6.18 one is led to an important conclusion. For the experimental second moment of the line at ω_p only the frequency interval $\omega_p - \delta$ to $\omega_p + \delta$ is of interest and consequently only those terms $S_{PkPk}(\omega, \vec{H}\vec{e}_i)$ with $\omega_p - \delta < \omega + \omega_k < \omega_p + \delta$. For a well resolved spectrum this is only one term: $S_{P_0P_0}(\omega, \vec{H}\vec{e}_i)$.

Apparently the secular part \mathcal{K}_0 of the interaction is the only source of the second moment *). The argument used is similar to Van Vleck's well known truncation procedure. Along these lines one gets for the second moment:

$$\begin{aligned} \langle \omega^2 \rangle_p I_p \beta^{-1} \mu_o H^2 &\sim \int_{\omega_p - \delta}^{\omega_p + \delta} (\omega - \omega_p)^2 S_{pp}(\omega, \vec{H}\vec{e}_i) d\omega \sim \int_{\omega_p - \delta}^{\omega_p + \delta} \sum_k S_{PkPk}(\omega, \vec{H}\vec{e}_i) d\omega \sim \\ &\sim \int_{\omega_p - \delta}^{\omega_p + \delta} S_{P_0P_0}(\omega, \vec{H}\vec{e}_i) d\omega \sim \int_{-\infty}^{+\infty} S_{P_0P_0}(\omega, \vec{H}\vec{e}_i) d\omega = (P_o, P_o), \end{aligned}$$

*) This implies that the constants c introduced by Mazur and Terwiel ²⁸⁾ are not only of order 1 but should be taken exactly equal to 1 (cf. also appendix K).

$$\begin{aligned} \text{hence } \langle \omega^2 \rangle_p I_p \beta^{-1} \mu_0 H^2 \sim (P_0, P_0) \sim \hbar^{-2} ([\mathcal{H}_0, \mathcal{H}_p], [\mathcal{H}_0, \mathcal{H}_p])_{\mathcal{H}_Z} = \\ = \hbar^{-2} (\beta \hbar \omega_p)^{-1} (1 - e^{-\beta \hbar \omega_p}) (\text{Tr } e^{-\beta \mathcal{H}_Z})^{-1} \text{Tr } e^{-\beta \mathcal{H}_Z} [\mathcal{H}_0, \mathcal{H}_p]^\dagger [\mathcal{H}_0, \mathcal{H}_p] \end{aligned} \quad 6.20$$

$$\text{and } \hbar^2 \langle \omega^2 \rangle_p \sim (\text{Tr } e^{-\beta \mathcal{H}_Z} \mathcal{H}_p^\dagger \mathcal{H}_p)^{-1} \text{Tr } e^{-\beta \mathcal{H}_Z} [\mathcal{H}_0, \mathcal{H}_p]^\dagger [\mathcal{H}_0, \mathcal{H}_p] \quad 6.21$$

which for high temperatures may again be approximated by

$$\hbar^2 \langle \omega^2 \rangle_p \sim (\text{Tr } \mathcal{H}_p^\dagger \mathcal{H}_p)^{-1} \text{Tr} [\mathcal{H}_0, \mathcal{H}_p]^\dagger [\mathcal{H}_0, \mathcal{H}_p] . \quad 6.22$$

For $p = 0$ eqs. 6.20 and 6.22 are seen to yield a zero second moment in this approximation. The zero frequency line may thus be expected to be relatively narrow. The special character of $(0, e^{iL\tau} 0)$ is described in an appendix (K), as it constitutes a low-frequency effect.

6.37 Some additional remarks.

One might ask how $S_{pp}(\omega, \vec{H}_i)$, which is supposed to have its domain around ω_p , can yield terms $S_{pkpk}(\omega, \vec{H}_i)$ at frequencies $\omega_p + \omega_k$ with $\omega_k \neq 0$, when it is multiplied by $(\omega - \omega_p)^2$. The answer is that $S_{pp}(\omega, \vec{H}_i)$ indeed contains satellite lines at frequencies $\omega_p + \omega_k$, but with an intensity which is two orders smaller than that of the main line. One may write for $\omega \sim \omega_p + \omega_k$

$$S_{pp}(\omega, \vec{H}_i) \sim \omega_k^{-2} S_{pkpk}(\omega, \vec{H}_i) .$$

The whole picture now agrees with inequality 6.13: The intensity of the main term $S_{pp}(\omega, \vec{H}_i)$ at ω_p is of second order in interaction strength. The satellite contribution of other main terms is fourth order (like that of $S_{pp}(\omega, \vec{H}_i)$ at $\omega_p + \omega_k$). In appendix I the contribution of cross terms is shown to be of third order and this is the geometrical mean indeed.

In principle the method used to derive the second moments could be extended to higher even moments but the accuracy suffers from too many subsequent approximations. One may however conclude that line broadening in the parallel configuration is almost exclusively due to the secular part of the interaction.

Contrary to the odd moments of the total spectrum with respect to zero frequency, those of the line at ω_p , with ω_p as reference frequency need not be zero. One has for the first moment:

$$\begin{aligned}
 \langle \omega \rangle_p I_p &\equiv \int_{\omega_p - \delta}^{\omega_p + \delta} (\omega - \omega_p) \frac{v}{\pi} \chi''_{ii}(\omega, \vec{H}\vec{e}_i) \omega^{-1} d\omega \approx \\
 &\approx \beta \mu_0^{-1} H^{-2} \int_{\omega_p - \delta}^{\omega_p + \delta} (\omega - \omega_p) S_{pp}(\omega, \vec{H}\vec{e}_i) d\omega \approx \beta \mu_0^{-1} H^{-2} \int_{\omega_p - \delta}^{\omega_p + \delta} S_{pp0}(\omega, \vec{H}\vec{e}_i) d\omega \quad 6.23 \\
 &\approx \beta \mu_0^{-1} H^{-2} h^{-1} (\mathcal{K}_p, [\mathcal{K}_0, \mathcal{K}_p]) \mathcal{K}_z.
 \end{aligned}$$

It can be shown that this lowest order approximation of the first moment is zero in high temperature approximation, at least for the usual types of interaction.

6.38 The Yarmus and Harkavy approach.

Yarmus and Harkavy³⁴⁾ claim, that the quantity closest related to experimental results is $\omega^2 \chi''_{ii}(\omega, \vec{H}\vec{e}_i) \omega^{-1}$ instead of $\chi''_{ii}(\omega, \vec{H}\vec{e}_i) \omega^{-1}$ (cf. 1.53). Apart from the merits of their claim, which are discussed in appendix L, the first quantity contains the same high frequency information as the latter and deserves further investigation. Instead of the function $\phi_{ii}(t, \vec{H}\vec{e}_i)$ its second time derivative is studied

$$\begin{aligned}
 \int_{-\infty}^{+\infty} e^{i\omega t} \omega^2 \frac{v}{\pi} \chi''_{ii}(\omega, \vec{H}\vec{e}_i) \omega^{-1} d\omega &= -\frac{\partial^2}{\partial t^2} \phi_{ii}(t, \vec{H}\vec{e}_i) = \\
 &= \beta \mu_0^{-1} H^{-2} (L \mathcal{K}_{int}, e^{iL t L} \mathcal{K}_{int}) = \beta \mu_0^{-1} H^{-2} \sum_{p, q = \pm 1, \dots, \pm n} (\omega_p^p, e^{iL t \omega_q})
 \end{aligned} \quad 6.24$$

which implies

$$\omega^2 \frac{v}{\pi} \chi''_{ii}(\omega, \vec{H}\vec{e}_i) \omega^{-1} = \beta \mu_0^{-1} H^{-2} \sum_{p, q = \pm 1, \dots, \pm n} S_{p, q}(\omega, \vec{H}\vec{e}_i) \quad 6.25$$

with $P' \equiv \omega_p^p$, $S_{p, q}(\omega, \vec{H}\vec{e}_i) = \omega_p \omega_q S_{pq}(\omega, \vec{H}\vec{e}_i)$. Thus an expression for $\omega^2 \chi''_{ii}(\omega, \vec{H}\vec{e}_i) / \omega$ is achieved analogous to that for $\chi''_{ii}(\omega, \vec{H}\vec{e}_i) \omega^{-1}$. The main difference is the lacking of terms with $p = 0$ or $q = 0$. The same argument, which led in section 6.34 to the approximation

$$\chi_{ii}''(\omega, \vec{H}_i) \omega^{-1} \sim S_{pp}(\omega, \vec{H}_i) \quad , \quad \omega_p - \delta < \omega < \omega_p + \delta \quad 6.14$$

now leads to

$$\omega^2 \chi_{ii}''(\omega, \vec{H}_i) \omega^{-1} \sim S_{p,p}(\omega, \vec{H}_i) = \omega_p^2 S_{pp}(\omega, \vec{H}_i) \quad 6.26$$

This constitutes a nice demonstration of the rather poor quality of these approximations. The intensity and moment calculations, however, could be somewhat more reliable. It is clear that in the approximation used the Yarmus and Harkavy lines differ only by a factor ω_p^2 from the usual $S_{pp}(\omega, \vec{H}_i)$. Hence they get the same moments and can use the computational material available for those. The only attractive feature of the approach is the fact that complications due to the $p = 0$, $q = 0$ low frequency terms can be avoided.

6.39 Frequency and field.

It was seen in section 6.33, that the parallel field absorption spectrum in the zero interaction approximation ($\kappa \rightarrow \kappa_2$) reduces to a set of δ -lines at frequencies $\omega_p = \gamma_p H$. Studying the field dependence for a fixed frequency ω one thus has a set of δ -lines at fields $H_p = \gamma_p^{-1} \omega$. As the inequality 6.13 may equally well be used in the fixed frequency variable field interpretation, one can give an argument analogous to that in section 6.34. Hence, if the field dependence consists of well resolved lines at fields H_p one may approximate

$$H^2 \frac{\nu}{\pi} \chi_{ii}''(\omega, \vec{H}_i) \omega^{-1} \sim \beta \mu_0^{-1} S_{pp}(\omega, \vec{H}_i) \quad , \quad H_p - \Delta < H < H_p + \Delta \quad 6.27$$

The Yarmus and Harkavy counterpart would be

$$H^2 \frac{\nu}{\pi} \chi_{ii}''(\omega, \vec{H}_i) \omega^{-1} \sim \beta \mu_0^{-1} S_{pp}(\omega, \vec{H}_i) \quad , \quad H_p - \Delta < H < H_p + \Delta \quad 6.28$$

As the experimental configuration usually permits continuous field variations, but only a restricted choice of fixed frequencies, one most often determines the intensities and moments of the field dependent lines. Making use of the approximate frequency-field symmetry of the functions $S_{pp}(\omega, \vec{H}_i)$ one can perform a conversion into frequency determined values. The symmetry used is based on the approximation, valid for high temperatures and small interaction strength (compared to the static field), that the intensity and moments of $S_{pp}(\omega, \vec{H}_i)$ (with respect to ω_p) are independent of the static field. In other words: the shape of $S_{pp}(\omega, \vec{H}_i)$ (as a

function of frequency) is invariant, when its center frequency $\omega_p = \gamma_p H$ is shifted by a field variation. Hence $S_{pp}(\omega, \gamma_p^{-1} \omega_p \vec{e}_i)$ is approximately a function f of $\omega - \omega_p$ alone. The moments can therefore be converted as follows

$$\int_{\omega_p - \delta}^{\omega_p + \delta} (\omega - \omega_p)^n S_{pp}(\omega, \gamma_p^{-1} \omega_p \vec{e}_i) d\omega \sim \int_{\omega_p - \delta}^{\omega_p + \delta} (\omega - \omega_p)^n f(\omega - \omega_p) d\omega = \int_{-\delta}^{+\delta} x^n f(x) dx =$$

$$= - \int_{\omega + \delta}^{\omega - \delta} (\omega - \omega_p)^n f(\omega - \omega_p) d\omega_p \sim \gamma_p^{n+1} \int_{H_p - \gamma_p^{-1} \delta}^{H_p + \gamma_p^{-1} \delta} (H_p - H)^n S_{pp}(\omega, H \vec{e}_i) dH. \quad 6.29$$

The frequency-field symmetry constitutes perhaps the only criterion for a choice between the usual and the Yarmus and Harkavy description. It would be natural to prefer of the functions $H^2 \frac{\nu}{\pi} \chi_{ij}^i(\omega, H \vec{e}_i) \omega^{-1}$, $H_p^2 \frac{\nu}{\pi} \chi_{ij}^i(\omega, H \vec{e}_i) \omega^{-1}$ and $\beta \mu_0 S_{pp}(\omega, H \vec{e}_i)$ the one that satisfies the approximation of field independent line shapes (vs. frequency) best, i.e. down to lowest fields. Only experiment can decide.

6.4 Simplifications due to the special structure of Cu Tutton salts.

6.41 The decomposition of \mathcal{K}_{int} for arbitrarily oriented \vec{H} .

The copper Tutton salts contain two subsystems (I and II) of magnetic ions (cf. section 6.1) corresponding to both types of tetragonal axis that occur. Within one subsystem all ions have the same g-tensor and A-tensor. According to 5.27 and 5.29 one may therefore write

$$\mathcal{K}_{hfs} = \sum_{u=I,II} \sum_{\alpha} \mathcal{K}_u^{\alpha} \quad 6.30$$

$$\mathcal{K}_{ex} + \mathcal{K}_d = \sum_{u,v=I,II} \sum_{\alpha,\beta} \mathcal{K}_{uv}^{\alpha\beta} \quad 6.31$$

with definitions 5.17, 5.18, 5.28 and 5.30. The exchange may be assumed to be of the Heisenberg type, $\vec{J}_{mn} = \bar{U} \frac{1}{3} \text{Tr} \vec{J}_{mn} = J_{mn} \bar{U}$. Eqs. 6.30 and 6.31 define a decomposition of $\mathcal{K}_{int} = \mathcal{K}_{hfs} + \mathcal{K}_{ex} + \mathcal{K}_d$ into eigenoperators \mathcal{K}_p of L_z in the sense of section 6.31. The eigenvalues ω_p , which according to sections 6.33 and 6.34 represent the centerfrequencies of the high-field absorption lines, are therefore given by

$$\omega_p = \alpha \omega_{Lu} + \beta \omega_{Lv} \quad , \quad \alpha, \beta = -1, 0, +1; \quad u, v = I, II \quad 6.32$$

(cf. 5.19, 5.20).

As thirteen different values can be seen to occur for $\omega_{LI} \neq \omega_{LII}$ one might number them $p = -6, -5, \dots, 0, \dots, +6$. Generally speaking the absorption spectrum in strong parallel fields is thus found to consist of thirteen lines.

6.42 The decomposition of \mathcal{K}_{int} for \vec{H} in the k2-k1 or k2-k3-plane.

An important simplification is achieved if $\vec{H} = H\vec{e}_i$ is chosen in the k2-k1- or k2-k3-plane. Then \vec{H} makes equal angles with both types of tetragonal axis implying $|\vec{H}_{eff,I}| \equiv |\vec{H} \cdot \vec{g}_I| = |\vec{H}_{eff,II}| \equiv |\vec{H} \cdot \vec{g}_{II}|$ and thus $\omega_{LI} = \omega_{LII} \equiv \omega_L$ (and $g_I = |\vec{e}_i \cdot \vec{g}_I| = g_{II} = |\vec{e}_i \cdot \vec{g}_{II}| \equiv g$, cf. 5.09). Consequently many of the thirteen lines coincide and only five are seen to result.

Taking together those eigenoperators of which the eigenvalues have become the same one gets the simple decomposition

$$\mathcal{K}_{int} = \sum_{p=-2,-1,\dots,+2} \mathcal{K}_p \quad 6.33$$

$$\text{with } \mathcal{K}_p \equiv \sum_{\alpha=-1,0,+1} \sum_{u=1,11} \mathcal{K}_u^\alpha \delta_{\alpha p} + \sum_{\alpha,\beta=-1,0,+1} \sum_{u=1,11} \mathcal{K}_{uv}^{\alpha\beta} \delta_{\alpha+\beta p} \quad 6.34$$

$$\text{and } L_z \mathcal{K}_p = \omega_p \mathcal{K}_p = p \omega_L \mathcal{K}_p, \quad p = \alpha + \beta = -2, -1, \dots, +2. \quad 6.35$$

For this case the constants $\gamma_p \equiv \omega_L H^{-1}$ equal

$$\gamma_p = p \hbar^{-1} \mu_o \mu_B g = p \gamma_1. \quad 6.36$$

The parallel field absorption spectrum for this case is thus found to consist of five lines at frequencies $0, \pm \omega_L$ and $\pm 2\omega_L$.

According to appendix I this implies that no crossterm contributions of third and lowest order are to be expected in the lines at $\pm 2\omega_L$. (Both ways to write $2\omega_L$ as a sum of ω_p 's, i.e. $\omega_L + \omega_L$ and $0 + 2\omega_L$, are excluded.) On the contrary such crossterm contributions can exist in the lines at $\pm \omega_L$ (as ω_L can be written as $2\omega_L + (-\omega_L)$).

This five-line spectrum resembles the case of absorption in a sample with the same isotropic g-tensor for all ions, considered by other authors^{27,22,28}). The g-anisotropy however is seen to complicate seriously the decomposition of \mathcal{K}_{int} and hence the expressions for intensities and second moments of the lines (cf. 6.17 and 6.22). Hillaert³⁵) has performed the laborious task of their computation on the basis of the argument given in section 5.2. His results will be used for a confrontation with experimental values (cf. section 6.5).

6.43 The static susceptibility in high temperature approximation.

It is convenient to present the experimental results for the field- and frequency-dependent susceptibility as values relative to the static susceptibility $\chi_o(H \vec{e}_i)$. To this end an expression for it will be derived. According to 4.06 one has - in zero interaction limit -

$$\chi_{o \quad ii}(H \vec{e}_i) = \beta \mu_o v^{-1} \{ (M_i, M_i)_{\mathcal{K}_z} - (P_i M_i, P_i M_i)_{\mathcal{K}_z} \}. \quad 6.37$$

As 3.01, 6.00 and 5.02 imply

$$M_i = - \mu_B \sum_n \vec{e}_i \cdot \vec{g}_n \cdot \vec{S}_n = - \mu_B \sum_n g_n S_n^o \quad 6.38$$

one has

$$\chi_{O_{ii}}(\mathbf{H} \vec{e}_i) = \beta \mu_o v^{-1} \sum_{m,n} g_m g_n \mu_B^2 \{ (S_m^O, S_n^O)_{\mathcal{H}_Z} - (1, S_m^O)_{\mathcal{H}_Z} (1, S_n^O)_{\mathcal{H}_Z} \} \quad 6.39$$

with $\mathcal{H}_Z = -\mu_o H M_i$.

One may evaluate 6.39 to be

$$\begin{aligned} \chi_{O_{ii}}(\mathbf{H} \vec{e}_i) = \beta \mu_o v^{-1} \sum_n g_n^2 \mu_B^2 \{ & (\text{Tr } e^{-\beta \mathcal{H}_{Z,n}})^{-1} \text{Tr } e^{-\beta \mathcal{H}_{Z,n}} (S_n^O)^2 \\ & - (\text{Tr } e^{-\beta \mathcal{H}_{Z,n}})^{-1} (\text{Tr } e^{-\beta \mathcal{H}_{Z,n}} S_n^O)^2 \} \end{aligned} \quad 6.40$$

with $\mathcal{H}_{Z,n} \equiv \mu_o H g_n \mu_B S_n^O$.

In high-temperature approximation, i.e. if β is negligible with respect to the single-ion Zeeman energy, one gets

$$\chi_{O_{ii}}(\mathbf{H} \vec{e}_i) \approx \beta \mu_o v^{-1} \sum_n g_n^2 \mu_B^2 \text{Tr} (S_n^O)^2 / \text{Tr} 1. \quad 6.41$$

For $\vec{H} = H \vec{e}_i$ in the k2-k1- or k2-k3-plane g_n is the same for all ions and

$$\chi_{O_{ii}}(\mathbf{H} \vec{e}_i) \approx \beta \mu_o v^{-1} N g^2 \mu_B^2 \frac{1}{3} S(S+1), \quad S = \frac{1}{2} \quad 6.42$$

which is the well-known Curie law for this case. Eq. 6.42 shows no dependence on H , therefore

$$\chi_{O_{ii}}(\mathbf{H} \vec{e}_i) \approx \chi_{O_{ii}}(0). \quad 6.43$$

One can prove that also

$$\chi_{O_{ii}}(\mathbf{H} \vec{e}_j) \approx \chi_{O_{ii}}(0). \quad 6.44$$

6.44 Expressions for intensity and moments.

According to 6.11, 6.14 and 6.42, 6.43 $\chi''/v\chi_o$, the central experimental quantity, and $S_{pp}(\omega, \mathbf{H} \vec{e}_i)$, the functions which play the main role in the theoretical analysis, are related by

$$2N \hbar^2 \frac{1}{3} S(S+1) \frac{\nu_L^2 \chi_{ii}''(2\pi\nu, 2\pi\nu_L \gamma_i^{-1} \vec{e}_i)}{\nu \chi_{oi}(0)} \approx S_{pp}(\omega, H \vec{e}_i),$$

$$\nu - \delta/2\pi < \nu_L < \nu + \delta/2\pi \quad 6.45$$

where $S = \frac{1}{2}$ and N is the number of magnetic ions in the sample ($\omega \equiv 2\pi\nu$; $\omega_L \equiv 2\pi\nu_L \equiv \gamma_i H$, cf. 6.36; \vec{e}_i in k_2-k_1 or k_2-k_3).

As was mentioned in section 6.39 $S_{pp}(\omega, H \vec{e}_i)$ is approximately a function of $\omega - p\omega_L \equiv \omega - p\gamma_i H$ alone. In analogy to 6.29 one thus has for intensity I_p and moments $\langle \omega_p^n \rangle$ ($\langle \omega_p^0 \rangle \equiv 1$)

$$\langle \omega_p^n \rangle \frac{I_p}{p} \beta^{-1} \mu_o H^2 \equiv \int_{p\omega_L - \delta}^{p\omega_L + \delta} (\omega - p\omega_L)^n S_{pp}(\omega, H \vec{e}_i) d\omega \approx$$

$$\approx (2\pi p)^{n+1} 2N \hbar^2 \frac{1}{3} S(S+1) \int_{\nu - \delta/2\pi p}^{\nu + \delta/2\pi p} (\nu p^{-1} - \nu_L)^n \frac{\nu_L^2 \chi_{ii}''}{\nu \chi_{oi}} d\nu_L. \quad 6.46$$

The experimental values obtained in this way can be confronted with the results of eqs. 6.17 and 6.22.

6.5 Experimental results. Absorption measurements in parallel fields at the highest frequencies.

6.51 Qualitative remarks.

As the theory given in section 6.3 requires a static field so strong as to yield a well-resolved absorption spectrum and as the centerfrequencies of the lines were seen to be proportional to the static field (6.08, 6.35) a measurement at fixed frequency and variable field should be performed at the highest available frequency. For the Cs- and Rb-salt a frequency $\omega/2\pi \approx 3$ GHz was found to give sufficient resolution. A new cavity at $\omega/2\pi = 4.8$ GHz was constructed in order to improve the K- and NH_4 -results.

The moderate maximum value of the static field needed in a measurement at these frequencies amounts to only 4 or 5 kOe and can easily be obtained.

One might wonder why no measurements were done at "X-band" or even higher frequencies. The reason is a technical one. According to eq. 6.17 the intensity of the lines is proportional to H^{-2} , thus decreasing rapidly with increasing measuring frequency. This intensity competes with spurious resonance absorption (with field independent intensity) due to misalignment of the static and alternating fields.

As the homogeneity of the fields used is only of restricted

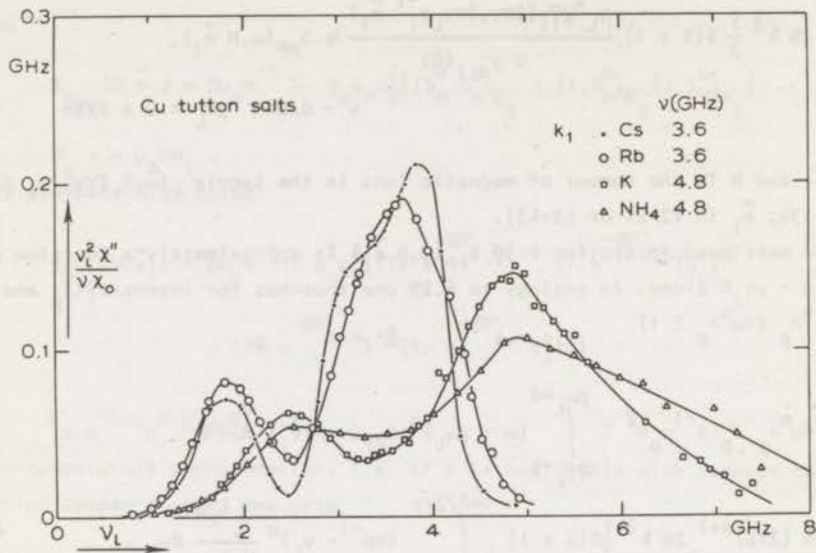


Fig. 6.30 High-frequency parallel-field absorption as a function of static field in four Cu Tutton salts. Fields along k_1 . The field is given in terms of the Larmor frequency ν_L .

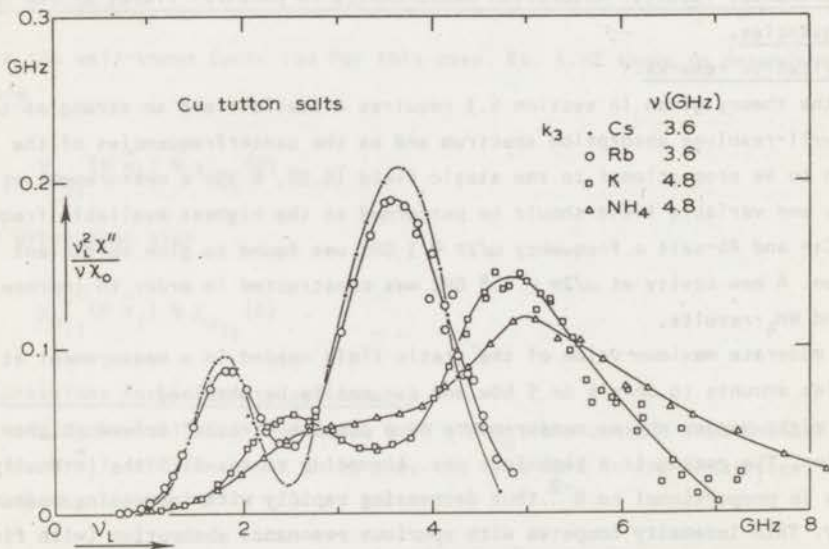


Fig. 6.31 High-frequency parallel-field absorption. Fields along k_3 .

quality, the same can be said of the optimal alignment. Another reason is the occurrence of unwanted modes in $\frac{1}{4} \lambda$ coaxial cavities of manageable size at these high frequencies. The use of a different type looks inevitable and so do the problems of design and construction connected to it.

Absorption measurements at 3 and 5 GHz have been performed with \vec{e}_i along k1-, k2- and k3-axis for the four Tutton salts. Two lines are observed centered at ν_L and $\nu_L/2$. They correspond to $|p| = 1$ and $|p| = 2$ respectively and represent all high-frequency information as, due to the frequency symmetry of the absorption spectrum lines of opposite p are physically equivalent.

In figs. 6.30, 6.31 and 6.32 the experimental results have been plotted. The linewidths are immediately seen to increase through the series Cs, Rb, K, NH_4 . This corresponds to the increasing second moment, determined fully by the secular interaction and thus mainly by the increasing exchange interaction (~~exchange interaction~~ isotropic g-tensor \mathcal{H}_{ex} is exactly secular; in the Rb-, K- and NH_4 -salt \mathcal{H}_{ex} is larger than the secular parts of \mathcal{H}_d and \mathcal{H}_{hfs} .)

In spite of the enhanced frequency the line separation in the K- and NH_4 -salt is rather poor. On the other hand traces of spurious resonance can already be recognized.

In the (Cs, k1)-measurement the line at ν_L is found to be asymmetric. Check measurements at other frequencies have confirmed this shape. Moreover special care has been given to the orientation of the crystal, in order to ensure that \vec{e}_i be parallel to k1. No satisfactory explanation of the asymmetry has been found so far.

6.52 Quantitative considerations, confrontation with theoretical results.

Combining eqs. 6.17 and 6.46 one finds that the total area under a curve in figs. 6.30, 6.31 and 6.32 is given by

$$\int_0^{\infty} \frac{\nu_L^2 \chi''}{\nu \chi_0} d\nu_L = 4\pi \left\{ \frac{\text{Tr } \mathcal{H}_1^+ \mathcal{H}_1}{N h^2 \text{Tr } I} + \frac{1}{2} \frac{\text{Tr } \mathcal{H}_2^+ \mathcal{H}_2}{N h^2 \text{Tr } I} \right\}$$

Theoretical values ³⁵⁾ for $N^{-1} h^{-2} \text{Tr } \mathcal{H}_p^+ \mathcal{H}_p / \text{Tr } I$ are given in table 6.4 together with the resulting predictions for the total area and the experimental values of the latter. The experimental results are systematically higher than the calculated ones. The difference varies from a few to 30 percent. Roughly speaking the k2-axis (and for the NH_4 -salt also the k1-axis) shows the largest discrepancies. For the K- and NH_4 -compound this could be ascribed to the increasing errors due to the multiplication by ν_L^2 , which occur in the high field region.

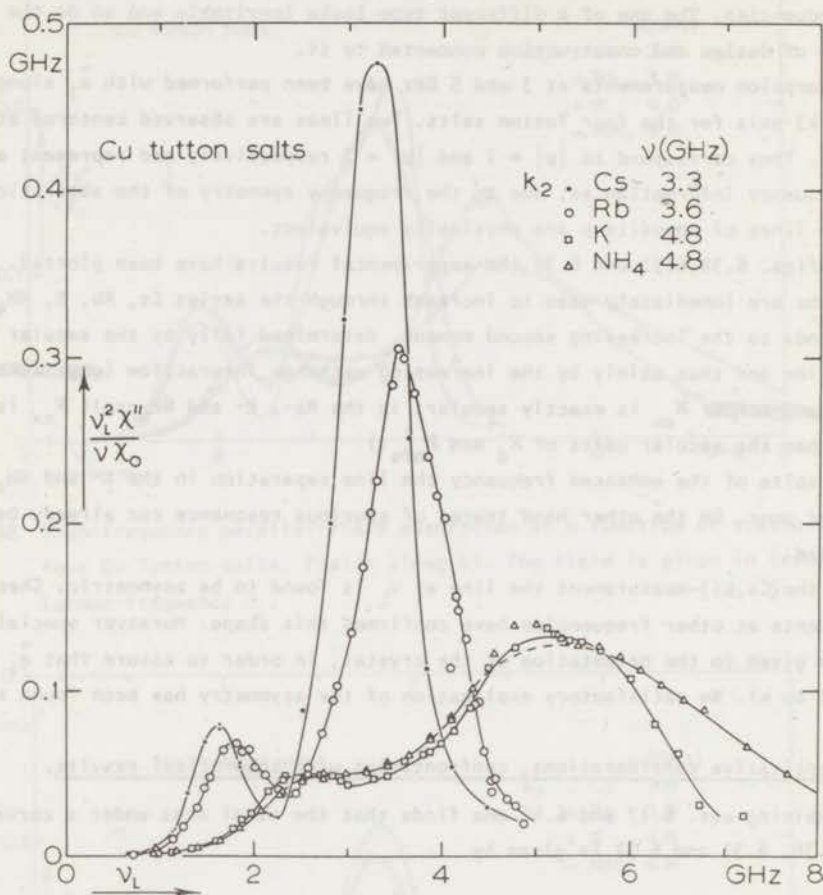


Fig. 6.32 High-frequency parallel-field absorption. Fields along k_2 .

The theoretical values for the traces have also been used for the calculation of the second moment of the zero field absorption line (cf. table 6.3) which should equal

$$8 \frac{\text{Tr } \mathcal{H}_1^+ \mathcal{H}_1}{N h^2 \text{Tr } I} + 32 \frac{\text{Tr } \mathcal{H}_2^+ \mathcal{H}_2}{N h^2 \text{Tr } I},$$

as can be found from an analysis of (LM_1, LM_1) . Again the

experimental values are too high and in this case the reason cannot be found in some gauge factor of the absorption measurement. Although the discrepancies are of the same order, no obvious correlations between the deviations in both sets of results are found.

The relative intensity of the lines at $\nu_L = \frac{1}{2}\nu$ and $\nu_L = \nu$ ($|p| = 2, 1$) constitutes another easy check, provided that the lines are sufficiently resolved.

In the Cs- and Rb-salt a reasonable agreement is found for the k_1 - and k_3 -direction. As in the total intensity a large deviation occurs in the k_2 -direction. This must be totally ascribed to the $|p| = 1$ line, as the intensities of the $|p| = 2$ line in these compounds agree within 10% (k_1, k_3 even 3%) with the predicted values (cf. $\text{Tr } \mathcal{H}_2^+ \mathcal{H}_2$ exp. in table 6.4). Nevertheless there is no reason to think of spurious resonance effects as similar anomalously large intensities are observed at other frequencies (cf. figs. 6.34, 6.38). Although one may remark that the conditions of appendix 1 exclude crossterms from contributing to the $|p| = 2$ line, whereas the other line lacks this feature, it is dubious if this is a sufficient ground. The satellite at ν_L of the line at $-\nu_L$ (cf. section 6.37) should at least amount to 13% allowing (cf. 6.13) a crossterm contribution of 36% in the intensity in order to account for the factor 1.5 discrepancy in the Rb k_2 case ($(\mathcal{H}_1, e^{iL\mathcal{H}_1})$ and $(\mathcal{H}_{-1}, e^{iL\mathcal{H}_{-1}})$ are the only cross terms present).

Relative intensity determination from the K- and NH_4 -measurements is largely a matter of artificial separation. The method followed - apparently with little success - consisted of an approximate fit of the $|p| = 2$ lineshapes observed in the Cs- and Rb-salts (using scaling factors) to the low field side of the K- and NH_4 -lines at $\nu_L = \frac{1}{2}\nu$. The need for sufficient resolution is clearly demonstrated.

Although the artificial separation described yields very poor results for the intensities, slightly better agreement is obtained for the second moments (cf. table 6.5). The experimental widths clearly follow the increasing theoretical prediction as exchange (and hence the secular part of the interaction) is enhanced from Cs to NH_4 . Apart from the second moments the first moments have been evaluated. On theoretical grounds these should be zero at high temperatures (cf. section 6.37).

In the Cs- and Rb-compounds, where the resolution is sufficient the experimental value for the first moment $\langle \nu \rangle_1$ of the $|p| = 1$ line is small as expected. It should be remarked that the asymmetry of this line for the k_1 -direction of the Cs-salt is not particularly reflected in the first moment and thus yields no contradiction with theory. The first moments of the $|p| = 2$ lines are also small and have not been given

Table 6.4

	$\frac{\text{Tr } \mathcal{K}_1^+ \mathcal{K}_1}{\text{Nh}^2 \text{Tr } 1}$	$\frac{\text{Tr } \mathcal{K}_2^+ \mathcal{K}_2}{\text{Nh}^2 \text{Tr } 1}$		$\frac{\text{Tr } \mathcal{K}_1^+ \mathcal{K}_1}{\text{Tr } \mathcal{K}_2^+ \mathcal{K}_2}$		$\frac{4\pi(\text{Tr } \mathcal{K}_1^+ \mathcal{K}_1 + \frac{1}{2}\text{Tr } \mathcal{K}_2^+ \mathcal{K}_2)}{\text{Nh}^2 \text{Tr } 1}$			$\frac{8\text{Tr } \mathcal{K}_1^+ \mathcal{K}_1 + 32\text{Tr } \mathcal{K}_2^+ \mathcal{K}_2}{(\text{Nh}^2 \text{Tr } 1)^{\frac{1}{2}}}$		
	th (Ghz ²)	th (Ghz ²)	exp	th	exp	th (Ghz ²)	exp	%	th	exp	%
Cs	0.02068	0.00946	0.0095	2.186	2.15	.3194	.32	0	.6843	.755	10
Rb	0.01875	0.01137	0.0117	1.650	1.7	.3070	.34	11	.7167	.796	11
K	0.01960	0.01279	0.0097	1.532	2.65	.3267	.38	16	.7525	.782	4
NH ₄	0.01983	0.01214	0.0088	1.634	3.3	.3255	.42	29	.7396	.776(p)	4
Cs	0.02956	0.008015	0.0089	3.689	4.3	.4219	.53	26	.7021	.745	6
Rb	0.02601	0.00878	0.0084	2.960	4.4	.3820	.43	13	.6994	.74	6
K	0.02302	0.00982	0.0118	2.344	2.3	.3510	.43	22	.7060		
NH ₄	0.03135	0.00850	0.0118	3.688	3.1	.4473	.54	20	.7230	.776(p)	4
Cs	0.01979	0.01120	0.0113	1.766	1.85	.3191	.335	5	.7198	.826	15
Rb	0.01979	0.01205	0.0124	1.642	1.7	.3243	.35	8	.7374	.80	9
K	0.01884	0.01330	0.0088	1.417	2.9	.3204	.37	15	.7591	.826	9
NH ₄	0.02284	0.01254	0.0060	1.820	5.2	.3657	.43	17	.7642	.776(p)	4

Table 6.5

	$\frac{1}{2\pi} \langle \omega \rangle_1$		$\frac{1}{2\pi} \langle \omega^2 \rangle_1^{\frac{1}{2}}$		%	$\frac{1}{2\pi} \langle \omega^2 \rangle_2^{\frac{1}{2}}$		%
	exp (GHz)	exp (GHz)	th			exp (GHz)	th	
k1								
Cs	0.04	0.46	0.50 ₁	- 8	0.67	0.65 ₀	+ 3	
Rb	0.03	0.54	0.67 ₂	- 20	0.75	0.81 ₀	- 7	
K	- 0.21	1.03	1.09 ₃	- 6	1.00	1.19 ₇	- 16	
NH ₄	- 0.60	1.52	1.35 ₃	+ 12	1.15	1.50 ₅	- 24	
k2								
Cs	- 0.09	0.51	0.49 ₅	+ 3	0.66	0.62 ₈	+ 5	
Rb	- 0.06	0.58	0.69 ₁	- 16	0.70	0.85 ₂	- 18	
K	- 0.25	1.03	1.11 ₀	- 7	1.2	1.26 ₀		
NH ₄	- 0.71	1.55	1.31 ₅	+ 18	1.2	1.49 ₀	- 20	
k3								
Cs	- 0.03	0.47	0.49 ₉	- 6	0.65	0.67 ₈	- 4	
Rb	- 0.02	0.59	0.66 ₉	- 12	0.74	0.84 ₅	- 12	
K	- 0.07	0.98	1.09 ₈	- 11	1.04	1.27 ₀	- 18	
NH ₄	- 0.53	1.54	1.34 ₃	+ 14	1.33	1.56 ₀	- 15	

as they can be changed arbitrarily by the details of separation otherwise unimportant in these salts.

The second moments measured in the Cs-salt yield satisfactory agreement with the theoretical results. The same cannot be said with respect to the Rb-compound which shows systematically too narrow lines (≈ 20%).

The second moments of the K- and NH₄-salt are less affected by separation problems than the intensities, as the uncertain centre region of the |p| = 2 lines has a less important weight. The high-field side of these lines has not been used, especially in the NH₄-salt even the low-field side may still be uncertain.

On the other hand separation details are not of great influence on the width of the |p| = 1 lines. The large experimental values for the NH₄-compound may again be attributed to inaccuracy in the high field region. The error may be estimated from the first moment values, which arise from the same effect, as theoretically they ought to be zero.

In general the difference between the three k-axes is hardly observable in the second moments. More accurate measurements with better separation, i.e. at higher frequencies, are needed. The spurious resonance occurring at $\nu_L = \nu$ will not affect the |p| = 2 line. Hence it is suggested that further experimental efforts in this field be focused on the |p| = 2 line in parallel static fields at high frequencies.

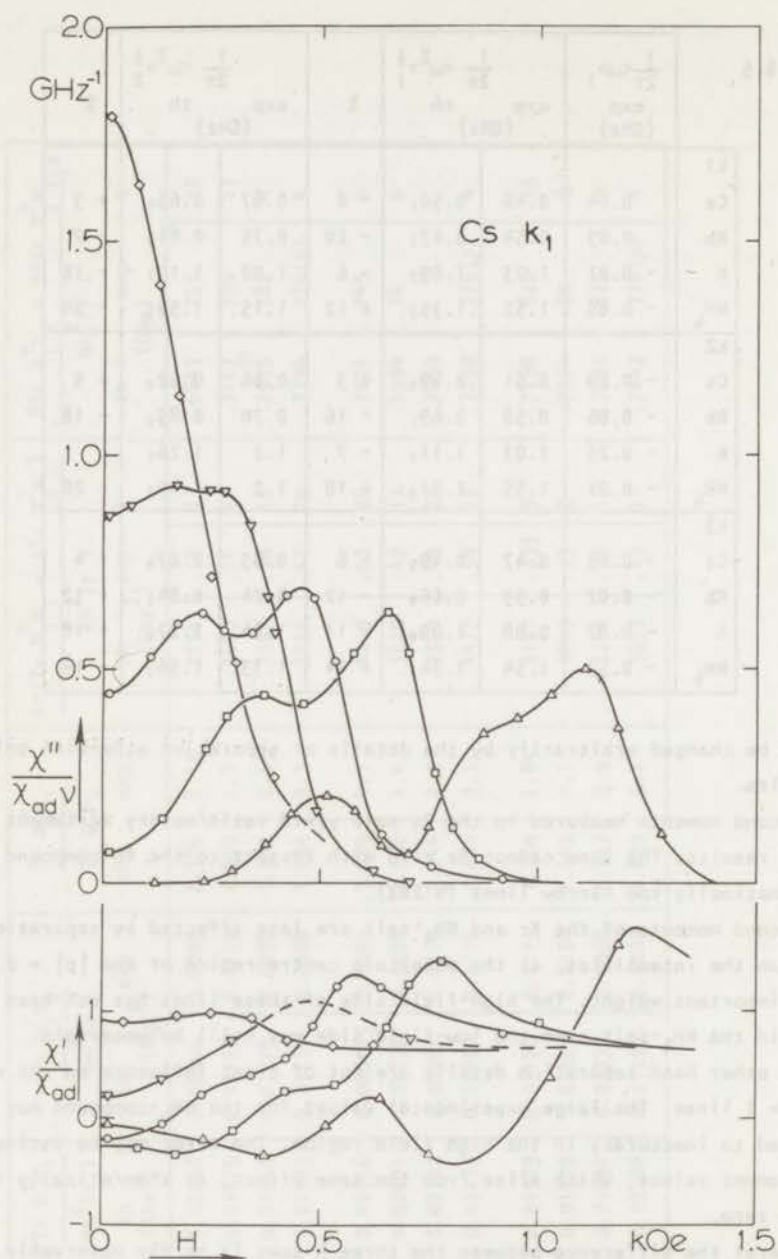


Fig. 6.33 Parallel-field dependence of absorption and dispersion in $\text{CuCs}_2(\text{SO}_4)_2 \cdot 2.6 \text{ aq.}$ at some frequencies (cf. fig. 6.34). Fields along k_1 .

$$\chi_{\text{ad}}^{-1} \chi_0 = 1 + H^2 (207 \text{ Oe})^{-2}.$$

6.6 Experimental results at frequencies below 3.6 GHz.

In the earlier stages of investigation the role of the high static field in the theoretical description was not yet felt so essential as it appeared to be later on. Hence many measurements have been performed at lower frequencies than 3.6 GHz.

As it may not be excluded that a theory should ever be conceived that does without the zero interaction approximation the results of these measurements are given in the following pages. As much of the information lies in the low-field region the factor ν_L^2 has been replaced by a factor containing χ_{ad} (cf. figure captions) analogous to the presentation in ref. 26.

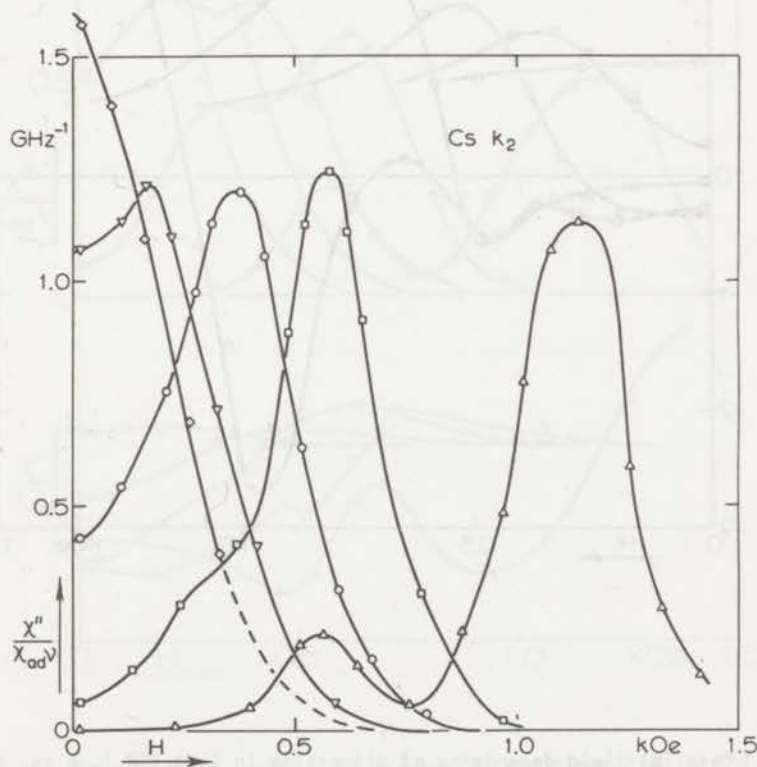


Fig. 6.34 Parallel-field dependence of absorption in $\text{CuCs}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$ at some frequencies. \diamond 0.18 GHz, ∇ 0.78 GHz, \circ 1.22 GHz, \square 1.78 GHz, \triangle 3.2 GHz. Fields along k_2 . $\chi_{ad}^{-1} \chi_0 = 1 + H^2 (230 \text{ Oe})^{-2}$.

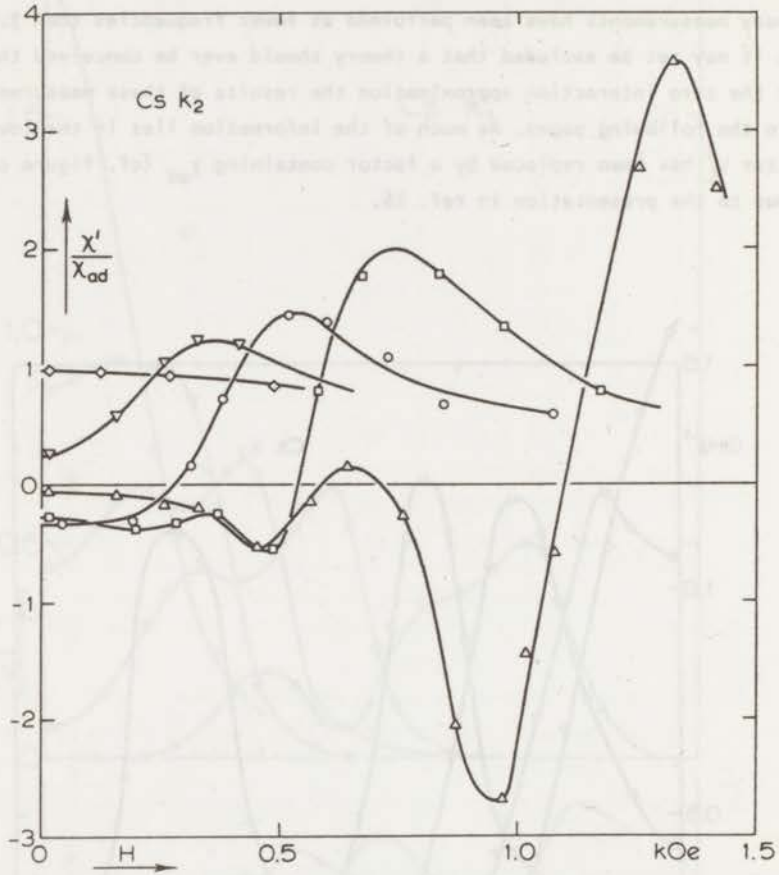


Fig. 6.35 Parallel-field dependence of dispersion in $\text{CuCs}_2(\text{SO}_4)_{2.6}$ aq. at some frequencies (cf. fig. 6.34). Fields along k_2 . $\chi_{ad} \chi_0 = 1 + H^2 (230 \text{ Oe})^{-2}$.

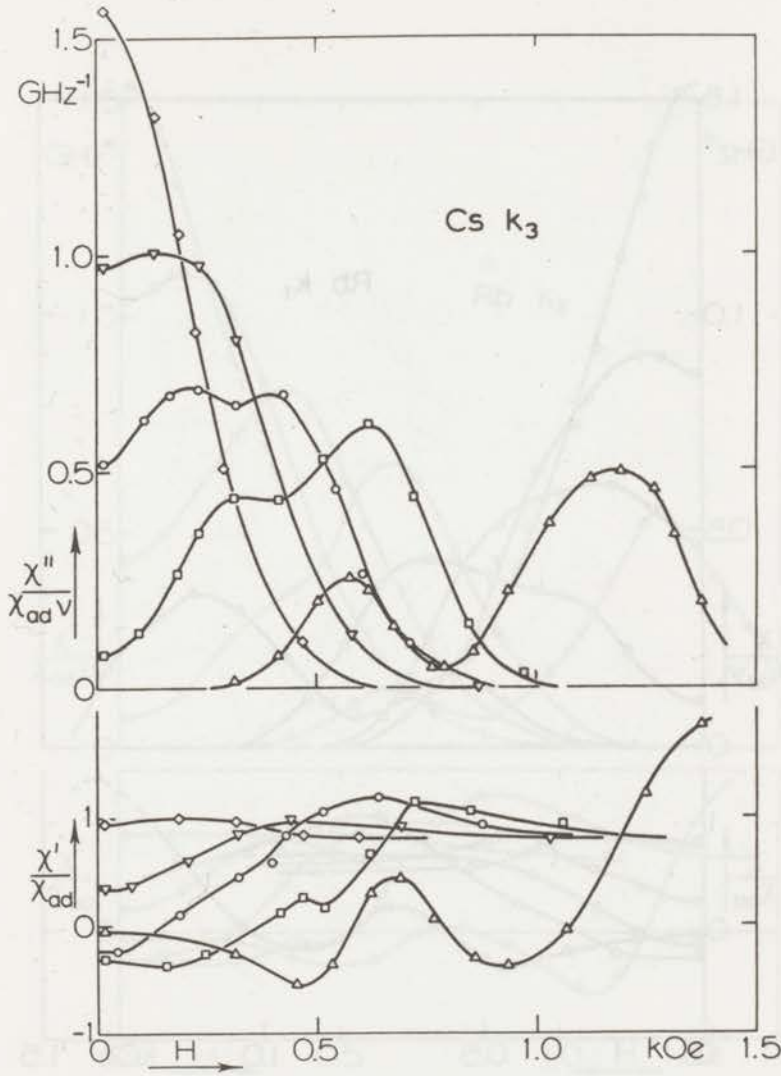


Fig. 6.36 Parallel-field dependence of absorption and dispersion in $\text{CuCs}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$ at some frequencies. Δ 3.6 GHz, further cf. fig. 6.34. Fields along k_3 .
 $\chi_{\text{ad}}^{-1} \chi_0 = 1 + H^2 (212 \text{ Oe})^{-2}$.

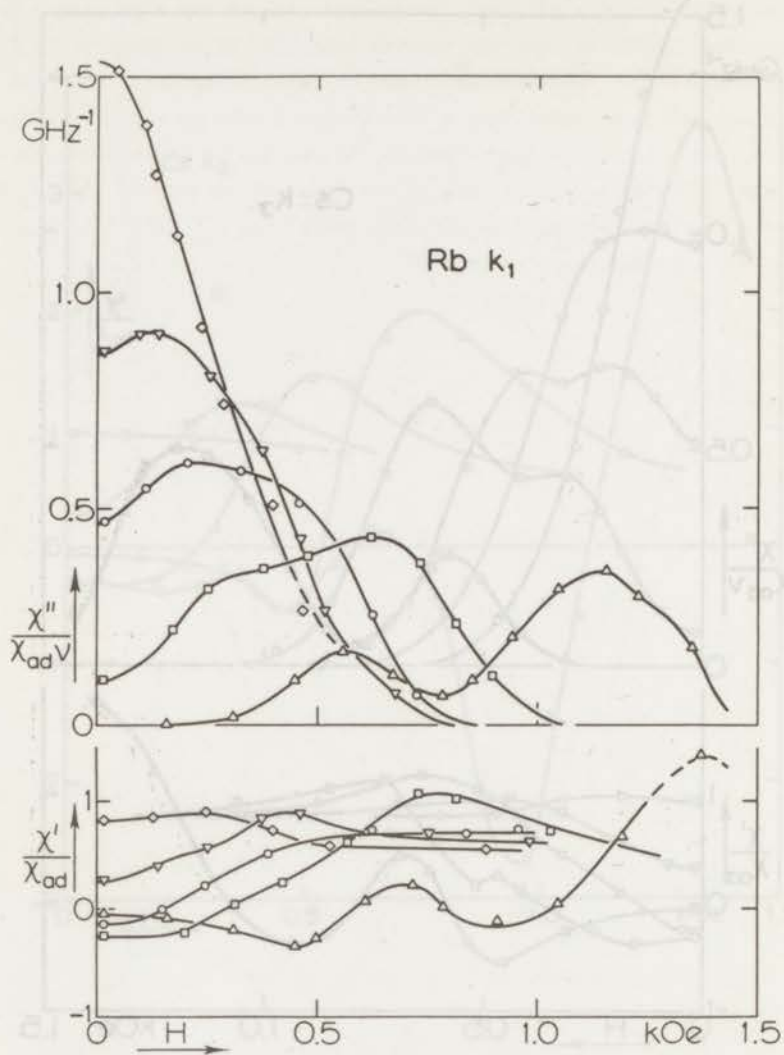


Fig. 6.37 Parallel-field dependence of absorption and dispersion in $\text{CuRb}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$ at some frequencies. \diamond 0.26 GHz, further cf. fig. 6.36. Fields along k_1 .
 $\chi''_{\text{ad}}^{-1} \chi''_0 = 1 + H^2 (232 \text{ Oe})^{-2}$.

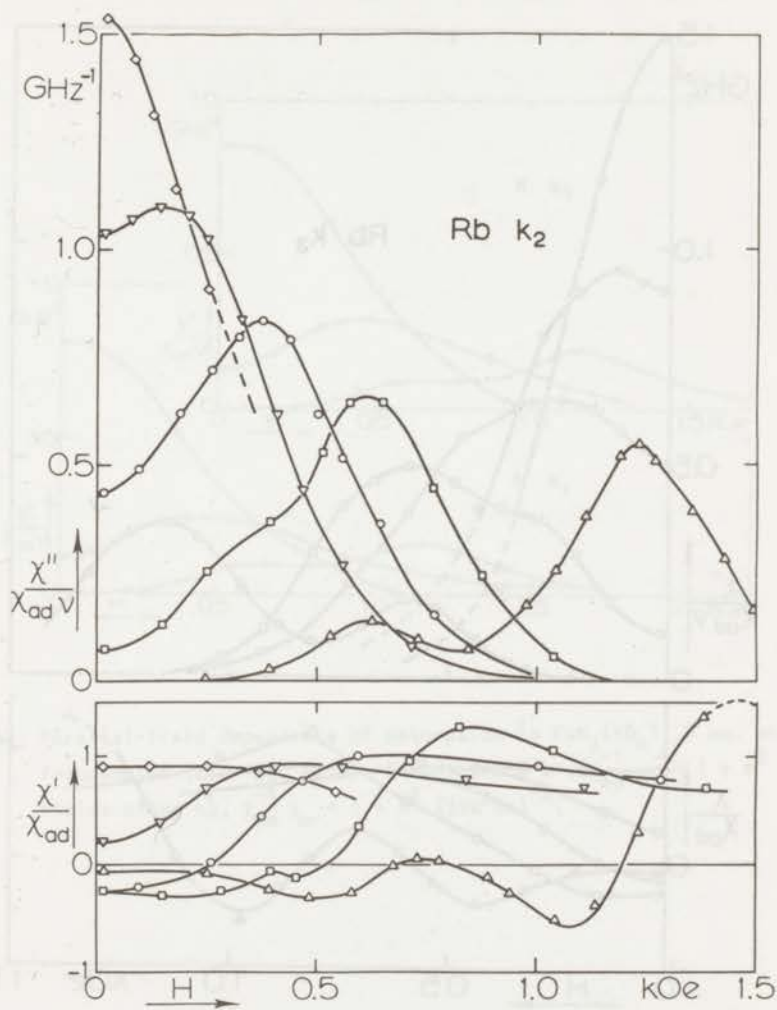


Fig. 6.38 Parallel-field dependence of absorption and dispersion in $\text{CuRb}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$ at some frequencies (cf. fig. 6.37). Fields along k_2 .
 $\chi_{\text{ad}}^{-1} \chi_0 = 1 + H^2 (257 \text{ Oe})^{-2}$.

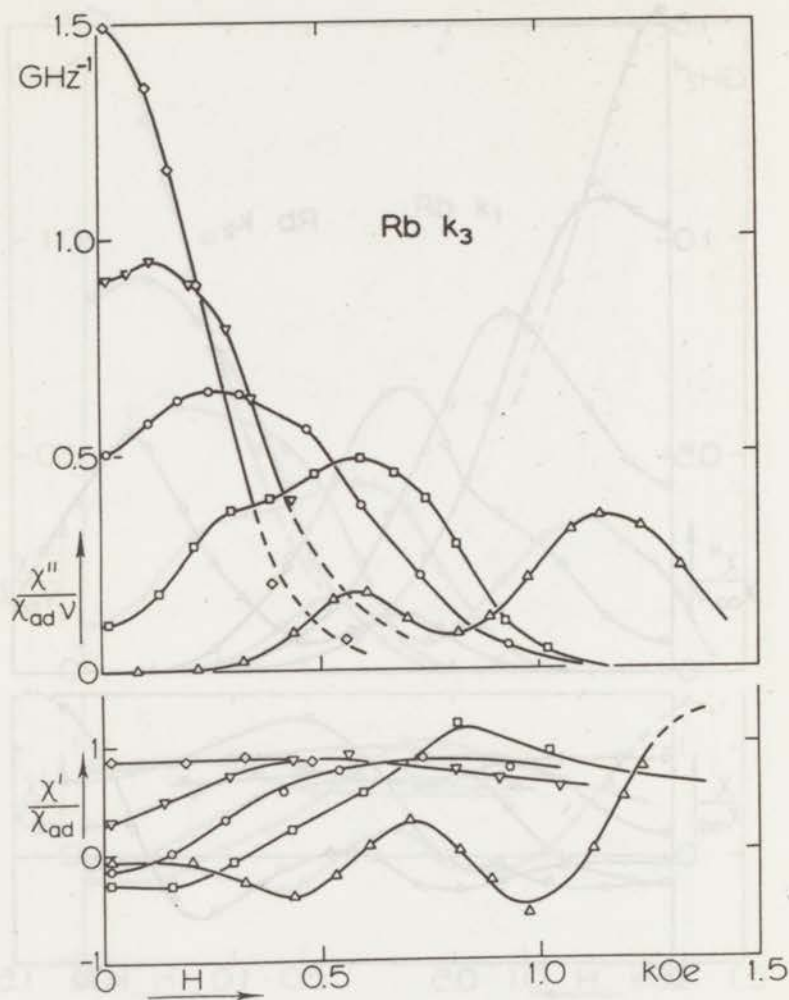


Fig. 6.39 Parallel-field dependence of absorption and dispersion in $\text{CuRb}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$ at some frequencies (cf. fig. 6.37). Fields along k_3 .
 $\chi_{ad}^{-1} \chi_0 = 1 + H^2 (239 \text{ Oe})^{-2}$.

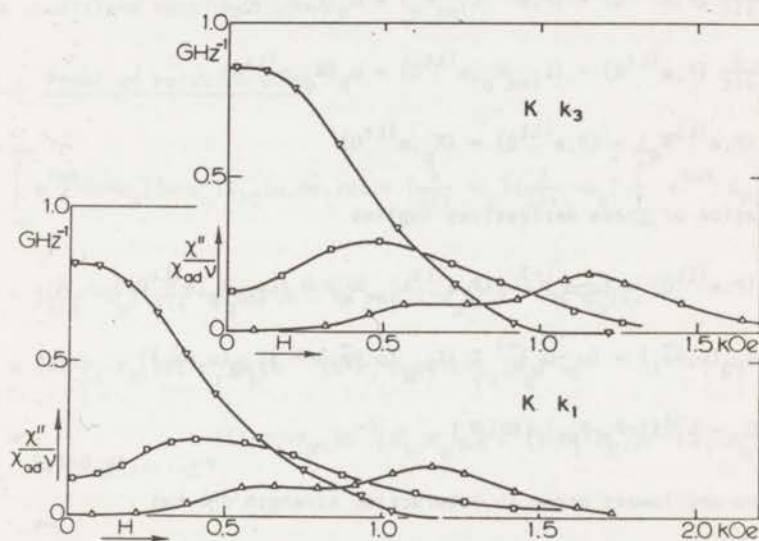


Fig. 6.40 Parallel-field dependence of absorption in $\text{CuK}_2(\text{SO}_4)_2 \cdot 6 \text{ aq.}$ at some frequencies (cf. fig. 6.37). Fields along k_1 , $\chi_{\text{ad}}^{-1} \chi_0 = 1 + H^2 (315 \text{ Oe})^{-2}$. Fields along k_3 , $\chi_{\text{ad}}^{-1} \chi_0 = 1 + H^2 (320 \text{ Oe})^{-2}$.

Appendix I. A further investigation of the cross terms.

Differentiating a cross term one gets

$$\frac{\partial}{\partial t} (P, e^{iLtQ}) = (P, e^{iLt} L_{int} \mathcal{H}_q) + \omega_q (P, e^{iLt} \mathcal{H}_q)$$

or
$$\frac{\partial}{\partial t} (P, e^{iLtQ}) = (L_{int} \mathcal{H}_p, e^{iLtQ}) + \omega_p (\mathcal{H}_p, e^{iLtQ}) .$$

As
$$(P, e^{iLt} \mathcal{H}_q) = (P, e^{iLtQ}) = (\mathcal{H}_p, e^{iLtQ})$$

identification of these derivatives implies

$$(P, e^{iLtQ}) = (\omega_p - \omega_q)^{-1} ((P, e^{iLt} L_{int} \mathcal{H}_q) - (L_{int} \mathcal{H}_p, e^{iLtQ}))$$

and
$$S_{PQ}(\omega, H\vec{e}_i) = (\omega_p - \omega_q)^{-1} \sum_r (S_{PQR}(\omega, H\vec{e}_i) - S_{PrQ}(\omega, H\vec{e}_i))$$

where
$$Q_r = h^{-1} (1 - P_i - P_{\mathcal{H}_i}) [\mathcal{H}_r, \mathcal{H}_q]$$

Up to third and lowest order in interaction strength one has

$$S_{PQR}(\omega, H\vec{e}_i) \sim h^{-1} (\mathcal{H}_p, [\mathcal{H}_r, \mathcal{H}_q]) \mathcal{H}_z \delta(\omega - \omega_p) \quad , p \neq 0$$

and
$$S_{PrQ}(\omega, H\vec{e}_i) \sim h^{-1} ([\mathcal{H}_r, \mathcal{H}_p], \mathcal{H}_q) \mathcal{H}_z \delta(\omega - \omega_q) \quad , q \neq 0$$

The S_{0QR} and S_{Pr0} contributions are narrow lines at $\omega = 0$.

One may state that the cross terms give a slight redistribution of the line intensities. The contribution of the cross terms to the line at $\omega_p \neq 0$ up to third order is

$$h^{-1} \sum_{q(\neq p)} \sum_{r(\neq q)} (\omega_p - \omega_q)^{-1} ((\mathcal{H}_p, [\mathcal{H}_r, \mathcal{H}_q]) \mathcal{H}_z + ([\mathcal{H}_r, \mathcal{H}_q], \mathcal{H}_p) \mathcal{H}_z) \delta(\omega - \omega_p) .$$

The intensity of this contribution is real (cf. 2.00). Due to the orthogonality only those terms \mathcal{H}_r contribute for which $\omega_p = \omega_q + \omega_r$. Consequently one may replace the restrictions $q \neq p$ and $r \neq q$ by the conditions

$$\omega_q + \omega_r = \omega_p \quad , \quad \omega_r \neq 0 \quad \text{and} \quad \omega_q \neq \frac{1}{2}\omega_p \quad *$$

Applying the high temperature approximation ($\beta \rightarrow 0$, average magnetisation $(I, M_i) \rightarrow 0$)

*) Due to the remark at eq. 6.23, $\omega_q \neq 0$ is often required as well.

one gets for the line intensity up to third order

$$I_p \beta^{-1} \mu_0 H^2 \approx (\text{Tr } I)^{-1} (\text{Tr } \mathcal{K}_p^\dagger \mathcal{K}_p + 2h^{-1} \sum_{q,r} (\omega_p - \omega_q)^{-1} \text{Re Tr } \mathcal{K}_p^\dagger [\mathcal{K}_r, \mathcal{K}_q])$$

under the conditions mentioned above.

Appendix J. Proof of relation 6.19.

$$\begin{aligned} & \int_{-\infty}^{+\infty} e^{i\omega t} (\omega - \omega_p)^{-1} (\omega - \omega_q)^{-1} S_{PQ}(\omega, \vec{H}e_i) d\omega = \left(\frac{\partial}{\partial i t} - \omega_p\right) \left(\frac{\partial}{\partial i t} - \omega_q\right) \int_{-\infty}^{+\infty} e^{i\omega t} S_{PQ}(\omega, \vec{H}e_i) d\omega = \\ & = \left(\frac{\partial}{\partial i t} - \omega_p\right) \left(\frac{\partial}{\partial i t} - \omega_q\right) (P, e^{iL t} Q) = ((L - \omega_p) P, e^{iL t} (L - \omega_q) Q) = \\ & = ((1 - P_1 - P_{\mathcal{K}_1}) (L - L_z) \mathcal{K}_p, e^{iL t} (1 - P_1 - P_{\mathcal{K}_1}) (L - L_z) \mathcal{K}_q) = \\ & = \sum_{k,l=0,\pm 1,\dots,\pm n} ((1 - P_1 - P_{\mathcal{K}_1}) h^{-1} [\mathcal{K}_k, \mathcal{K}_p], e^{iL t} (1 - P_1 - P_{\mathcal{K}_1}) h^{-1} [\mathcal{K}_l, \mathcal{K}_q]) \equiv \\ & \equiv \int_{-\infty}^{+\infty} e^{i\omega t} \sum_{k,l=0,\pm 1,\dots,\pm n} S_{PkQl}(\omega, \vec{H}e_i) d\omega. \end{aligned}$$

Appendix K. Truncation procedure and strong coupling memory function.

Following Mazur and Terwiel ²⁸⁾ one may study the term $(0, e^{iL t} 0)$ with the aid of 2.53

$$\frac{d}{dt} (0, e^{iL t} 0) = - \int_0^t \frac{((1 - P_0)L_0, e^{i(1 - P_0)L(t-\tau)} (1 - P_0)L_0)}{(0, 0)} (0, e^{iL \tau} 0) d\tau.$$

The memory spectrum defined by 2.64 is real and positive semidefinite

$$s'_{0,0}(\omega, \vec{H}e_i) \geq 0.$$

The same holds for the main terms of the sum

$$s'_{0,0}(\omega, \vec{H}e_i) = \sum_{p,q=\pm 1,\dots,\pm n} s'_{pq}(\omega, \vec{H}e_i)$$

with $((1-P_0)h^{-1}[\mathcal{K}_0, \mathcal{K}_p], e^{i(1-P_0)Lt} (1-P_0)h^{-1}[\mathcal{K}_0, \mathcal{K}_q]) \equiv \int_{-\infty}^{+\infty} e^{i\omega t} s'_{pq}(\omega, \vec{H}_i) d\omega$.

As long as correlations between operators orthogonal to 0 are concerned, the special propagator $(1-P_0)L$ gives the usual properties of correlation functions.

In particular the counterpart of 2.45 holds (for $\omega \neq 0$; $s'_{pq}(\omega, \vec{H}_i)$ may contain $\delta(\omega)$ contributions)

$$|s'_{pq}(\omega, \vec{H}_i)| \leq (s'_{pp}(\omega, \vec{H}_i) s'_{qq}(\omega, \vec{H}_i))^{\frac{1}{2}}$$

Unlike the proper term $(0, e^{iLt_0})$ its memory spectrum $s'_{0,0}(\omega, \vec{H}_i)$ is not reduced to irrelevance by replacing $\mathcal{K} \rightarrow \mathcal{K}_c$. The main terms $s'_{pp}(\omega, \vec{H}_i)$ contract to δ -lines at frequency ω_p , with intensity $h^{\frac{1}{2}}([\mathcal{K}_0, \mathcal{K}_p], [\mathcal{K}_0, \mathcal{K}_p])_{\mathcal{K}_c}$, the cross terms vanish.

In this approximation the intensities and truncated second moments (with respect to the centre ω_p and within the interval $\omega_p - \delta$ to $\omega_p + \delta$) of the main terms can be calculated ^{*}, but contrary to the situation in section 6.36 they cannot be confronted with experimental evidence. The reason for this awkward detachment lies in the following:

The theoretical information consisting of lower moments of lines concentrated around frequencies $\omega_p \neq 0$ ($p=+1, \dots, +n$) only concerns frequency regions far away from $\omega \approx 0$. The experimental data on $(0, e^{iLt_0})$ however can only be gathered at $\omega \approx 0$ and the same necessarily holds for $s'_{0,0}(\omega, \vec{H}_i)$. (If one should try to look at $(0, e^{iLt_0})$ in the frequency interval $\omega_p - \delta$ to $\omega_p + \delta$ the experiment would yield (P, e^{iLt_P}) instead). The range of experimental interest lies thus way off in the tails of the theoretically pictured lines.

Making some assumptions about the line shape of the main terms one can still try to extrapolate the memory spectrum at $\omega \approx 0$ for a given field strength H from the theoretically derived intensities and second moments around $\omega_p \neq 0$. One should however keep in mind that doing so one cannot show the cross terms to be negligible. As no main term occupies the $\omega \approx 0$ domain in the memory spectrum, the inequality is of no help in estimating the relative importance of main and cross terms there. In principle they can all be of the same order of magnitude.

^{*}) One may even prove, that again (cf. section 6.36), in the approximation $\mathcal{K} \rightarrow \mathcal{K}_c$, the secular part \mathcal{K}_0 of the interaction constitutes the only source of these second moments.

The three assumptions to be made are (all for $\mathcal{H} \approx \mathcal{H}_2$):

- 1) Cross terms are absent at $\omega \approx 0$.
- 2) Main terms have a field independent line shape.
- 3) Main terms have a particular, e.g. Gaussian, line shape.

Both first assumptions are implicit in the notion of secular effective interaction introduced by Mazur and Terziel²⁸). One could say that they suppose the weak coupling features 1) and 2) to be maintained in the strong coupling situation. As one cannot be sure that this be the case, one is - contrary to the weak coupling custom - not able to conclude decisively from experimental results about line shapes in the memory spectrum.

It is nevertheless remarkable that some of the nicest examples of Gaussian field dependence of the relaxation frequency (which corresponds to Gaussian line shapes if 1) and 2) are fulfilled) have been measured in strong coupling compounds²⁹).

Appendix L. Criticism on Yarmus and Harkavy.

1. Yarmus and Harkavy³⁴) do not distinguish between ω_p and ω ; they give a relation of the form

$$\omega = \gamma_p H + \text{correction terms}$$

instead of

$$\omega_p = \gamma_p H + \text{correction terms.}$$

The correction terms only apply to more complicated hamiltonians than the Cu^{2+} type. Their way of doing erroneously leads to an integral over ω instead of one over ω_p for eq. (3) l.c. Having emended this failure one must assume the validity of a frequency field conversion (cf. section 6.39) in order to obtain the uncorrected version of eq. (3) l.c. which is used in the remainder of their article. With this necessary addition, which spoils the simplicity to a certain extent, their approach is not much different from the Locher - Gorter²⁶) method. In either way the anisotropy of γ_p , the central parameter in the conversion procedure, is neglected as otherwise the description of the powdered samples used would become highly complicated.

2. Their reproach that Locher and Gorter neglect electric field and hyperfine zero field splittings in the Cu²⁺ Tutton salts is unjustified. The Cu^{2+} ion having a

spin $S = \frac{1}{2}$ does not experience an electrostatic field in the sense that this could cause a zero field splitting. The hyperfine interaction is of the same order as the dipole interaction, i.e. small compared to the static magnetic field.

3. Fig. 2 l.c. poses another problem. The first and second "Larmor lines" in the parallel configuration, which are known to occur at center fields differing by a factor of two, do not appear to follow this rule. This probably indicates a real experimental discrepancy, as it cannot be corrected through multiplication by χ_{ad}^{-1} or H^2 , which would yield the Locher - Gorter presentation. In the measurements of the latter no such deviation is found.

4. Concerning their criticism on Locher's use of χ_{ad} one can admit that it seems arbitrary and suggests a higher accuracy than is justified by the approximations made. But if χ_{ad}/χ_0 is replaced by $(\mathcal{H}_{int}, \mathcal{H}_{int})/(\mathcal{H}_z, \mathcal{H}_z)$ (which equals χ_{ad}/χ_0 in second and lowest order of interaction strength) these objections are met. The Locher-Gorter approach is then seen to correspond to the method followed in section 6.32, which has already been compared to Yarmus and Harkavy in section 6.38 and 6.39.

I'll tell thee everything I can; There 's little to relate.

L. Carroll, Through the Looking Glass.

CHAPTER 7

MEASUREMENTS ON MnF_2

7.1 Introductory remarks.

7.11 Introduction.

In order to extend the field of measurements to phenomena, which are essentially temperature dependent and cannot be described in the high-temperature approximation, temperature must be lowered to a value corresponding with the strength of the interactions in the sample. Beneath this value many substances show an ordering of the magnetic moments and a sudden change of certain macroscopic quantities. The temperature at which this change takes place is called the critical temperature of the magnetic phase transition (from paramagnetic to ordered phase and v.v.). Two types of ordering are most frequently encountered: ferromagnetism and antiferromagnetism; the critical temperature for antiferromagnetic ordering is called Neél temperature (T_N). Very much work has been done on the behaviour of long-time averages of quantities as a function of temperature: the static aspects of magnetic transitions. But the character of the variations in time of a quantity equally depends on temperature. These dynamical aspects are far more complicated to describe and constitute a more restricted area of investigation, to which the underlying work intends to be a contribution.

7.12 Choice of the sample material.

Manganous fluoride has been called the fruitfly of antiferromagnetism. It has been the subject of various types of experiment^{36,37,38,39}) and only rubidium manganous fluoride has reached equal popularity lately. The Neél temperature of 67.3 K lies conveniently in the liquid nitrogen range. Thus for a first step in the study of

dynamical aspects of a magnetic phase transition the choice of manganous fluoride was obvious. One might ask why an antiferromagnet was chosen rather than a ferromagnet. Indeed the latter shows its phase transition directly by a divergence in the static susceptibility and the dynamical behaviour would be interesting to look into, but on the other hand hysteresis, size effects and domain formation are complicating factors, virtually absent in an antiferromagnetic substance.

7.13 Crystal structure and interactions.

The unit cell is tetragonal with dimensions $c = 3.3103\text{\AA}$, $a = 4.8734\text{\AA}$. The magnetic ions (Mn^{2+}) occupy the corners and center thus forming a body-centered cubic lattice compressed along the c-axis. The tetragonal symmetry facilitates orientation of the crystal by X-ray diffraction. In the antiferromagnetic phase one of both congruent sublattices consists of the corner ions, the other contains the center ions. A strong antiferromagnetic exchange interaction between corner and nearest center ions, together with a weaker ferromagnetic exchange between nearest ions of the same sublattice are responsible for the occurrence of magnetic ordering.

In the ordered state the magnetic moments are aligned along the c-axis (easy axis). This anisotropy has been shown to be mainly due to the dipole-dipole interaction between the magnetic ions as they are situated on the non-cubic lattice. As the spin quantum number of the Mn^{2+} -ions is $\frac{5}{2}$, one might expect them also to be sensitive to electric fields within the crystal, but these appear to be of minor importance. A third possible source of anisotropy, the g-value, can equally be ruled out, as for all ions the g-tensor is isotropic with $g = 1.98$.

As anisotropy is fully accounted for by the dipole-dipole interaction⁴⁰⁾, the exchange interactions, which are stronger by some orders of magnitude, may be supposed purely isotropic (Heisenberg type). Diamagnetic effects in Mn^{2+} ions are negligible in the temperature range of interest. The hyperfine interactions - essential in NMR measurements - are weak even when compared to the dipole-dipole coupling between the electron spins. The existence of spin-lattice interaction is manifest from sound-attenuation measurements, but the characteristic frequencies⁴¹⁾ (≤ 50 MHz) lie well below the frequency range used in the present work.

One may thus hope that the following hamiltonian in which only spin variables occur may give a reasonable description

$$\mathcal{H} = \mathcal{H}_{\text{ex}} + \mathcal{H}_Z + \mathcal{H}_d \quad 7.01$$

with

$$\mathcal{H}_{\text{ex}} = \sum_{m < n} 2J_{mn} \vec{S}_m \cdot \vec{S}_n \quad 5.07 \equiv 7.02$$

$$\chi_Z = \mu_0 \vec{H} \cdot \mu_B g \sum_n \vec{\xi}_n \quad 7.03$$

$$\chi_d = \mu_0 g^2 \mu_B^2 \sum_n \{ |\vec{r}_{mn}|^{-3} \vec{\xi}_m \cdot \vec{\xi}_n - 3 |\vec{r}_{mn}|^{-5} (\vec{\xi}_m \cdot \vec{r}_{mn}) (\vec{\xi}_n \cdot \vec{r}_{mn}) \}. \quad 7.04$$

7.14 Magnetic resonance.

Depending on temperature two types of resonance have been observed. Above T_N several authors have reported electron paramagnetic resonance (EPR); among them Seehra and Castner³⁹⁾ give the most recent and detailed results. Below T_N antiferromagnetic resonance (AFMR) has been found by Burgiel and Strandberg (BS)³⁸⁾. EPR is usually measured at frequencies of 9 GHz or higher. The resonance frequency ν_L is proportional to the applied magnetic field, and practically independent of temperature

$$\nu_L = g \mu_B h^{-1} \mu_0 |\vec{H}|. \quad 7.05$$

The linewidth broadens when the Neel point is approached from above. At the usual resonance field of 3 kOe or more the linewidth depends on the direction of the static field, not on that of the alternating field, of which only the component perpendicular to the static field contributes to the resonance.

AFMR has been observed at frequencies of the order of 100 GHz. In zero static field there is one pair of resonance lines with center frequencies $\pm \nu_A$,

$$\nu_A = 46.5 \text{ GHz} \times \left(\frac{T_N - T}{TK} \right)^{0.483 \pm 0.025} \quad 7.06$$

henceforth the exponent will be taken equal to the molecular field value 0.50.

(The zero field behaviour is maintained in presence of a static field parallel to the alternating field, both perpendicular to the c-axis). Applying a static field parallel to the c-axis one gets two pairs of lines with centerfrequencies $\pm \nu_+$ and $\pm \nu_-$,

$$\nu_{\pm} = (\nu_A^2 - \frac{1}{2} \nu_L^2)^{\frac{1}{2}} \pm \frac{1}{2} \nu_L \quad (\vec{H} \parallel \text{c-axis}). \quad 7.07$$

For static field, alternating field and the c-axis all mutually perpendicular one has

$$\nu_A = (\nu_A^2 + \nu_L^2)^{\frac{1}{2}} \quad (\vec{H} \perp \text{c-axis}). \quad 7.08$$

These are predictions from molecular field theory by Keffer and Kittel⁴²⁾, confirmed

experimentally up to a few K below T_N by the measurements of Burgiel and Strandberg and given here in the approximation $\chi_{O\parallel}(0) \approx \chi_{O\perp}(0)$ valid near and above T_N . The intensity of AFMR depends on the direction of the alternating field: the resonance is driven by the component perpendicular to the c-axis. The relative intensity of both lines for $\vec{H} \parallel c$ has not been studied. Within 5 K below T_N the widths of AFMR lines in MnF_2 have not been determined unambiguously. They have been reported to differ as much as a factor 3 depending on the experimental approach followed. (This has been tentatively ascribed to an improbably strong field dependence at relatively low fields.) At temperatures this close to T_N one should be reluctant in assuming Lorentzian or even symmetrical line shapes. The only statement that can be safely made is that above 62 K AFMR lines continue broadening with increasing temperature.

7.15 Present work.

Resonance absorption has been measured as a function of the static field (oriented perpendicular to the c-axis) for several temperatures in the region 63 K - 77 K and for room temperature, at frequencies of 0.179, 0.263, 0.565, 1.21, 1.78, 3.05 and 4.84 GHz with the alternating field parallel to the c-axis. In a check measurement at 3.05 GHz no significant difference was found between the results for static field along (1, 0, 0) and (1, 1, 0). At 1.78 GHz measurements were performed with the alternating field perpendicular to c for both main orientations of the static field: $H \parallel c$ and $H \perp c$. In all situations the alternating field was perpendicular to the static field.

In two aspects the present work differs from the investigations of other authors mentioned in the previous section: First the range of frequencies lies considerably lower than "X-band" such that for EPR the zero field behaviour and the development into the high-field region, where the lines become narrow compared to the center-frequency, can be studied. At low field the orientation of the alternating field plays an essential role. In the second place measurements have been made in the antiferromagnetic phase with the alternating field parallel to the c-axis. In this orientation no AFMR is known to occur, while the non-zero $\chi_{O\parallel}(0)$ indicates that absorption must exist somewhere in the frequency spectrum. For zero static field this intensity can be fully accounted for by the relaxation absorption measured in the low frequency region. Moreover the relaxation time for this orientation of the alternating field is found to be practically independent of temperature right through the transition. The field dependence of these measurements will be treated with the aid of the more general approach given in the next section.

7.2 Theory.

7.21 The frequency dependent susceptibility in a static field according to Tjon.

In section 3.3 it has been derived, that under certain mathematical assumptions the complex frequency dependent susceptibility $\chi_{ii}(\omega, \vec{H})$ satisfies the relation

$$\frac{\chi_{ii}(\omega, \vec{H}) - \chi_{ii}(0, \vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} (-i\omega)^{-1} = \frac{1}{i\omega + l'(i\omega, \vec{H}) (A_i, A_i)^{-1}} \quad 3.14 \equiv 7.09$$

The index i corresponds to the direction of the alternating magnetic field of the resonance experiment; furthermore

$$l'(z, \vec{H}) \equiv \int_0^\infty e^{-zt} (A', e^{iL't} A') dt \quad 2.56$$

$$A' \equiv (1 - P_{A_i}) L A_i, \quad L' \equiv (1 - P_{A_i}) L \quad 2.57$$

$$A_i \equiv (1 - P_i - P_{\partial C'}) M_i = M_i - (l, M_i) l - (\mathcal{K}', \mathcal{K}')^{-1} (kT_B \frac{\partial}{\partial T_B} (l, M_i)) \mathcal{K}'$$

where (l, M_i) is proportional to the average magnetization in the i -direction, and the field dependence of L, \mathcal{K}', P and the scalar product has been omitted from the notation. Let the hamiltonian be given by

$$\mathcal{K} = \mathcal{K}_{ex} + \mu_0 \vec{H} \cdot \mu_B \sum_n \vec{g}_n \cdot \vec{S}_n + \mathcal{K}_d$$

The magnetization operators for this hamiltonian do not contain the static field

$$M_i = -\mu_B \sum_n \sum_j (\vec{g}_n)_{ij} (\vec{S}_n)_j$$

and

$$\chi_{\infty ii}(\vec{H}) = 0$$

as \mathcal{K} is linear in the field.

Tjon has reduced the expression 7.09 by two successive approximations, based on the relative weakness of the static field compared to the exchange interaction. The first consists of replacing the function $l'(i\omega, \vec{H})$ by the zeroth and second order terms of a Taylor expansion in the strength of the static field \vec{H} ; odd order terms are identically zero, as $\chi_{ii}(\omega, \vec{H}) = \chi_{ii}(\omega, -\vec{H})$ (cf. 7.09, section 3.5, section 3.6). Hence

$$l'(i\omega, H\vec{e}_j) \approx l'(i\omega, 0) + \frac{1}{2} H^2 \left[\frac{\partial^2}{\partial H^2} l'(i\omega, H\vec{e}_j) \right]_{H=0} \quad 7.10$$

where \vec{e}_j is the unit vector in the direction of \vec{H} (j -direction). The zeroth order term can be expressed in the zero field susceptibility by inversion of 7.09

$$\chi'(\omega, 0) = -i\omega(A_i, A_i)_{H=0} \left(1 + \frac{\chi_{ii}(\omega, 0)}{\chi_{ii}(0, 0)} - 1\right)^{-1} \quad 7.11$$

As the hamiltonian can be written as $\mathcal{H} = \mathcal{H}_{ex} - \mu_0 H M_j + \mathcal{H}_d$ the second order term can be split according to

$$\begin{aligned} & \left[\frac{\partial^2}{\partial H^2} \chi'(\omega, H \vec{e}_j) \right]_{H=0} = \\ & = \int_0^\infty e^{-i\omega t} \hbar^{-2} \left[\frac{\partial^2}{\partial H^2} ([\mathcal{H}_d, M_i], e^{iL't} [\mathcal{H}_d, M_i]) \right]_{H=0} dt \quad 7.12 \\ & - 2 \int_0^\infty e^{-i\omega t} \hbar^{-2} \mu_0 \left[\frac{\partial}{\partial H} ([\mathcal{H}_d, M_i], e^{iL't} [M_j, M_i]) + ([M_j, M_i], e^{iL't} [\mathcal{H}_d, M_i]) \right]_{H=0} dt \\ & + 2 \int_0^\infty e^{-i\omega t} \hbar^{-2} \mu_0^2 \left[([M_j, M_i], e^{iL't} [M_j, M_i]) \right]_{H=0} dt \end{aligned}$$

where use has been made of $[\mathcal{H}_{ex}, M_i] = 0$ (\mathcal{H}_{ex} denotes isotropic exchange).

If the alternating field is parallel to the static field ($i=j$) the first term in the right hand side of eq. 7.12 is the only non-zero contribution. Nevertheless this term is very small: the resulting field dependence is expected to be negligible in fields which are weak compared to the exchange interaction. In MnF_2 for $T \geq T_N$ this is indeed experimentally found (cf. also the remark at eq. 7.06). In $CuCl_2 \cdot 2aq.$ the orientation along the easy axis shows a dependence on very low fields (\approx dipolar field), which persists in the high-temperature region and looks akin to similar mysterious effects in other Cu^{2+} compounds reported by van der Molen⁴⁴).

From here the investigation will be restricted to the resonance configuration in which the alternating field is perpendicular to the static field ($i \neq j$). In that case the last term of eq. 7.12 plays the main role and Tjon makes the second approximation dropping both other terms, which - at least in high-temperature approximation - can be shown to be of the order $(\mathcal{H}_d, \mathcal{H}_d) / (\mathcal{H}_{ex}, \mathcal{H}_{ex})$. If all ions have the same g -tensor and if the j - and i - directions are different principal axes of this tensor, one has

$$[M_j, M_i] = i\mu_B g_j g_i g_k^{-1} \epsilon_{ijk} M_k$$

where k is the third axis, $g_j \equiv g_{jj}$ etc. and $\epsilon_{ijk} = \pm 1$, depending on the sign of the

permutation ijk . Thus

$$\frac{1}{2}H^2 \left[\frac{\partial^2}{\partial H^2} 1'(i\omega, \vec{H}\vec{e}_j) \right]_{H=0} = \omega_L^2 \int_0^\infty e^{-i\omega t} g_i^2 g_k^{-2} [(M_k, e^{iL't} M_k)]_{H=0} \quad 7.13$$

where $\omega_L = \hbar^{-1} g_j \mu_B \nu_0 H$ (cf. 7.05).

It is perhaps elucidating to make the following note here: Use has been made of $[M_i, \mathcal{H}_{ex}] = 0$ and $[M_i, M_j] \neq 0$, i.e. \mathcal{H}_{ex} is secular and $-\nu_0 H M_j$ is non-secular. The static field H determines the strength of the non-secular contribution in the hamiltonian and is assumed so small as to make this contribution a small perturbation compared with the secular exchange term. Therefore the low-field approximation may be looked upon as an analogon of the usual weak-coupling limit, where the non-secular part of the dipole-dipole interaction plays the role of the perturbation. Contrary to the situation in the weak-coupling limit the replacement of the propagator L' by the normal Liouville operator L will be seen to be often exact and no part of the limit procedure for low field.

If the hamiltonian for $\vec{H} = 0$ is invariant with respect to the inversion of the i -direction (e.g. in a crystal with mirror symmetry for a j - k -plane and symmetric interactions) one has $x_{ki}(\omega, 0) = 0$ and hence

$$[(M_i, L^n M_k)]_{H=0} = 0 \text{ for } n = 0, 1, 2, \dots$$

This implies

$$[e^{iL't} M_k]_{H=0} = [e^{iL't} M_k]_{H=0} \quad 7.14$$

By definition no spontaneous total magnetization occurs in a pure antiferromagnet.

Therefore, for $\vec{H} = 0$, one has $(I, M_i) = 0$ and $\frac{\partial}{\partial T_b} (I, M_i) = 0$, hence $A_i = M_i, (1 - P_i) M_i = M_i$ and $x_{ii}(0, 0) = x_{oi}(0)$, and the same for k . Moreover, if the hamiltonian for $\vec{H} = 0$ is invariant with respect to the inversion of the j -direction as well, one has $(I, M_i) = 0$ for any value of H , and hence $x_{ii}(0, \vec{H}\vec{e}_j) = x_{oi}(\vec{H}\vec{e}_j)$.

According to 2.56, 7.14 and section 3.3 eq. 7.10 takes the form

$$\begin{aligned} 1'(i\omega, \vec{H}\vec{e}_j) (A_i, A_i)^{-1} &= \\ &= \frac{x_{oi}(0)}{x_{oi}(\vec{H}\vec{e}_j)} \left\{ -i\omega + \left(\frac{x_{ii}(\omega, 0)}{x_{oi}(0)} - 1 \right)^{-1} (-i\omega) + \right. \\ &\quad \left. + \omega_L^2 g_i^2 g_k^{-2} x_{oi}(0) x_{ok}(0) \left(\frac{x_{kk}(\omega, 0)}{x_{ok}(0)} - 1 \right)^{-1} \right\} \quad 7.15 \end{aligned}$$

At this stage it is essential to know how strongly the isothermal susceptibility in one direction, χ_{oi} , depends on a static field $H\vec{e}_j$ perpendicular to that direction. If $\chi_{oi}(H\vec{e}_j) \approx \chi_{oi}(0)$ holds in a good approximation, one can derive (cf. 7.09 and 7.15) that 3.16 yields

$$\frac{\chi_{ii}''(2\pi\nu, H\vec{e}_j)}{\chi_{oi}(0)} \approx \frac{\frac{a_i}{d_i^2+a_i^2} + \eta^{2\nu-2} a_k}{\left(\frac{d_i}{d_i^2+a_i^2} - \eta^{2\nu-2} d_k\right)^2 + \left(\frac{a_i}{d_i^2+a_i^2} + \eta^{2\nu-2} a_k\right)^2} \quad 7.16$$

with

$$a_i \equiv \frac{\chi_{ii}''(2\pi\nu, 0)}{\chi_{oi}(0)}, \quad d_i \equiv \frac{\chi_{ii}'(2\pi\nu, 0)}{\chi_{oi}(0)} - 1$$

and

$$\eta \equiv g_i g_k^{-1} \chi_{oi}^{-\frac{1}{2}}(0) \chi_{ok}^{\frac{1}{2}}(0) h^{-1} g_j \mu_B \mu_o H \equiv H/\gamma$$

Instead of ω the experimentally more convenient $\nu \equiv \omega/2\pi$ has been used. The extrema in the field dependence given by eq. 7.16 occur for $H = H_e \equiv \gamma \eta_e$ with

$$\eta_e^{2\nu-2} = \frac{a_i a_k^{-1}}{d_i^2+a_i^2} (-1 \pm (1+a_i^{-1} d_i a_k d_k^{-1}) (1+a_k^2 d_k^{-2})^{-\frac{1}{2}}) \quad 7.16a$$

The analogue of 7.16 for χ' reads (cf. 3.15)

$$\frac{\chi_{ii}'(2\pi\nu, H\vec{e}_j)}{\chi_{oi}(0)} - 1 \approx \frac{\frac{d_i}{d_i^2+a_i^2} - \eta^{2\nu-2} d_k}{\left(\frac{d_i}{d_i^2+a_i^2} - \eta^{2\nu-2} d_k\right)^2 + \left(\frac{a_i}{d_i^2+a_i^2} + \eta^{2\nu-2} a_k\right)^2} \quad 7.16b$$

The essential point in eq. 7.16 is the fact that the frequency-dependent susceptibility for a given frequency in a static field has been expressed in the frequency-dependent susceptibility for the same frequency in zero field, represented by the four variables a_i, d_i, a_k, d_k . This number can often be reduced to two as will be seen below.

If the zero field susceptibility for alternating fields in the i -direction behaves according to a single relaxation (with relaxation time $(2\pi\tau_i)^{-1}$):

$$a_i = \nu \Gamma_i^{-1} (1 + \nu^2 \Gamma_i^{-2})^{-1} \quad (\text{property I})$$

$$d_i = -\nu^2 \Gamma_i^{-2} (1 + \nu^2 \Gamma_i^{-2})^{-1}$$

or else,

if it satisfies the relation $|d_i| \ll a_i$ in the frequency region of interest

(property II)

and if also the susceptibility in the k-direction has one of those properties, equation 7.16 may be considerably simplified:

I for i and k:

$$\begin{aligned} \frac{\chi_{ii}''(2\pi\nu, \vec{H}_j)}{\chi_{oi}(0)} &= \frac{\Gamma_i \nu^{-1} + n^2 \nu^{-2} a_k}{(-1 - n^2 \nu^{-2} d_k)^2 + (\Gamma_i \nu^{-1} + n^2 \nu^{-2} a_k)^2} = \\ &= A(\Gamma_i, \Gamma_k, n, \nu) \equiv \frac{\Gamma_i \nu^{-1} + n^2 \nu^{-2} \Gamma_k^{-1} (1 + \nu^2 \Gamma_k^{-2})^{-1}}{(-1 + n^2 \Gamma_k^{-2} (1 + \nu^2 \Gamma_k^{-2})^{-1})^2 + \text{numerator}^2} \end{aligned} \quad 7.17$$

I for i, II for k:

$$\frac{\chi_{ii}''(2\pi\nu, \vec{H}_j)}{\chi_{oi}(0)} = \frac{\Gamma_i \nu^{-1} + n^2 \nu^{-2} a_k}{1 + \text{numerator}^2}$$

If the experimental results can be approximated by $A(\Gamma_i, \Gamma_k, n, \nu)$, with $\Gamma_k \gg \nu$, then one may identify $\Gamma_k = a_k^{-1} \nu$.

II for i, I for k:

$$\begin{aligned} \frac{\chi_{ii}''(2\pi\nu, \vec{H}_j)}{\chi_{oi}(0)} &= \frac{a_i^{-1} + n^2 \nu^{-2} a_k}{(-n^2 \nu^{-2} d_k)^2 + (a_i^{-1} + n^2 \nu^{-2} a_k)^2} = \\ &= \frac{a_i^{-1} + n^2 \nu^{-2} \Gamma_k^{-1} (1 + \nu^2 \Gamma_k^{-2})^{-1}}{(-n^2 \Gamma_k^{-2} (1 + \nu^2 \Gamma_k^{-2})^{-1})^2 + \text{numerator}^2} \end{aligned}$$

If the experimental results can be approximated by $A(\Gamma_i, \Gamma_k, n, \nu)$, with $\Gamma_i \gg \nu$, then one may identify $\Gamma_i = a_i^{-1} \nu$.

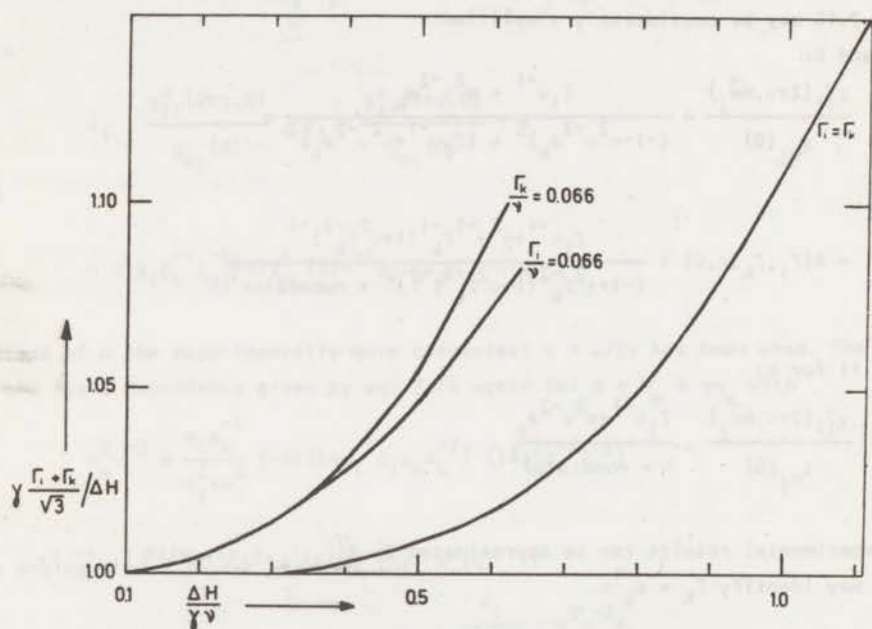


Fig. 7.01 Relative deviation of the high frequency linewidth $3^{-\frac{1}{2}}\gamma(\Gamma_i + \Gamma_k)$ from the linewidth ΔH , measured at a frequency ν , as a function of $\Delta H/\gamma\nu$.

II for i and k:

$$\frac{\chi''_{ii}(2\pi\nu, \vec{H}e_j)}{\chi_{oi}(0)} \approx (a_i^{-1} + \eta^2 \nu^{-2} a_k)^{-1}.$$

If the experimental results can be approximated by $A(\Gamma_i, \Gamma_k, \eta, \nu)$, with $\Gamma_i \gg \nu$ and $\Gamma_k \gg \nu$, then one may identify $\Gamma_i = a_i^{-1}\nu$ and $\Gamma_k = a_k^{-1}\nu$.

7.22 Application 1, linewidth in paramagnetic resonance.

In the paramagnetic temperature region the zero field susceptibility of a compound which has the symmetries supposed in the preceding section and in which isotropic exchange is the main type of interaction, can usually be described by single relaxations such that both i- and k-direction have property I. Hence eq. 7.17 is expected to hold. For high frequencies ($\nu \gg \Gamma_k$) one may write

$$\frac{\chi''_{ii}(2\pi\nu, \vec{H}e_j)}{\nu\chi_{oi}(0)} \approx (\frac{1}{2} + \frac{1}{2}\eta^2 \nu^{-2})^{-\frac{1}{2}} \Gamma^{-1} ((1 + (\nu - \eta)^2 \Gamma^{-2})^{-1} + (1 + (\nu + \eta)^2 \Gamma^{-2})^{-1}) \quad 7.18$$

where

$$\Gamma \equiv (\frac{1}{2} + \frac{1}{2}\eta^2 \nu^{-2})^{\frac{1}{2}} \left(\frac{\Gamma_i + \Gamma_k}{2} + \frac{\nu^2 - \eta^2}{\nu^2 + \eta^2} \frac{\Gamma_i - \Gamma_k}{2} \right).$$

For fields

$$H \approx \pm \gamma \nu \text{ (or } \eta \approx \pm \nu)$$

eq. 7.18 gives absorption values close to those of a sum of two Lorentz shaped lines centered around $\pm \gamma \nu$, with full width at half height

$$2\gamma\Gamma = \gamma(\Gamma_i + \Gamma_k) \quad 7.19$$

(If $\nu \gg \Gamma$ is satisfied, the condition $H \approx \pm \gamma \nu$ is fulfilled throughout the width of these Lorentz lines). Eq. 7.18 may equally well be taken as a function of frequency ν . In the region where not only $\nu \gg \Gamma_k$ but also $\nu \approx \pm \eta$ holds, the frequency spectrum given by eq. 7.18 nearly coincides with a pair of Lorentz lines at frequency $\pm \eta$ with half width at half height (Γ) given by the simple relation

$$\Gamma = \frac{\Gamma_i + \Gamma_k}{2}$$

7.20

(if $|\eta| \gg \Gamma$ is satisfied, the condition $\nu \approx \pm \eta$ is fulfilled throughout the width of these Lorentz lines). Eqs. 7.19, 7.20 relate resonance linewidth for a static field along the j-direction with zero field relaxation times for an alternating field

along i- and k-direction respectively. Apart from the present experimental work the measurements on $\text{CuCl}_2 \cdot 2\text{aq}$ by de Jong⁴⁵⁾ and Zimmerman⁴⁶⁾ have confirmed relation 7.19, for temperatures down to less than 2% above T_N . The conditions for the validity of 7.19, 7.20 can be summarized as follows:

1. The static field should be weak compared to the exchange interaction.
2. All ions should have the same g-tensor.
3. The static field should be oriented along a principal axis (j) of this common g-tensor.
4. The static field should not influence the static susceptibility along both other principal axes.
5. No spontaneous magnetization should occur and the hamiltonian should be invariant with respect to inversion of the direction (j) parallel to the static field and of one (i) of the other principal g-tensor axes.
6. The zero field susceptibility with alternating fields along i and j direction should allow a description by single relaxations.
7. The resonance frequency should be high compared to the inverse zero field relaxation time (with alternating field along the third principal axis k).

As the width of resonance lines is often characterized by the distance ΔH between the inflection points, one may ask which value is predicted for it by eq. 7.17. For high frequencies ($\nu \gg \Gamma_i, \Gamma_k$) there is no problem: a solitary Lorentzian of which the full (field-)width at half height equals $2\gamma\Gamma$ has an inflection-point distance given by $\Delta H = \frac{2\gamma\Gamma}{\sqrt{3}}$; therefore the value $\Delta H = \frac{\gamma}{\sqrt{3}}(\Gamma_i + \Gamma_k)$ is expected for the lines described by eq. 7.17. At lower frequencies however the lines at $+\gamma\nu$ and $-\gamma\nu$ meet and, for $\nu = 0$, eventually merge. It is clear that the width at half height soon loses its practical meaning. The inflection-point distance ΔH however stays well-defined and is found to vary but little down to surprisingly low frequencies ($\nu \geq \Gamma_i + \Gamma_k$). An analytical expression for ΔH , derived from eq. 7.17, has not been achieved; for some special cases (Γ_i/ν fixed, Γ_k/ν fixed, or $\Gamma_i = \Gamma_k$) a numerical calculation has been performed, which gives the relative deviation of the high-frequency value $\gamma \frac{\Gamma_i + \Gamma_k}{\sqrt{3}}$ from the exact value ΔH , as a function of the latter (cf. fig. 7.01).

7.23 Application 2, field dependence of antiferromagnetic resonance absorption in the low-frequency region.

In section 7.21 the simplification of eq. 7.16 has been seen to rest on the properties I or II of the zero field susceptibilities. One may wonder if these conditions are fulfilled in the antiferromagnetic case. Below T_N the zero field susceptibility for alternating fields perpendicular (L) to the easy axis can usually

be described by one or two pairs of antiferromagnetic resonance lines. This susceptibility has property II (i.e. $|d_{\perp}| \ll a_{\perp}$) in a frequency region $|\nu| < \frac{1}{5} \nu_0$, if the antiferromagnetic spectral density function $\frac{\chi''(2\pi\nu, 0)}{\nu\chi_{O\perp}(0)}$ can be approximated by a sum of Lorentz shaped lines with center frequencies and widths all greater than ν_0 . In order to account for deviations from such a sum one may need a correction term. Such a term may be added without loss of property II, provided that for frequencies $|\nu| \leq \nu_0$ the correction has a frequency independent value, and for $|\nu| \geq \nu_0$ either stays below this value or is so restricted that its intensity in this region at most equals its intensity in the frequency range $|\nu| \leq \nu_0$. As these conditions look rather moderate, $|d_{\perp}| \ll a_{\perp}$ will be assumed to hold. In some cases the susceptibility for alternating fields parallel to the easy axis is experimentally found to behave according to a single relaxation (with relaxation time $(2\pi\Gamma_{\parallel})^{-1}$) and thus has property I. Hence for static and alternating fields parallel or perpendicular to the easy axis, the simplifications of eq. 7.16 given in section 7.21 may be used. Consequently one may try to approximate the experimental results by the A-function defined in eq. 7.17 through an appropriate choice of Γ_i and Γ_k values. If the best fit yields $\Gamma_{\perp} \gg \nu$, this value may be identified with

$$a_{\perp}^{-1} \nu \equiv \left(\frac{\chi''(2\pi\nu, 0)}{\nu\chi_{O\perp}(0)} \right)^{-1} \quad 7.21$$

In such a case both in the paramagnetic and in the antiferromagnetic region an analysis in terms of single relaxations gives a reasonable description. This is due to the fact that in the antiferromagnetic phase (for $\nu \ll$ frequencies and widths) the low-frequency part of the antiferromagnetic resonance lines may be replaced by the broad top of a fake relaxation band with equal height, which determines the effective relaxation time $(2\pi\Gamma_{\perp})^{-1}$. This can only be done if this top is indeed broad with respect to ν ($\Gamma_{\perp} \gg \nu$) and if dispersion plays a minor role (II).

7.24 Application 3, field dependence of the antiferromagnetic frequencies in MnF_2 .

For narrow resonance lines, which vary mainly in centerfrequency and scarcely in shape as the field is changed, the maxima in the field dependence practically coincide with those in the frequency dependence. In order to find the relation between static field and resonance frequency one may therefore start from eq. 7.16a which gives the extrema in the field dependent absorption for a given frequency. It is true that following this method one may not hope to detect any field independent modes. The rather tedious check made to ensure that the frequency dependence of eq. 7.16 shows only those extrema, which are found in the field dependence, will not be given here. As only the usual resonance configuration with alternating field perpendicular to the

static field is studied no field independent modes are to be expected (cf. 7.07 and 7.08).

In MnF_2 the zero field absorption for alternating fields perpendicular to the easy (c) axis is commonly described by the sum of two Lorentz lines at frequencies $\pm v_A$ with half width at half height Γ_A . The dispersion is bound to follow corresponding expressions. This gives the following quantities to be inserted in eq. 7.16a

$$a_{\perp}(d_{\perp}^2 + a_{\perp}^2)^{-1} = \Gamma_A v^{-1} (1 + v_A^2 (\Gamma_A^2 + v^2)^{-1}) \quad 7.22$$

$$a_{\perp} d_{\perp}^{-1} = -\Gamma_A v^{-1} (1 + 2v_A^2 (\Gamma_A^2 + v^2 - v_A^2)^{-1}) \quad 7.23$$

in which also a_{\perp} can be expressed

$$a_{\perp}^{-1} \equiv a_{\perp}(d_{\perp}^2 + a_{\perp}^2)^{-1} (a_{\perp}^{-2} d_{\perp}^2 + 1) \quad .$$

The zero field susceptibility for alternating fields parallel to c is at low frequencies measured (cf. section 7.31) to behave according to a single relaxation with relaxation time $(2\pi\Gamma_{\parallel})^{-1}$, $\Gamma_{\parallel} \ll \Gamma_A$.

As the frequencies typically used in AFMR satisfy $v \geq \Gamma_A$ one may write

$$a_{\parallel} \ll -d_{\parallel} \approx 1. \quad 7.24$$

Static field parallel to the c-axis.

In this case one has for the directions: $i = \perp$, $j = \parallel$, $k = \perp$. Eq. 7.16a then takes the form (only the + sign in 7.16a gives $\eta_e^2 \geq 0$)

$$\eta_e^2 v^{-2} = (1 - v_A^2 (\Gamma_A^2 + v^2)^{-1})^2 (1 + a_{\perp}^2 d_{\perp}^{-2}) (-1 + 2(1 + a_{\perp}^2 d_{\perp}^{-2})^{-\frac{1}{2}}) \quad 7.25$$

For $v_A \geq 10 \Gamma_A$ and $|v^{-1}(v^2 - v_A^2)| \geq 4 \Gamma_A$ this may be (within 5%) approximated by

$$\eta_e \approx \pm v^{-1} (v^2 - v_A^2) \quad 7.26$$

implying

$$|v| \approx \frac{1}{2} \eta_e \pm (v_A^2 + \frac{1}{4} \eta_e^2)^{\frac{1}{2}} \quad 7.27$$

with $\eta_e \equiv h^{-1} g_{\parallel} \mu_B \mu_0 H_e$.

This is to be compared with eq. 7.07, which holds near T_N

$$|v_{\text{top}}| = \frac{1}{2}v_L \pm (v_A^2 + \frac{1}{2}v_L^2)^{\frac{1}{2}} \quad 7.07$$

with

$$v_L \equiv h^{-1}g_{\parallel}\mu_B\mu_0H_e,$$

or rather with the more general form given by Keffer and Kittel⁴²), of which 7.07 is an approximation

$$|v_{\text{top}}| = (1 - \frac{1}{2}\chi_{o1}^{-1}(0)\chi_{o//}(0))v_L \pm (v_A + (\frac{1}{2}\chi_{o1}^{-1}(0)\chi_{o//}(0)v_L)^2)^{\frac{1}{2}}. \quad 7.28$$

The only discrepancy lies in the ratio $\chi_{o1}^{-1}(0)\chi_{o//}(0)$, which may differ from one. This may indicate that the approximations applied to eq. 7.12 breaks down at temperatures $T \ll T_N$ where such a deviation occurs.

Static field perpendicular to the c-axis.

In this case one has for the directions: $i = 1, j = 1, k = //$. Using the approximation 7.24 one may approximate eq. 7.16a (as $\Gamma_{//} \leq 2\Gamma_A$ only the + sign in 7.16a gives $n_e^2 \geq 0$) by

$$n_e^2 v^{-2} = 1 - v_A^2 (\Gamma_A^2 + v^2)^{-1} \quad 7.29$$

or

$$v^2 = \frac{1}{2}(v_A^2 + n_e^2 - \Gamma_A^2) + \frac{1}{2}((v_A^2 + n_e^2 - \Gamma_A^2)^2 + 4n_e^2 \Gamma_A^2)^{\frac{1}{2}} \quad 7.30$$

which for $\Gamma_A \ll v_A$ may be written as

$$v \approx \pm (v_A^2 + n_e^2)^{\frac{1}{2}} \quad \text{with} \quad n_e \equiv g_{\perp}g_{//}\chi_{o1}^{-\frac{1}{2}}(0)\chi_{o//}^{\frac{1}{2}}(0)h^{-1}g_{\perp}\mu_B\mu_0H_e. \quad 7.31$$

This is to be compared with eq. 7.08, which gives

$$v_{\text{top}} = \pm (v_A^2 + v_L^2)^{\frac{1}{2}} \quad \text{with} \quad v_L \equiv h^{-1}g_{\perp}\mu_B\mu_0H. \quad 7.08$$

As for MnF_2 g_{\perp} equals $g_{//}$ the only discrepancy is again the factor $\chi_{o1}^{-\frac{1}{2}}(0)\chi_{o//}^{\frac{1}{2}}(0)$.

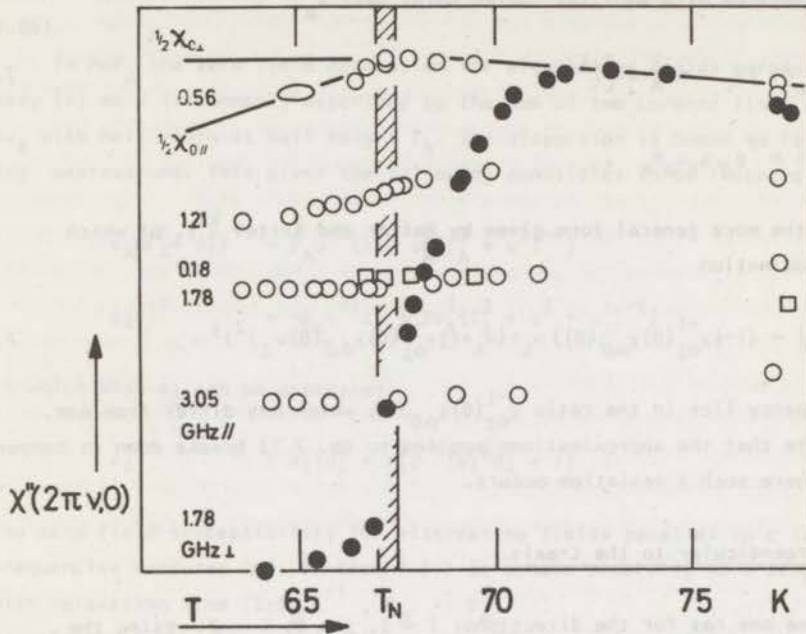


Fig. 7.02 Magnetic absorption in zero field as a function of temperature.

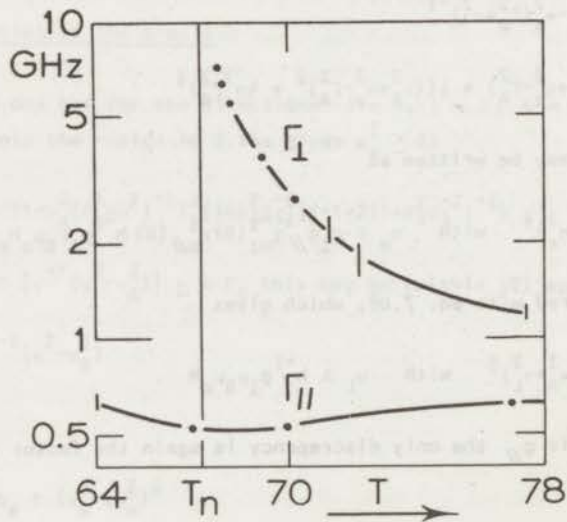


Fig. 7.03 Zero field relaxation rates $\Gamma = (2\pi\tau)^{-1}$ as a function of temperature.

7.3 Experimental results concerning magnetic absorption in MnF₂

7.31 Zero field absorption.

In fig. 7.02 both types of temperature dependence that occur in the zero field absorption can clearly be distinguished. For alternating fields perpendicular to the easy (c) axis $\chi''_{\perp}(2\pi\nu, 0)$ shows a distinct jump at the phase transition, whereas for the orientation parallel to c only small variations (of the same order as those in the isothermal static susceptibility $\chi_{o//}(0)$) are found in $\chi''_{//}(2\pi\nu, 0)$. The first of these observations stands to reason, as it is shown that below T_N an alternating field $\perp c$ excites antiferromagnetic resonance (at a centerfrequency typically far above the measuring frequencies used here), whereas above T_N paramagnetic resonance must be expected (at zero center frequency). This zero frequency resonance, having a Lorentzian line shape, is identical to a single relaxation with relaxation time $(2\pi\Gamma_{\perp})^{-1}$. The width Γ_{\perp} derived from the measurement at 1.78 GHz is given in fig. 7.03 as a function of temperature. It has been assumed that the intensity of the relaxation varies with temperature proportional to the isothermal static susceptibility $\chi_{o\perp}(0)$ as measured by Bizette and Tsai (BT)⁴⁷⁾. The temperature dependence of Γ_{\perp} will be studied in more detail in section 7.33. At about 73 K the absorption (1.78 GHz) reaches its maximum value (cf. fig. 7.02). Taking this to be the usual $0.5\chi_{o\perp}(0)$ one finds for $\chi_{o\perp}(0)$ a value $5 \pm 2\%$ bigger than that of BT.

The behaviour in an alternating field parallel to the c-axis embodies a new phenomenon. The frequency dependence of this absorption is given in fig. 7.04. At temperatures above 63 K it is seen to have a Debye lineshape (i.e. Lorentz shape around $\nu = 0$) and thus to correspond to a single relaxation with relaxation time $(2\pi\Gamma_{//})^{-1}$. A check on the true Debye character, the widths $\Gamma_{//}$ and the intensities of the lines has been made by means of fig. 7.05 in which straight lines represent Debye curves. As could be conjectured from fig. 7.04 the relaxation time ($\Gamma_{//}$ is shown in fig. 7.03) varies but little between 63 K and 77 K. It varies even less from there up to room temperature (where $\Gamma_{//} = 0.65$ GHz is reached). The small variation of $\Gamma_{//}$ around T_N is about opposite to that in $\chi_{o//}(0)$. This might be a weak support to Suzuki's prediction⁴⁸⁾ that the relaxation time could be proportional to the static susceptibility in the critical region. This would account for the observed temperature independent $\chi''_{//}(2\pi\nu, 0)$ at high frequencies ($\gg \Gamma_{//}$) (cf. fig. 7.02). Again the isothermal static susceptibility corresponding to the intensity of this relaxation absorption amounts to a value $5 \pm 2\%$ higher than that found by BT. These deviations need not be totally ascribed to inaccuracy of the present work as can be seen from the comparative survey given in table 7.1. Consequently the higher value found in this work has been used throughout.

*) The rates calculated in high temperature approximation are $\Gamma_{//} = 0.362$ GHz, $\Gamma_{\perp} = 0.433$ GHz³⁵⁾, for $J_{mn} h^{-1} = -36.6, +6.7, -0.8$ GHz⁴³⁾.

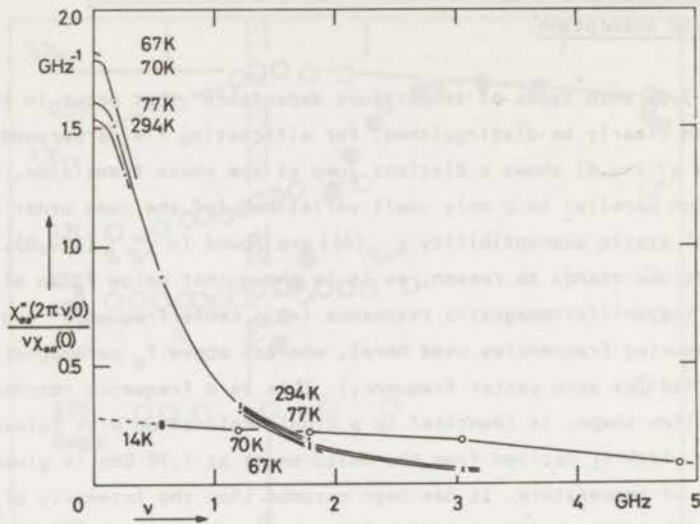


Fig. 7.04 The absorption spectrum in zero field for some temperatures.

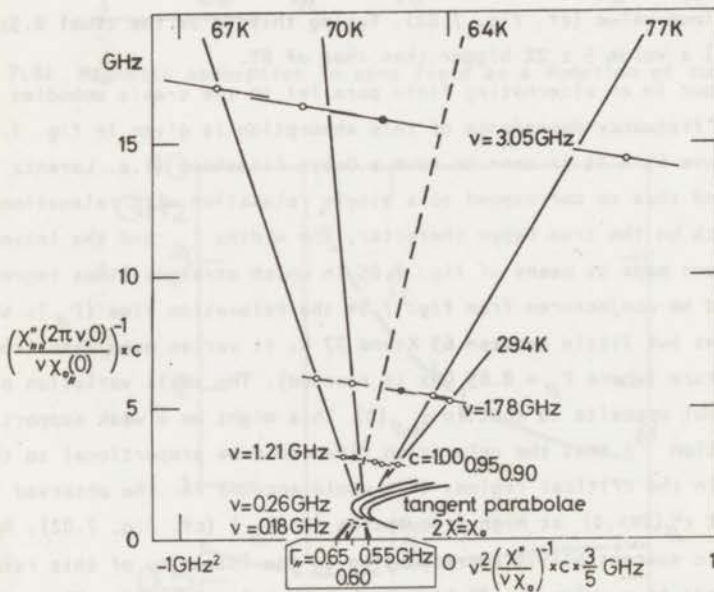


Fig. 7.05 Debye fits for $\chi''_{\parallel}(2\pi\nu,0)$ at several temperatures.

$$c \equiv \chi''_{o\parallel} BT(0) / \chi''_{o\parallel} \text{ this work } (0).$$

Some additional measurements were done at hydrogen temperatures. As those at 20 K suffer from uncertainty of the zero absorption level only measurements at 14 K have been used. At these low temperatures the absorption band is about an order of magnitude broader than the characteristic widths at liquid nitrogen temperatures and up, and its shape is no longer Debye-like (cf. fig. 7.04).

An appreciable part of the intensity may still be found at frequencies above the measuring range (i.e. > 5 GHz). The intensity measured below 5 GHz equals 70% of the total intensity according to the rather inaccurate values for the isothermal static susceptibility $\chi_{o//}(0)$, reported by BT. It may also be compared to the results of Griffel and Stout⁴⁹⁾ for $\chi_{o//}(0) - \chi_{o\perp}(0)$ combined with the $\chi_{o\perp}(0)$ value of BT. If the latter is enhanced by 2 to 3% (cf. table 7.1) the intensity measured below 5 GHz takes about 60% of the total intensity. In fig. 7.04 $\chi_{o//}(0)$ at 14 K is assumed to equal a value that would yield 65%.

Table 7.1. Isothermal static susceptibility

Measurement	ν	T	Deviation from Bizette and Tsai ⁴⁷⁾
Corliss ⁵⁰⁾ $\chi_{o\text{ powder}}(0)$	0	293 K 195 K	6 % 5 %
This work $\chi_{\perp}''(2\pi\nu, 0)$	1.78 GHz	73 K 77 K	3..7 % 4..8 %
$\chi_{//}''(2\pi\nu, 0)$	0.18..3.05 GHz	70 K 67 K	3..7 % 2..6 %
Griffel and Stout ⁴⁹⁾ $\chi_{o\perp}(0) - \chi_{o//}(0)$	0	20 K 14 K	1..35% -1..4 %
extrapolation	0	4 K	≥ 2 %

7.32 Field dependence.

According to the properties of MnF_2 summarized in section 7.13 and especially those reported in the preceding section, the theory of field dependence given in section 7.2 is expected to apply. The behaviour in static fields perpendicular to the alternating field has been measured at liquid nitrogen temperatures and the results have been successfully analyzed along the lines of section 7.2 both above and below T_N . The measurements of the absorption as a function of the static field

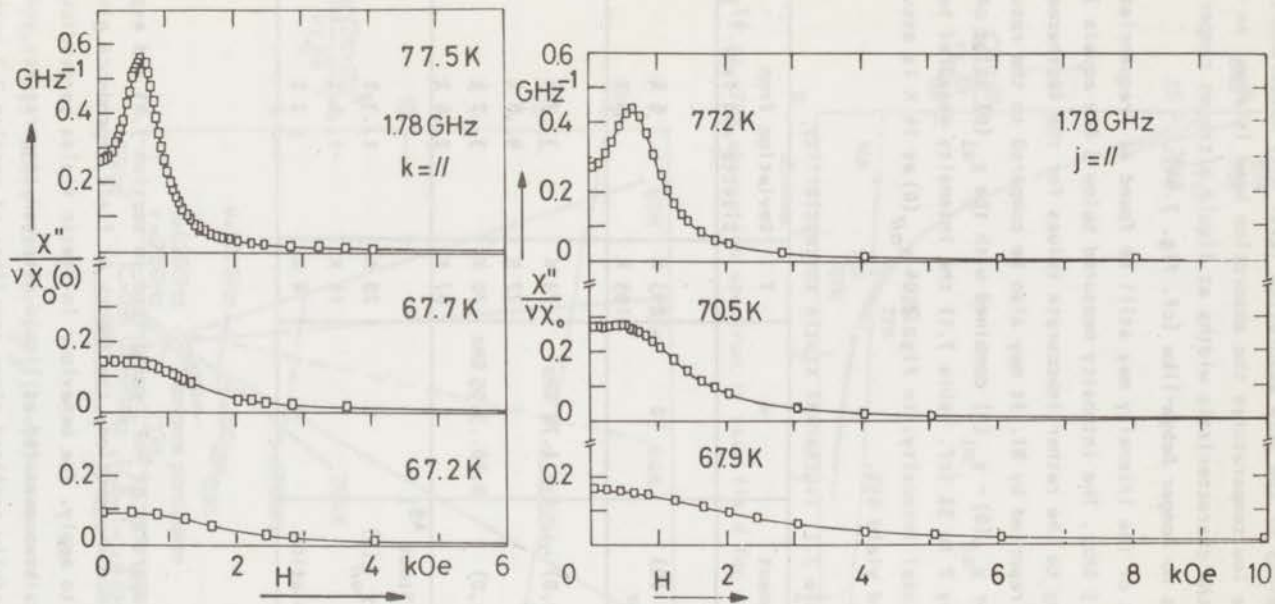


Fig. 7.06 Resonance absorption at 1.78 GHz as a function of field for some temperatures. The solid lines represent the theoretical fit achieved by a proper choice of the parameters $\Gamma_{//}$ and Γ_{\perp} . The r.f. field is perpendicular to c . Left: static field perpendicular to c . Right: static field along c .

were performed at fixed frequency, temperature and orientation. In order to avoid systematic errors every field run has been analyzed separately. Basically the analysis consists of searching the values for the zero field relaxation rates Γ_i , Γ_k and normalization factor, which yield the best fit when approximating the experimental results by a function $A(\Gamma_i, \Gamma_k, n, \nu)$ defined in eq. 7.17. It was discussed in section 7.23 that such an approach may stay useful below T_N . A first search was made shifting specially devised double logarithmic plots of the measurements over a series of gauge plots based on the A-function of eq. 7.17. It revealed that a good fit could be made and that its quality depends strongly on Γ_{\perp} but far less on Γ_{\parallel} . With this knowledge in mind the second step was performed. An average value $\Gamma_{\parallel} = 0.595$ GHz was inserted and by adapting Γ_{\perp} the differences between the experimental values and the A-function were minimized. (The resulting values for Γ_{\perp} and normalization factor have been checked to undergo only minor changes if a different value (10%) is chosen for Γ_{\parallel} .) Some typical fits produced in this way are shown in figs. 7.06, 7.07, 7.08. Their quality may be taken as an indication for the validity of Tjon's approximations and the theory based thereupon. The standard deviation achieved (determined from the differences between theory and experiment) is typically a few percent of the mean value (of all measuring points in one field run). The values of Γ_{\perp} determined by this procedure have been plotted in fig. 7.09. Every point corresponds to one field run and thus to one combination of frequency, temperature and orientation. A nice agreement is found with the result of the zero field measurements above T_N with alternating field \perp c. (cf. fig. 7.10) The points below T_N are seen to satisfy the condition $\Gamma_{\perp} \gg \nu$, which justifies the identification with

$$a_{\perp}^{-1} \nu \equiv \left(\frac{\chi_{\perp}''(2\pi\nu, 0)}{\chi_{\perp}''(0)} \right)^{-1} \quad 7.21$$

the inverse of the zero field AFMR tail (cf. Appl. 2).

7.33 Temperature dependence of Γ_{\perp} .

For reasons of clarity no error bars have been drawn in fig. 7.09. Therefore it is necessary to mention here that the typical errors in temperature are about 0.2 to 0.3 K, due to the uncertain correction for the hydrostatic pressure, applied to the reading of the vapour pressure above the liquid nitrogen. (The resulting temperature gradient is compensated to an unknown extent by heat flow in the apparatus.) The remaining errors must be ascribed to imperfections in the theory or the method of analysis. Even when these errors are taken into account

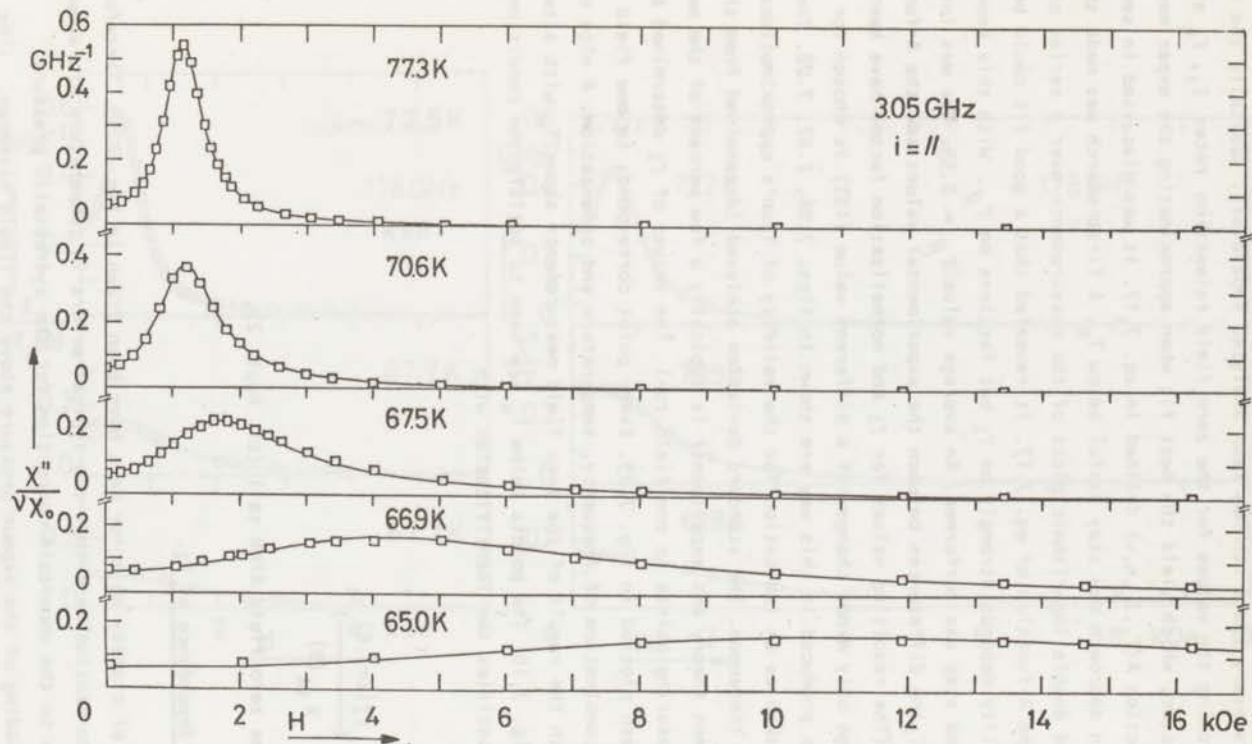


Fig. 7.07 Resonance absorption at 3.05 GHz as a function of field for some temperatures. The solid lines represent the theoretical fit achieved by a proper choice of the parameters $\Gamma_{//}$ and Γ_{\perp} . The r.f. field is parallel to c .

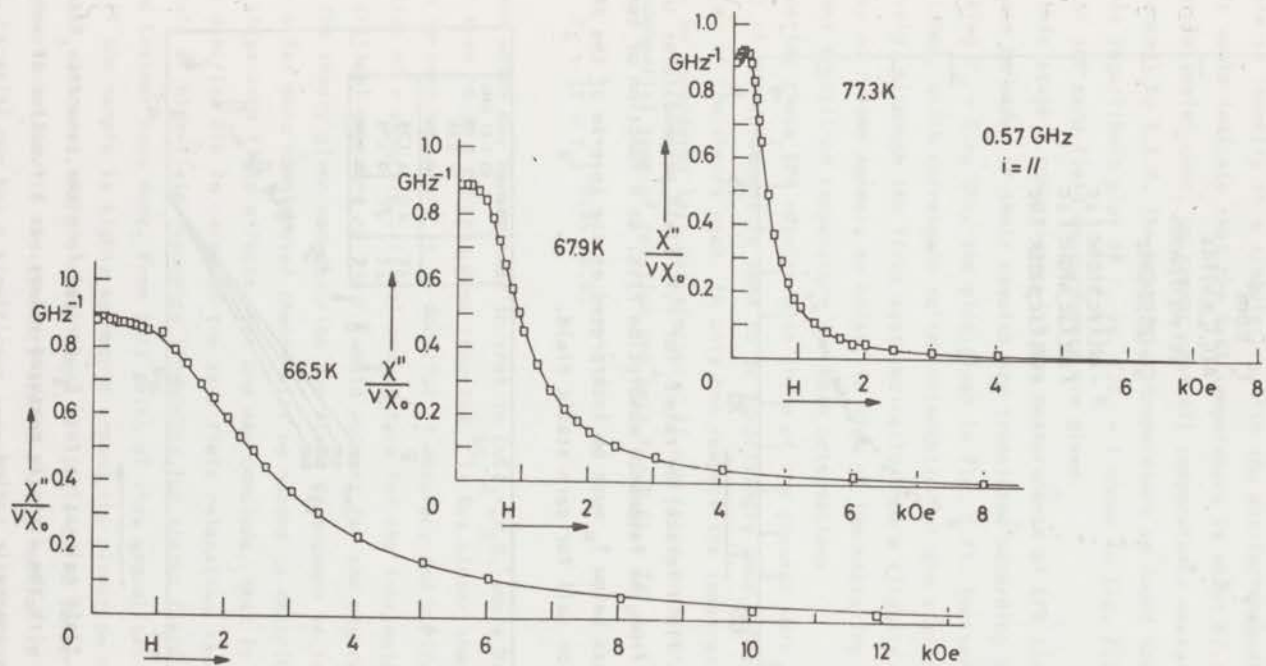


Fig. 7.08 Resonance absorption at 0.57 GHz as a function of field for some temperatures. The solid lines represent the theoretical fit achieved by a proper choice of the parameters $\Gamma_{//}$ and Γ_{\perp} . The r.f. field is parallel to c .

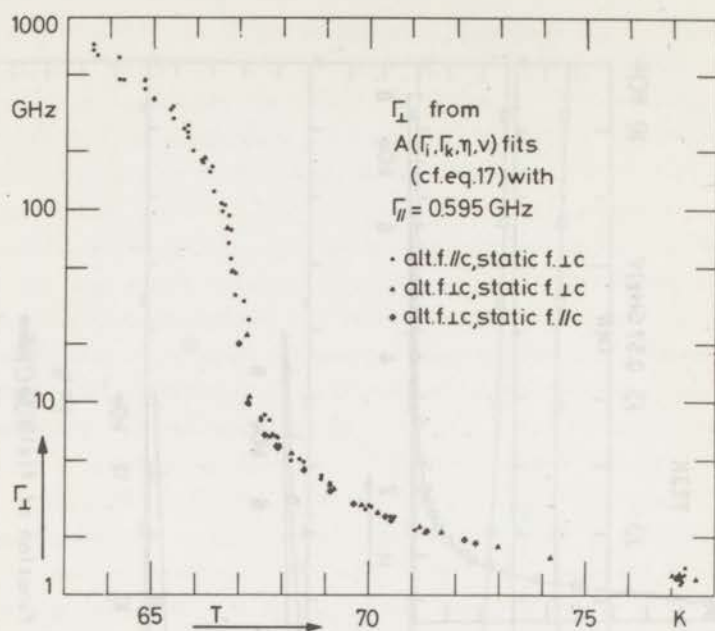


Fig. 7.09 The zero field relaxation rate Γ_{\perp} for r.f. field perpendicular to c derived from the resonance absorption fits, as a function of temperature. The values below T_N must be interpreted as the inverse of the AFMR absorption tail for zero static field.

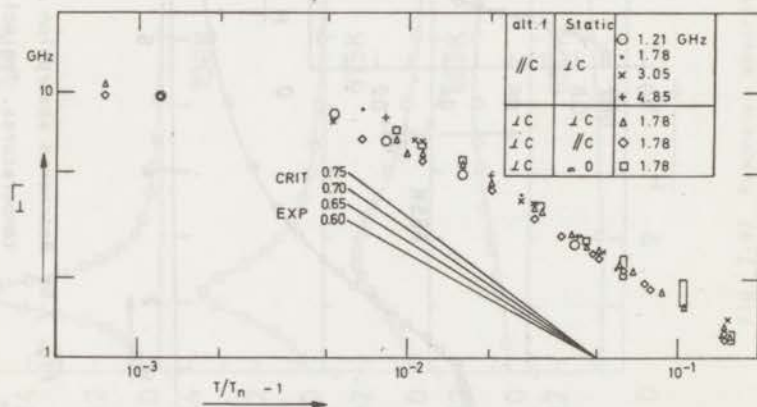


Fig. 7.10 The zero field relaxation rate Γ_{\perp} derived from the resonance fits, together with the directly measured values, as a function of temperature in the paramagnetic region.

there stays a gap or at least a very steep temperature dependence between 11 GHz and 20 GHz. In view of the inaccuracy in the determination of temperature it looks reasonable to identify this singularity with the antiferromagnetic transition.

This would indicate that the Néel temperature is about 67.1^5 K according to the "temperature scale" used, or rather that all temperatures measured should be corrected (enhanced) by 0.2 K. The transition temperature so found has been used to make the double logarithmic plot of Γ_{\perp} vs. $T/T_N - 1$ shown in fig. 7.10, in which also the results of the zero field measurements are given.

At this stage a comparison with the measurements of EPR linewidths by Seehra and Castner can be made. If their results are translated according to Application 1 one gets, taking $\Gamma_{//} = 0.6_0$ GHz, the plot given in fig. 7.11. Two series of points can be distinguished, which correspond to the orientation of the static field $\perp c$ and $//c$ respectively. Although the first systematically show a slightly stronger temperature dependence no reason appears to exist, in view of the measuring errors, to assume a different transition temperature for both orientations.

Comparing these EPR results with those of the present work (the tiny dots in fig. 7.11) the agreement is seen to be surprisingly good, which again supports the credibility of the theory used. In only one respect the temperature dependence of Γ_{\perp} found may be considered less satisfactory. If one tries to describe it by the celebrated exponential type of relation one gets for $0.01 < T/T_N - 1 < 0.2$

$$\Gamma_{\perp} \sim (T - T_N)^{-0.65 \pm 0.03}$$

an exponent which may be compared to that in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, where for all three principal axes -0.59 ± 0.03 has been reported⁴⁵). But closer than 1% from T_N a deviation is seen to occur. It is doubtful if accuracy and purity justify the introduction of a separate critical temperature for the \perp -orientation ($T_c = 66.8 \pm 0.1$ K and critical exponent -0.7 ± 0.1 would account for the observed deviation). Although the theory given can describe the field dependence in terms of zero field behaviour, a far more complicated theory will be needed to describe the critical aspects of these zero field effects. Yet one may conclude, that it seems more fundamental to describe EPR in terms of the zero field relaxation rates $\Gamma_{//}$ and Γ_{\perp} , than on the basis of high-field resonance linewidths for static field $\perp c$ and $//c$, as Seehra and Castner have done. From this point of view a qualitative conjecture can be made: If the sample is highly symmetric around the direction of the alternating field (RbMnF_3 all axes, MnF_2 c-axis) there is little or no temperature dependence in the relaxation time. If the symmetry around that direction is low ($\text{CuCl}_2 \cdot 2\text{aq}$ all axes, MnF_2 $\perp c$ -axis) one has a significant temperature dependence. This empirical rule might support the argument of Huber⁵¹).

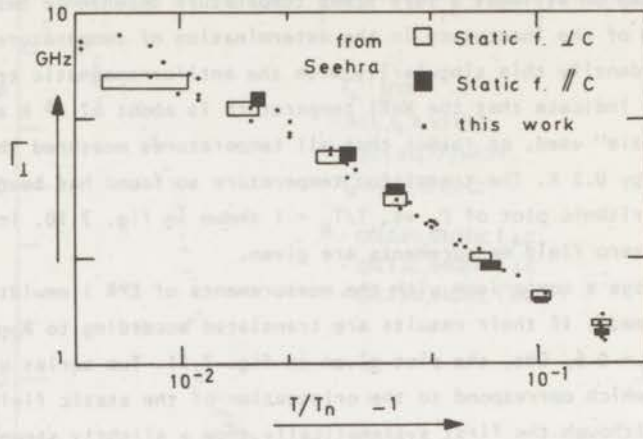


Fig. 7.11 The zero field relaxation rate Γ derived from the resonance linewidths of ref.39, compared to those of fig. 7.10.

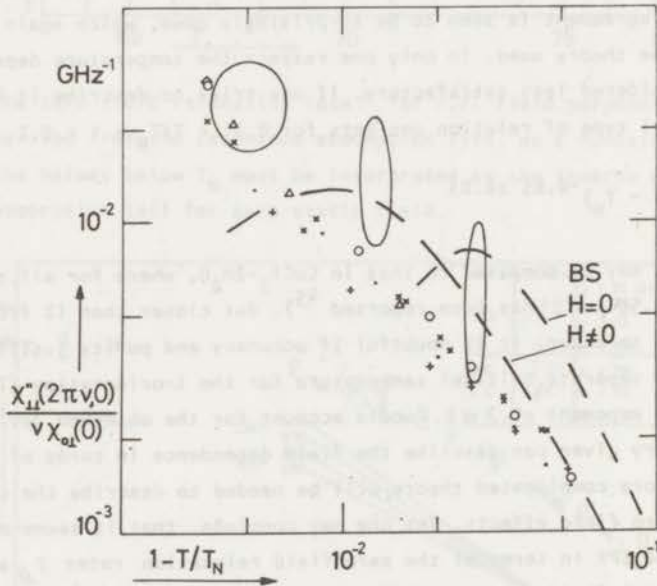


Fig. 7.12 The zero field AFMR absorption tail derived from the resonance fits as a function of temperature in the antiferromagnetic region. The large elliptic areas indicate the result of the direct absorption measurements. The broken lines give the extrapolations from the work of ref.38, under the assumption that the AFMR lines are Lorentzian.

7.34 Temperature dependence of the AFMR tail.

At the end of section 7.23 it was seen that for $T < T_N$ the Γ_{\perp} values may be interpreted as the inverse of the zero field AFMR tail at low frequencies. With the aid of the temperature correction introduced in the preceding sections this tail has been plotted in fig. 7.12 together with the rather inaccurate results of the direct zero field measurement at 1.78 GHz. For comparison with the AFMR measurements of Burgiel and Strandberg³⁸⁾ two curves have been added. BS have determined the zero field AFMR frequency (cf. eq. 7.06) and zero field AFMR linewidth up to 64 K. Extrapolating their results to higher temperature and assuming both lines (at $\pm v_A$) of which the AFMR absorption consists to be Lorentzian all the way down their low frequency tail one can estimate the zero field AFMR tail as a function of temperature. This yields the $H = 0$ curve in fig. 7.12. From a different type of measurement at 10 kOe BS got quite different values for the AFMR width. As no strong field dependence of AFMR width in low fields can be derived from eq. 7.16, it might well be that these 10 kOe values are closer to the actual zero field values than those measured in zero field. Therefore a second extrapolation and estimate have been made, based on the 10 kOe widths (cf. the $H \neq 0$ curve in fig. 7.12). The agreement with present results, especially around 64 K is much better than for the $H = 0$ curve. This might be a second reason for doubt concerning the BS zero field measurement. Within 3% below the Neel temperature only qualitative agreement is found. The deviations can be attributed to a failure of the extrapolations and the assumption about the Lorentzian character of the lineshape.

*How nicely microscopic forces yield
In Units growing Visible the World we wield.*

John Updike

CHAPTER 8

MEASUREMENTS ON SOME COPPER ALKALI HALIDES

8.1 Introductory remarks.

8.11 Introduction.

In both preceding chapters two examples representing extreme choices for the strength of the exchange interaction have been treated. In chapter 6 the Cu Tutton salts were studied in which exchange interaction is not large, compared to dipole-dipole interaction and Zeeman energy. In chapter 7 manganous fluoride was seen to have an exchange interaction much larger than dipole-dipole interaction or Zeeman energy; hence relaxation rates in MnF_2 cannot be changed by the parallel static fields available and temperature becomes the central parameter.

In this chapter the intermediate case is investigated: a series of three compounds of the $Cu(NH_4)_2Cl_4 \cdot 2$ aq. type, where the exchange is still large compared to the dipole-dipole interaction but of the same order of magnitude as the Zeeman energy in highest obtainable field. The dependence of the relaxation rate on parallel static fields is studied in the high-temperature region, i.e. at temperatures where no ordering effects are to be expected and where relaxation rates are independent of temperature. Hence the fact that the exchange in these compounds is mainly of the ferromagnetic type is of little importance.

8.12 Choice of the sample material.

The copper alkali halides were chosen for the following reasons:

- The exchange interaction corresponds to fields of the order of 10 kOe to be compared to the highest available static field of 16 kOe.
- The dipole-dipole interaction is weak compared to the exchange.
- The crystal structure is well-known and relatively simple (cf. section 8.13).
- Single crystals are readily available.

- The work of Van der Molen⁴⁴) below 0.2 GHz and 7 kOe shows the need for an extension to higher frequencies and fields.

8.13 Crystal structure and hamiltonian.

The Cu^{2+} ions in the copper alkali halides studied constitute a body-centered almost-cubic lattice. The deviation from the cubic form is given by the ratio $c/a \approx 1.05$ (cf. table 8.1). Just like in the Tutton salts the copper ions being surrounded by stretched octahedrons of charged particles, have an anisotropic g -tensor with tetragonal symmetry. Here, however, the charges are not only localized in water molecules as the octahedron consists of four halogen ions and two H_2O groups. Depending on the direction of the tetragonal axis two types of ion can be distinguished, with axis along $(1, 1, 0)$ and $(1, -1, 0)$ respectively. Corner ions are all of one type, centre ions all of the other. Both c - a -planes make equal angles with both types of tetragonal axis. The elements of the g -tensor are given by $g_{//} = 2.38$, $g_{\perp} = 2.06$, which values are in reasonable agreement with the present experimental results.

As was mentioned in section 8.11 the interaction in these compounds mainly consists of exchange. A more detailed discussion is given in section 8.14. Furthermore one has dipole-dipole interaction and hyperfine interaction. According to Wielinga⁵²) the latter being much smaller than the former, can be neglected in this case. One may thus expect that the hamiltonian of the spin system in a sample of a copper alkali halide is given by eq. 6.00 where \mathcal{H}_{hfs} can be omitted.

In analogy to section 6.31 (cf. also section 5.22) \mathcal{H}_{int} will be decomposed into eigenoperators of L_z in section 8.21. For the parallel static field ($\vec{H} \equiv H\vec{e}_z$) in a c - a -plane a situation occurs analogous to that in the k_2 - k_1 or k_2 - k_3 -plane of the Tutton salts. Hence the decomposition is then given by eqs. 6.33, 6.34, 6.35, 6.36.

Table 8.1

compound	a (\AA)	c (\AA)	T_c (K)	$J_{\text{mn}} \text{h}^{-1}$ (GHz)
$\text{Cu}(\text{NH}_4)_2\text{Cl}_4 \cdot 2 \text{ aq.}$	7.58	7.96	0.70	5.0
$\text{CuK}_2\text{Cl}_4 \cdot 2 \text{ aq.}$	7.45	7.88	0.88	6.3
$\text{Cu}(\text{NH}_4)_2\text{Br}_4 \cdot 2 \text{ aq.}$	7.98	8.41	1.74	12.6

8.14 Exchange interaction in the Cu alkali halides.

In eq. 5.06 the exchange tensor \vec{J}_{mn} is seen to consist of three parts. The isotropic (Heisenberg) part $\frac{1}{3}(\text{Tr } \vec{J}_{\text{mn}}) \vec{1}$ contributes to the secular part \mathcal{H}_0 of the interaction. In the underlying compounds it corresponds to the major part of \mathcal{H}_{ex} and also of \mathcal{H}_0 . The values of $\frac{1}{3} \text{Tr } \vec{J}_{\text{mn}}$ for nearest neighbours are given in table 8.1. Those for next nearest neighbours are four times smaller. Farther neighbours may be ignored.

It is a well-known feature of spin-spin relaxation (cf. e.g. section 8.21) that the relaxation rate τ^{-1} strongly depends on the non-secular part of the interaction. Van der Molen⁴⁴) has found for these compounds that the non-secular part of the dipole-dipole interaction is too small to allow a satisfying description of his experiments. Hence he postulated the existence of non-secular contributions in the exchange, akin to Van Vleck's pseudo-dipolar exchange, which is anisotropic and symmetric^{*})⁵³).

This correction to isotropic exchange, however, is not the first to be made. As was pointed out by Moriya⁵⁴) one may roughly estimate the relative contributions (isotropic) : (antisymmetric-Dzialoshinsky) : (pseudo-dipolar) to be of the order

$$1 \quad : \quad \left(\frac{g-2}{g}\right) \quad : \quad \left(\frac{g-2}{g}\right)^2,$$

which implies that the antisymmetric exchange can play an important role in spin-spin relaxation. The introduction by De Jong⁵⁵) of antisymmetric exchange in the description of dynamical spin-spin effects has proven successful in many Cu^{2+} -compounds and probably constitutes the biggest step forward in this field during the last decade.

It is not surprising that neither in the Cu Tutton salts nor in MnF_2 the need for an introduction of antisymmetric exchange has been felt. In the first case the total exchange is not much larger than the dipole-dipole interaction such that only a minor correction can be expected. In MnF_2 g is very close to 2 (within 1%). Yet one might thus try to explain the difference between 295 K results and high T calculations

8.15 Antisymmetric exchange in the Cu alkali halides.

The Dzialoshinsky-Moriya part of the exchange may be written as

$$2 \sum_{m < n} \vec{S}_m \cdot \left(\frac{1}{2} \vec{J}_{mn} - \frac{1}{2} \vec{J}_{mn}^{\sim} \right) \cdot \vec{S}_n = 2 \sum_{m < n} \vec{D}_{mn} \cdot (\vec{S}_m \wedge \vec{S}_n) \quad 8.01$$

with $(\vec{D}_{mn})_i \equiv \epsilon_{ijk} \left(\frac{1}{2} \vec{J}_{mn} - \frac{1}{2} \vec{J}_{mn}^{\sim} \right)_{jk}$, $m < n$

and $\epsilon_{xyz} \equiv \epsilon_{yzx} \equiv \epsilon_{zxy} \equiv 1$, $\epsilon_{yxz} \equiv \epsilon_{xzy} \equiv \epsilon_{zyx} \equiv -1$.

The axial vectors \vec{D}_{mn} representing an interaction in the crystal satisfy the symmetry conditions of the total crystal. Using these De Jong⁵⁶) has proven that in the Cu alkali halides no antisymmetric exchange between next nearest neighbours occurs and that for nearest neighbours all \vec{D}_{mn} -vectors have the same length and are parallel to the a - a -plane, with $\vec{D}_{mn} \perp \vec{r}_{mn}$. Exchange between farther neighbours has

^{*}) These contributions are part of, but may not be identified with the second term in 5.06, which is traceless and may still contribute a secular component to \mathcal{K}_{ex} . As the definition of "secular" depends on the orientation of the static field, eq. 5.06 gives the only universal way of splitting \mathcal{K}_{ex} .

been ignored. Designating both types of ion by I and II and realizing that an ion and its nearest neighbours are of different types one can indicate the direction of the vectors by the following rules

$$(\vec{D}_{mn} + \vec{D}_{ml}) \perp \vec{r}_{nl} \quad \text{and} \quad (\vec{D}_{mn} + \vec{D}_{kn}) \perp \vec{r}_{mk},$$

$$\vec{D}_{mn} + \vec{D}_{ml} = 0, \text{ if } \vec{r}_{nl} // c \quad \text{and} \quad \vec{D}_{mn} + \vec{D}_{kn} = 0, \text{ if } \vec{r}_{mk} // c,$$

where the numbering has been chosen so as to satisfy $m \in I, n \in II \rightarrow m < n$. Thus the antisymmetric exchange in these compounds can be characterized by one parameter $|\vec{D}_{mn}|$, which should be of the order of $\frac{g-2}{g} \left| \frac{1}{3} \text{Tr } \bar{J}_{mn} \right|$, where m and n are nearest neighbours.

8.2 Theory for the field dependence of the relaxation rate in compounds with relatively strong exchange interaction.

The case of compounds that have exchange as the main type of interaction more or less constitutes the standard problem in spin-spin relaxation theory ^{22,17}). It is characterized by the feature that the secular part of the interaction (cf. section 5.23) - mostly due to the presence of strong isotropic exchange ^{*}) - is much larger than the remaining non-secular part. This allows a simplifying assumption concerning the field dependence of the memory spectrum at high temperatures. The situation is sometimes referred to as the weak coupling case ¹⁷).

8.21 The memory spectrum and the weak coupling limit.

In section 6.33 it was seen that in strong parallel fields and at high temperatures (zero interaction limit) the secular part \mathcal{K}_0 of the interaction yields a narrow line at $\omega = 0$. In section 6.36 this line was found to be narrower than the lines at other frequencies, its second moment being approximately zero. In the present case where non-secular interaction is negligible this narrow line at zero frequency, usually called Kronig - Bouwkamp relaxation, is the only line in the absorption spectrum. Experimentally this is found to be true for all values of the parallel static field. As the analysis of the absorption spectrum by means of moment calculations breaks down it is useful to try an analysis of the memory spectrum. Due to the single-line

^{*}) This holds for an almost isotropic g-tensor. An interesting case of possibly small but mainly secular interaction occurs for $\mathcal{K}_{ex} \approx 0$ and very anisotropic g-tensor with $g_{ij} = g_i \delta_{ij}$ and $g_i \gg g_j, g_k$, such that \mathcal{K}_d hardly contains non-secular contributions. The same holds for \mathcal{K}_{hfs} , if the A-tensor has similar characteristics. This situation is found in some rare-earth compounds.

character of the absorption spectrum this may well be done for the memory spectrum that corresponds to the total absorption spectrum (rather than for the one that can be derived from the zero-frequency term alone, as was done in appendix K). It will be seen that the strong field condition, implicit in the zero interaction limit, can then be omitted, the only approximation to be made being that of negligible non-secular interaction (weak coupling limit).

According to 3.12 the memory function and memory spectrum pertaining to the total spectrum are given by

$$(LM_i, e^{i(1-P_A)Lt} LM_i) = \int_{-\infty}^{+\infty} e^{i\omega t} s'_{LM_i, LM_i}(\omega, \vec{H}) d\omega . \quad 3.12$$

Up to second and lowest order in the non-secular part of the interaction the memory function equals ($L_z M_i = L_o M_i = 0$)

$$(LM_i, e^{i(L_z + L_o)t} LM_i)_{\mathcal{H}_z + \mathcal{H}_o}, \text{ with } L_o B \equiv \hbar^{-1} [\mathcal{H}_o, B] .$$

If this is a good approximation in the long time region (i.e. for times of the order of the inverse - very narrow - linewidth) one says that the weak coupling limit applies. One can then write

$$(LM_i, e^{i(1-P_A)Lt} LM_i) \approx (LM_i, e^{i(L_z + L_o)t} LM_i)_{\mathcal{H}_z + \mathcal{H}_o} . \quad 8.02$$

In analogy to section 6.31 one may split

$$\begin{aligned} (LM_i, e^{i(L_z + L_o)t} LM_i)_{\mathcal{H}_z + \mathcal{H}_o} &= \mu_o^{-2} H^{-2} (L_z \mathcal{H}_z, e^{i(L_z + L_o)t} L_z \mathcal{H}_z)_{\mathcal{H}_z + \mathcal{H}_o} = \\ &= \mu_o^{-2} H^{-2} \sum_{p, q, = 0, \pm 1, \dots, \pm n} \omega_p \omega_q (\mathcal{H}_p, e^{i(L_z + L_o)t} \mathcal{H}_q)_{\mathcal{H}_z + \mathcal{H}_o} . \end{aligned} \quad 8.03$$

As $[\mathcal{H}_z, \mathcal{H}_o] = 0$, one has for all B $L_z L_o B = L_o L_z B$ implying

$$\begin{aligned} (\mathcal{H}_p, e^{i(L_z + L_o)t} \mathcal{H}_q)_{\mathcal{H}_z + \mathcal{H}_o} &= (\mathcal{H}_p, e^{iL_o t} e^{iL_z t} \mathcal{H}_q)_{\mathcal{H}_z + \mathcal{H}_o} = \\ &= (\mathcal{H}_p, e^{iL_o t} \mathcal{H}_q)_{\mathcal{H}_z + \mathcal{H}_o} e^{i\omega_q t} . \end{aligned} \quad 8.04$$

One can prove by inspection of 3.07 that

$$(\mathcal{H}_p, e^{iL_0 t} \mathcal{H}_q)_{\mathcal{H}_Z + \mathcal{H}_O} = (\mathcal{H}_q, e^{iL_0 t} \mathcal{H}_p)_{\mathcal{H}_Z + \mathcal{H}_O} \delta_{pq} \quad 8.05$$

Hence the memory function in weak coupling limit equals

$$(LM_i, e^{i(1-P_A)Lt} LM_i) \approx \mu_0^{-2} \sum_{p=0, \pm 1, \dots, \pm n} \gamma_p^2 (\mathcal{H}_p, e^{iL_0 t} \mathcal{H}_p)_{\mathcal{H}_Z + \mathcal{H}_O} e^{i\omega_p t} \quad 8.06$$

The corresponding approximation for the memory spectrum is given by

$$s_{LM_i, LM_i}^i(\omega, \vec{H}) \approx \mu_0^{-2} \sum_{p=0, \pm 1, \dots, \pm n} \gamma_p^2 s_{\mathcal{H}_p, \mathcal{H}_p}^o(\omega - \omega_p, \vec{H}) \quad 8.07$$

with
$$(\mathcal{H}_p, e^{iL_0 t} \mathcal{H}_p)_{\mathcal{H}_Z + \mathcal{H}_O} \equiv \int_{-\infty}^{+\infty} e^{i\omega t} s_{\mathcal{H}_p, \mathcal{H}_p}^o(\omega, \vec{H}) d\omega \quad 8.08$$

where the functions $s_{\mathcal{H}_p, \mathcal{H}_p}^o(\omega, \vec{H})$ are centered around $\omega = 0$ and have intensities $(\mathcal{H}_p, \mathcal{H}_p)_{\mathcal{H}_Z + \mathcal{H}_O}$ and second moments $(L_0 \mathcal{H}_p, L_0 \mathcal{H}_p)_{\mathcal{H}_Z + \mathcal{H}_O} (\mathcal{H}_p, \mathcal{H}_p)_{\mathcal{H}_Z + \mathcal{H}_O}^{-1}$.

Their shape, though fully determined by their moments, is in most cases not explicitly known but probably resembles a broad line.

8.22 High-temperature approximation and rigid line shapes.

Contrary to the situation in section 6.3 one can achieve an essential simplification excluding low-temperature effects through application of the high-temperature approximation ($\beta \rightarrow 0$) at this stage, instead of postponing it to the calculation of intensities and moments. The functions $s_{\mathcal{H}_p, \mathcal{H}_p}^o(\omega, \vec{H})$ defined through 8.08 depend on the static field through the definition of the scalar product only. Making the high-temperature approximation one gets field independent functions

$$\lim_{\beta \rightarrow 0} s_{\mathcal{H}_p, \mathcal{H}_p}^o(\omega, \vec{H}) \equiv s_{\mathcal{H}_p, \mathcal{H}_p}^o(\omega) \quad 8.09$$

The memory spectrum may thus be approximated by a sum of lines $s_{\mathcal{H}_p, \mathcal{H}_p}^o(\omega - \omega_p)$ at centerfrequencies ω_p with linewidths of the order of $\hbar^{-1} (\mathcal{H}_p, \mathcal{H}_p)_{\mathcal{H}_Z + \mathcal{H}_O}^{\frac{1}{2}} \beta \rightarrow 0$. Contrary to

the general parallel-field absorption-spectrum (cf. section 6.3) it contains no crossterms*) or satellite lines and, as $\gamma_0 \equiv 0$, no zero-frequency line. It is important that in the double approximation of weak coupling and high temperature the line shapes may be assumed independent of the static field. At a field variation the lines simply shift rigidly keeping their form. Hence one may speak of "lines" and not only of "terms" as in section 6.3; the name memory lines will be used (only well-defined at high temperatures).

Due to the symmetry with respect to inversion of the static field (cf. section 3.5) one has

$$s_{LM_i, LM_i}^i(\omega, \vec{H}) = s_{LM_i, LM_i}^i(\omega, -\vec{H}) . \quad 8.10$$

Hence eqs. 8.07 and 8.09 imply

$$\sum_{p=+1, \dots, +n} \gamma_p^2 s_{\mathcal{H}_p}^0(\omega - \omega_p) \approx \sum_p \gamma_p^2 s_{\mathcal{H}_p}^0(\omega + \omega_p) .$$

Moreover, due to 2.46, one has

$$s_{\mathcal{H}_p}^0(\omega) = s_{\mathcal{H}_{-p}}^0(-\omega) . \quad 8.11$$

As $\gamma_p = -\gamma_{-p}$ one gets

$$\gamma_p^2 s_{\mathcal{H}_p}^0(\omega) = \gamma_{-p}^2 s_{\mathcal{H}_{-p}}^0(-\omega) \quad 8.12$$

and hence

$$\begin{aligned} & \sum_{p=1, \dots, n} \gamma_p^2 (s_{\mathcal{H}_p}^0(\omega - \omega_p) + s_{\mathcal{H}_p}^0(-\omega + \omega_p)) \approx \\ & \approx \sum_{p=1, \dots, n} \gamma_p^2 (s_{\mathcal{H}_p}^0(\omega + \omega_p) + s_{\mathcal{H}_p}^0(-\omega - \omega_p)) . \end{aligned} \quad 8.13$$

At least for $n \leq 2$ this implies

*) This implies that a narrower upper bound (in terms of the relative importance of \mathcal{H}_p , $p \neq 0$ and \mathcal{H}_0) than 6.13 must exist. A search for such a relation is suggested as it would greatly clarify the mechanism of the weak coupling approximation.

$$s_{\mathcal{H}_p \mathcal{H}_p}^0(\omega) \approx s_{\mathcal{H}_p \mathcal{H}_p}^0(-\omega) \quad 8.14$$

i.e. if the weak coupling and high-temperature approximation apply the memory lines are approximately symmetric with respect to their centre. If the calculation of an odd moment ($\sim \text{Tr } \mathcal{H}_p^\dagger (L_o)^{2n+1} \mathcal{H}_p$) yields a non-zero value, this proves the breakdown of the approximation.

8.23 Single relaxation at high temperatures.

If the memory lines are smoothly curved and contain no fine structures it follows from 8.12 that $s_{LM_i, LM_i}^1(\omega, \vec{H})$ is approximately constant ($\approx s_{LM_i, LM_i}^1(0, \vec{H})$) in a frequency interval around $\omega = 0$. The width of this interval may be estimated to be one order of magnitude smaller than the linewidth $h^{-1}(\mathcal{H}_o, \mathcal{H}_o)_{\beta \rightarrow 0}^{\frac{1}{2}}$. As was mentioned in section 3.3. this implies single-relaxation absorption in that interval ²⁸). The relaxation rate τ^{-1} is proportional to the constant value

$$\tau^{-1} = \pi s_{LM_i, LM_i}^1(0, \vec{H}) (A, A)_{\beta \rightarrow 0}^{-1} \quad \text{cf. 3.19}$$

This value is field dependent according to

$$s_{LM_i, LM_i}^1(0, \vec{H}) = \mu_o^{-2} \sum_{p=\pm 1, \dots, \pm n} \gamma_p^2 s_{\mathcal{H}_p \mathcal{H}_p}^0(-\omega_p) \quad 8.15$$

For increasing static field the memory lines shift away from the interval around $\omega = 0$ yielding a decreasing relaxation rate ^{*}). When the field dependence of τ^{-1} has been experimentally determined it can be confronted with the theoretical values for intensities and moments of the memory lines $s_{\mathcal{H}_p \mathcal{H}_p}^0(\omega)$.

Thus in compounds with negligible non-secular interaction and at high temperatures the memory spectrum, approximated by a sum of rigid lines, can be recorded through measurements of τ^{-1} at fixed low frequencies in a variable field. The maximal value of this field should be of the order of $\gamma_p^{-1} h^{-1}(\mathcal{H}_o, \mathcal{H}_o)_{\beta \rightarrow 0}^{\frac{1}{2}}$. Without the simplification of rigid line shapes the same result could only be achieved through a measurement of the frequency dependent susceptibility up to frequencies of the order of $h^{-1}(\mathcal{H}_o, \mathcal{H}_o)_{\beta \rightarrow 0}^{\frac{1}{2}}$, an experiment which is much more difficult to perform (cf. section 6.2).

The single relaxation derived above on the basis of the weak coupling and

^{*}) This decrease may be compensated to some extent by the field dependence of $(A, A)_{\beta \rightarrow 0}$.

high-temperature approximation and under the assumption of smooth unstructured memory lines is often experimentally found. One usually checks the single-relaxation character and determines the relaxation rate and its field dependence measuring the absorption at some fixed frequencies around τ^{-1} and fitting the results to a Debye line (i.e. a Lorentz line at $\omega = 0$, cf. eq. 3.17 with $\omega_0 = 0$).

It should be emphasized that no other than experimental evidence is available to support the assumed absence of fine structures in the memory lines. In some cases deviations from single-relaxation behaviour are found that imply such fine structures (cf. e.g. 3.22).

8.24 The high-frequency tail of a single relaxation.

Once the single-relaxation (Debye) character within a frequency interval around $\omega = 0$ has been established (or assumed), the field dependence of τ^{-1} can be determined in a still easier way. Choosing one fixed measuring frequency within that interval, and far above τ^{-1} *) (or rather its maximum as a function of field), one may approximate (cf. 3.17, 3.19, $\omega_0 = 0$, $\alpha = 1$)

$$\omega^2 \frac{\chi''_{ii}(\omega, \vec{H})}{\omega(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))} = \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \approx \tau^{-1} \approx \pi s'_{LM_i, LM_i}(\omega, \vec{H}) (A, A)^{-1}. \quad 8.16$$

This means that at these high frequencies the field dependence of τ^{-1} can be immediately observed and that the memory spectrum is directly proportional to $\omega^2 \chi''_{ii} \omega^{-1}$.

The complicating field dependence of (A, A) can easily be dealt with. Due to 4.04, 4.06 and section 3.3 one has

$$(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})) (A, A)^{-1} = (\chi_{0 ii}(\vec{H}) - \chi_{\infty ii}(\vec{H})) ((M_i, M_i) - (I, M_i)^2)^{-1} \quad 8.17$$

which in absence of diamagnetic effects (χ linear in \vec{H}) and for negligible average magnetization (I, M_i) approximately equals $\chi_{0 ii}(\vec{H}) (M_i, M_i)^{-1}$ implying

$$\omega^2 \frac{\chi''_{ii}(\omega, \vec{H})}{\omega \chi_{0 ii}(\vec{H})} \approx \pi s'_{LM_i, LM_i}(\omega, \vec{H}) (M_i, M_i)^{-1}. \quad 8.18$$

As often the field dependence of $\chi_{0 ii}(\vec{H})$ and (M_i, M_i) is of little importance

*) If such a choice is impossible one should not speak of a relaxation.

8.18 shows the equivalence of $\omega^2 \chi'' \omega^{-1}$ and s' at high frequencies.

8.25 The direct measurement of the memory spectrum.

The approximate equivalence of $\omega^2 \chi'' \omega^{-1}$ and the memory spectrum s' derived in the preceding section for the high-frequency tail of a single relaxation can be given a more general significance. Inspecting eqs. 3.14 and 3.13 one sees that if

$$| \chi_{ii}(\omega, \vec{H}) - \chi_{\infty ii}(\vec{H}) | \ll \chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}) \tag{8.19}$$

holds, one may approximate

$$\begin{aligned} l'(i\omega)(A, A)^{-1} &= -i\omega \frac{\chi_{ii}(\omega, \vec{H}) - \chi_{\infty ii}(\vec{H})}{\chi_{ii}(\omega, \vec{H}) - \chi_{ii}(0, \vec{H})} \approx \\ &\approx i\omega \frac{\chi_{ii}(\omega, \vec{H}) - \chi_{\infty ii}(\vec{H})}{\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H})} \end{aligned} \tag{8.20}$$

and thus

$$\pi s'_{LM_i LM_i}(\omega, \vec{H}) = \text{Re } l'(i\omega) \approx \omega^2 \frac{\chi''_{ii}(\omega, \vec{H})}{\omega(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))} (A, A) \tag{8.21}$$

This allows a general and simple experimental determination of the memory spectrum. In most cases inequality 8.19 holds outside a narrow zero-frequency absorption-line leaving the bulk of the broad functions $s_{p \beta p}^0(\omega, \vec{H})$ (cf. 8.08) open for direct investigation. Combining 8.21 and 8.07 one has (if 8.19 holds)

$$\begin{aligned} \omega^2 \frac{\chi''_{ii}(\omega, \vec{H})}{\omega \chi_{0 ii}(\vec{H})} (M_i, M_i) &\approx \omega^2 \frac{\chi''_{ii}(\omega, \vec{H})}{\omega(\chi_{ii}(0, \vec{H}) - \chi_{\infty ii}(\vec{H}))} (A, A) \approx \\ &\approx \pi \mu_0^{-2} \sum_{p=1, \dots, n} \gamma_p^2 s_{p \beta p}^0(\omega - \omega_p, \vec{H}) \end{aligned} \tag{8.22}$$

to which 8.09 may be applied.

As far as a confrontation with theoretical values for intensities and moments of the functions $s_{p \beta p}^0(\omega, \vec{H})$ (for $\beta \rightarrow 0$ memory lines) is concerned the excluded interval plays a minor role. This suggests that in such a confrontation no use is made of the distinct features of s' at $\omega \approx 0$ and that an analysis of $\omega^2 \chi'' \omega^{-1}$ would be sufficient. In the next section it is shown that at low frequencies and high temperatures the application of the weak coupling approximation in such an analysis leads to definitely wrong results.

8.26 Tentative analysis of $\omega^2 \chi'' \omega^{-1}$.

A direct analysis of $\omega^2 \chi'' \omega^{-1}$ seems to have the advantage of doing without condition 8.19. However it will be seen that the interval around $\omega = 0$ must again be excluded or otherwise the weak-coupling approximation does not hold.

Taking the second time-derivative of 3.08 one gets

$$\beta \mu_0 (LM_i, e^{iLt} LM_i) = \int_{-\infty}^{+\infty} e^{i\omega t} \omega^2 S_{ii}(\omega, \vec{H}) d\omega \quad . \quad 8.23$$

Comparing this to eq. 3.12 one may remark that 8.23 shows a simpler type of time development. Consequently one would expect the weak coupling approximation to be valid such that up to second and lowest order in the non-secular part of the interaction one has

$$\beta \mu_0 (LM_i, e^{i(L_z + L_o)t} LM_i)_{\mathcal{H}_z + \mathcal{H}_o} \approx \int_{-\infty}^{+\infty} e^{i\omega t} \omega^2 S_{ii}(\omega, \vec{H}) d\omega \quad 8.24$$

and thus analogous to 8.07 (cf. 1.38, 1.45, 3.10)

$$\begin{aligned} \omega^2 \frac{\chi''_{ii}(\omega, \vec{H})}{\omega(\chi'_{ii}(0, \vec{H}) - \chi'_{\infty ii}(\vec{H}))} (A, A) &= \pi \omega^2 S_{ii}(\omega, \vec{H}) \approx \\ &\approx \pi \mu_0^{-2} \sum_{p=0, \pm 1, \dots, \pm n} \gamma_p^2 S_{\mathcal{H}_p}^o(\omega - \omega_p, \vec{H}) . \end{aligned} \quad 8.25$$

This would constitute an alternative and more general way to derive eq. 8.22.

It is instructive to compare both weak-coupling approximations 8.02 and 8.24 for the special case of a single relaxation at high temperature. For a single relaxation eq. 3.19 yields

$$\pi S'_{LM_i, LM_i}(\omega, \vec{H}) = \pi S'_{LM_i, LM_i}(0, \vec{H}) = \tau^{-1}(A, A) \quad 8.26$$

whereas eq. 3.17 implies

$$\pi \omega^2 S_{ii}(\omega, \vec{H}) = \tau^{-1}(A, A) \left(1 - \frac{1}{1 + \omega^2 \tau^2} \right) . \quad 8.27$$

Although both expressions have been approximated by the same sum

$$\pi \mu_0^{-2} \sum_{p=+1, \dots, +n} \gamma_p^2 \sum_{p,p}^o \chi_{p,p}(\omega - \omega_p, \vec{H}) \quad 8.28$$

the first expression is frequency independent, whereas the second contains a narrow line (a negative replica of the absorption line) which stays at zero frequency for all fields. The occurrence of a constant value was seen to be plausible in section 8.28 but the zero-frequency line in eq. 8.27 indicates a serious difficulty. For high temperatures 8.28 becomes a sum of (positive non-definite) memory lines which have a rigid shape and only shift when the field is varied. Their sum cannot yield an anomaly of the type found in eq. 8.27, whatever their shape may be. Therefore the weak coupling approximation for $\omega^2 S_{ii}(\omega, \vec{H})$ is seen to break down in the frequency interval around $\omega = 0$, where 8.19 does not hold either. Even outside this interval and certainly at lower temperatures the validity of eq. 8.22 would be dubious without the argument of section 8.25.

Again the importance of experimental evidence concerning the single-relaxation character has appeared. Without it one would be tempted to prefer the erroneous method given in this section ^{*}). The weak coupling approximation is a subtle method.

8.27 The extremely high-frequency tail of relaxation absorption.

A well-known paradox in relaxation absorption is the fact that a pure Debye (or Lorentz) line has infinite even moments. This means that relaxation absorption cannot exactly satisfy such a frequency dependence. The divergence can be understood realizing that the time development corresponding to a pure Debye line is proportional to $e^{-|t|\tau^{-1}}$ thus having a singularity at $t = 0$. The high-frequency region of the Fourier spectrum is essential for the short-time behaviour and may therefore be expected to be anomalous. In physical situations however the sharp bend at $t = 0$ is rounded and the absorption spectrum must be cut off. It has often been put that this occurs at frequencies of the order of $\hbar^{-1}(\chi_o, \chi_o)^{\frac{1}{2}}$. Eq. 8.22 clearly shows the shape of this cut-off.

8.3 Experimental results on Cu alkali halides.

Absorption measurements at a frequency $\nu \equiv \omega/2\pi = 1.78$ GHz have been performed as a function of the parallel static field $\vec{H} \equiv H\vec{e}_i$, for $\text{Cu}(\text{NH}_4)_2\text{Cl}_4 \cdot 2 \text{ aq.}$ and its two variants $\text{CuK}_2\text{Cl}_4 \cdot 2 \text{ aq.}$ and $\text{Cu}(\text{NH}_4)_2\text{Br}_4 \cdot 2 \text{ aq.}$, with \vec{e}_i both along a- and c-axis.

^{*}) However, a further analysis by an estimate of the cross terms, as suggested in the note to section 8.22, could indeed be easier for $\omega^2 S_{ii}$ than for s' .

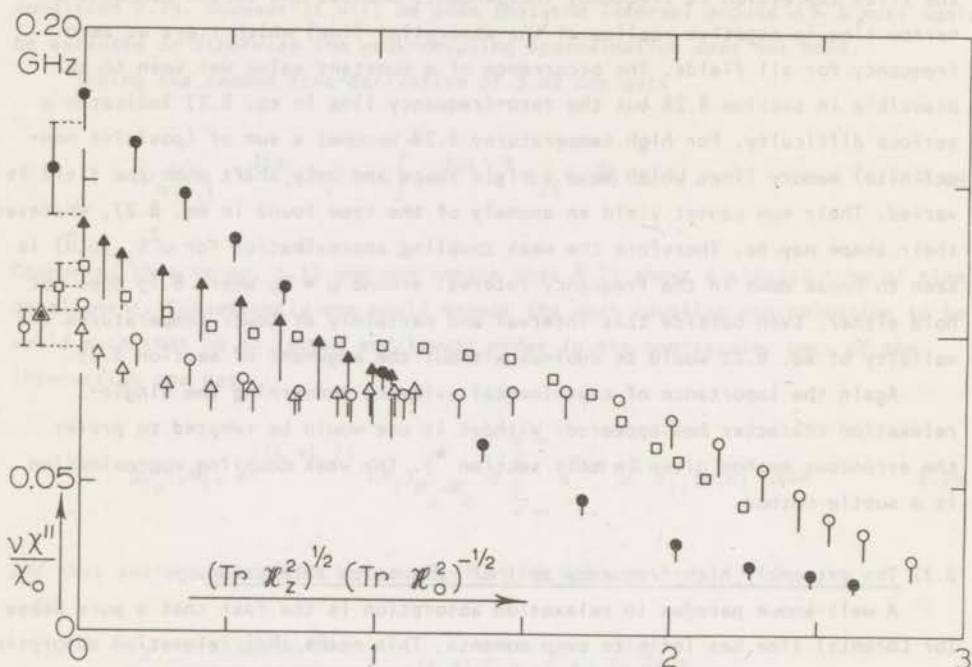


Fig. 8.01 Field dependence of $v_{X''}/\chi_0$ in some Cu alkali halides at 1.78 GHz. Open points: $\vec{e}_i // a$, full points: $\vec{e}_i // c$. Circles: $\text{Cu}(\text{NH}_4)_2\text{Cl}_{4.2}$ aq.; squares: $\text{CuK}_2\text{Cl}_{4.2}$ aq.; triangles: $\text{Cu}(\text{NH}_4)_2\text{Br}_{4.2}$ aq.; the tails represent the change when the temperature T_b is reduced from 20 K to 14 K. The extrapolations from the low-frequency zero field measurements of τ^{44} are indicated on the left.

(for the K-compound only the a-axis). A slight difference was found between the results for the two temperatures 14 K and 20 K, which are high compared to the ferromagnetic transition temperatures (cf. table 8.1). Measurements at other temperatures were too inaccurate to justify further analysis.

Moreover the routine of the measurement included a determination of the EPR line. A discussion of the observed linewidths will be given in section 8.32.

8.31 Intensity and second moment of a sum of memory lines.

For the underlying compounds Van der Molen⁴⁴) gives zero-field low-frequency relaxation-rates τ^{-1} which all lie below $2\pi \cdot 0.2$ GHz. Consequently 8.19 is expected to apply at the measuring frequency. In presence of a parallel static field τ^{-1} usually decreases, apart from the field dependence of $(A, A) \sim \chi_{ii}(0, \vec{H}) = \chi_{ad, ii}(\vec{H})$. The latter factor, however, does not invalidate 8.19 for the measuring frequency used.

Hence eq. 8.22 applies. Moreover the temperature is high and $\chi_{o, ii}(\vec{H})$ is almost field independent (cf. section 6.43) such that

$$2N\hbar^2 \frac{1}{3} S(S+1) \frac{\nu \chi_{ii}''(2\pi\nu, 2\pi\nu_L \gamma_1^{-1} \vec{e}_i)}{\chi_{o, ii}(0)} \approx \sum_{p=+1, +2} p^2 s_{\mathcal{K}_p}^o(\omega - p\omega_L) \quad 8.29$$

where use has been made of the decomposition given by eqs. 6.33, 6.34, 6.35 and 6.36, as \vec{e}_i lies in a c-a-plane (cf. section 8.13). As the memory lines are broad (width of the order of $\approx \hbar^{-1} (\mathcal{K}_o, \mathcal{K}_o)^{\frac{1}{2}}$) compared to the measuring frequency one may approximate (cf. 8.11, 8.14)

$$2N\hbar^2 \frac{1}{3} S(S+1) \frac{\nu \chi_{ii}''}{\chi_{o, ii}} \approx 2 s_{\mathcal{K}_1}^o(\omega_L) + 8 s_{\mathcal{K}_2}^o(2\omega_L) \quad 8.30$$

Thus the absorption measurement yields a rather clear picture of the memory lines.

In analogy to 6.29 and 6.46 one may derive from 8.29 (cf. 8.11, 8.14) that

$$2N\hbar^2 \frac{1}{3} S(S+1) \int_0^\infty \nu_L^{2n} \frac{\nu \chi_{ii}''}{\chi_{o, ii}} d\nu_L \approx \sum_{p=1, 2} (2\pi p)^{-(2n+1)} p^2 \int_{-\infty}^{\infty} \omega^{2n} s_{\mathcal{K}_p}^o(\omega) d\omega =$$

$$= (2\pi)^{-(2n+1)} (\text{Tr } I)^{-1} \{ \text{Tr}((L_{o1}^n \mathcal{K}_1)^\dagger L_{o1}^n \mathcal{K}_1) + 2^{1-2n} \text{Tr}((L_{o2}^n \mathcal{K}_2)^\dagger L_{o2}^n \mathcal{K}_2) \}. \quad 8.31$$

The traces in 8.31 can be calculated with the aid of 6.34 and 6.30, 6.31 with definitions 5.17, 5.18, 5.28, 5.30, where \mathcal{K}_{ex} includes the antisymmetric exchange introduced in section 8.15.

Table 8.2

Cu alkali chloride	$J_{mn} h^{-1}$ (GHz)	$\vec{H} = \vec{H}_e \vec{I}$ along	T_b (K)	$A \equiv \int_0^\infty \frac{\nu X''}{X_0} d\nu_L$		$C_A \equiv \frac{ \vec{D}_{mn} ^2}{h^2}$		$B \equiv \int_0^\infty \nu^2 \frac{\nu X''}{X_0} d\nu_L$		$C_B \equiv \frac{ \vec{D}_{mn} ^2}{h^2}$	
				exp. (GHz ²)	theor. (GHz ²)	(GHz ²)	$\frac{ \vec{D}_{mn} }{J_{mn}}$	exp. (GHz ⁴)	theor. (GHz ⁴)	(GHz ²)	$\frac{ \vec{D}_{mn} }{J_{mn}}$
NH ₄	5.0	a	20	3.61	0.50+12.60C _A	0.247	0.100	0.22	0.0280+0.749C _B	0.255	0.099
			14	3.22		0.215	0.093	0.20		0.24	0.098
		c	20	3.44 (6.81)	0.51+25.20C _A	0.116	0.068	0.110 (0.399)	0.0239+1.50 C _B	0.057	0.048
			14	3.18		0.106	0.065	0.10		0.053	0.046
K	6.3	a	20	4.52	0.54+12.60C _A	0.315	0.089	0.34	0.0475+1.165C _B	0.25	0.079

Using the approximation of isotropic g-tensor in \mathcal{K}_z and \mathcal{K}_d and neglecting the contribution of antisymmetric exchange to \mathcal{K}_o with respect to that of the isotropic exchange De Jong⁵⁶⁾ has performed these calculations, the results of which are given in table 8.2.

The experimental results for the field dependence of $v_{X_{ii}}''/X_{O_{ii}}$ are given in fig. 8.01. In order to simplify the comparison between compounds with different strength of the isotropic exchange (which through L_o in the second moment mainly determines the widths of the memory lines) the absorption has been plotted vs. a normalized field value, the ratio $(\text{Tr } \mathcal{K}_z^2)^{\frac{1}{2}} (\text{Tr } \mathcal{K}_o^2)^{-\frac{1}{2}} \approx 12^{-\frac{1}{2}} h\nu_L J_{mn}^{-1}$, rather than vs. v_L . A check measurement in $\text{Cu}(\text{NH}_4)_2\text{Cl}_4 \cdot 2 \text{ aq.}$ (a-direction) at 4.84 GHz confirmed the approximate frequency independence predicted by 8.30. For reasons of clarity it has been omitted from fig. 8.01.

It follows from eq. 8.30 that fig. 8.01 showing their weighted sum gives an impression of the right halves of the two memory lines $S_{\mathcal{K}_1\mathcal{K}_1}^o$ and $S_{\mathcal{K}_2\mathcal{K}_2}^o$ (*). One may improve the picture imagining the negative field region to be present as well such that symmetric figures appear. It will be seen that $S_{\mathcal{K}_2\mathcal{K}_2}^o$ may probably be neglected, which implies that fig. 8.01 immediately shows the approximate shape of $S_{\mathcal{K}_1\mathcal{K}_1}^o$.

It is clear from fig. 8.01 that the symmetrized $v_{X_{ii}}''/X_o$ figures for $\vec{e}_i // a$ and $\vec{e}_i // c$ have a different shape respectively being broad and sharp. Neither type can be analyzed to equal the sum of two Gaussians around $v_L = 0$, such that the celebrated assumption of Gaussian memory lines (which has been carefully avoided in the present work) is found to be wrong in this case. The shape of the memory lines constitutes a problem which should be further investigated both experimentally and theoretically.

The present results are in good agreement with the Debye-extrapolations based on the τ values of ref. 44, such that the single relaxation behaviour is seen to persist up to frequencies of ten or twenty times the relaxation rate.

The temperature dependence observed cannot be explained from spin-spin effects. It is suggested that interionic distances and orientations change with temperature and that this influences the exchange interaction (**). Strong dependence on temperature has been observed in the resonance linewidths (cf. table 8.3).

The experimental values for $A \equiv \int_0^{\infty} \frac{v_{X_{ii}}''}{X_{O_{ii}}} dv_L$ and $B \equiv \int_0^{\infty} v_L^2 \frac{v_{X_{ii}}''}{X_{O_{ii}}} dv_L$ are listed

in table 8.2. As can be seen from fig. 8.01 the measurements for the Br-compound

*) The latter horizontally compressed by a factor 2.

**) Probably mainly its antisymmetric part.

should be extended to higher fields before values for intensity and second moment can be given. As far as could be observed it shows characteristics similar to the Cl- compounds.

The theoretical values for A and B are given in table 8.2 as functions of the strength $|\vec{D}_{mn}|$ of antisymmetric exchange between nearest neighbours. Thus the experiment yields two formally independent *) ways to determine this constant. The values derived from A and B are presented separately in the form $|\vec{D}_{mn}|^2 h^{-2}$. As according to Moriya the ratio $|\vec{D}_{mn}| J_{mn}^{-1}$ should be of the order $\frac{g-2}{g}$ (cf. section 8.14), the former ratio is given as well.

In the a-direction of $\text{Cu}(\text{NH}_4)_2\text{Cl}_4 \cdot 2 \text{ aq.}$ both values for $|\vec{D}_{mn}|$ agree. An acceptable difference is found for the a-direction of the K-compound. Both $|\vec{D}_{mn}| J_{mn}^{-1}$ ratios are slightly lower.

The c-direction of $\text{Cu}(\text{NH}_4)_2\text{Cl}_4 \cdot 2 \text{ aq.}$, however, shows a remarkable discrepancy, not only between the $|\vec{D}_{mn}|$ values that result from A and B but also when these values are compared to those found for the a-direction. One may try to ascribe this to an experimental error and calculate A and B for the c-direction based on the $|\vec{D}_{mn}|$ values measured in the a-direction. The results (in brackets) are about twice and four times larger respectively. The difference could at most be explained by a narrow line at $\nu_L \approx 30 \text{ GHz}$, which would lie well within the measuring range but has not been observed. Another explanation, a possible error in the zero absorption level can also be ruled out as reasonable agreement with ref. 44 has been found in zero field. A closer investigation is needed.

The $|\vec{D}_{mn}| J_{mn}^{-1}$ ratios found in the a-direction of both compounds give almost too good an agreement with $\frac{g_a-2}{g_a} = 0.10$ as derived from the average g in the a-a-plane. Even the results of the c-direction of the NH_4 compound, taken on their own, satisfy Moriya's estimate for the order of magnitude of the ratio.

The improvement achieved by the introduction of antisymmetric exchange may be seen when one takes $|\vec{D}_{mn}| = 0$ in the theoretical expressions in table 8.2. The remaining values for A and B are totally due to \mathcal{H}_d with about equal contributions from $s_{\mathcal{H}_1}^o$ and $s_{\mathcal{H}_2}^o$ (44). As the antisymmetric exchange (for almost isotropic g-tensor) hardly contributes to the $s_{\mathcal{H}_2}^o$ memory line, this becomes negligible upon introduction of a large amount of this exchange. Hence one may interpret fig. 8.01 in the simple way mentioned above.

*) For large $|\vec{D}_{mn}|$, compared to \mathcal{H}_d , an erroneous gauge factor in the absorption measurement may cause the same error in both results.

8.32 Resonance linewidths in low fields.

The resonance linewidths observed (half width at half height) are listed in table 8.3. Apart from present results those of Henderson and Rogers ⁵⁷⁾ determined at room temperature have been added in order to stress the temperature dependence. Moreover the observed values for g are given, through which the frequency measured half widths Γ have been derived. As the measuring frequency is only 1.78 GHz the resonance field corresponds to $(\text{Tr } \mathcal{H}_c^2)^{\frac{1}{2}} (\text{Tr } \mathcal{H}_o^2)^{-\frac{1}{2}} < 0.10$ which may be called a low field (condition 1 of section 7.22).

Although the other conditions of section 7.22 are poorly satisfied one may try a description by eq. 7.20, where k is the direction perpendicular to the alternating field (i) and the static field (j). The zero-field relaxation rates might be taken from ref. 44 but are also - and perhaps in somewhat more detail - directly available in the present work (cf. section 8.24), as $(A, A) = (M_i, M_i)$ for $H = 0$. The latter results have been used for a tentative calculation of the resonance linewidth according to 7.20 (cf. table 8.3 values in brackets). The agreement is surprisingly good. One might state that antisymmetric exchange once again ^{55), 45)} gives a reasonable description both of relaxation rates and of resonance linewidths.

Table 8.3

Cu alkali halide	$\vec{H} = H \vec{e}_j$ along	T_b (K)	$\frac{1}{2}$ width at $\frac{1}{2}$ height (Oe)	g	Γ (GHz)	$\frac{\Gamma_a + \Gamma_c}{2}$
NH ₄ -Cl	c	14	34	2.04	0.097	(0.100)
		20	36	2.06	0.104	(0.109)
		77	42	2.10	0.124	(0.11)
		295	84	2.10	⁵⁷⁾	
K-Cl	c	20	40	2.11	0.118	(0.120)
		77	49	2.1	0.15	(0.20)
		295	95	2.09		
NH ₄ -Br	c	14	29	2.07	0.084	(0.092)
		20	30	2.11	0.089	(0.10)
						$\frac{\Gamma_a + \Gamma_c}{2}$
NH ₄ -Cl	a	14	42	2.24	0.132	(0.133)
		20	42	2.21	0.130	(0.143)
		77	52	2.24	0.163	(0.18)
NH ₄ -Br	(1, 1, 0)	14	31	2.24	0.098	(0.104)
		20	33	2.20	0.098	(0.12)

.... (*horresco referens*)

*P. Vergilius, Aeneis,
Second Book, verse 204.*

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SAMENVATTING

De tijdontwikkeling van een systeem, ook al bestaat het uit veel deeltjes, wordt in de quantummechanica beschreven door de Schrödinger vergelijking. Dit lijkt een eenvoudige uitspraak maar aangezien deze vergelijking bepaald wordt door de hamiltoniaan van het systeem, waarin alle gegevens over zijn wisselwerkingen, zowel inwendig als met de buitenwereld zijn bevat, kan of hoeft er nauwelijks meer van worden gezegd. Zulke korte maar veel omvattende uitspraken komen in het theoretisch gedeelte (hoofdstuk 1 tot en met 5) veelvuldig voor.

Aanvankelijk is weinig over de aard van de hamiltoniaan verondersteld. De belangrijkste aanname is dat deze van een uitwendige vector-parameter \vec{H} afhankelijk is. Voor de magnetische systemen die hier in het bijzonder zijn beschouwd is \vec{H} het magnetisch veld.

De voornaamste reden om magnetische systemen te onderzoeken is gelegen in het feit dat men in magnetische systemen alle wisselwerkingen denkt te kennen. Daarom vormen zij een vrijwel ideale toetssteen voor de theorie der quantumstatistica, zoals het Kubo-formalisme en de uitbreidingen daarvan.

Een confrontatie van theorie en experiment in zulke systemen is mogelijk aan de hand van het frequentiespectrum van de lineaire respons op veranderingen van \vec{H} . Experimenteel valt dit spectrum te bepalen door meting van energie-absorptie in magnetische wisselvelden van verscheidene frequenties. Theoretisch komt het overeen met het spectrum van een bepaalde correlatiefunctie.

Hoewel dit spectrum in het algemeen te ingewikkeld is om een volledige numerieke berekening ervan mogelijk te maken, kunnen toch enige karakteristieke grootheden zoals momenten of relaxatietijden worden berekend en worden vergeleken met de experimentele uitkomsten. Als zelfs zo'n berekening te moeilijk is kan men zoeken naar het onderling verband tussen de experimentele resultaten zoals dat door de theorie wordt voorspeld.

De hier beschreven onderzoeken vormen een uitbreiding van Locher's werk over spin-spin effecten in de paramagnetische susceptibiliteit van poeders bij frequenties van ongeveer 1 GHz ²⁶). Aangezien zijn meetopstelling voor het einde der hier beschreven metingen geen wezenlijke veranderingen heeft ondergaan, wordt de lezer voor een beschrijving van de experimentele methode verwezen naar ref. 26.

De belangrijkste uitbreiding wordt gevormd door het onderzoek op het gebied van overgangsverschijnselen (MnF_2 , hoofdstuk 7). Hierdoor werd een theoretische beschrijving van relaxatie nodig waarin de hoge temperatuur benadering niet wordt verondersteld.

Een overzicht van de mogelijkheden daartoe vindt men in de hoofdstukken 1 tot en met 4.

Een tweede uitbreiding is gelegen in het gebruik van éénkristallen in plaats van poeders. Dit betekent dat de anisotropie van de g-tensor meer op de voorgrond treedt. De veranderingen die aangebracht moeten worden in de gebruikelijke ontbinding van de hamiltoniaan zijn behandeld in hoofdstuk 5.

Hoofdstuk 6 beschrijft de onmiddellijke voortzetting van Locher's werk. Hierin worden de koper Tutton zouten besproken, die verhoudingsgewijs kleine exchange-interactie hebben. Wat de theorie betreft wordt het bewijs geleverd van de regel, dat de breedte van de verboden parallel veld resonantielijnen praktisch uitsluitend door het z.g. seculaire deel van de wisselwerking wordt bepaald. De experimentele resultaten zijn hiermee niet geheel in strijd.

De overgangsverschijnselen in MnF_2 zijn besproken in hoofdstuk 7. Uitgaande van een aanpak van Tjon wordt een verband afgeleid tussen resonantie-absorptie in lage velden en relaxatie in nulveld voor stoffen waarin sterke exchange-interactie optreedt. Dit verband kan worden toegespitst en levert dan een vertaalrecept op tussen paramagnetische resonantie lijnbreedtes enerzijds en relaxatietijden in nulveld anderzijds, welk recept blijft gelden tot vlak boven het overgangspunt in antiferromagneten.

Hoofdstuk 8 is gewijd aan de meest onderzochte vorm van spin-spin relaxatie, de veldafhankelijkheid bij hoge temperatuur van de relaxatietijd in stoffen met verhoudingsgewijs sterke exchange-interactie. Experimenteel blijkt de gebruikelijke veronderstelling van Gaussische lijnen voor de integraalkern van de relaxatie in de koper alkali halogeniden niet op te gaan. De theorie in dit hoofdstuk is daarom gegeven in een vorm die deze aanname vermijdt. De confrontatie tussen theorie en experiment is uitgevoerd aan de hand van oppervlakte en momenten van de waargenomen veldafhankelijkheden en niet in de vorm van relaxatietijden.

Bovendien blijkt, dat men, door de aanwezigheid van antisymmetrische exchange in deze stoffen aan te nemen, de experimentele resultaten redelijk kan beschrijven.

De bruikbaarheid van het vertaalrecept uit hoofdstuk 7 wordt ook door deze metingen bevestigd. De overigens slecht begrepen temperatuurafhankelijkheden van lijnbreedtes en relaxatietijden kunnen zo onder een noemer worden gebracht.

Those were the days my friend,

Op verzoek van de faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn studie.

Na een gymnasium- β opleiding aan het Coornhert Lyceum der Gemeente Haarlem, waar Dr. J.K. van den Briel mijn door mijn vader gewekte belangstelling voor de natuurkunde verder aanwakkerde, begon ik in 1958 mijn studie aan de Rijksuniversiteit te Leiden. Het kandidaatsexamen met de hoofdvakken natuurkunde en wiskunde en bijvak scheikunde werd in 1961 afgelegd. Sinds november van dat jaar ben ik verbonden aan de werkgroep spin-spin relaxatie van het Kamerlingh Onnes Laboratorium, waarvoor Prof.dr. C.J. Gorter de verantwoordelijkheid heeft. Aanvankelijk assisteerde ik tezamen met Dr. R.G. van Welzenis bij het onderzoek van Dr. P.R. Locher, vervolgens bij dat van de eerste onder toezicht van Dr. J.C. Verstelle.

Enige tijd vóór het behalen van het doctoraal examen, afgelegd in 1965, nam ik de zorg voor het onderzoek van spin-spin relaxatie bij frequenties rond 1 GHz op mij eveneens onder directe leiding van Dr. J.C. Verstelle.

Sinds 1963 ben ik verbonden aan het electronica practicum voor tweede- en derdejaars studenten (sedert 1969 als hoofdassistent).

Degenen die mij in staat gesteld hebben dit proefschrift te schrijven zijn te verdelen in vier, hier en daar overlappende groepen.

Allereerst zij die als directe samenwerkers de sfeer bepalen of bepalen waarin leven en werken tot een harmonisch geheel verenigd zijn. Hiervan wil ik er één als voorbeeld noemen: Henk van Noort, die vanaf 1964 in alles, voor- en tegenspoed, heeft meegeleefd.

Vervolgens zij die door hun ervaring en belangstelling mijn denken en ons onderzoek hebben gevormd en gericht. Dr. J.C. Verstelle, hoewel zeker eveneens behorend tot de eerste groep, neemt hier een onvervangbare plaats in. Hij was het, die, door in 1967 het onderzoek van overgangsverschijnselen te suggereren, aan de werkzaamheden in de groep spin-spin relaxatie een noodzakelijke en succesvolle wending gaf. Bovendien wil ik de vele gesprekken memoreren, die ik als kandidaat met Dr. P. Locher had (of liever omgekeerd), welke toen juist zijn proefschrift voorbereidde. Het gelukkig toeval dat bij het begin van het onderzoek (in 1965) een opbloei van de theoretische belangstelling ervoor juist in het Instituut Lorentz plaatsvond is van groot belang geweest. Met Prof.dr. P. Mazur en Dr. R.H. Terwiel heeft een vruchtbare wisselwerking plaats gehad en hetzelfde kan worden gezegd over het contact met Prof.dr. J.A. Tjon (Utrecht).

De computerberekeningen van C. de Lezenne Coulander en in het bijzonder die van J.G.A. Hillaert hebben de analyses in hoofdstukken 7 en 6 mogelijk gemaakt. De hechte samenwerking met de drie collega-promovendi H.L. van Noort, J.G.A. Hillaert en W.M. de Jong is van onmiskenbaar nut geweest.

In de derde plaats zij die door hun functie in het Kamerlingh Onnes Laboratorium, doch vaak met groter hulpvaardigheid dan alleen daaruit te verklaren valt, het onderzoek hebben gesteund. Weer vallen hier slechts voorbeelden te noemen: de kamer-technici D. de Jong en J. Turenhout komen mij het eerst in gedachten.

Ten vierde zij die de directe uitvoering van het proefschrift hebben verzorgd. Geen van hen zal het mij kwalijk nemen, dat ik hier het eerst Sary Kranenburg-Ginjaar noem, die ongeveer de helft van het typewerk (waaronder de beide eerste hoofdstukken!) en bovendien nog de afwerking heeft verricht. Een groot deel van de hoofdstukken 5 en 6 werd enthousiast verzorgd door Marja Muns. De hoofdstukken 3, 4 en 7 werden uitgevoerd door mevr. E. de Haas-Walraven. Het tekenwerk werd in hoog tempo uitgevoerd door de heren H.J. Rijskamp, W.J. Brokaar en W.F. Tegelaar, welke laatste tevens voor de speciale fotografische afwerking zorg droeg en de indeling van de omslag ontwierp.

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