NUCLEAR MAGNETIC RESONANCE IN PARAMAGNETIC AND ANTI-FERROMAGNETIC SINGLE CRYSTALS

N. J. POULIS

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PROEFSCHRIFT
TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFICUS Dr J. H. BOEKE, HOOGLERAAR IN DE FACULTEIT DER RECHTSGELEERDHEID, PUBLIEK TE VERDEDIGEN OP WOENSDAG 7 MEI 1952 TE 14 UUR

DOOR

NICOLAAS JOHANNES POULIS
GEBOREN TE ROTTERDAM IN 1923

Promotor: PROF. DR C. J. GORTER

AAN MIJN OUDERS

VOORWOORD

Ofschoon met enige schroom voldoe ik aan de wens van mijn promotor, een korte schets te geven van mijn wetenschappelijke opleiding en van de wijze waarop het in dit proefschrift besproken onderwerp tot stand is gekomen.

Geboren op 5 Augustus 1923 te Rotterdam, bezocht ik de Openbare Lagere School, welke onder leiding stond van de Heer R. A. C. Sneep. Op deze school ontving ik in de hogere klassen van de heer L. C. Varossieau de grondslag voor mijn verdere ontwikkeling.

Van 1935 tot 1940 doorliep ik de Libanon H.B.S. te Rotterdam.

In September 1940 volgde mijn inschrijving aan de Technische Hogeschool te Delft, waar ik in October 1947 het diploma van natuurkundig ingenieur behaalde.

In de laatste jaren studeerde ik hier bij wijlen Prof. Dr. E. C. Wiersma en bij Prof. Dr. J. A. Prins. Gedurende het jaar 1946 was ik medewerker van de Technisch Physische Dienst-T.N.O. te Delft.

In Januari 1947 werd ik als opvolger van Dr. S. Broersma benoemd tot hoofdassistent in de natuurkunde aan de Technische Hogeschool. Tot Januari 1949 werkte ik te Delft aan verschillende onderwerpen, o.a. problemen op het gebied der warmtegeleiding en warmteoverdracht, temperatuurmeting en verstrooiing van röntgenstralen.

In Januari 1949 werd ik als opvolger van Dr. N. Bloembergen benoemd als wetenschappelijk medewerker in de werkgroep Leiden van de „Stichting voor Fundamenteel Onderzoek der Materie". Leider van deze werkgroep is Prof. Dr. C. J. Gorter. Door hen werd ik ingewijd in de problemen der magnetische kernresonantie. Het eerste jaar werd het werk van Dr. Bloembergen nml. het meten van kernspin-relaxatietijden voortgezet.

Met de bestaande meetbrug werd ook getracht de splitsing van de

resonantielijnen te meten in mono-kristallen van $CuSO_4.5H_2O$.

De brugmethode hoe geschikt ook voor het meten van relaxatietijden bleek onbruikbaar voor de metingen der fijnstructuur der resonantielijnen in mono-kristallen. Van de verschillende te volgen methoden bleek de oscillatormethode de meest geschikte.

Volgens hetzelfde principe probeerde mijn promotor in 1942 reeds kernresonantie waar te nemen. Wegens de, zoals later gebleken is, ongeschikt gekozen stof, was het resultaat negatief.

Met deze nieuwe apparatuur werden metingen verricht aan mono-kristallen van $CuSO_4.5H_2O$, $CuCl_2.2H_2O$, $CuK_2Cl_4.2H_2O$, CuH_2SiO_4 speciaal bij zeer lage temperaturen, waarvan de resultaten in dit proefschrift beschreven zijn.

Deze metingen zijn verricht met medewerking van G. E. G. Hardeman, Dr. E. D. Kunst en B. Bölger. Bij deze metingen werd veel steun ondervonden van de technische staf van het Kamerlingh Onnes Laboratorium, in het bijzonder van de heer D. de Jong.

Dit onderzoek is een onderdeel van het research programma van de „Stichting voor Fundamenteel Onderzoek der Materie" en is mogelijk gemaakt door de financiële steun van de „Stichting voor Zuiver Wetenschappelijk Onderzoek".

SAMENVATTING

In de inleiding van deze dissertatie wordt een kort overzicht gegeven van de theorie van de splitsing van de proton resonantie lijn van een mono-kristal van $CuSO_4.5H_2O$. De metingen met behulp van een hoogfrequentbrug bleken niet de gewenste nauwkeurigheid te geven. Het bouwen van een oscillator met bijbehorende versterkers wordt gemotiveerd in § 2. Daarna worden de methode van meten en de resultaten van de metingen aan de paramagnetische kristallen $CuSO_4.5H_2O$ en $CuK_2Cl_4.2HO_2$ besproken. Het aantal resonantielijnen voor $CuSO_4.5H_2O$ (maximaal 20) en ook de trikline structuur maken, dat de resultaten moeilijk te interpreteren zijn. Na lang experimenteren gelukte het mono-kristallen van $CuCl_2.2H_2O$ te laten groeien. Het voordeel van Cu $Cl_2.2H_2O$ is de eenvoudige structuur en het kleine aantal lijnen, dat verwacht kan worden (maximaal 8).

Bij temperaturen van vloeibare waterstof is het gedrag van $CuCl_2.2H_2O$ hetzelfde als van de paramagnetische kristallen. Beneden 4°K blijkt het kristal anti-ferromagnetisch te worden, waardoor aan dit kristal meer dan gewone aandacht besteed is.

In hoofdstuk I en II worden deze metingen aan $CuCl_2.2H_2O$ beschreven bij verschillende waarden van het magnetisch veld. Het blijkt, dat het gedrag van de Cu-spins bij zwakke velden verschilt van dat bij sterke velden. Bij zwakke velden zijn de Cu-spins vast georiënteerd langs de *a*-as van het kristal. Bij sterke velden staan ze altijd loodrecht op de richting van het magneetveld. Het blijkt dat de overgang tussen beide toestanden plaats vindt bij ongeveer 7000 Ø. Uit de positie van de maxima in de resonantie-diagrammen werd de plaats van de protonen in de elementair cel bepaald. Uit de berekening blijkt, dat alle Cu-spins in een *ab*-vlak van het kristal parallel staan, terwijl in de naburige vlakken de spins antiparallel ten opzichte daarvan gericht zijn.

De vorm van de resonantie-diagrammen in het overgangsgebied tussen zwakke en sterke velden wordt verklaard in hoofdstuk II met

de in hoofdstuk I ontwikkelde theorie en die van G o r t e r en H a a n t j e s betreffende de richting van de Cu-spins.

In hoofdstuk III worden de metingen besproken bij de overgang van de paramagnetische in de anti-ferromagnetische toestand. De overgang blijkt bij een scherp gedefinieerde temperatuur plaats te vinden. Deze zogenaamde N é e l-temperatuur blijkt nog afhankelijk te zijn van de sterkte van het magneetveld en van de richting hiervan t.o.v. de kristalassen.

DECOMPOSITION OF THE PROTON MAGNETIC RESONANCE LINE IN PARAMAGNETIC CRYSTALS

Synopsis

The fine structure of the proton magnetic resonance line in single-crystals of $CuSO_4.5H_2O$ and $CuK_2Cl_4.2H_2O$ has been observed. The position and number of the lines are strongly dependent on temperature and on the direction of the externally applied magnetic field. In $CuSO_4.5H_2O$ always fewer lines than the theoretical number of 20 were observed. For $CuK_2Cl_4.2H_2O$ the theoretical number of 8 lines is reached.

The temperature dependence is measured for both crystals at different orientations at four temperatures in liquid helium and at two temperatures in liquid hydrogen. At the higher temperatures the deviation from the central position is in first approximation inversely proportional to $T-\Theta$, as should be expected from the law of Curie–Weiss. At the lowest temperatures deviations from this law were found.

At 1.5°K the position and width of the lines are measured as functions of the angle between the magnetic field and the crystal axis. This dependence is in good agreement with the theoretical expectation.

1. *Introduction.* The first nuclear magnetic resonance measurements on single-crystals were made by P a k e [1]). A fine structure of the proton line in crystals of gypsum was found, which could be explained by the magnetic proton-proton interaction in a water molecule of hydration.

We measured the proton resonance in single-crystals containing paramagnetic ions which influenced profoundly the width and shape of the resonance line. Measurements on single-crystals of chromium alum give a very broad proton resonance line (more than 100 oersteds wide).

On the other hand we found by studying the proton resonance in single-crystals of copper sulphate at room temperature a line of about 10 oersteds wide, which is split at lower temperatures

into a number of lines, each of which is no more than about 10 oersteds wide. In the case of $CuSO_4.5H_2O$ the broadening action of the cupric ions is apparently considerably reduced by exchange interaction between them.

The time average of magnetization of the copper ions is responsible for a local magnetic field which varies strongly with the space coordinates in the unit cell. The different protons in the unit cell are placed in different local fields which leads to a different resonance frequency in each proton.

In order to calculate the position of the lines Bloembergen [2]) uses the following Hamiltonian for the proton system:

$$\mathfrak{H}_P = -\sum_i \gamma_i I_i H_0 + \sum_{ic} U_{ic} + \sum_{ij} V_{ij}, \qquad (1)$$

where U_{ic} is the magnetic interaction between the ith proton and the cth copper ion and V_{ij} is the magnetic interaction between the ith and the jth proton. From this Hamiltonian we can calculate

TABLE I

2 protons without interaction	2 protons with pr — Cu^{++} interaction	2 protons with pr — pr interaction	2 protons with pr — pr and pr — Cu^{++} interaction
— $+\gamma\hbar H_0$	— $+\gamma\hbar H_0 - a$	— $\gamma\hbar H_0 + d$	— $+\gamma\hbar H_0 - a + d$
	— $+ b$		— $-d+\sqrt{b^2+d^2}$
— 0	— $- b$	— 0	
	— $-\gamma\hbar H_0 + a$	— $- 2d$	— $-d-\sqrt{b^2+d^2}$
		— $-\gamma\hbar H_0 + d$	— $-\gamma\hbar H_0 + a + d$
— $-\gamma\hbar H_0$			
one line	two lines	two lines	four lines
$h\nu =$	$h\nu =$	$h\nu =$	$h\nu =$
$\gamma\hbar H_0$	$\gamma\hbar H_0 - a + b$	$\gamma\hbar H_0 + 3d$	$\gamma\hbar H_0 - a + 2d + \sqrt{b^2+d^2}$
	$\gamma\hbar H_0 - a - b$	$\gamma\hbar H_0 - 3d$	$\gamma\hbar H_0 - a - 2d - \sqrt{b^2+d^2}$
			$\gamma\hbar H_0 - a + 2d - \sqrt{b^2+d^2}$
			$\gamma\hbar H_0 - a - 2d + \sqrt{b^2+d^2}$

the different energy levels in the following cases for one water molecule of hydration in a constant field H_0:

1. two protons without magnetic interaction,
2. two protons with interaction between proton and Cu^{++},
3. two protons with proton-proton interaction, and
4. two protons with proton-proton and proton-Cu^{++} interaction.

B l o e m b e r g e n computed the values of a, b and d (table I):

$$\begin{aligned} a &= \tfrac{1}{2}\gamma\hbar(H_z' + H_z''), \\ b &= \tfrac{1}{2}\gamma\hbar(H_z' - H_z''), \text{ and} \\ d &= -\tfrac{1}{4}\gamma^2\hbar^2(1 - 3\cos^2\Theta_{12})r_{12}^{-3}, \end{aligned} \tag{2}$$

where

$$H_z' = \sum_c \bar{\mu}_c(1 - 3\cos^2\Theta_{1,c})r_{1,c}^{-3} \tag{3}$$

with in first approximation

$$\bar{\mu}_c = \beta^2 g^2 H_0 S(S+1)\,(3kT)^{-1}. \tag{4}$$

H_z' and H_z'' are the z-components of the field produced by the Cu-ions at the position of the two protons respectively.

Following a method of V a n V l e c k one could find for the line-width in first approximation

$$(\Delta\omega)^2 = \gamma^2 g^2 \beta^2 \frac{S(S+1)}{3} \sum_c (1 - 3\cos^2\Theta_{ic})^2 r_{ic}^{-6} + \\ + \frac{9}{4}\gamma^4\hbar^2 \frac{I(I+1)}{3} \sum_j (1 - 3\cos^2\Theta_{ij})^2 r_{ij}^{-6}. \tag{5}$$

The contribution of the cupric ions given by the first term is greatly reduced by exchange interaction. B l o e m b e r g e n computed this $(\Delta\omega)^2_{\text{eff.Cu}}$ to be about 1 oersted [2]).

2. *Experimental arrangement.* The experimental method and apparatus we used for the first measurements on $CuSO_4.5H_2O$ have already been described elsewhere [3]). The use of the high-frequency bridge requires a constant frequency, so it is necessary to vary the magnetic field, which gives many difficulties:

a. The magnetic field from the electromagnet must be varied in one direction, for instance from weaker to stronger fields, in order to avoid hysteresis effects. The rate of increase of the field has to be small in order to find each peak in the real position on the screen of the oscillograph. The hysteresis of the magnet also prevents to project a central line of the protons in water for the different graphs.

b. It is necessary to calibrate the magnetic field. The current of the electromagnet flows through a manganin resistance. The e.m.f.

over this resistance is measured with a Tinsley potentiometer. The e.m.f. of the potentiometer was calibrated against the field measured with a flip coil. In view of the hysteresis effect of the magnet it is impossible to calibrate the e.m.f. absolutely against the magnetic field.

The bridge method is slow and the accuracy of the position of the lines is not very high.

In order to increase the accuracy the autodyne oscillator method is used. The crystal is placed directly in the coil of a transmitter. A normal Colpitt oscillator is used, the capacities c_1 and c_2 are chosen in such a way that the frequency of oscillation is about 30 MHz (See fig. 1).

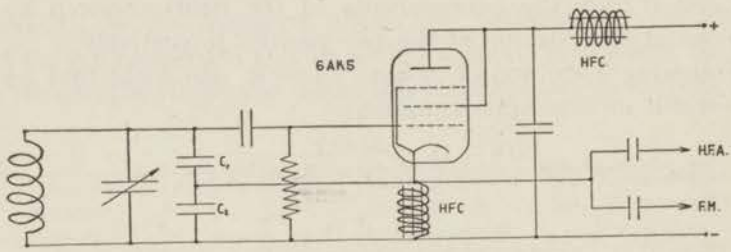

Fig. 1. Schematic diagram of the oscillator. The 6AK5 is used as a triode.

In order to prevent saturation of the nuclear absorption the oscillations should be weak. Since by changing the tuning capacity the transconductance of the tube alters, it is necessary to regulate the plate voltage in such a way that the generator is just on the verge of oscillation. The coil, placed in the cryostat, is connected with a quartz-insulated tuning capacity (Ducati 20–350 pF) by means of a coaxial cable of $\frac{1}{2}$ wave length at 30.5 MHz. With this cable it is possible to cover a frequency range of 3 MHz (29.8 to 33.1 MHz). For measurements on $CuSO_4.5H_2O$ this variation in frequency is in most cases sufficient but the decomposition of the hydrogen band in $CuCl_2.2H_2O$ at the lowest temperatures proves to be larger than 3 MHz. In order to increase the frequency band of the oscillator the cable was shortened or lengthened by about 20 cm.

The signal of the oscillator is amplified in a special high-frequency amplifier with a broad band and low noise factor (cascode; band

width 6 MHz). This cascode consists of three 6AK5-tubes. As detector a 6H6-diode is used.

The magnetic field of about 7000 oersteds is modulated at 25 Hz by means of two auxiliary coils on the pole pieces, with an amplitude of about 15 oersteds.

The high-frequency signal is modulated (25 times per second) with the absorption and dispersion signal. The 25 Hz-modulation is amplified after detection in the 6H6-diode by two 6AC7-tubes.

Behind the low-frequency amplifier an oscillograph is used with an external time base from the same 25 Hz-oscillator as used for the modulation of the field. Weak signals were detected with the help of the "lock in" amplifier as described by B l o e m b e r g e n[4]).

Fig. 2 gives the block scheme of the electrical circuit.

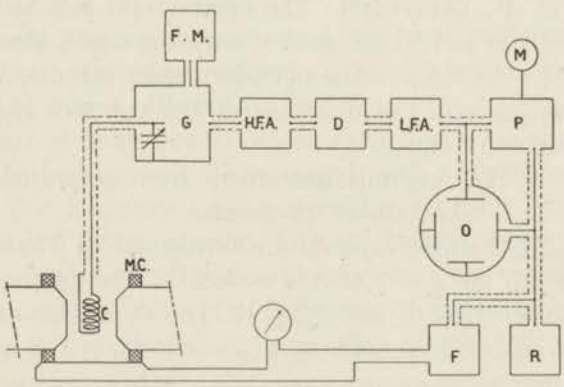

Fig. 2. Block diagram of the electrical circuit.
G = oscillator; C = coil + crystal; F.M. = frequency meter; H.F.A. = high-frequency amplifier (cascode); D = detector; L.F.A. = low-frequency amplifier; O = oscillograph; P = phase-sensitive 25 c.p.s.-mixer; R = 25 Hz-oscillator; F = phase shifter and power amplifier; M.C. = modulation coils.

The cryostat is of the type normally used in the Kamerlingh Onnes Laboratory. The crystals are sealed with molten paraffin wax in thin-walled glass tubes and are placed in the right orientation in the coil between the pole pieces. To prevent vibration of the coil the wirings are glued on the glass tube with polystyrene glue and thin cigarette paper. The coil is shielded by a copper tube which could be evacuated by means of a vacuum pump and afterwards filled with helium gas in order to assure a good heat contact between the crystal and the liquid in the cryostat.

3. *Crystallographic data.* We give a short outline of the crystallographic data known from literature [5]).

$CuSO_4.5H_2O$ belongs to the triclinic system. The three axes $a = 6.12$ Å, $b = 10.7$ Å and $c = 5.97$ Å make the angles $\alpha = 82°16'$, $\beta = 107°26'$ and $\gamma = 102°40'$.

The unit cell contains two non-equivalent cupric ions in (0, 0, 0) and $(0, \frac{1}{2}, \frac{1}{2})$. From the X-ray data of Beevers and Lipson [5]) follows that each Cu^{++}-ion is surrounded by two oxygen atoms and four water molecules in a nearly octahedral arrangement. The remaining two of the ten water molecules in the unit cell are at somewhat larger distances from the copper ions.

Large clear crystals of copper sulphate are used (dimensions 5, 5, 2 cm) on which we could find most of the faces given in the handbook of P. Groth [6]). The crystals are polished with fine emery powder in water, and are cut with the *c*-axes along and perpendicular to the axes of the cylinder, while the direction of the *a*-plane was known. The diameter of the cylinder is 9 mm, the length about 4 to 5 cm.

The $CuSO_45H_2O$ crystals are grown from saturated solutions, a proces which takes about six months.

$CuK_2Cl_4.2H_2O$ single crystals are tetragonal *). The dimensions of the unit cell are $a = 7.45$ A. $c = 7.88$ A. The unit cell contains two Cu-ions at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The O of H_2O are situated at $(0, 0, -w)$, $(0, 0, w)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + w)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - w)$.

As our first measurements on $CuSO_4.5H_2O$ gave a very complicated dependence of the positions of the lines as a function of the orientation of the magnetic field, we tried to make single-crystals of other Cu-salts of simpler structure and containing less crystal water.

$CuCl_2.2H_2O$ as well as $CuK_2Cl_4.2H_2O$ are crystals that fulfill both requirements. After long experimenting we succeeded in growing large crystals of $CuCl_2.2H_2O$ by slowly cooling a solution, saturated at 45°C, in an automatically regulated thermostat (drop 0.5°C per 24 hours).

Later on we succeeded in growing large single crystals of $CuK_2Cl_4.2H_2O$ by evaporation of a saturated solution over a period of many months.

*) We are very much indebted to Prof. Dr. E. Niggli for his identifications of the different axes of the crystal.

4. *Experiments.* Before the experiment, when the cryostat is being filled with liquid helium at the liquefactor, an identical coil with water is placed in the same position in the magnet. The magnetic field is regulated (with 3 parallel resistances) until the proton resonance line is found at a definite frequency (at about 31.5 MHz). The current through the magnet is measured with the Tinsley potentiometer and kept constant during the whole day. The potentiometer current from a battery is controlled every two hours with a Weston standard cell.

After fixing the magnetic field, the cryostat is filled with liquid helium and placed in the magnet.

The measurements in liquid helium are performed at 4.2, 3.1, 2.1 and 1.1°K; on a previous day measurements in liquid hydrogen, at 20.1 and 14.1°K, were made.

Working with the autodyne method, we have sufficient time to measure the temperature dependence in five to ten positions of the magnetic field on one helium day.

The resonance frequency at which each line is obtained in the centre of the oscillograph, is measured with a frequency meter (BC221K). The frequency meter is calibrated each MHz on the check points of a quartz crystal. With a Standard Signal Generator (GR 805-C) calibrated at the same check points, the region between these points is calibrated. At the beginning of a measuring day the frequency meter is controlled at these check points; this is repeated twice a day.

5. *Results and discussions. a.* $CuSO_4.5H_2O$. According to theory the five different water molecules of hydration in $CuSO_4.5H_2O$ should lead to twenty lines in five groups of four. Each group of four should consist of two pairs, the centres of which are separated by a distance $2b$ (see formula 2). The separation of these two lines in a pair is $4d$ (equal intensity). However, the experiments on $CuSO_4.5H_2O$ never give twenty lines, thus it may be concluded that certain lines overlap.

The results of the measurements of the temperature dependence are given in fig. 3. The position of the lines is given in the frequency scale. As one should expect that the dependence is in a first approximation as $1/T$, we made a graph of $\nu_{res.} = f(1/T)$. The graphs were made in nine different positions of the magnet. In most cases the temperature dependence appears to be as $1/(T-\Theta)$ down

to temperatures of 2°K, in accordance with the Curie-Weiss law. Below that temperature the distances from the central line are considerably smaller than indicated by such a dependence. It is our intention to measure the temperature dependence at lower temperatures, reached by demagnetization of the crystal.

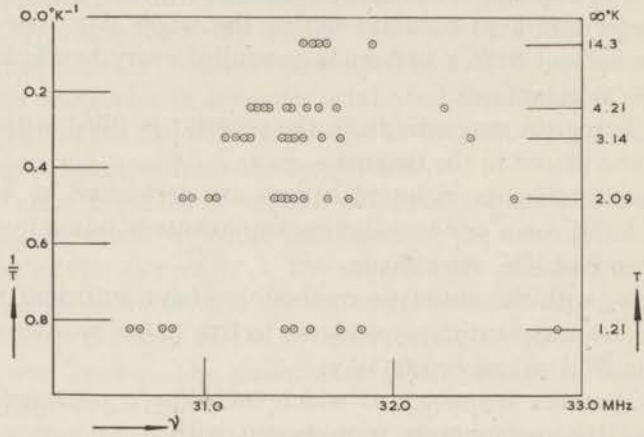

Fig. 3. Position of the proton magnetic resonance lines in a single-crystal of $CuSO_4.5H_2O$ as a function of $1/T$ for one orientation of the magnetic field.

Fig. 4 give the positions of the resonance lines of $CuSO_4.5H_2O$ as functions of the direction of the magnetic field (α) at the same temperature (1.5°K). Measurements are taken after every 10 degrees of rotation of the magnet.

According to formula (3) one expects the position of the lines to go as

$$\sum_c \bar{\mu}_c (3\cos^2 \Theta_{1,c} - 1) r_{1,c}^{-3} = \sum_c \bar{\mu}_c (3\cos^2 \alpha \cos^2 \beta_{1,c} - 1) =$$

$$= \sum_c \bar{\mu}_c \left(\tfrac{3}{2}\cos^2 \beta_{1,c} \cos 2\alpha + \tfrac{3}{2}\cos^2 \beta_{1,c} - 1\right) r_{1,c}^{-3}; \qquad (6)$$

$\beta_{1,c}$ = angle between line Cu to proton 1 and its projection on the plane of rotation of the magnet,

α = angle of rotation of the magnet.

From the graphs we could see directly that for $\alpha = 0°$ and $\alpha = 180°$ the same pattern is found. This was also controlled in a few other positions of the magnet (for $\alpha = 90°$ and $\alpha = 270°$) but for the sake of clearness these lines are omitted here.

The measurements could be carried out with a high accuracy

(better than $1^0/_{00}$) while the greatest difficulty is only to place a broad line with its centre in the right position on the oscillograph.

As in formula (6) $\beta_{1,c}$ is constant for a proton, one should expect the form of the curve to be as cos 2α. Careful examination of figs. 4 and 5 shows that this is not the case for most of the exterior lines. So one could conclude that in most of the cases $\overline{\mu}_c$ must also be a function of the direction of the magnetic field.

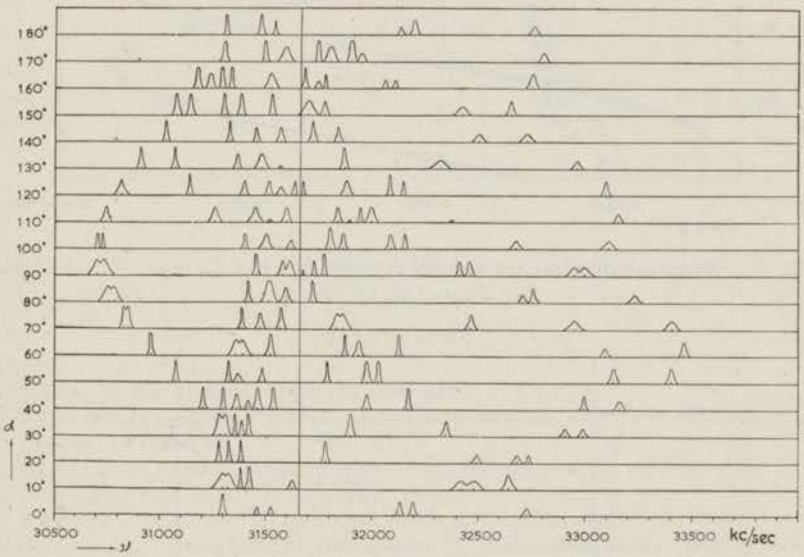

Fig. 4. Position and width of the proton magnetic resonance lines in single-crystals of $CuSO_4.5H_2O$, at different angles α of the constant magnetic field H_0. H_0 horizontally. For $\alpha = 90°$ c-axis // H_0. Plane a, containing b- and c-axis, vertically. Temperature $T = 1.53°$K. Resonance frequency of protons in water 31.662 MHz in H_0.

The measurements on $CuCl_2.2H_2O$ showed that this crystal becomes anti-ferromagnetic in the liquid helium ergion. The results obtained with this salt will be discussed later.

However, single crystals of $CuK_2Cl_4.2H_2O$ proved to be paramagnetic at these temperatures. The crystal was orientated so that the magnetic field could be rotated in the bc-plane. The resonance diagram for a temperature of 3,03°K is shown in fig. 5. The maximum number of eight lines found is in good agreement with the predictions of the theory. The resonance curves are sine functi-

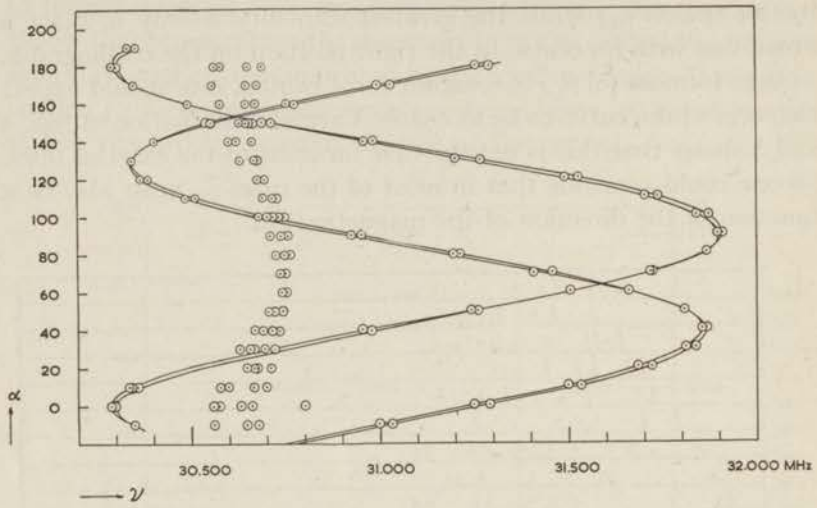

Fig. 5. Resonance diagram for a single crystal of $CuK_2Cl_4.2H_2O$. $T = 3.03°K$. H_0 rotated in bc plane.

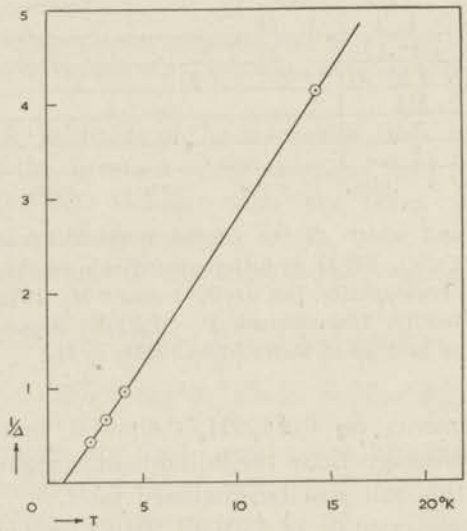

Fig. 6. Temperature dependence of the distance Δ between the extreme resonance lines.

ons with periods 180° just as one should expect from formula (5). This same formula leads to the expectation that the temperature dependence of the resonance lines will be as $1/(T-\Theta)$. To control

this we plotted in fig. 6, $1/\Delta$ as a function of T, where Δ is the distance between the extreme resonance lines for one of the protons in a molecule of water of crystallization. Figure 9 shows a striking agreement with the theory, Θ is found to be 0.9°K.

At temperatures lower than 1.5°K the resonance lines become broader, while the intensity decreases. Down to a temperature of 1,2°K the shape of the resonance diagrams shows that the crystal remains, however, paramagnetic.

REFERENCES

1) Pake, G. E., J. chem. Phys. **16** (1948) 327.
2) Bloembergen, N., Commun. Kamerlingh Onnes Lab., Leiden No. 280*c*; Physica, 's-Grav. **16** (1950) 95.
3) Bloembergen, N., Commun. No. 277*a*; Physica, 's-Grav. **15** (1949) 386.
4) Bloembergen, N., Thesis Leiden (1949).
5) Beevers, C. A., and Lipson, H., Proc. roy. Soc., London A**146** (1934) 570.
6) Groth, P., Physikalische Kristallographie (W. Engelmann, Leipzig) (1905), p. 349.

CHAPTER I

NUCLEAR MAGNETIC RESONANCE IN AN ANTI-FERROMAGNETIC SINGLE CRYSTAL. PART I.

Synopsis

Nuclear magnetic resonance absorption of protons in a single-crystal of $CuCl_2.2H_2O$ has been studied. At temperatures of liquid hydrogen the resonance diagrams are similar to those in single-crystals of the paramagnetic salt $CuSO_4.5H_2O$. In the liquid helium region, however, the resonance diagrams are always symmetrical about the proton line in water. This symmetry and also the temperature dependence of the resonance lines indicate that $CuCl_2.2H_2O$ is anti-ferromagnetic below about $T = 4.3°K$.

A threshold value of the magnetic field as predicted by N é e l has been found. Measurements have been carried out both in a field below and in a field above this threshold value.

From the measurements in weak fields the position of the protons in the crystal can be calculated.

1*a*. *Introduction.* According to theoretical considerations on the decomposition of the nuclear magnetic resonance line of the protons in a single-crystal of $CuSO_4.5H_2O$ a maximum number of twenty lines was to be expected [1] [2]). The resonance diagram, in which the positions of the resonance frequencies are plotted for different orientations of the magnetic field, showed for a single-crystal of $CuSO_4.5H_2O$ a very complicated structure, while the theoretical number of twenty lines was never reached.

The following objections may be raised against the choice of $CuSO_4.5H_2O$ for the investigation of the decomposition of the hydrogen line in paramagnetic crystals:

1°. the number of protons in the elementary cell is large, the expected number of twenty lines is too large to permit good insight into the behaviour of the curves in the resonance diagram, and

2°. the crystal structure is not so easy to handle, being triclinic.

To avoid these difficulties we tried to grow single-crystals of another copper salt. $CuCl_2.2H_2O$ proved to be suitable, since it contains only two molecules of crystal water. The number of lines expected for single-crystals of $CuCl_2.2H_2O$ is thus considerably smaller than for $CuSO_4.5H_2O$. Besides, the rhombic structure of $CuCl_2.2H_2O$ is much simpler. The drawbacks of $CuCl_2.2HO_2$ are the difficulty of growing large single-crystals and its hygroscopic behaviour. The first measurements [2]) on a not very homogeneous single-crystal suggested that $CuCl_2.2H_2O$ is anti-ferromagnetic in the temperature region of liquid helium which makes the experiments on this salt of particular interest. After repeated attempts we succeeded in growing larger and more homogeneous single-crystals of this salt. The results of the measurements on these crystals will be discussed.

1*b*. *Method*. For the measurements on $CuCl_2.2H_2O$ the same autodyne oscillator method is used as in the experiments with $CuSO_4.5H_2O$, already described [2]). The crystal is situated in the coil of a Collpit oscillator which is held on the verge of oscillation by regulating the plate voltage of the oscillator triode (6AK5). The coil is placed in the homogeneous region of the magnetic field of a Weiss magnet. The field is fixed at a constant value by controlling the current through the magnet with a Tinsley potentiometer.

Working at low temperatures requires a long connecting cable between the coil in the cryostat and the tuning capacity. By shortening or lengthening this cable the frequency region covered by the oscillator can be enlarged. The constant magnetic field is modulated by an oscillating field with a frequency of 25 Hz and an amplitude of 10 oersteds, while the 25 Hz-signal is made visible on an oscillograph.

The experiments on single-crystals of $CuCl_2.2H_2O$ are carried out at frequencies of about 7.8, 17.8, 25.4, 31.6 and 38.0 MHz. Each of these frequencies requires an amplifier with a band width of at least 5 MHz. Originally a special cascode (low-noise amplifier) for 8 MHz was constructed to increase the signal to noise ratio. Later on, in the experiments with larger crystals, the signal to noise ratio proved to be large enough to permit the use of a normal broad band amplifier in which of course the noise factor was held as low as possible by using 6AK5-pentodes. The schematic diagram of these different amplifiers is shown in fig. 1. The last stage is inserted to reduce the

damping of the cable which connects the high-frequency amplifier with the diode detector and low-frequency amplifier. As the signal is much smaller at low than at high frequencies, the 8 MHz amplifier is constructed with five 6AK5-tubes, while in the other amplifiers only four stages are used.

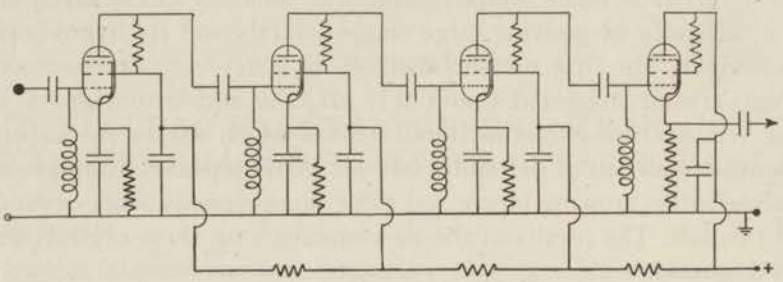

Fig. 1. The general scheme of the broad-band high-frequency amplifier. The tubes are 6 A.K. 5. For each frequency range different coils, resistances and condensers are used.

The cryostat of the type normally used in our laboratory consists of two Dewar vessels, the outer one for liquid air, the inner one for liquid helium or hydrogen. The magnetic field is calibrated at the beginning of each measuring day with the proton resonance in water.

1*c*. *Crystal structure*. The crystals of $CuCl_2.2H_2O$ belong to the rhombic bi-pyramidal class. The dimensions of the elementary cell are:

$$a = 7.38 \text{ Å}, \; b = 8.04 \text{ Å}, \; c = 3.72 \text{ Å}.$$

The positions of the different ions in the elementary cell are:

2 Cu at $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$;

4O at $(0, q, 0)$, $(0, -q, 0)$ and $(\frac{1}{2}, \frac{1}{2}+q, 0)$, $(\frac{1}{2}, \frac{1}{2}-q, 0)$;

4 Cl at $(p, 0, r)$, $(-p, 0, -r)$ and $(\frac{1}{2}-p, \frac{1}{2}, r)$, $(\frac{1}{2}+p, \frac{1}{2}, -r)$,

where $q = 0.25 \pm 0.02, \; p = 0.25, \; r = 0.37.$

As this structure is determined by X-ray diffraction the positions of the protons are unknown. The crystal has three binary axes of symmetry perpendicular to each other and three planes of symmetry through these axes.

2. *Measurements on paramagnetic* $CuCl_2.2H_2O$. H_0 *in plane ab.* At temperatures of liquid hydrogen $CuCl_2.2H_2O$ proves to be paramagnetic. The shape of the resonance diagrams obtained at different temperatures (20.1°K and 14.3°K) are similar, only the distances between the lines being altered. The diagram for measurements at 14.3°K with the constant magnetic field rotating in the *ab*-plane is shown in fig. 2.

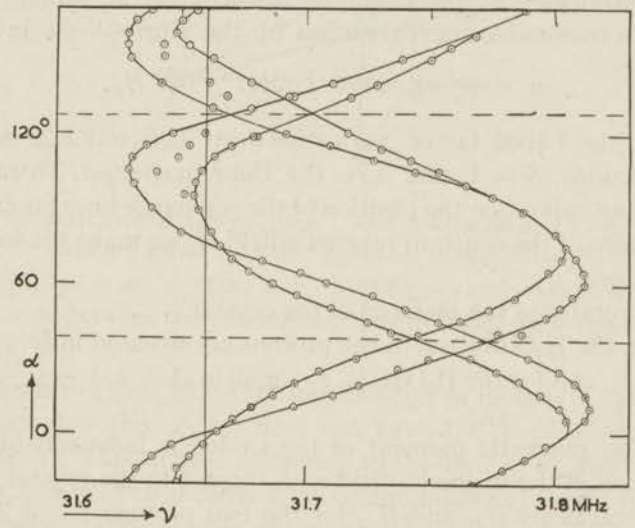

Fig. 2. Resonance diagram for H_0 in the *ab*-plane. $T = 14.3$°K. The resonance line for the protons in water is found at $\nu_0 = 31.66$ MHz. In the diagram the *a*- and *b*-axes are shown by the dashed lines at $\alpha_a = 128°$ and $\alpha_b = 38°$.

The most striking characteristics of the different diagrams are:

1°. the curves are symmetrical about the *a*-axis and also about the *b*-axis,

2°. the curves in the resonance diagrams behave in first approximation as sine functions with a period of 180°,

3°. the angle between the maxima in the resonance curves and the *b*-axis is 25°, and

4°. the maximum number of lines is five.

Following theory one would expect for the two protons in one crystal water four lines in two pairs of two [1] [2]). The distance between the two lines in one pair, due to the proton-proton interaction should be of the order of 10 oersteds, while the distance between the two

pairs can be calculated from the formula for the dipole-dipole interaction

$$H_d = \mu_0^{-1} \Sigma_c \{3(\boldsymbol{\mu}_c . \mathbf{r})\ (\boldsymbol{\mu}_0 . \mathbf{r})/r^5 - (\boldsymbol{\mu}_c . \boldsymbol{\mu}_0)/r^3\}, \qquad (1)$$

where H_d is the component of the local magnetic field parallel to the constant field H_0, $\boldsymbol{\mu}_c$ the magnetic moment of the c-th Cu-ion, and $\boldsymbol{\mu}_0$ that of the proton. In the temperature region where the salt is paramagnetic the magnetic moment of the Cu-ion can be given in a reasonable approximation by the Curie-Weiss law:

$$\mu_c = \{g^2 \mu_B^2\ S(S + 1)/3k(T - \theta)\}\ H_0, \qquad (2)$$

where g, the Landé factor, varies between 2.05 and 2.25 in different directions, $S = \frac{1}{2}$, and μ_B is the Bohr magneton. To calculate in first approximation the position of the resonance lines for different orientations of the constant magnetic field H_0 we make the following assumptions:

I. H_0 rotates in the plane ab of the crystal,

II. for the H_2O in $(0, q, 0)$ the protons are situated in (x, y, z) and $(-x, y, z)$, and for the H_2O in $(\frac{1}{2}, \frac{1}{2} + q, 0)$ in $(\frac{1}{2} + x, \frac{1}{2} + y, -z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$,

III. the magnetic moment of the Cu-ion is independent of the orientation of the magnetic field with respect to the crystal axes.

The local fields H_{d1} and H_{d2} for the two protons 1 and 2 in one crystal water on interaction with Cu-ion in $(0, 0, 0)$ are then found to be:

$$\begin{aligned} H_{d1} &= (\boldsymbol{\mu}_c/r_1^3)\ \{3 \cos^2 (a - a) \cos^2 b - 1\} \\ H_{d2} &= (\boldsymbol{\mu}_c/r_2^3)\ \{3 \cos^2 (a + a) \cos^2 b - 1\}, \end{aligned} \qquad (3)$$

while a, a and b are indicated in fig. 3. The qualitative characteristics of the measurements given under 1° and 2° are in good agreement with these formulae.

In the calculation of the position of the protons in the unit cell discussed in section 3*d* the interactions of the considered proton with several of the Cu-ions did not prove to be negligible. The formulae giving the total interaction consist of sums of nine functions of the form (3). The calculated curves remain thus sine functions with periods of 180° in good agreement with the measurements at 20.1°K and 14.3°K. The formulae for the positions of the maxima and minima deduced are given in section 3*d*.

However, the resonance curves are not exactly sine functions since the anisotropy of the susceptibility introduces higher harmonics.

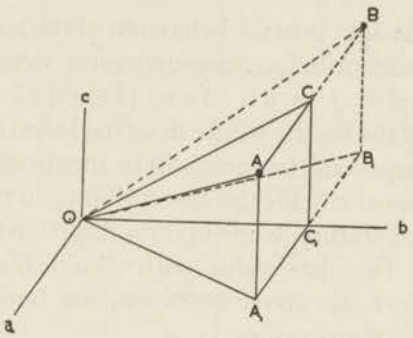

Fig. 3. The positions of the protons 1 and 2 with respect to the crystal axes are given by A and B. In all calculations
$\angle A_1OC_1 = a$; $\angle AOA_1 = b$; $\angle COC_1 = c$; $\angle AOC = d$.
The angle between the rotating magnetic field and the b-axis is α.

The number of lines being not four but five or more is perhaps due to the fact that the crystal does not have the *ab*-plane precisely parallel to H_0. The protons belonging to the H_2O in $(0, q, 0)$ and in $(\frac{1}{2}, \frac{1}{2} + q, 0)$ would then cause a maximum number of eight lines, of which several could coincide approximately (for most directions of the field). A further discussion of these measurements is given after calculation of the position of the protons.

3. *Experiments on anti-ferromagnetic* $CuCl_2.2H_2O$. 3*a*. Introduction. The results of the first experiments at liquid helium temperatures show the following characteristics:

1°. the resonance diagram has a striking symmetry about the central proton resonance line,

2°. the temperature dependence of the resonance lines is very different from that in the paramagnetic region, and

3°. the resonance diagram and the number of resonance lines change essentially in passing from hydrogen to helium temperatures.

Because of these three points we suspected that the crystal becomes anti-ferromagnetic at liquid helium temperatures. The shapes of the resonance diagrams measured at many temperatures in a constant field of about 7400 oersteds are not comprehensible from

Bloembergen's theory [1]) of the decomposition of the proton resonance which is successful for $CuSO_4.5H_2O$ and paramagnetic $CuCl_2.2H_2O$.

To get a better insight into the behaviour of the anti-ferromagnetic single-crystals, susceptibility measurements were carried out in cooperation with Dr. J. van den Handel and Mr. H. M. Gijsman [3]). As the results will be described soon in another paper, only their most important features will be mentioned here.

1°. In weak magnetic fields the susceptibility in the *b*-directions is dependent on temperature, while in the *a*-direction the susceptibility decreases rapidly to a low value with diminishing temperatures.

2°. In magnetic fields above 8000 oersteds both susceptibilities are independent of temperature.

3°. Between 6000 and 8000 oersteds a transition from 1° to 2° occurs.

4°. The crystal becomes anti-ferromagnetic at a temperature just above the boiling point of liquid helium.

According to the theory of Néel one must assume the crystal to consist of two magnetic lattices with anti-parallel spin directions. At weak fields the Cu-spins should be anti-parallel, but fixed with respect to the crystal axes, while at strong fields the anti-parallel Cu-spins are rotating with the magnetic field but perpendicularly to it. We had derived this result from our observations before we realised that it was predicted in Néel's paper of 1936 [4]). The first experiments on the decomposition of the proton magnetic resonance line were carried out in a field of 7400 oersteds, *i.e.* just in the threshold region. Later on we repeated our measurements both in weaker and stronger fields. Only the results at the weakest and at the strongest field will be presented in this paper [5]).

3*b*. H_0 in plane *ab*, $H_0 = 1705$ Ø. The resonance frequency for the protons in water was 7.26 MHz, from which the value of H_0 is calculated to be 1705 oersteds. The results obtained in the experiments at temperatures 4.1, 3.5, 3.0 and 1.2°K are shown in figs. 4, 5, 6 and 7 respectively.

With regard to the measurements on the paramagnetic $CuCl_2.2H_2O$ the following results are important.

1°. The diagram is symmetrical about the proton resonance line in water.

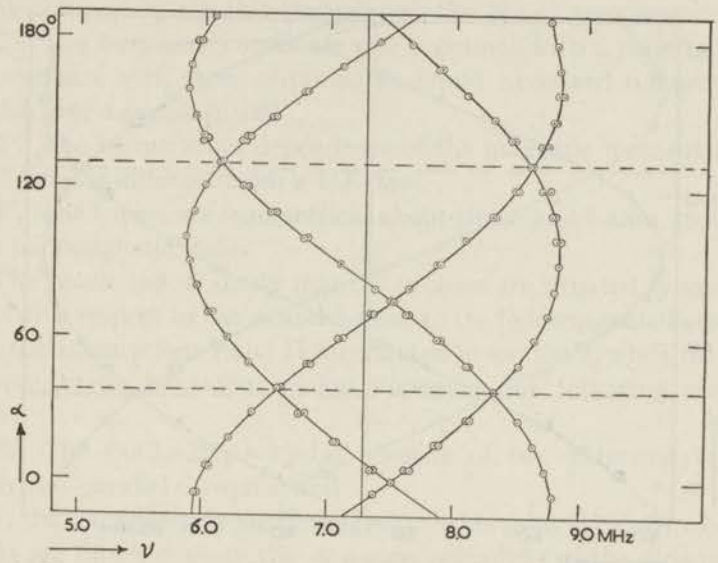

Fig. 4. Resonance diagram for H_0 rotating in the *ab*-plane. $T = 4.13°K$. The resonance line for the protons in water is found at $\nu_0 = 7.26$ MHz. In the diagrams the *a*- and *b*-axes are shown by the dashed lines at $\alpha_a = 125°$ and $\alpha_b = 35°$.

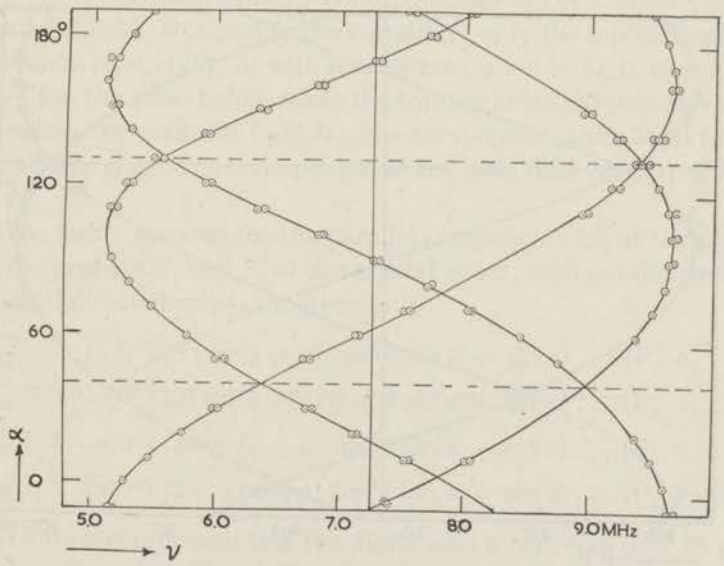

Fig. 5. The same data as for fig. 4. $T = 3.44°K$.

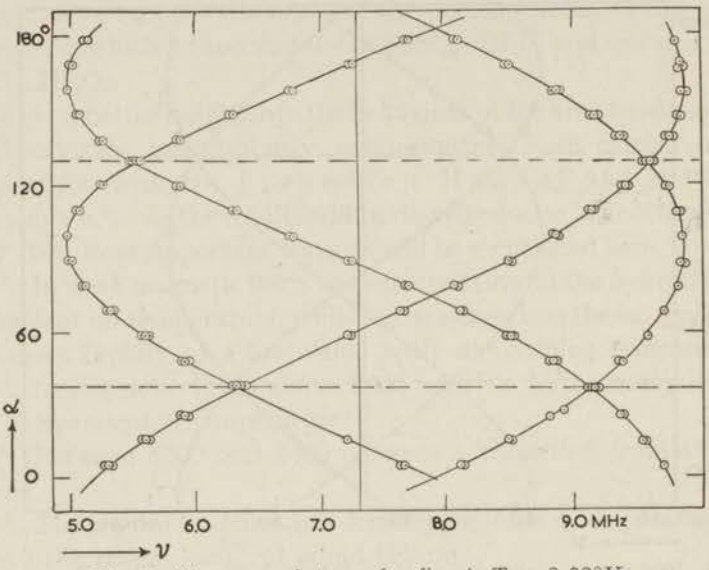

Fig. 6. The same data as for fig. 4. $T = 3.03°$K.

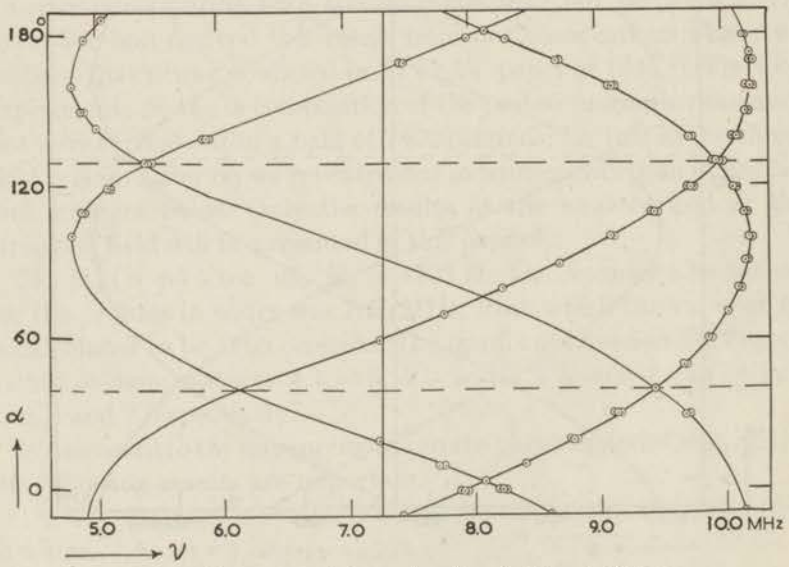

Fig. 7. The same data as for fig. 4. $T = 1.19°$K.

We propose to call this temperature the Néel temperature.

2°. The resonance curves are sine functions with a period of 360° in contrast with those obtained at liquid hydrogen temperatures which give a period of 180°.

3°. The temperature dependence of the magnetic moment of the Cu^{++}-ion is different from a $1/T$- law.

4°. The curves are symmetrical about the *a*- and *b*-axes, just as in the paramagnetic state.

The result *sub* 4° shows that the protons are situated symmetrically with respect to the *a*- and *b*-axes. In the following calculation we use the assumptions I and II formulated in section 2, while the antiferromagnetic behaviour makes necessary the following assumptions:

IV. The $CuCl_2.2H_2O$-crystal consists of two magnetic lattices with anti-parallel Cu-spins, and

V. In the relatively small magnetic fields used (1705 Ø), the Cu-spins are directed along the $\pm$ *a*-axes regardless of the direction of the magnetic field.

In order to calculate the position of the resonance lines as a function of the direction of the magnetic field H_0 the vector of the local magnetic field at the position of the proton is added vectorially to H_0. The resonance frequency is proportional to the absolute value of the total field. To simplify the equations, only the interaction of the proton in (x, y, z) (fig. 3) with its nearest Cu-ion in (0, 0, 0) is considered for the time being, while the total field is split into three components: the constant field H_0, the component of the local field H_d parallel to H_0 and the component of the local field H_p perpendicular to H_0.

The four equations for the parallel components H_d at the position of the protons P_1 and P_2 of one crystal water, with parallel and anti-parallel directed spins, are given in (6)

$$\begin{aligned}
H_{d1} &= \quad (\mu_c/r^3)\,\{3\cos(a-a)\cos^2 b\sin a - \sin a\} \ldots (P_1, a_+),\\
H_{d2} &= (-\mu_c/r^3)\,\{3\cos(a+a)\cos^2 b\sin a + \sin a\} \ldots (P_2, a_+),\\
H_{d3} &= (-\mu_c/r^3)\,\{3\cos(a-a)\cos^2 b\sin a - \sin a\} \ldots (P_1, a_-),\\
H_{d4} &= \quad (\mu_c/r^3)\,\{3\cos(a+a)\cos^2 b\sin a + \sin a) \ldots (P_2, a_-).
\end{aligned} \tag{6}$$

The formulae represent sine functions with a period of 360° in agreement with section 3*b*, *sub* 2°. As pointed out in section 3*b*, *sub* 4°. the

curves given by (6) are symmetrical with respect to the a- and b-axes. The positions of the maximum and minimum values of H_d (P, $a \pm$) in the resonance diagram are such that

$$\text{tg } \alpha_m = (3 \sin^2 a \cos^2 b - 1)/{}^3/_2 \sin 2a \cos^2 b, \quad (7)$$

where α_m is the angle with the b-axis. From formula (7) one can calculate directly the distances D between the exterior lines if H_0 is parallel to the a- or b-axis, by substituting $a = \pi/2$ or $a = 0$ respectively:

$$a = \tfrac{1}{2}\pi, \quad D_{H_0//a} = (2\mu_c/r^3)\,(3 \sin^2 a \cos^2 b - 1), \text{ and} \quad (8)$$

$$a = 0, \quad D_{H_0//b} = (3\mu_c/r^3) \sin 2a \cos^2 b. \quad (9)$$

The values of α_m found from the different resonance diagrams are:

$$\alpha_m = 56° \text{ or } \alpha_m = 90° + 34°. \quad (10)$$

In addition to the displacement of the resonance lines due to the parallel component H_d of the local field, there is also a small influence of the perpendicular component H_p, which causes a slight lack of symmetry of the resonance diagrams about the proton resonance line in water.

The resonance frequencies of the protons as derived from the observations should be corrected by:

$$\Delta\nu_p = -(\gamma^2\mu_c^2/r^6)\{3 \sin(\alpha - a) \cos^2 b \sin a + \cos a\}^2/2\gamma H_0 \quad (11)$$

in order to find the influence of H_d only. The maximum value of $\Delta\nu_p$ lies at the intersection of the resonance curves, while in the maxima of the resonance curves this factor $\Delta\nu_p$ disappears. The correction is of the order of:

$$\Delta\nu_p \approx -(\Delta\nu_d^2/2\nu^6) \approx (2{,}45)^2/(2 \times 7.28) = 0.42 \text{ MHz}$$

at 3.0°K. By using these values of $\Delta\nu_p$ in the resonance diagrams, we find that the curves become practically symmetrical with respect to the proton resonance line in water.

A small correction for the demagnetizing field has to be made, which is proportional to the magnetization M. The demagnetization is thus dependent on the direction and strength of the magnetic field and on the temperature. The largest correction is of the order of 5 Ø.

The distance between the exterior resonance lines when H_0 is in a certain direction is a direct measure of the dependence of μ_c on

temperature. In fig. 8 we have plotted the value of $\mu_c = f(T)$ calculated from the distance between the exterior lines on the b-axis. Absolute values of μ_c can only be calculated when the distance between the Cu-ion and proton is known.

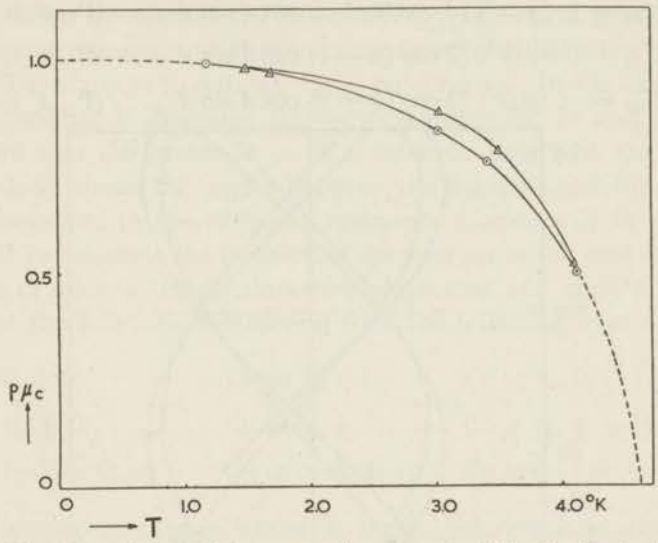

Fig. 8. The dependence of the magnetic moment of the Cu-ion in the antiferromagnetic state on temperature.
⊙ Measurements in a field of 1705 Ø.
△ Measurements in a field of 8920 Ø.
The value of p is dependent on the direction of the magnetic field with respect to the crystal axes.

3c. H_0 in plane bc, $H_0 = 1750$ Ø. The crystals of $CuCl_2.2H_2O$ always grow as needles with the needle axis along the c-axis of the crystal. For measurements with the c-axis perpendicular to the magnetic field, the crystal need not be thicker than 8 mm. Later on we succeeded in growing one single-crystal large enough to permit two cylinders to be cut from it, one with the a-axis, and a very small one with the b-axis vertically. The crystal was not very homogeneous so that it was impossible to fix the a-axis exactly vertically. The results of the measurements at 4.1°K with $H_0 = 1750$ Ø in plane bc, shown in fig. 9, are, however accurate enough to permit some conclusions to be made.

Just as in section 3b we assume, in order to simplify the formulae, that the considered protons have a magnetic interaction only with

their nearest Cu-ion. The magnetic moment of this Cu-ion would be directed along the + or — a-axis.

$$\begin{aligned} H_{d1} &= \quad (\mu_c/r^3)\,\{3\cos(\alpha - c)\cos d \sin d \;\ldots\; (P_1, a_+),\\ H_{d2} &= (-\mu_c/r^3)\,\{3\cos(\alpha + c)\cos d \sin d \;\ldots\; (P_2, a_+),\\ H_{d3} &= (-\mu_c/r^3)\,\{3\cos(\alpha - c)\cos d \sin d \;\ldots\; (P_1, a_-),\\ H_{d4} &= \quad (\mu_c/r^3)\,\{3\cos(\alpha + c)\cos d \sin d \;\ldots\; (P_2, a_-). \end{aligned} \tag{12}$$

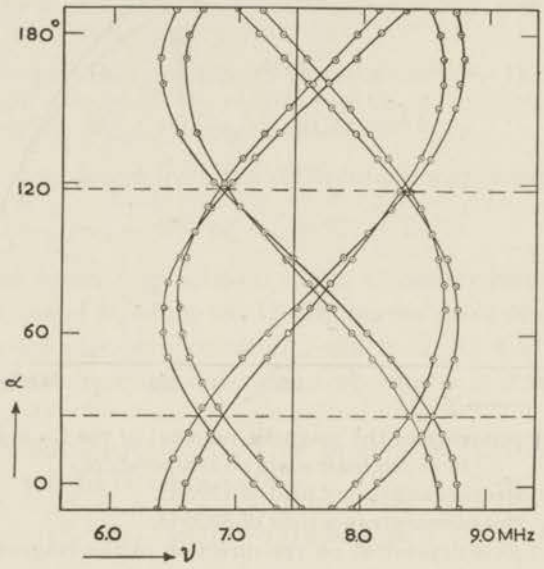

Fig. 9. Resonance diagram for H_0 rotating in the bc-plane. $T = 4.14°$K. The resonance line for the protons in water is found at $\nu_0 = 7.45$ MHz. In the diagram the b- and c-axes are shown by the dashed lines at $a_b = 27°$ and $a_c = 117°$.

The resonance diagram of fig. 9 shows a sine function with a period of 360°, while the resonance curves are symmetrical about the b- and c-axes, in agreement with formulae (12). For the position of the maximum of the resonance curves with respect to the b-axis we find $a_m = 41°$. Substition of $\alpha = 0$ and $\alpha = \pi/2$ in equation (12) gives directly the distances between the exterior lines if H_0 is parallel to the b- and c-axis respectively:

$$\alpha = 0, \quad D_{H_0//b} = (6\mu_c/r^3)\cos c \sin d \cos d, \tag{13}$$

$$\alpha = \pi/2, \; D_{H_0//c} = (6\mu_c/r^3)\sin c \sin d \cos d. \tag{14}$$

Equation (13) can also be written as

$$D_{H_0//b} = (6\mu_c/r^3) \cos c \sin d \cos d = (3\mu_c/r^3) \sin 2a \cos^2 b, \quad (15)$$

which is just the value of $D_{H_0//b}$, when the field is rotated in the *ab*-plane. When we measure the values of $D_{H_0//b}$ in both diagrams taken at the same temperature, the distances agree to within a few percent.

3*d*. The position of the protons. In the discussion of the resonance diagrams shown in sections 3*a*, 3*b* and 3*c* it is assumed that the proton in (x, y, z) interacts only with the Cu-ion in (0, 0, 0). From the angles between the maxima and the crystal axes measured in the different resonance diagrams it is perhaps possible to calculate the position of the protons in the unit cell. The results of such attempts, however, show that one must take into account the magnetic interaction with the following nine Cu-ions:

Cu in (0, 0, 0),	Cu in (0, 0 1),	Cu in (0, 0, —1),
Cu in $(\frac{1}{2}, \frac{1}{2}, 0)$,	Cu in $(\frac{1}{2}, \frac{1}{2}, 1)$,	Cu in $(\frac{1}{2}, \frac{1}{2}, -1)$,
Cu in $(-\frac{1}{2}, \frac{1}{2}, 0)$,	Cu in $(-\frac{1}{2}, \frac{1}{2}, 1)$,	Cu in $(-\frac{1}{2}, \frac{1}{2}, -1)$.

In the temperature region where the crystal behaves paramagnetically the local field due to the nine Cu-ions consists of a sum of nine terms of the form (3). Only the formulae for the angle between the maximum and the *b*-axis, a_h, becomes more complicated:

$$\operatorname{tg} 2a_h = \frac{\sum_1^9 i\, 2(x - X_i)(y - Y_i) r_i^{-5}}{\sum_1^9 i \{(x - X_i)^2 - (y - Y_i)\} r_i^{-5}}, \quad (16)$$

where

$$r_i^2 = (x - X_i)^2 + (y - Y_i)^2 + (z - Z_i)^2. \quad (17)$$

In these formulae, the position (X_i, Y_i, Z_i) of the i-th Cu-ion and the position (x, y, z) of the proton, are expressed in Å. As to the orientation of the Cu-spins in the anti-ferromagnetic regions two possibilities were considered:

1. the nearest neighbours of each Cu-spin are directed anti-parallel to it,

2. in each *ab*-plane the Cu-spins are all parallel, while in adjacent *ab*-planes they are anti-parallel.

The results discussed in sections 3*b* and 3*c* remain unaltered. Only formula 7 is more complicated. Rather lengthy calculations, especially concerning the shape of the resonance diagrams in magnetic fields in the threshold region [5]), showed that possibility 2 about the direction of the Cu-spins gives the most satisfactory results.

The value of the maximum α_{ab}, when H_0 rotates in the ab-plane and α_{bc}, when H_0 rotates in the bc-plane, can be calculated from

$$\operatorname{tg} \alpha_{ab} = \frac{\sum_1^9 q_i \{3(x - X_i)^2 - r_i^2\} r_i^{-5}}{\sum_1^9 q_i 3(x - X_i)(y - Y_i) r_i^{-5}}, \tag{18}$$

$$\operatorname{tg} \alpha_{bc} = \frac{\sum_1^9 q_i (x - X_i)(z - Z_i) r_i^{-5}}{\sum_1^9 q_i (x - X_i)(y - Y_i) r_i^{-5}}, \tag{19}$$

where, according to possibility 2 concerning the direction of the Cu-spins, the values of q_i are:

$$q_1 = q_4 = q_7 = +1;$$

and

$$q_2 = q_3 = q_5 = q_6 = q_8 = q_9 = -1.$$

In formulae (16), (17), (18) and (19) r_i are the distances between the i-th Cu ions in (X_i, Y_i, Z_i) and the proton in (x, y, z). With the help of the three formulae (17), (18), (19), and the values of $\alpha_h = 25°$, $\alpha_{ab} = 56°$ and $\alpha_{bc} = 41°$ known from the resonance diagrams, we found by a method of trial and error as most probable values of x, y and z:

$$x = 0.98 \text{ Å}, \quad y = 3.05 \text{ Å}, \quad z = 0.92 \text{ Å}.$$

Adopting these values of x, y and z and the orientation of the Cu-spins mentioned in 2 we shall discuss briefly the various results.

1°. Paramagnetic $CuCl_2.2H_2O$ (section 2). The consideration of the magnetic interaction between the protons at a distance of about 1.9 Å from each other leads to a splitting in a pair of resonance lines which is in agreement with the measurements. The distances between the different pairs of lines in the resonance diagrams can be calculated from a sum of nine functions of the form (3).

It follows that the resonance lines for all orientations of the magnetic field will be situated at higher frequencies than the central proton line in water, which is in good agreement with the resonance diagram shown in fig. 2. To get approximate agreement with the measurements at 20.0°K and 14.3°K it proves to be necessary to use a value of θ of about —4°K in the formula (2) for the magnetic moment.

2°. Anti-ferromagnetic $CuCl_2.2H_2O$. From the resonance diagrams one finds immediately the frequency difference between the exterior lines in each position of the magnetic field. We calculated the value of the splitting $\Delta\nu$ due to the parallel component at $T = 0$°K by extrapolation from the measurements at 7.2 MHz, when H_0 is along the b-axis (fig. 8).

With the help of the formula for the parallel component at the position of a proton due to nine Cu-ions and this value of $\Delta\nu$ it was possible to calculate the magnetic moment of a Cu-ion μ_c in the b-direction at $T = 0$°K:

$$\mu_c = 1.05 \times 10^{-20} \text{ erg } Ø^{-1}.$$

While in this direction the magnetic moment in the paramagnetic state is $g\mu_B = 0.95.10^{-20}$ erg $Ø^{-1}$. To calculate the position of the protons we used the room temperature values of the distances and part of the discrepancy mentioned may be attributed to the error thus introduced.

3*e*. H_0 in plane ab, $H_0 = 8920$ Ø. In these experiments a central proton frequency in water of 37.91 MHz is used, which corresponds to a magnetic field of about 8920 oersteds. The resonance diagrams with H_0 rotating in the ab-plane are shown in figs. 10, 11 and 12 belonging to temperatures of 4.1, 3.5 and 3.0°K respectively. The diagram measured at a temperature of 1.2°K has practically the same shape and dimensions as that given in fig. 12. It is therefore omitted.

To explain the shape of the resonance diagram we use the assumptions I and II, mentioned in section 2; and assumption IV, mentioned in section 3*b*; however, assumption V concerning the direction of the Cu-spin must be changed.

Previously it has been found [3]) that the susceptibility in both main directions is nearly independent of temperature in these magnetic fields above the transition region. This is in agreement with the

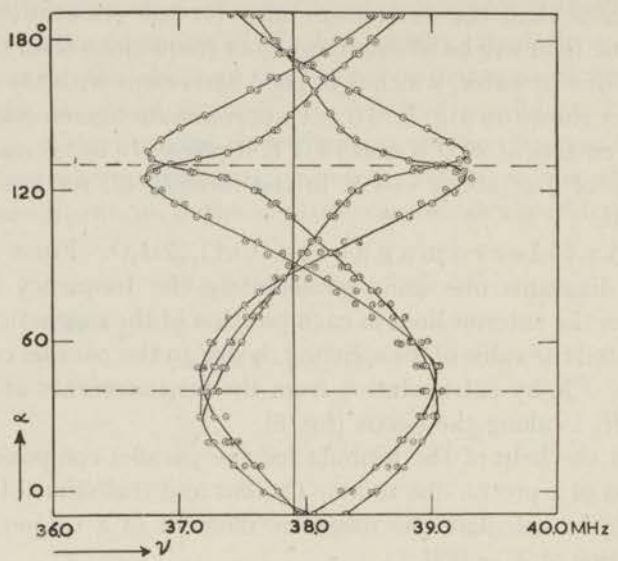

Fig. 10. Resonance diagram for H_0 rotating in the *ab*-plane. $T = 4.13°$K. The resonance line for the protons in water is found at $\nu_0 = 37.91$ MHz. In the diagram the *b*- and *c*-axes are shown by the dashed lines at $a_a = 130°$ and $a_b = 40°$.

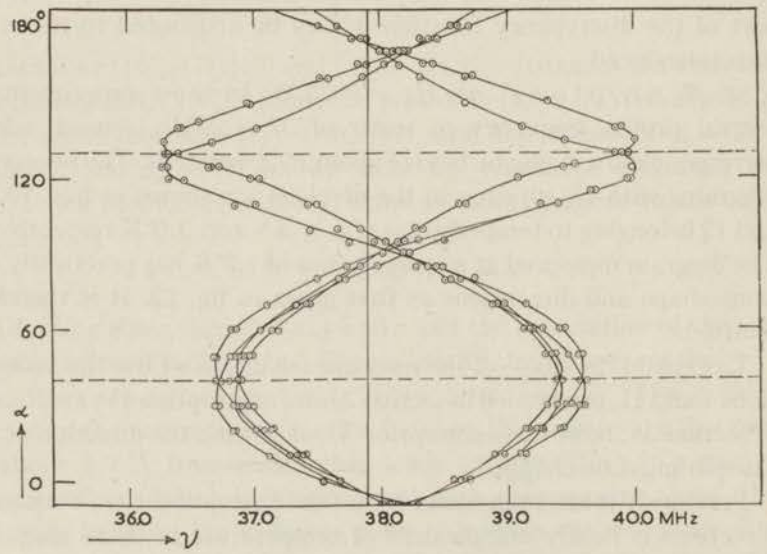

Fig. 11. The same data as for fig. 10. $T = 3.69°$K.

theoretical expectation that the antiparallel Cu-spins rotate with the magnetic field, but perpendicularly to it. Since for a rotating Cu-spin the resonance diagram will be totally different from that for a fixed Cu-spin (see sections 3*b* and 3*c*), these measurements in strong fields are a test for the assumption of rotating spins.

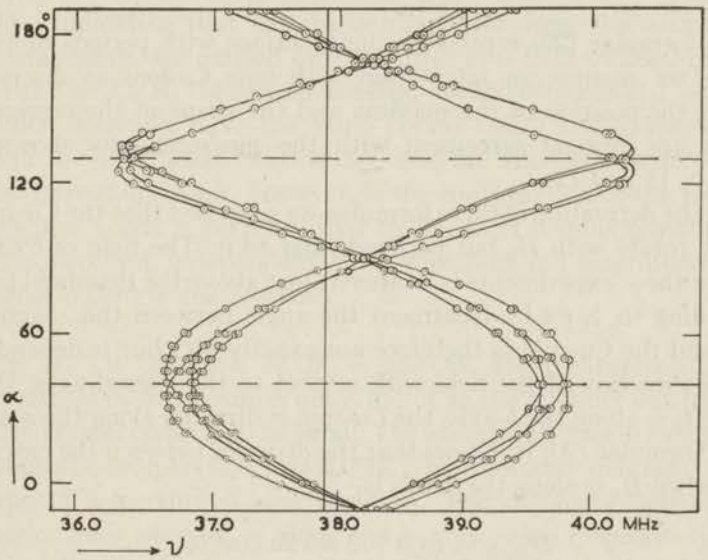

Fig. 12. The same data as for fig. 10. $T = 3.02°K$.

The most striking results obtained in these strong fields are the following:

1°. the resonance curves show a period of 180° in contrast with the measurements in weak fields (1705 Ø) which had a period of 360°,

2°. the symmetry of the resonance diagram due to the anti-ferromagnetic behaviour, is more strict than in the measurements in weak fields (compare fig. 6 and fig. 12 at the same temperature), and

3°. a rapid change of the resonance appears to occur when H_0 is in the neighbourhood of the *a*-axis.

Therefore to calculate the local field, we use the assumptions I, II and IV, while for the behaviour of the Cu-spin we also use the assumption VI:

In strong fields in the *ab*-plane the Cu-spins rotate in this plane with H_0 but perpendicular to it.

One finds for the local field parallel to H_0 the following formulae:

$$\begin{aligned}
H_{d1} &= (\mu_c/r^3)\,\{3\cos(\alpha - a)\cos^2 b \sin(\alpha - a)\} \ldots (P_1, a_+),\\
H_{d2} &= (\mu_c/r^3)\,\{3\cos(\alpha + a)\cos^2 b \sin(\alpha + a)\} \ldots (P_2, a_+),\\
H_{d3} &= (\mu_c/r^3)\,\{3\cos(\alpha - a)\cos^2 b \sin(\alpha - a)\} \ldots (P_1, a_-),\\
H_{d4} &= (\mu_c/r^3)\,\{3\cos(\alpha + a)\cos^2 b \sin(\alpha + a)\} \ldots (P_2, a_-).
\end{aligned} \tag{20}$$

These formulae (20) represent sine functions with periods of 180°. When we assume an interaction with nine Cu-ions as discussed before, the position of the maxima and the shape of the resonance curves are in good agreement with the measurements shown in figs. 10, 11 and 12.

For the derivation of these formulae we supposed that the Cu-spins would rotate with H_0 but perpendicular to it. The field of 8920 Ø used in these experiments is, however, just above the threshold field. According to N é e l's treatment the angle between the magnetic field and the Cu-spin is therefore not exactly 90°, but is dependent on the direction of the field with respect to the crystal axes. Only when H_0 is along the b-axis, the Cu-spin is directed along the a-axis. From formulae (20) it follows that the distance between the exterior lines when H_0 is along the b-axis is,

$$D_{H_0//b} = (\mu_c/r^3).3 \sin 2a \cos^2 b,$$

which is precisely the value found in formula (9). Comparison of the distance $D_{H_0//b}$ measured in section 3b with those from section 3e at equal temperatures shows that there is an agreement within a few percent.

In fig. 8, which shows μ_c as a function of temperature, the values found in these strong fields are also plotted. The curve for μ_c in strong fields is a few percent higher than in weak fields. By extrapolating these curves to $T = 0°\mathrm{K}$ one could find the value of $D_{H_0//b}$ at the absolute zero discussed at the end of section 3c.

There are three reasons for the occurrence of higher harmonics in our curves:

1. the Cu-spin rotates with H_0 but does not lie exactly perpendicular to it, as has been discussed above [4]),

2. susceptibility measurements [3]), and also paramagnetic resonance experiments in the liquid hydrogen region, show an anisotropy of the magnetic moment, and

3. the effect of the demagnetization is of the order of 25 Ø with a difference of about 12% when H_0 is along the *a*- and the *b*-direction.

3*f*. H_0 in plane *bc*, $H_0 = 8880$ Ø and $H_0 = 9560$ Ø. In section 3*c* we discussed the resonance diagram when the crystal is orientated with the *a*-axis perpendicular to H_0. The curves found behave in the same way as those mentioned in section 3*b* for weak fields, indicating that the Cu-spin is fixed along the *a*-axis. Two measurements are carried out: the first in a field of 8880 oersteds and at $T = 3.5°$K, the second in a field of 9560 oersteds at $T = 1.2°$K.

Both diagrams have the same period (360°) and shape as that found in weak fields (section 3*c*), and are therefore omitted. The most important result, however, is the confirmation of the fact that when the *x*-axis is perpendicular to H_0, the Cu-spins remain along this *a*-direction, independent of the direction and magnitude of the magnetic field in the *bc*-plane.

3*g*. H_0 in plane *ac*, $H_0 = 8880$ Ø. The measurements with the crystal in this position are difficult as the cylinder cut from the single-crystal could only be small. The absorption lines are very weak though the temperature was 3.0°K. The resonance diagram has the shape of a perturbed sine function. The distances between the exterior lines when H_0 is along the *a*- and *c*-axes respectively agree very well with the distances measured when H_0 is in the *ab*- and in the *bc*-plane respectively. Both results lead to the expectation that the Cu-spins turn from the *a*- to the *b*-axis, when H_0 is rotating from the *c*- to the *a*-axis. In consequence of the sudden jump of the Cu-spin from a direction in the *ac*-plane to the *b*-axis, the resonance curves show a steep gradient at an angle of about 25° from the *a*-axis.

REFERENCES

1) Bloembergen, N., Commun. Kamerlingh Onnes Lab., Leiden No. 280*c*; Physica, 's-Grav. **16** (1950) 95.
2) Poulis, N. J., Commun. No. 283*a*; Physica, Amsterdam **17** (1951) 392.
3) van den Handel, J., Poulis, N. J., and Gijsman, H. M., Magnetization of an anti-ferromagnetic single-crystal at low temperatures (to be published in Physica).
4) Néel, L., Ann. Physique (11) **5** (1936) 232.
5) Poulis, N. J. and Hardeman, G. E. G. Nuclear magnetic resonance in an anti-ferromagnetic single crystal. II (to be published in Physica).

CHAPTER II

NUCLEAR MAGNETIC RESONANCE IN AN ANTI-FERROMAGNETIC SINGLE CRYSTAL II

Synopsis

The decomposition of the proton magnetic resonance line in an anti-ferromagnetic single crystal of $CuCl_2.2H_2O$ in different magnetic fields in the transition region is discussed [1]. With different orientations of fields of 4170 Ø and 5970 Ø in the *ab*-plane of the crystal the resonance diagrams are perturbed sine functions with periods of 360°. The perturbation is more pronounced in stronger fields. In a field of 7460 Ø the transition of a perturbed sine function with a period of 360° into one with a period of 180° is studied as a function of temperature.

1. *Introduction.* In connection with the different behaviour of the anti-ferromagnetic single crystal of $CuCl_2.2H_2O$ in weak (1700 Ø) and strong (9000 Ø) magnetic fields discussed in I [1], a large number of experiments were carried out in the transition region. These experiments in different fields and at different temperatures, show the gradual transition of the magnetic lattice with anti-parallel Cu-spins fixed along the *a*-axis into one with the Cu-spins orientated perpendicular to the magnetic field.

In 1936 N é e l [2]) discussed the behaviour of anti-parallel magnetic moments. He pointed out that the magnetic moments have a tendency to orientate themselves perpendicular to an applied magnetic field. This tendency may be opposed by a crystalline anisotropy, which favours other orientations. The experiments in weak fields (1700 Ø) on a single crystal of $CuCl_2.2H_2O$ showed the *a*-axis to be the preferred direction for the magnetic moments [1]) [3]). In stronger fields, however, the Cu-spins will deviate from this *a*-direction. The angle between the magnetic moments and the *a*-axis, which depends on the orientation and strength of the mag-

netic field, was derived by Néel[2]) by consideration of the magnetic energy and the energy associated with the crystalline anisotropy.

Gorter and Haantjes[4]) extended the theory of Néel to a three-dimensional case which takes into account rhombic crystalline anisotropy. It is assumed that the crystal consists of two magnetic lattices (+ and —). Following the theory of Néel[4]) and Van Vleck[5]) each magnetic moment is considered to be influenced by the external field H_0 and a virtual field (Weiss field) proportional to minus the average magnetization of the other lattice.

The six equations for the x-, y- and z-components of the total field exerted upon the ions of the two lattices can be written concisely as:

$$H_x^{\mp} = H_{0x} - \alpha_x \mu_x^2 H_x^{\mp}/W^{\mp} \operatorname{tgh}(W^{\mp}/kT), \tag{1}$$

where:

$$W^{\pm} = \sqrt{\mu_x^2 H_x^{\pm 2} + \mu_y^2 H_y^{\pm 2} + \mu_z^2 H_z^{\pm 2}}. \tag{2}$$

For a single crystal of $CuCl_2.2H_2O$ the constants α_x, α_y and α_z as well as the magnetic moments μ_x, μ_y and μ_z may be supposed to have rhombic symmetry. In this case the solutions of the above equations for $T = 0°K$ is straightforward.

Introducing
$$\begin{aligned} \gamma_x &= \alpha_x \mu_x^2 \qquad (etc.) \\ h_x &= \mu_x H_{0x} \qquad (etc.) \\ p_x &= \tfrac{1}{2}\mu_x (H_x^+/W^+ - H_x^-/W^-) \quad (etc.) \end{aligned} \tag{3}$$

Gorter and Haantjes deduce the following relations from equations (1) and (2):

$$\begin{aligned} (\gamma_y^2 - \gamma_z^2)\, p_y p_z + (p_x h_x + p_y h_y + p_z h_z)(p_y h_z - p_z h_y) &= 0, \\ (\gamma_z^2 - \gamma_x^2)\, p_z p_x + (p_x h_x + p_y h_y + p_z h_z)(p_z h_x - p_x h_z) &= 0, \\ (\gamma_x^2 - \gamma_y^2)\, p_x p_y + (p_x h_x + p_y h_y + p_z h_z)(p_x h_y - p_y h_x) &= 0, \end{aligned} \tag{4}$$

but only as a first approximation ($h \ll \gamma$)

$$p_x^2 + p_y^2 + p_z^2 = 1. \tag{5}$$

Equation (5) for the direction cosines of the antiparallel Cu-spins is valid in the approximation that the magnetic field H_0 is weak. As a result of the increase of H_0 the Cu-spins of both lattices deviate towards the field direction by an angle ε. This angle ε, though being responsible for the resulting magnetization of the sample, is in these measurements always smaller than 4°.

As the nuclear magnetic resonance experiments with magnetic fields in the transition region are all carried out with this field lying in the *ab*-plane, we may solve equations (4) and (5) setting $h_z = 0$.

The solution realised in this case will be:

$$(\gamma_x^2 - \gamma_y^2) p_x p_y + (p_x h_x + p_y h_y)(p_x h_y - p_y h_x) = 0 \qquad (6)$$

Substitution of $p_y^2 = 1 - p_x^2$ leads to the equation

$$(u^2 + 4h_x^2 h_y^2)\, p_x^4 + (-u^2 - 4h_x^2 h_y^2)\, p_x^2 + h_x^2 h_y^2 = 0, \qquad (7)$$

where:

$$u = (\gamma_x^2 - \gamma_y^2 + h_y^2 - h_x^2). \qquad (8)$$

For an isotropic magnetic moment ($\mu_x = \mu_y = \mu_z$) the solution of equation (7) gives the same relation between ψ^* and the variables β^* and H_0 as deduced by N é e l [2]):

$$\operatorname{tg} 2\psi^* = \sin 2\beta^* / \{\cos 2\beta^* - (H_0/H_{\text{thr}})^2\}, \qquad (9)$$

where H_0 is the external magnetic field,
β^* is the angle between H_0 and the *a*-axis (see fig. 1),
and H_{thr} is the threshold field.

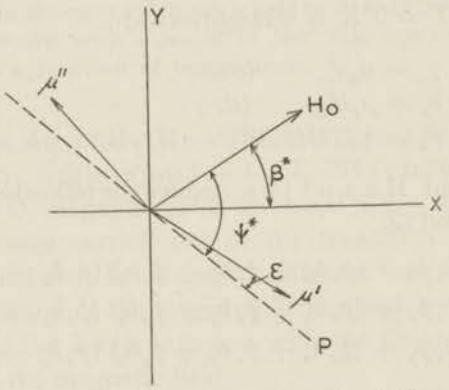

Fig. 1. Orientation of the magnetic moment μ' and the magnetic field H_0 to the crystal axes, when the magnetic moment is isotropic ($\mu_x = \mu_y = \mu_z$).

The angle ψ^* thus defined from (9) is nearly equal to the angle ψ introduced by Gorter and Haantjes [4]) for the anisotropic case. As the largest deviation between ψ^* and ψ is of the order of 2°, formula (9) will be used throughout.

By further extension of this theory, Gorter and Haantjes deduce a simple relation between the total magnetization M of the

crystal and the angle ψ^* calculated from formula (9). By introducing the assumption that the magnetic moment is isotropic ($\mu_x = \mu_y = \mu_z$), the relation becomes

$$M = M_0 \sin^2 \psi^*, \qquad (10)$$

where M_0 is the magnetization when H_0 is along the b-axis. Formula (10) was already deduced by N é e l [2]). When the temperature has a value different from zero, (9) and (10) become considerably more complicated [6]). Magnetization measurements [1]) carried out in the transition region show striking agreement with this theory, when a suitable choice of the threshold field H_{thr} has been made.

To calculate the positions of the proton resonance lines theoretically, it is necessary to know the direction of the magnetic moments relative to the crystal axes for each orientation of the magnetic field. The magnetization measurements confirm that it is justified to use formula (9) for the calculation of ψ^*.

2. *Discussion of the results of the nuclear magnetic resonance experiments on single crystals of* $CuCl_2.2H_2O$ *in the transition region.* 2*a*. H_0 in plane *ab*; $H_0 = 4170$ Ø. The proton resonance line in water was found at a frequency of 17.75 MHz, from which the value of H_0 is calculated to be 4170 Ø. The resonance diagrams measured at temperatures of 4.14, 3.03 and 1.21°K are shown in fig. 2, 3 and 4 respectively. In comparison with the resonance diagrams shown in section 3*b* of I the following results are seen to be significant.

1°. The resonance curves are perturbed sine functions with periods of 360°. The perturbation is stronger at lower temperatures.

2°. The distances between the exterior lines when H_0 is along the *a*- or *b*-axis are equivalent to those found at the same temperature and the same orientation of a field of 1705 Ø.

3°. The resonance curves remain symmetrical about the central proton line in water.

Assumptions I, II, IV formulated in I, section 3*b*, remain valid except that now the orientations of the Cu magnetic moments with respect to the crystal axes have to be calculated from (9).

Just as before we can calculate the position of the lines in the resonance diagrams, using the formula (I, 1)

$$H_d = \mu_0^{-1} \Sigma_c \{3 (\boldsymbol{\mu}_c . \mathbf{r}) (\boldsymbol{\mu}_0 . \mathbf{r})/r^5 - (\boldsymbol{\mu}_c . \boldsymbol{\mu}_0)/r^3\}.$$

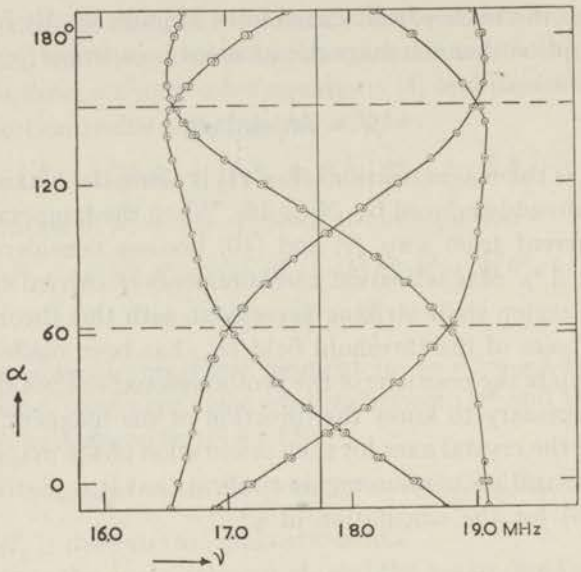

Fig. 2. Resonance diagram for H_0 rotating in the ab-plane. $T = 4.14°$K. The resonance line for the protons in water is found at $\nu_0 = 17.75$ MHz. In the diagrams the a- and b-axes are shown by the dashed lines at $\alpha_a = 153°$ and $\alpha_b = 63°$.

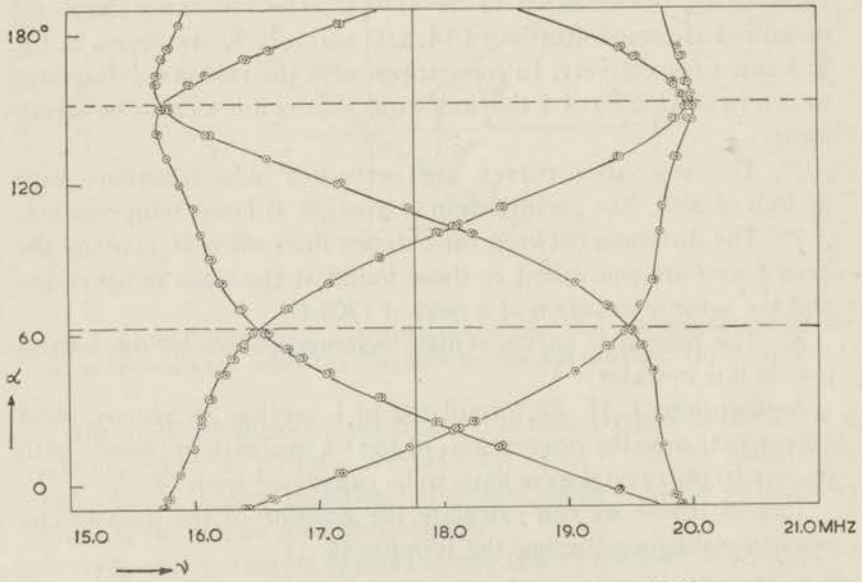

Fig. 3. The same data as for fig. 2. $T = 3.03°$K.

The only difference is that the magnetic moment of the Cu-ion and the a-axis now form an angle φ^* (see fig. 5).

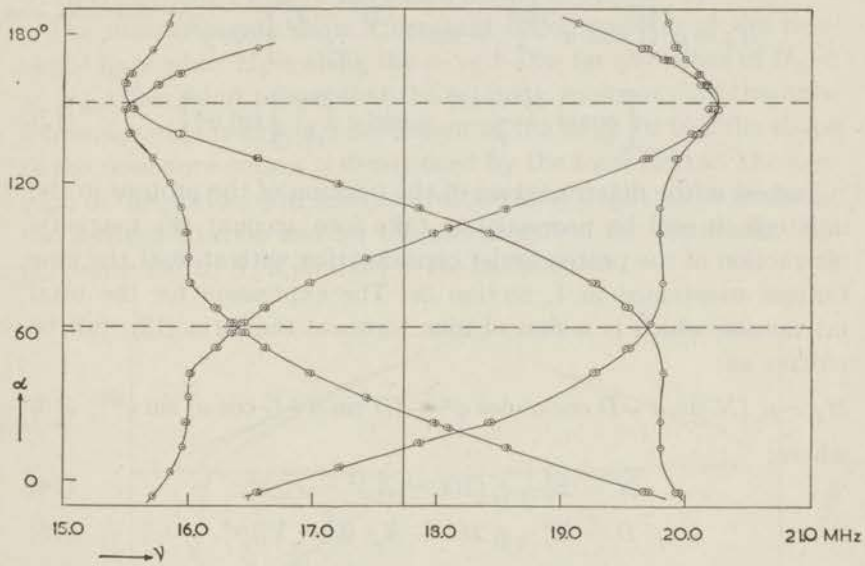

Fig. 4. The same data as for fig. 2. $T = 1.21°$K.

The component of the local field H_d parallel to H_0 at the position of the proton P_1 is then given by:

$$H_{d1} = \left(\frac{\mu_c}{r^3}\right) . [3 \cos (a - a) \cos^2 b \sin (a - \varphi^*) - \sin (a - \varphi^*)] \quad (11)$$

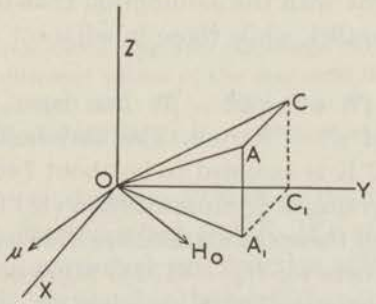

Fig. 5. A is the position of the proton. In the calculations the following angles are used: $\angle A_1OC_1 = a$; $\angle AOA_1 = b$. The angle between the rotating magnetic field H_0 and the b-axis is a. The angle between the magnetic moment μ and the a-axis is φ^*.

After transformation to the Cartesian coordinates of the proton (x, y, z), formula (11) becomes:

$$H_{d1}=\mu_c\left\{\left[\cos\alpha\,\frac{3xy}{r_1^5}+\sin\alpha\,\frac{3x^2-r_1^2}{r_1^5}\right]\cos\varphi^*-\right.$$
$$\left.-\left[\cos\alpha\,\frac{3y^2-r_1^2}{r_1^5}+\sin\alpha\,\frac{3xy}{r_1^5}\right]\sin\varphi^*\right\}. \qquad (12)$$

Just as in the determination of the position of the protons in the unit cell, it will be necessary to take into account the magnetic interaction of the proton under consideration with at least the nine Cu-ions mentioned in I, section 3*c*. The expression for the total interaction which is a sum of nine terms of the form (12), can be written as:

$$H_{d1}=\mu_c\,[N\sin\alpha+D\cos\alpha)\cos\varphi^*-(D\sin\alpha+G\cos\alpha)\sin\varphi^*], \qquad (13)$$

where:

$$N=\Sigma_{i=1}^{9}\,q_i\,\{3(x-X_i)^2-r_{i1}^2\}/r_i^5, \qquad (14)$$

$$D=\Sigma_{i=1}^{9}\,q_i\,3(x-X_i)\,(y-Y_i)/r_i^5, \qquad (15)$$

$$G=\Sigma_{i=1}^{9}\,q_i\,\{3(y-Y_i)^2-r_i^2\}/r_i^5. \qquad (16)$$

In formulae (14), (15) and (16) (x, y, z) are the coordinates of the proton and (X_i, Y_i, Z_i) those of the Cu-ion $(i = 1, \ldots, 9)$, while the values of q_i are

$$q_1=q_4=q_7=+1 \text{ and } q_2=q_3=q_5=q_6=q_8=q_9=-1.$$

Ångström units are used throughout. These values of q_i are chosen in agreement with the assumption that the Cu-spins in one *ab*-plane are all parallel, while those in adjacent *ab*-planes are anti-parallel.

Using formula (9) $\varphi^*=\psi^*-\beta^*$ has been determined for a series of values of $\beta^*=90-\alpha$. The threshold field H_{thr} for a temperature of 3.0°K is assumed to be about 7460 Ø. The shape of the resonance diagrams is determined from (13) for different values of H_0. The results of these calculations are shown in fig. 6. The shape of the calculated curve for $H_0=4170$ Ø is in good agreement with the resonance diagram for 3.03°K shown in fig. 3.

In weak fields $\varphi^*=0$ for all orientations of the magnetic field. Then formula (13) becomes:

$$H_{d_1}=\mu_c\,(N\sin\alpha+D\cos\alpha). \qquad (17)$$

Below the threshold field formula (9) shows that $\varphi^* = 0$ when $\beta^* = 0°$ or $\beta^* = 90°$. For all fields $H_0 < H_{thr}$, the value of H_{d_1} when H_0 is along the a- or the b-axis is only dependent upon μ_c.

The measurements show a constant decomposition of the resonance lines when H_0 is along the a- or b-axis for all values of $H_0 < < H_{thr}$. This result proves that the magnetic moment μ_c of the antiferromagnetic Cu-ions is independent of the field. In fact the shape of the resonance curves is determined by the total field at the position of the proton. The small correction that ought to be made for the demagnetization and for the component of the disturbing field perpendicular to H_0 is omitted in the calculations.

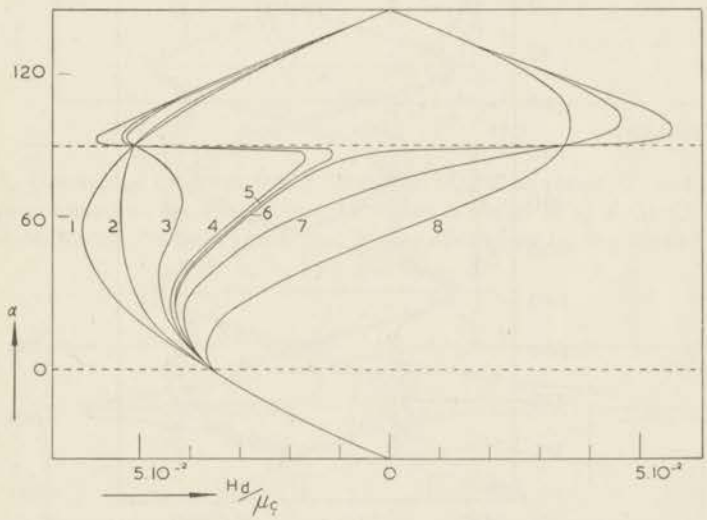

Fig. 6. Shape of the resonance diagrams calculated from formulae (13) and (9), for different values of the magnetic field H_0.
1: $H_0 = 0$ Ø, 2: $H_0 = 4170$ Ø, 3: $H_0 = 5970$ Ø, 4: $H_0 = 7400$ Ø, 5: $H_0 = 7440$ Ø, 6: $H_0 = 7480$ Ø, 7: $H_0 = 8900$ Ø and 8: $H_0 = \infty$.

2*b*. H_0 in plane ab; $H_0 = 5970$ Ø. In this field only one resonance diagram was determined at 4.14°K. It is shown in fig. 7. The resonance curve is a perturbed sine function with a period of 360° just as are those in section 2*a*, the perturbation being more pronounced than at 4170 Ø. The shape of the calculated curve for $H_0 = 5970$ Ø shown in fig. 6 is in good agreement with that of the measured one.

As the magnetic field did not rotate exactly in the *ab*-plane of the crystal due to a slight deviation of the adjustment of the crystal, some of the resonance lines are doubled.

2*c*. H_0 in plane *ab*; $H_0 = 7460$ Ø. In the introduction of I (section 3*a*), the difficulties encountered in the explanation of the results of the first experiments carried out in a field of 7460 Ø at many temperatures were mentioned. The following discussion will make it clear that at this field the transition from a perturbed sine function with a period of 360° into one with a period of 180° is dependent upon temperature.

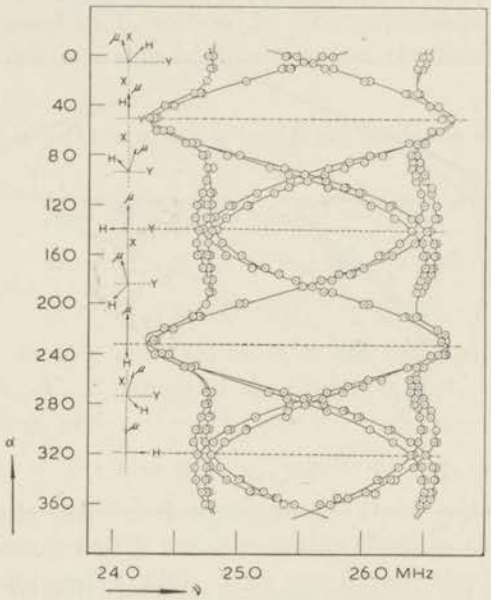

Fig. 7. Resonance diagram for $H_0 = 5970$ Ø. $T = 4.14$°K. The magnetic field is rotated in the *ab*-plane over 360°. The orientation of the magnetic moment to the crystal axes is shown for each rotation over 45° of H_0.

The transition which takes place at a temperature of about 3°K is shown clearly by the susceptibility measurements. In weak fields ($\approx$ 2000 Ø) the susceptibility $\chi_{||}$, when H_0 is along the *a*-axis increases continuously with increasing temperature to the Néel point where $\chi_{||}$ becomes equal to the perpendicular susceptibility, $\chi_{\perp}$, which is independent of temperature. In a field of 7460 Ø, the parallel susceptibility $\chi_{||}$, however, shows a minimum at a temper-

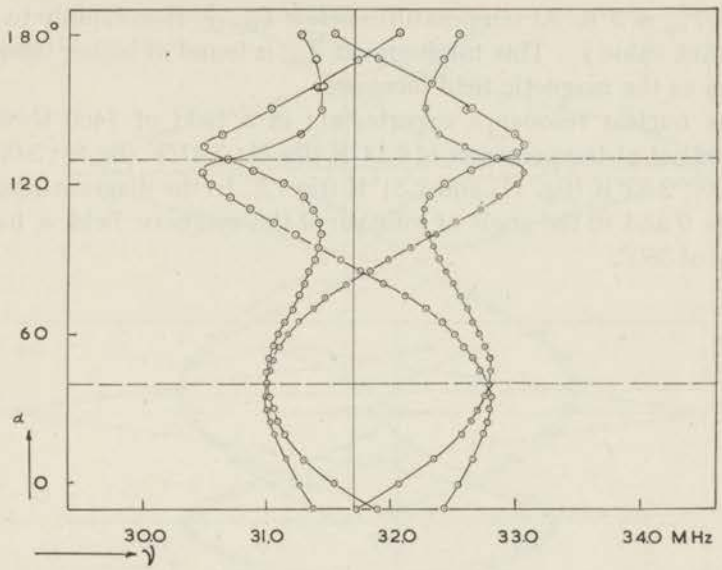

Fig. 8. Resonance diagram for H_0 rotating in the *ab*-plane. $T = 4.14°$K. The resonance line for the protons in water is found at $\nu_0 = 31.62$ MHz. In the resonance diagram the *a*- and *b*-axes are shown by the dashed lines at $\alpha_a = 130°$ and $\alpha_b = 40°$.

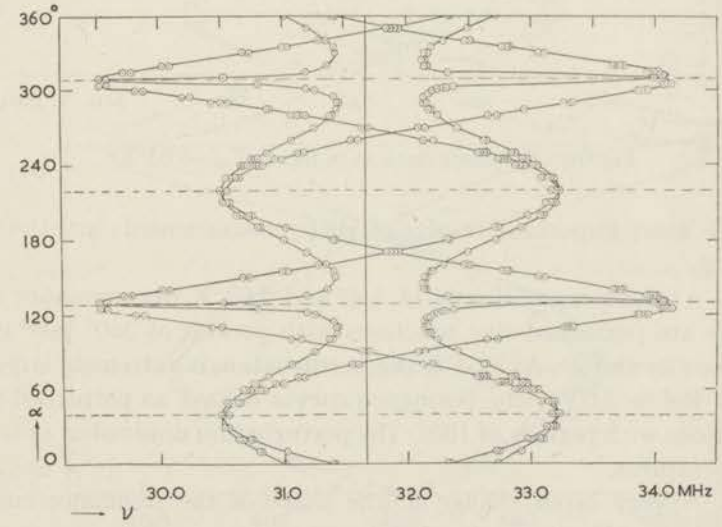

Fig. 9. The same data as in fig. 8. $T = 3.47°$K. The magnetic field is rotated over 360°.

ature $T_{thr} \approx 3°K$. At temperatures below T_{thr}, $\chi_{||}$ rises rapidly to the constant value $\chi_{\perp}$. This minimum at T_{thr} is found at higher temperatures as the magnetic field increases.

The nuclear resonance experiments in a field of 7460 Ø were carried out at temperatures of 4.14°K (fig. 8); 3.47°K (fig. 9); 3.03°K (fig.10); 2.52°K (fig. 11) and 1.51°K (fig.12). In the diagrams shown in figs. 9 and 10 the angle of rotation of the magnetic field, α, has a range of 360°.

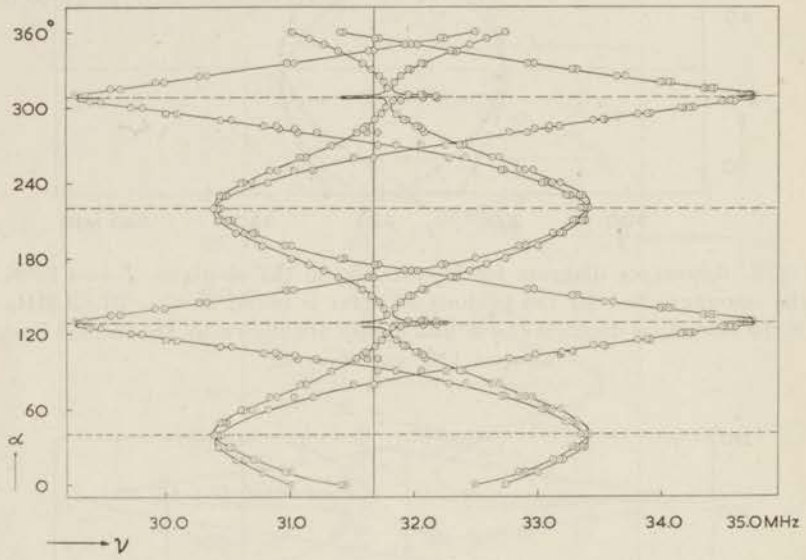

Fig. 10. The same data as in fig. 9. $T = 3.03°K$.

The most important results of these measurements are the following.

1°. At the temperatures 4.14, 3.47 and 3.03°K the resonance diagrams are perturbed sine functions with periods of 360° just as in sections 2*a* and 2*b*. At 3.03°K the perturbation is extremely large.

2°. Below 3.03°K the resonance curves behave as perturbed sine functions with periods of 180°. The perturbation diminishes at lower temperatures.

3°. A very rapid change in the shape of the resonance curves occurs when H_0 approaches the *a*-axis.

4°. At all temperatures the distances between the exterior lines

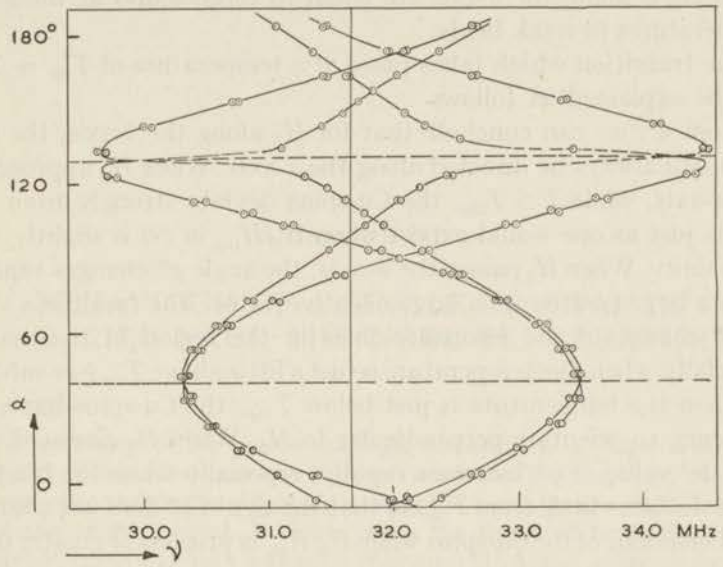

Fig. 11. The same data as in fig. 8. $T = 2.52°$K.

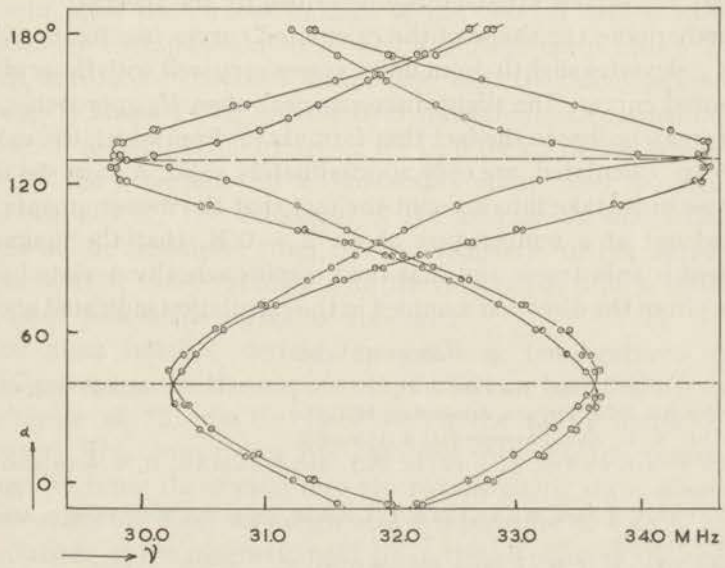

Fig. 12. The same data as in fig. 8. $T = 1.51°$K.

when H_0 is along the b-axis are equal to those found at the same temperatures in weak fields.

The transition which takes place at a temperature of $T_{thr} \approx 3°K$ can be explained as follows

From 4°. we can conclude that for H_0 along the b-axis, the Cu-spins will always be directed along the a-axis. When H_0 approaches the a-axis, while $T > T_{thr}$, the Cu-spins deviate strongly from the a-axis just as one would expect when H_0/H_{thr} in (9) is slightly less than unity. When H_0 passes the a-axis, the angle φ^* changes rapidly from a large positive to a large negative value. The result is a very rapid change of the resonance lines in the region of the a-axis, especially when the temperature is just a little above T_{thr} (see sub 3°).

When the temperature is just below T_{thr}, the Cu-spins have the tendency to orientate perpendicular to H_0. When H_0 passes the a-axis the value of φ^* increases rapidly, especially when the temperature deviates little from T_{thr}, so that the sign of φ^* does not change. The behaviour of the Cu-spins when H_0/H_{thr} is just less or greater than unity described above, causes the resonance curve calculated from formula (13) to be transformed from one with a period of 360° into one with a period of 180°. The transition which takes place at a temperature T_{thr} of about 3°K found in the measurements (see *sub* 1°. and 2°.) is thus satisfactorily described by the theory.

Furthermore the shape of the calculated curves (see fig. 6), when H_0/H_{thr} deviates slightly from unity agrees very well with those of the measured curves. The slight discrepancies, when H_0 approaches the a-axis may be due to the fact that formula (9) from which the values of φ^* are calculated, are only approximately valid. A more detailed analysis must take into account the fact that the measurements are carried out at a temperature above $T = 0°K$, that the magnetic moment is anisotropic and that the Cu-spins actually deviate by an angle ε from the direction assumed in the calculation indicated above.

REFERENCES

1) Poulis, N. J., and Hardeman, G. E. G., Commun. Kamerlingh Onnes Lab., Leiden No. 287*a*; Physica, Amsterdam **18** (1952).
2) Nėel, M. L., Ann. Physique (11) **5** (1936) 232.
3) van den Handel, J., Poulis, N. J., and Gijsman, H. M., to be published in Physica.
4) Gorter, C. J., and Haantjes, J., Commun. Suppl. No. 104*b*; Physica, Amsterdam **18** (1952).
5) Van Vleck, J. H., J. chem. Phys. **9** (1941) 85.
5) Nagamiya, T., Progress of theor. Phys., Kyoto, **6** (1951) 342.

CHAPTER III

BEHAVIOUR OF A SINGLE CRYSTAL OF $CuCl_2.2H_2O$ NAER THE NÉEL TEMPERATURE

Synopsis

The behaviour of the proton magnetic resonance in a single crystal of $CuCl_2.2H_2O$ is studied near the Néel temperature T_N. It is found that T_N is lower when the magnetic field H_0 is along the a-axis than when H_0 is along the b-axis of the crystal. In fields below the threshold field ($H_{thr.}$) this difference $T_{Nb} - T_{Na}$ has a maximum of about 0.015 deg. K, while above $H_{thr.}$ this difference is of the order of 0.041 deg. K.

Results and discussions. In two preceding articles [1] [2] the dependence on temperature of the time-averaged magnetic moment μ_c of the Cu-ions in each of the two sublattices was discussed. By extrapolation to $\mu_c = 0$ the Néel temperature T_N at which anti-ferromagnetism disappears can be calculated to lie between 4.3 and 4.4°K. Specific heat measurements carried out on a powder of $CuCl_2.2H_2O$ by Dr. S. F r i e d b e r g in this laboratory indicate the occurrence of a remarkably sharp Néel temperature at about 4.31°K. The behaviour of the average Cu magnetic moments in the transition from the paramagnetic to the anti-ferromagnetic state can be studied with the help of the proton magnetic resonance in a single crystal of this salt.

The most suitable method for obtaining temperatures up to 4.4°K proved to be the use of a liquid helium bath boiling under a pressure of 781 mm Hg (well within the safety limits of the cryostat). The temperature rise obtained with this overpressure is enough to bring the crystal into the paramagnetic state. The resonance peaks are then very high at a temperature of 4.43°K for all orientations of the magnetic field H_0 in the ab-plane of the crystal. In the temperature region from 4.43°K to 4.36°K the distance Δ

between the extreme resonance lines increases with decreasing temperature. At hydrogen temperature this distance Δ is proportional to $1/(T + \theta)$, where θ is about 4°K ($\Delta = 0.170$ MHz at 14.15°K).

The splitting at 4.43°K is 0.26 MHz which is considerably smaller than expected by extrapolation from the hydrogen measurements. Below 4.36°K the splitting is nearly independent of the temperature. The behaviour of the resonance lines in the transition region between the paramagnetic and anti-ferromagnetic states proves to be very complicated.

For a magnetic field $H_0 = 7160$ Ø, orientated along the *b*-axis of the crystal, the intensity of the resonance lines decreases very rapidly in a temperature region of about 0.002 degrees at 4.33°K. A thousandth of a degree lower the very weak resonance lines belonging to the anti-ferromagnetic state are found at another frequency. When the field is orientated along the *a*-axis at the same temperature, the crystal shows, however, the normal paramagnetic behaviour with very high resonance peaks. If a constant magnetic field H_0 is rotated from the *a*- to the *b*-axis, the intensities of the resonance peaks belonging to the paramagnetic state of the crystal decrease when the *b*-axis is approached, while in the immediate neighbourhood of the *b*-axis the anti-ferromagnetic lines appear with small intensity.

With H_0 along the *a*-axis, the crystal becomes anti-ferromagnetic at a temperature of about 4.31^7°K. Experiments were also carried out in fields of 1460, 6070, 7160, 7860 and 9250 Ø. The difference between the Néel temperatures for H_0 along the *a*- and *b*-axes is plotted in fig. 1 as a function of the magnetic field.

As shown in fig. 1 this difference in T_N appears to be more pronounced in fields above the threshold region. The Néel temperature for H_0 along the *b*-axis, $T_{Nb} = 4.33^3$°K, is nearly the same as in weak fields, while for H_0 along the *a*-axis $T_{Na} = 4.29^2$°K.

The Néel temperature is influenced by two factors:
1°. the direct influence of the magnetic fields, and
2°. the influence of the anisotropy of the crystal.

Garrett [3]) has discussed the dependence of the Néel temperature on the strength of the magnetic field in the case where H_0 is along the *a*-axis of the crystal. For small values of H_0 the curve $H_0 = f(T_N)$ is a parabola. In a field of 7000 Ø the Néel temperature will be 0.014 deg. K lower than in zero field.

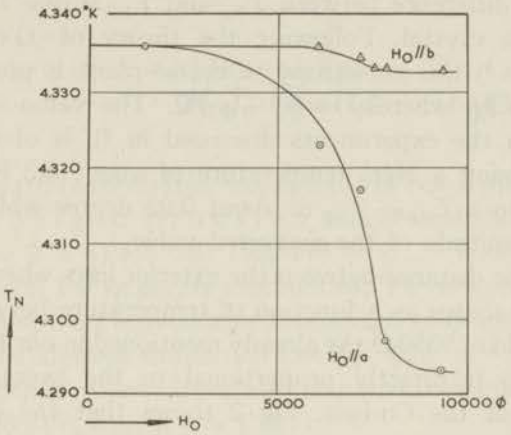

Fig. 1. The Néel temperature as a function of the magnetic field H_0.
△ H_0 // b-axis,
⊙ H_0 // a-axis.

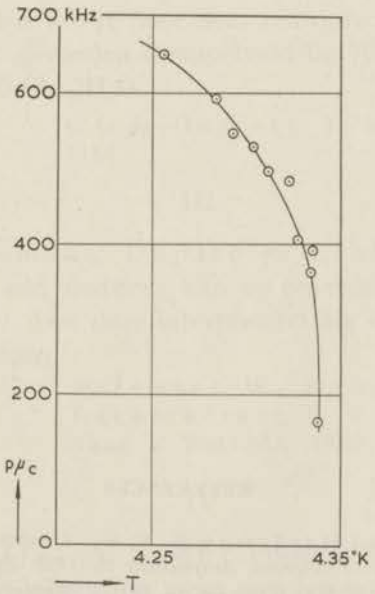

Fig. 2. The dependence of the magnetic moment μ_c of the Cu-ions in the anti-ferromagnetic state on temperature in the temperature region from 4.1 to 4.4°K; p is a constant.

The large difference between T_{Na} and T_{Nb} is due to the anisotropy of the crystal. Following the theory of Gorter and Haantjes [4]) this anisotropy in the *ab*-plane is proportional to $\gamma_x^2 - \gamma_y^2 = 2\gamma\Delta\gamma$, where $\gamma = (\gamma_x + \gamma_y)/2$. The value of $\Delta\gamma/\gamma$, calculated from the experiments discussed in [2]), is of the order of 0.7%. Assuming a Néel temperature of about 4.3°K this effect would lead to a $T_{Na} - T_{Nb}$ of about 0.03 degree which is of the order of magnitude of the measured value.

In fig. 2 the distance between the exterior lines when H_0 is along the *b*-axis is shown as a function of temperature between 4.1 and 4.4°K in a field of 9350 Ø. As already mentioned in our first paper [1]), this splitting is directly proportional to the average magnetic moment μ_c of the Cu-ions. Fig. 2 shows that the curve for μ_c intersects the temperature axis perpendicularly.

REFERENCES

1) Poulis, N. J., and Hardeman, G. E. G., Commun. Kamerlingh Onnes Lab., Leiden No. 287*a*; Physica, Amsterdam 18 (1952) 201.
2) Poulis, N. J., and Hardeman, G. E. G., Nuclear magnetic resonance in an anti-ferromagnetic single crystal. II (to be published in Physica).
3) Garrett, C. G. B., J. chem. Physics 19 (1951) 1154.
4) Gorter, C. J., and Haantjes, J., Commun. Suppl. No. 104*b*; Physica, Amsterdam **18** (1952) (to be published in Physica).

STELLINGEN

N. J. Poulis 1952

I

Voor de warmteoverdracht van een bol in een stromend medium hebben Kronig en Bruysten aangetoond, dat voor $Re < 1$ geldt: $Nu = 2 + \frac{1}{2}Pé + 581/1920\ Pé^2 + \ldots\ldots$ Voor die waarden van Pé, waarbij $Pé^2$ en hogere machten van Pé verwaarloosd kunnen worden, kan op veel eenvoudiger manier het volgende verband tussen Nu en Pé afgeleid worden: $Nu = 2 + \frac{1}{2}Pé$.

Onder dezelfde voorwaarden kan men voor een cylinder afleiden $Nu = 2/\ln(8/\gamma Pé)$ waarin $\gamma = 1{,}7811$.

Kronig, R. and Bruysten, J., Appl. sci. Res. (A) **2** (1951) 439.

II

Het door Garrett beschouwde kritische veld voor anti-ferromagnetische stoffen wordt door hem ten onrechte geïdentificeerd met het door ons gevonden drempelveld bij 7000 oersted in anti-ferromagnetisch $CuCl_2.2H_2O$.

C. G. B. Garrett, J. chem. Phys. **19** (1951) 1154.

III

De door Peremans, Duparc en Lekkerkerker afgeleide eigenschap van matrices kan op eenvoudige manier worden bewezen, wanneer men deze interpreteert als een eigenschap van kwadratische vormen.

Peremans, W., Duparc, H. J. A. and Lekkerkerker, C. G., Proc. Kon. Ned. Akad. v. Wet. 55A (1952) 24

IV

De door Griffel en Stout opgegeven toeneming van de loodrechte susceptibiliteit ($\chi_\perp$) van anti-ferromagnetisch MnF_2 bij afnemende temperatuur kan toegeschreven worden aan de keuze van een minder geschikte methode van meten.

Griffel, M. and Stout, J. W., J. chem. Phys. **18** (1950) 1455.

V

Metingen van de verstrooiing van röntgenstralen door vloeibare zwavel bij verschillende temperaturen doen vermoeden, dat bij 160°C slechts een klein gedeelte van de acht-ringen openbreken en zich tot lange ketens aaneensluiten.

Prins, J. A. and Poulis, N. J., Physica **15** (1949) 696.

VI

Men kan gegevens verkrijgen over het voorkomen van vrije organische radicalen door de bepaling van de kernmagnetische relaxatietijd en wel juist bij die concentraties, waarbij andere meetmethoden geen uitsluitel geven.

VII

Het is van belang de proeven van Flood bij hogere temperaturen voort te zetten ter contrôle van de door Becker-Döring en Volmer afgeleide formule voor de graad van oververzadiging waarbij druppels zich spontaan vormen.

Flood, H., Diss. (Berlin 1933).

VIII

De bij lage temperaturen aan metalen gemeten afwijking der kernspin relaxatietijden van de wet van Heitler en Teller doen vermoeden, dat metalen gebruikt zouden kunnen worden voor het bereiken en meten van uiterst lage temperaturen.

Hatton, J. and Rollin, N., Proc. Royal Soc. (A) **199** (1949) 222.

IX

Metingen van kernresonantie aan MnF_2 doen onderstellen, dat in anti-ferromagnetica met een Néel-temperatuur groter dan 10°K de relaxatietijd T_1 te klein wordt ($T_1 < 10^{-6}$ sec.) om nog pieken in de kernresonantie te kunnen waarnemen.

Bloembergen, N. and Poulis, N. J., Comm. Kamerlingh Onnes Lab. No. 284*a*, Leiden.

X

Soortelijke warmtemetingen aan Zn tonen aan, dat de onderstelling van Jones en Mott dat de dichtheid van de energieniveaux N(E) altijd groter is dan de waarde volgens Sommerfeld, in het geval van hexagonale roosters met $c/a > 1{,}63$ onjuist is.

Jones, H. and Mott, N. F., Proc. Royal Soc. (A) **162** (1937) 49.

XI

De hoge temperaturen, welke men in de industrie moet bepalen, wijken indien gemeten met een kleurpyrometer doorgaans minder af van de thermodynamische temperatuur dan indien gemeten met een totaalstralings- of deelstralings pyrometer.

Campbell, C. H., Modern pyrometry (1951) 120.

XII

Verschillende moeilijkheden bij de verklaring van het gedrag van een nernststift vervallen, wanneer men aanneemt dat de geleiding hoofdzakelijk door electronen geschiedt (halfgeleider).