

Gorter's Footprints on the Trail That Led to Magnetic Resonance

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The Dutch physicist Cornelis Jacobus Gorter (1907–80) was the first to demonstrate the phenomenon of paramagnetic relaxation. Understanding its implications, he recognized that—at least in principle—the magnetic dipole transitions between the Zeeman components of a nuclear spin system might be observed as a resonance effect. To his regret, Gorter's attempts at observing such resonances in a solid, made in the years 1936 and 1942, remained fruitless. However, since Zavoisky a few years later reported a successful electron spin resonance experiment (1945), and Bloch, Hansen, and Packard, and Purcell, Torrey, and Pound reported nuclear magnetic resonance experiments (1946), it seems appropriate to give a brief historical sketch of Gorter's seminal efforts in this field (Figure 1).

Gorter studied in Leiden where at the age of 25 years he defended a Ph.D. thesis entitled 'Paramagnetische Eigenschappen von Salzen' (paramagnetic properties of salts). He then began his professional career at the renowned but modest physics laboratory of the Teyler's foundation in Haarlem, moved



Figure 1 The Dutch physicist Cornelis Jacobus Gorter (Photograph by E. de Jong)

as reader to the University of Groningen in 1936, and was appointed Professor of Physics at the University of Amsterdam in 1940, to a chair formerly held by Zeeman. While in Groningen he had a very fruitful collaboration with his colleague in theoretical physics, R. de L. Kronig; during the difficult war years in Amsterdam he struggled to keep his research going with the help of bright young students, amongst whom was L. J. F. Broer. Gorter's true allegiance, however, remained with the Kamerlingh Onnes Laboratory in Leiden with, at the time, its almost unique low-temperature facilities. Thus, shortly after the war, Gorter seized the opportunity to move from Amsterdam to Leiden, where in 1948 he became the Director of the Kamerlingh Onnes Laboratory. In retrospect, this promotion must have been a challenge for an ambitious young physicist, but also a mixed blessing to be burdened with the directorship of a famous physics institute in those years just after World War II. While physics in the United States had continued to flourish in places like Harvard or the MIT Radiation Laboratory, the situation in Holland after five years of war was dismal. There is no question that Gorter and some of the leading scientists of his generation in Holland were saddled with tasks that interfered with their creative work.

Gorter might, perhaps, best be characterized as one of the last true, general physicists; a man who frowned on specialization and considered almost the whole of physics as his playground. Together with his Ph.D. students or colleagues in theoretical physics, he made major contributions in subjects as diverse as paramagnetic relaxation, nuclear orientation, and the anisotropy of γ - and β -emissions, superconductivity, superfluidity, and the Senftleben effect. Thus, one may wonder, as did Gorter himself in his acceptance speech when honoured with the Fritz London award in 1967, whether he had perhaps spread his efforts too thinly.¹

I shall merely consider here Gorter's efforts in relation to magnetic resonance. In his student days, Gorter had already been impressed by Ehrenfest's argument² that the validity of the Curie–Langevin formula for the magnetization of a paramagnetic material implied relaxation processes induced by thermal motion. After a preliminary, unsuccessful experiment by Breit and Kamerlingh Onnes, Gorter became the first to demonstrate the reality of such relaxation.³ Heeding Ehrenfest's suggestion, he measured the heat effects accompanying the (electron–spin lattice) relaxation of Fe^{3+} , Cr^{3+} , V^{3+} , Ti^{3+} , and Gd^{3+} ions in alum crystals placed in an rf magnetic field ($\nu = 10\text{--}21$ MHz, $B_1 = 0.5\text{--}0.8$ mT) in a calorimeter cooled by boiling hydrogen or nitrogen.

In parallel with these experiments, Gorter and Kronig worked on the theory of absorption and dispersion in paramagnetic crystals under the influence of an alternating magnetic field.⁴ Their work was inspired by Debye's treatment of the dielectric behavior of an assembly of rigid dipoles subject to frictional forces and Brownian motion. Gorter realized that when a system of spins $S = \frac{1}{2}$ (or $I = \frac{1}{2}$) is placed in a constant magnetic field B_0 and subjected to a second, alternating magnetic field perpendicular to B_0 , its response can be described by the real and imaginary parts of the magnetic susceptibility, as sketched in Figure 2. The figure, which is a copy of Gorter and Broer's original drawing,⁵ shows the now familiar fact that at the frequency ν_0 where the resonance condition $h\nu_0 \approx \mu B_0$ is fulfilled, a magnetic dipole transition occurs which manifests itself by a maximum in the absorption A , accompanied by a

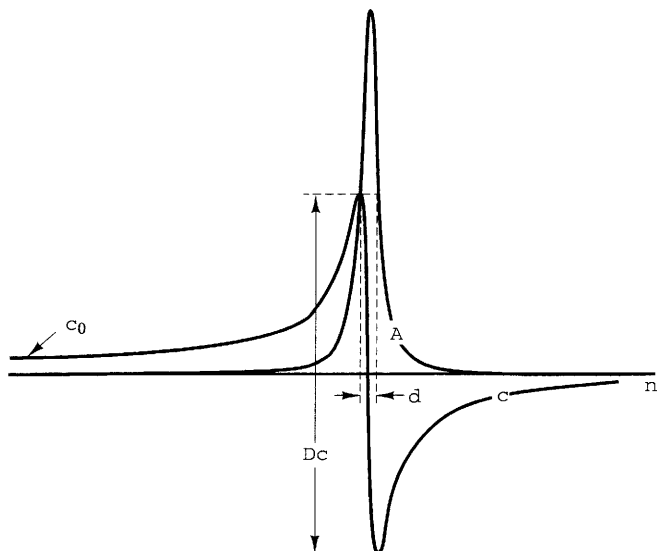


Figure 2 Absorption A and susceptibility χ as a function of frequency ν . The halfwidth δ has been taken equal to $0.05\nu_0$. Reproduced from Gorter and Broer⁵ [in current terminology χ denotes the real part (χ') of the susceptibility and A is proportional to its imaginary part (χ'')]. Reproduced by permission of Elsevier Science Publishers

'jump', $\Delta\chi$, in the (real part of the) susceptibility χ . According to Gorter and Broer, this jump, is given by

$$\Delta\chi/\chi_0 = \nu_0/\delta \quad (1)$$

where δ denotes the halfwidth of the spectral transition and χ_0 the static susceptibility due to the spins concerned. If thermal equilibrium obtains, then

$$\chi_0 = N\mu^2/3kT \quad (2)$$

where N is the number of spins per gram and μ is the spin magnetic moment.

Because of the limitation in frequency of the rf equipment at his disposal, Gorter's experiments on the relaxation of paramagnetic salts in strong external fields⁶ were restricted to frequencies below those where resonance occurs as depicted in Figure 2. However, Gorter realized that, because of the smallness of the nuclear magnetic moment compared with that of an electron, his equipment should be well suited to investigate *nuclear* paramagnetic relaxation phenomena in the resonance region depicted in Figure 2. Using the calorimetric method that had proved so successful in the demonstration of electron paramagnetic relaxation the same year (1936), Gorter made his first, negative, attempt to detect magnetic resonance transitions of ^1H and ^7Li nuclei in $\text{K}[\text{Al}(\text{SO}_4)_2] \cdot 12\text{H}_2\text{O}$ (alum) and LiF crystals, respectively.⁷ In these experiments, carried out at liquid hydrogen temperature (14–20 K), the crystals were subjected to a 20 MHz alternating field with a strength B_1 as high as 1 mT and a constant field that could be varied between 0 and 1.4 T. Provided Boltzmann equilibrium was maintained between the $m = \pm\frac{1}{2}$ spin states at the temperature of the lattice, Gorter expected to observe a temperature rise of $0.3^\circ\text{C min}^{-1}$ in the experiment on protons in alum. However, the actual tem-

perature rise was at most 1% of this estimate and remained hidden in the background due to the heat leakage of the calorimeter. With our present knowledge it is clear that Gorter's explanation....

The only reasonable explanation of this negative result is that the absorption of energy by the nuclear spin disturbs the Boltzmann distribution over the nuclear energy levels

...is the correct one. He further concluded that the 'nuclear temperature' in the experiment must have been in excess of 1400 K and that the spin-lattice relaxation time was longer than 10^{-2} s. Gorter's reasoning, in a sense, anticipated the thermodynamic interpretation of paramagnetic relaxation phenomena by Casimir and du Pré.⁸ These authors were the first to formulate clearly that it is reasonable to assume that in the relaxation experiments thermal equilibrium is rapidly established within the lattice and spin systems individually, each at its own temperature, whereas the relaxation reflects the slow heat transfer between the two systems.

A year later, in September 1937, Gorter visited Rabi's laboratory at Columbia University. It proved a fateful visit for both parties and a boost for science. Rabi and his collaborators were pioneers in molecular beam techniques. In their experiments designed to determine the sign of the magnetic moments of the proton and deuteron,⁹ changes of the quantum states of hydrogen and deuterium atoms in the incoming beam were effected by passing the beam through a region in which (dc) electric currents in a set of parallel wires generated a highly anisotropic magnetic field pattern. In a coordinate system moving with a given atom, the applied field T then varies in direction and strength as a function of time. If the field pattern relative to the direction of propagation is chosen suitably, non-adiabatic changes in the magnetic quantum number result, from which by a somewhat involved argument the *sign* of the magnetic moment of the nucleus may be derived.⁹ The absolute *magnitude* of the nuclear moment, however, must be determined via another beam experiment. Because, as the authors of Ref. 9 stated:

Since the form of the field T [felt by a particular nucleus] is not known exactly it is not possible to calculate α [an angle specifying the change in quantum state] as a function of the field and of the velocity. There will also be a different value of α for every atomic velocity. We cannot, therefore, begin by setting the field at some particular value and expect to find nonadiabatic transitions.

In other words, in the configuration in which it existed in 1936, with all applied fields of a static nature in the laboratory frame, the beam equipment was not suited for carrying out quantitative magnetic resonance experiments.

In January 1938, a few months after Gorter's visit, the Columbia group heralded the first successful nuclear magnetic resonance experiment. It was carried out on Li and Cl nuclei in a beam of LiCl molecules, and reported in a Letter entitled 'A New Method of Measuring Nuclear Moment'.¹⁰ From Gorter's own account,^{1,5} contemporary sources, and the acknowledgement at the end of the Letter,¹⁰ it transpires that Gorter had provided a stimulus which was crucial for this success. Apparently he had asked why, instead of trying to change the Zeeman state of the particles by passing the beam through a

highly anisotropic but poorly-defined static field, this was not done by irradiating a magnetic dipole transition between two of the Zeeman states—as in his own recent, unsuccessful calorimetric experiment! This means that between the first, inhomogeneous magnetic field and the refocusing field of the earlier experimental configuration,⁹ the beam should be passed through a region with a constant field plus a weak radio-frequency field at right angles to it that could be generated by a simple coil driven at the resonance frequency. This worked, and six years later Rabi was awarded the Nobel Prize in Physics for his superb beam experiments.

As Gorter saw, Rabi's method had the great advantage that the absorptive ($m \rightarrow m'$) and stimulated emission ($m' \rightarrow m$) transitions have an additive effect on the signal of the beam detector. In contrast, in his own calorimetric experiment they had cancelled one another out. Now, with nuclear magnetic resonance no longer being a figment of the physicist's imagination, Gorter renewed his attempts to detect it in a solid. Or, in his own words:⁵

The success however obtained by Rabi and his collaborators in 1938 when they combined, on our instigation, the principle of a constant and an oscillating magnetic field perpendicular to each other with their marvellous molecular beam technique, encouraged us to continue the experiments we had undertaken along a somewhat different line. These experiments again related to nuclear magnetic spins in solids, but as the transfer of absorbed energy to the crystal lattice had appeared to be too slow, they aimed at observing the anomalous dispersion which must occur in the neighbourhood of a spectral line. This anomalous dispersion should lead to a rather sharp jump in the susceptibility (compare Figure 2).

In their publication⁵ Gorter and Broer then refer to equations (1) and (2) to estimate the magnitude of this jump and somewhat glibly pass over the effect of saturation. If the thermal contact between spins and lattice is insufficient and the spin temperature becomes very high due to saturation, χ_0 tends to zero and so does $\Delta\chi$ according to equations (1) and (2). Yet, they must have realized that with increasing saturation the vertical distance between the two extremes of χ in Figure 2 goes to a finite, asymptotic value, although the absorption A vanishes (for a discussion in modern terminology, cf. Abragam¹¹).

The susceptibility experiments by Gorter and Broer were carried out on the ^7Li and ^{19}F nuclei in LiCl and KF polycrystalline powders in which the coil of a resonant circuit operating at 3.7 MHz was embedded. These particular substances were chosen in order to minimize the linewidth δ by keeping the local fields due to the neighboring counterions (Cl or K) small. After preliminary experimentation at the boiling point of nitrogen in the Zeeman Laboratory of the University of Amsterdam, the final experiments were carried out at the Kamerlingh Onnes Laboratory at the boiling points of hydrogen (LiCl and KF) and helium (LiCl).

On the basis of a (realistic) estimate of the linewidth due to Kronig and Bouwkamp,¹² a susceptibility change leading to a frequency shift of the oscillator of ≈ 80 Hz was expected on passing with the magnetic field through resonance in the experiment on LiCl in helium, provided the static susceptibility χ_0 was that predicted by the Langevin formula for a temperature of 4.2 K. However, no shift was detected and it must have

remained smaller than about 1 Hz. Another experiment, carried out at Casimir's suggestion, in which the sample was cooled down from room temperature to 4.2 K in a strong stationary field of 1 T, was equally unsuccessful. The authors concluded that, as in Gorter's earlier calorimetric experiment, the negative result was most likely due to slow spin-lattice relaxation. They wrote:

The time characterizing the establishment of equality between the "nuclear spin temperature" and the lattice temperature would have to be considerably larger than 10^3 seconds at the low temperatures.

It is sad that Gorter came so close to making a great discovery and then gave up. Bloembergen later determined the relaxation time T_1 in the LiCl crystals used by Gorter and Broer, and found $T_1 = 600$ s at 2.1 K. So, if the estimate given in the above quotation was realistic, the authors might have observed a small effect. Although a reasonable knowhow of electron paramagnetic relaxation existed, no quantitative information whatsoever was available on nuclear relaxation, and no one was aware of the effect paramagnetic impurities might have. On the basis of Waller's¹³ theoretical analysis, however, there was every reason to suspect that the Li nuclei in a pure, diamagnetic LiCl crystal would be very slow in coming to thermal equilibrium with the lattice. On considering this dearth of information, the authors might have been well advised to try a few, quite different samples. But hindsight is easy, and the wartime conditions in 1942 were far from conducive to experiments in physics.

Gorter had the advantage of starting his work in the intellectual company of theoretical physicists like Kronig, Casimir, and Kramers, who were all actively interested in problems in magnetism. Together, they had by 1940 arrived at a reasonable understanding of electron paramagnetic relaxation. When, during the later years of World War II further experimentation was out of the question, Gorter gathered his knowledge of the field in a small monograph entitled 'Paramagnetic Relaxation'.¹⁴

In 'My Early Years in NMR, 1946–48', Bloembergen gives a lucid description of the realization of NMR in condensed phase by the groups at Harvard and Stanford in 1945. This, together with the discovery of electron paramagnetic resonance by Zavoiskii¹⁵ and the formulation of the Bloch equations, opened an entirely new door for looking at the mysteries of relaxation processes in ensembles of spins. Gorter's book, therefore, soon became dated. However, his interest in the field by no means waned, as is apparent from Bloembergen's account. For example, he discovered the phenomenon of exchange narrowing and discussed it with Van Vleck.¹⁶ He was also the first to identify cross relaxation ('third relaxation' in Gorter's terminology),¹⁷ a process for which Bloembergen et al.¹⁸ gave a detailed explanation and which constitutes one of the cornerstones of today's pulsed NMR techniques.

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Biographical Sketch

J. H. van der Waals. *b* 1920. Ph.D., 1950 University of Groningen. Research physicist and subsequently Associate Director of Research with Shell, 1946–67; Professor of Physics, University of Leiden, 1967–89. Worked as an undergraduate in C. J. Gorter's laboratory (1941); shared an office with Harden McConnell at Shell Development Co., Emeryville, when the Varian #1 NMR spectrometer arrived (1953–54). Current research interest: study of excited states of molecules, frequently by EPR.

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