JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Magnetism at Low Temperature II

Recent Developments on Spin-Spin Relaxation

C. J. GORTER
Kamerlingh Onnes Laboratory, Leiden
The Netherlands

A review of the field of spin-spin relaxation is given. In connection with experimental work of *Verstelle* some remarks are made on exchange narrowing of the spin-spin relaxation band in DPPH and on the so-called third relaxation in substances with $J>\frac{1}{2}$. Caspers solution of the old controversy between the theories of *Kronig* and *Bouwkamp* and of *Broer* on spin-spin relaxation in large fields is given. Also the nature of *Broer*'s isolated susceptibility is clarified. Data obtained by *Locher* on absorption and dispersion in parallel and perpendicular fields in two copper Tutton salts with differing exchange interactions are given and discussed.

Study at low temperatures of the magnetic response of paramagnetic samples, that obey Curie's law, to oscillating magnetic fields usually reveals the existence of a wide range of frequencies in which the real part of the susceptibility χ' is an almost constant fraction of the static susceptibility χ_0[1]. This region is situated at frequencies well above those where spin-lattice relaxation occurs. In this region the imaginary part χ'' of the susceptibility, often called the absorption coefficient, is much smaller than χ_0 and proportional to the frequency ν. In the early investigations on spin-spin relaxation the determination of the temperature independent coefficient $\rho'=\chi''/\chi_0\nu$ was the main result; $\rho'/2\pi$ was sometimes called the spin-spin relaxation time. In agreement with Waller's theoretical prediction[2], ρ' was in many cases found to be of the order of $\nu_i^{-1}=h/g\beta H_i$, where h is Planck's constant, β is the Bohr magneton, g is Landé's splitting factor and H_i the root mean square dipole-dipole interaction field.

Van Vleck[3] has remarked that the second moment $\int\chi''\nu d\nu$ of the absorption at these and higher frequencies must, in zero field, be equal to $(1/2)\pi\chi_0\nu_i^2$. Since this second moment would diverge for a Debije shape of the absorption $(\chi''/\chi_0=\rho'\nu(1+\rho'^2\nu^2)^{-1})$ the absorption coefficient χ'' must vanish more rapidly at very high frequencies. Often it has been described by a Gauss shape $(\chi''/\chi_0=(\nu/\nu_i)(\pi/2)^{1/2}\exp(-\nu^2/2\nu_i^2))$.

In substances with a strong exchange interaction between the magnetic ions, larger values of ρ' were found indicating a decrease of the effective value of the dipole-dipole field H_i. This led, with the narrowing of the paramagnetic resonance line in transversal fields, to the conception of exchange narrowing[4]. This narrowing should be accompanied by strong deviations from the Gauss shape in the sense of a Lorentz shape for the resonance line in a perpendicular field and in that of a Debije curve for the spin-spin relaxation band in zero field.

In DPPH the narrowing was found to lead to values of 10^{-7} seconds for the order of ρ' while, within the limits of the accuracy, χ''

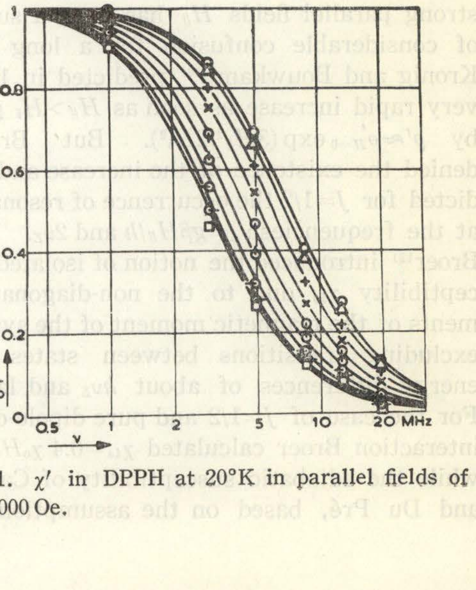

Fig. 1. χ' in DPPH at 20°K in parallel fields of 0-4000 Oe.

and χ' behave according to Debije functions[5]. In agreement with the theoretical prediction ρ' is of the order of ν_e/ν_t^{-2} where ν_e represents the exchange frequency. It is found to increase by a factor of about 2.5 in a parallel field which is still considerably below $h\nu_e/g\beta$. This increase might be connected with Anderson's factor 10/3[6].

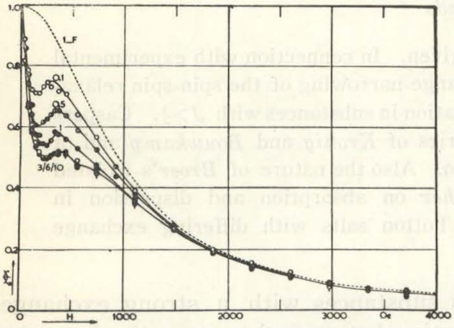

Fig. 2. χ'/χ_0 in $Cr_{0.05}Al_{0.95}K(SO_4)_2.12H_2O$ as a function of the parallel field at frequencies from 0.1-10 MHz. The dotted line follows from Casimir and Du Pré's formalism.

In salts with $J>1/2$, in which the electrical splitting of the basic levels is at least of the order of the dipole-dipole interaction $h\nu_t$, a phenomenon sometimes called third relaxation is observed[7),8]. This phenomenon can be considered as a special kind of spin-spin relaxation and might be attributed to simultaneous transitions in neighbouring magnetic ions which energetically almost compensates each other (one of the processes classified by Bloembergen as cross relaxation[9]).

The behaviour of spin-spin relaxation in strong parallel fields $H_{/\!/}$ has been a subject of considerable confusion for a long time. Kronig and Bouwkamp[10] predicted in 1938 a very rapid increase as soon as $H_{/\!/}>H_t$ given by $\rho'\approx\rho'_{H=0}\exp(3H_{/\!/}^2/2H_t^2)$. But Broer[11] denied the existence of the increase and predicted for $J=1/2$ the occurrence of resonances at the frequencies $\nu_L=g\beta H_{/\!/}/h$ and $2\nu_L$. Later Broer[12] introduced the notion of isolated susceptibility χ_{is} due to the non-diagonal elements of the magnetic moment of the system, excluding transitions between states with energy differences of about $h\nu_L$ and larger. For the case of $J=1/2$ and pure dipole-dipole interaction Broer calculated $\chi_{is}=0.4\,\chi_0H_t^2/H_{/\!/}^2$ while the adiabatic susceptibility of Casimir and Du Pré, based on the assumption that the system of spins remains at every moment practically in internal equilibrium, is for this case $\chi_{ad}=0.5\chi_0H_t^2/H_{/\!/}^2$. In spite of the contributions of other theoreticians[13] on the nature of this difference it remained obscure. Recently these questions have been cleared up by experimental investigations of Verstelle and Locher[8),14] and theoretical work of

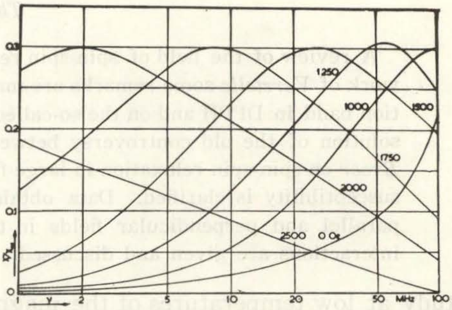

Fig. 3. χ''/χ_{ad} in $Cu(NH_4)_2(SO_4)_2.6H_2O$ in different parallel fields as a function of the frequency (logarithmic scale).

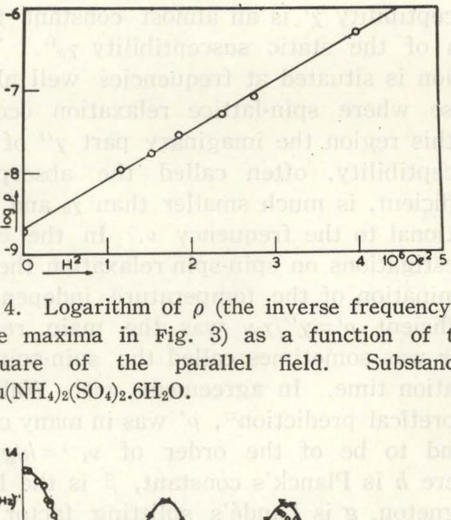

Fig. 4. Logarithm of ρ (the inverse frequency of the maxima in Fig. 3) as a function of the square of the parallel field. Substance: $Cu(NH_4)_2(SO_4)_2.6H_2O$.

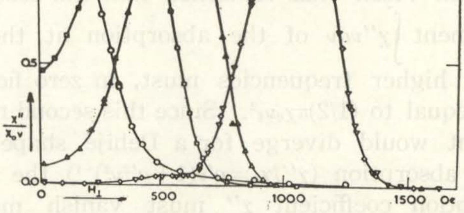

Fig. 5. $\chi''/\chi_0\nu$ in $CuCs_2(SO_4)_2.6H_2O$ as a function of the perpendicular field at the frequencies of 0.41, 1.21, 1.76 and 3.18 GHz.

Caspers[15].

It was observed in a number of salts that an absorption band shifts rapidly in high fields towards low frequencies, the character of the displacement resembling that predicted by Kronig and Bouwkamp, though in substances with little exchange interaction the band is only weak and the shift not quite so rapid as was predicted. But Broer's two parallel resonances for $J=1/2$ have also been observed at much higher frequencies.

Thus, with increasing frequency, χ' decreases in several steps from χ_{ad} to zero. For $J=1/2$ there are three steps: one due to the Kronig-Bouwkamp relaxation and two due to the Broer resonances.

According to Caspers' analysis the only meaning of χ_{is} is that it gives the value of χ' in the frequency interval between the Kronig-Bouwkamp relaxation and the different resonances in case that interval is sufficiently wide. In case of pure dipole-dipole interaction and $J=1/2$ where, in agreement with Broer's calculation $\chi_{is=(4/5)\chi_{ad}}\int\chi'' d\ln\nu$ over the Kronig-Bouwkamp band should be 1/4 of that integral over the two resonance bands. Exchange interaction should lead to a decrease of χ_{is} and to a strengthened Kronig-Bouwkamp and weakened resonance bands.

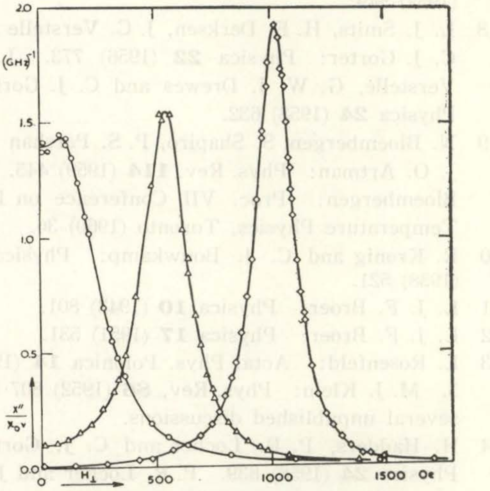

Fig. 6. $\chi''/\chi_0\nu$ in $Cu(NH_4)_2(SO_4)_2.6H_2O$ as a function of the perpendicular field at frequencies of 0.41, 1.76 and 3.18 GHz.

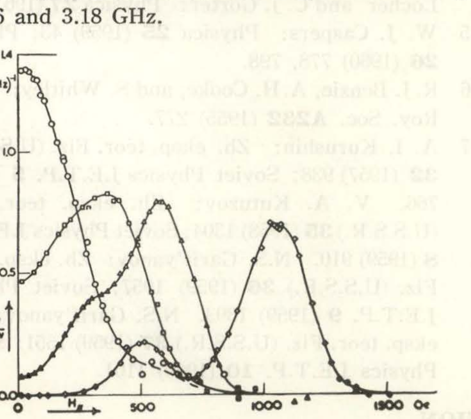

Fig. 7. $\chi''/\chi_{ad}\nu$ in $CuCs_2(SO_4)_2.6H_2O$ as a function of the parallel field. The same frequencies as Fig. 5.

Caspers' predictions have been tested[14] in the two powdered Tutton salts $CuCs_2(SO_4)_2\cdot 6H_2O$ and $Cu(NH_4)_2(SO_4)_2\cdot 6H_2O$. It was known from the work of Benzie and Cooke[16] that the exchange is small in the CuCs salt but that it is considerably larger than the dipole-dipole interaction in the $CuNH_4$ salt. The diagrams 5, 6, 7 and 8 give some results of Locher obtained between 0.4 and 3.2 GHz. In fig. 9 containing also Verstelle's results the three bands are clearly visible. General agreement with the theory is found. The ratio of the intensities of the two re-

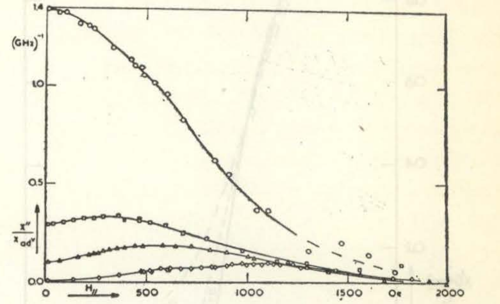

Fig. 8. $\chi''/\chi_{ad}\nu$ in $Cu(NH_4)_2(SO_4)_2\cdot 6H_2O$ as a function of the parallel field. The same frequencies as Fig. 5.

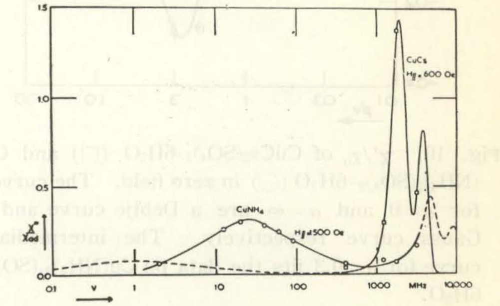

Fig. 9. χ''/χ_{ad} of $CuCs_2(SO_4)_2\cdot 6H_2O$ and $Cu(NH_4)_2(SO_4)_2\cdot 6H_20$ in parallel fields of respectively 600 and 1500 oersteds as a function of the frequency (logarithmic scale).

sonance bands depends theoretically on the hyperfine structure which is of the same order of magnitude as the dipole-dipole interaction. Also for this reasonable agreement with theory is found. Several separate less simple results did not yet find adequate theoretical discussion[17)].

For the same Cu Tutton salts the absorption χ'' has been studied in perpendicular fields and χ' as well as χ'' in zero field. In perpendicular fields marked exchange narrowing is observed in the $CuNH_4$ salt while a line at the double paramagnetic resonance frequency (half the resonance field at constant frequency) is observed in the CuCs salt. In zero field the absorption and dispersion are found to have a Lorentz character in the $CuNH_4$ salt while in the CuCs salt it is a more Gauss like shape with a peak of χ'' that is considerably higher than $\chi_0/2$ and negative χ' values at frequencies above ν_i. A proposed intermediate formula describes the shapes in zero field satisfactorily for the $CuNH_4$ salt.

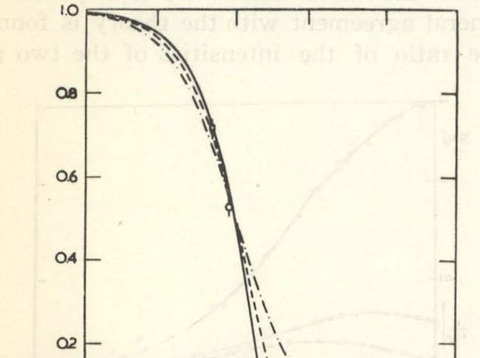

Fig. 10. χ'/χ_0 of $CuCs_2(SO_4)_2\cdot 6H_2O$ (□) and $Cu(NH_4)_2(SO_4)_2\cdot 6H_2O$ (○) in zero field. The curves for $\alpha=0$ and $\alpha=\infty$ are a Debije curve and a Gauss curve respectively. The intermediate curve for $\alpha=0.3$ fits the data on $Cu(NH_4)_2.(SO)_2.6H_2O$.

References

1 C. J. Gorter: Paramagnetic Relaxation, Elsevier (1947); Progress in Low Temperature Physics II, Ch. XI (1957).

2 I. Waller: Z. Phys. **79** (1932) 370.

3 J. H. Van Vleck: J. Chem. Phys. **5** (1938) 320; Nuovo Cimento, X, VI, Suppl. (1957) 1081. L. J. F. Broer: Physica **10** (1943) 801.

4 C. J. Gorter and J. H. Van Vleck: Phys. Rev. **74** (1948) 1168; J. H. Van Vleck: Phys. Rev. **72** (1947) 1128.

5 J. C. Verstelle, G. W. J. Drewes and C. J. Gorter: Physica **26** (1960) 520.

6 P. W. Anderson and P. R. Weiss: Rev. Mod. Phys. **25** (1953) 269. P. W. Anderson: J. Phys. Soc. Japan **9** (1954) 316. R. Kubo and K. Tomita: Proc. Phys. Soc. Japan **9** (1954) 888.

7 F. W. De Vrijer and C. J. Gorter: Physica **18** (1952) 549.

8 L. J. Smits, H. E. Derksen, J. C. Verstelle and C. J. Gorter: Physica **22** (1956) 773. J. C. Verstelle, G. W. J. Drewes and C. J. Gorter: Physica **24** (1958) 632.

9 N. Bloembergen, S. Shapiro, P. S. Pershan and J. O. Artman: Phys. Rev. **114** (1959) 445. N. Bloembergen: Proc. VII Conference on Low Temperature Physics, Toronto (1960) 36.

10 R. Kronig and C. J. Bouwkamp: Physica **5** (1938) 521.

11 L. J. F. Broer: Physica **10** (1943) 801.

12 L. J. F. Broer: Physica **17** (1951) 531.

13 L. Rosenfeld: Acta. Phys. Polonica **14** (1955) 3. M. J. Klein: Phys. Rev, **86** (1952) 807 and several unpublished discussions.

14 H. Hadders, P. R. Locher and C. J. Gorter: Physica **24** (1958) 839. P. R, Locher and J. C. Verstelle: Proc. VII Conference on Low Temperature physics, Toronto (1960) 56. P. R. Locher and C. J. Gorter: Physica **27** (1961) 997.

15 W. J. Caspers: Physica **25** (1959) 43; Physica **26** (1960) 778, 798.

16 R. J. Benzie, A. H. Cooke, and S. Whitley: Proc. Roy. Soc. **A232** (1955) 277.

17 A. I. Kurushin: Zh. eksp. teor. Fiz. (U.S.S.R.) **32** (1957) 938; Soviet Physics J.E.T.P. **5** (1957) 766. V. A. Kutuzov: Zh. eksp. teor. Fiz. (U.S.S.R.) **35** (1958) 1304; Soviet Physics J.E.T.P. **8** (1959) 910. N.S. Garif'yanov: Zh. eksp. teor. Fiz. (U,S.S.R.) **36** (1959) 1957; Soviet Physics J.E.T.P. **9** (1959) 1393. N.S. Garif'yanov: Zh. eksp. teor. Fiz. (U.S.S.R.) **37** (1959) 1551; Soviet Physics J.E.T.P. **10** (1960) 1101.

DISCUSSION

J. H. VAN VLECK: I might mention that the effect calculated by Broer at low frequencies is presumably actually present, but the difficulty is that it is not the main effect, as it is concerned essentially with a satellite zero-frequency line, and so has not been observed, as it is masked by the main decay phenomenon of Kronig and Bouwkamp.

C. J. Gorter: Indeed, in the pure dipole-dipole case with $S=1/2$ the difference between χ_{ad} and Broer's χ_{is} which is due to the satellite zero-frequency band is 20%. 80% goes to Broer's bands at the Larmor and the double Larmor frequencies.

A. H. Cooke: Do I understand that the line shape has been measured in the case where exchange narrowing occurs, and that it is not Gaussian?

C. J. Gorter: Yes, the $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ presents an example. A better example is DPPH where the exchange is relatively larger.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

The Splitting of the NMR Lines in Vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$

N. J. POULIS AND W. VAN DER LUGT
Kamerlingh Onnes Laboratorium, Leiden
The Netherlands

Nuclear magnetic resonance diagrams of the protons as well as phosphorus nuclei were determined in vivianite at temperatures between 1°K and 77°K. Vivianite becomes antiferromagnetic at a temperature between 4°K and 11°K. The phosphorus nuclei exhibit an isotropic shift. There are two types of Fe^{++} ions with a different magnetic behaviour.

Resonance diagrams with an external field rotating in the *ac* plane and in a plane perpendicular to the *c*-axis were obtained. The crystal of vivianite is monoclinic, the *ac* plane is a reflection plane. Thus, if the external field H_0 is rotated parallel to the *ac* plane the number of resonance lines found is half of that found for H_0 rotating in a plane perpendicular to the *c*-axis, in the paramagnetic state as well as in the antiferromagnetic state.

The diagrams show that the crystal is paramagnetic at liquid hydrogen temperatures and antiferromagnetic at liquid He temperatures. The resonance of the phosphorus nuclei exhibit apart from the anisotropic shift also an isotropic shift towards higher frequencies. The isotropic shift must be due to the interaction with an amount of magnetic spin moment transferred from the Fe^{++} ions to the phosphorus atoms. The temperature dependence of the splitting of the lines in the paramagnetic state is not the same for all nuclei. Two types of nuclei can be distinguished, the splittings of the first group having a much larger dependence on temperature than the splitting of the other group (Fig. 1). At liquid He temperatures the crystal is antiferromagnetic. Sixteen lines were found for $H_0 \perp c$ axis (Fig. 2). The internal fields at the position of the nuclei were measured without the use of an external field. Also here two types of temperature

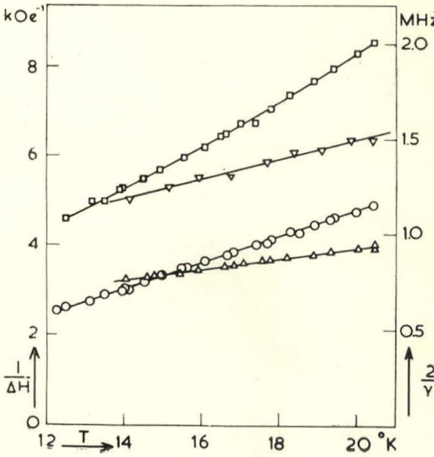

Fig. 1.