Observations on Antiferromagnetic $CuCl_2 \cdot 2H_2O$ Crystals

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Four series of observations carried out in the Kamerlingh Onnes Laboratory on $CuCl_2 \cdot 2H_2O$ crystals are reviewed. The magnetization curves confirm the general picture given by the theoretical analysis of Gorter and Haantjes. At the lower temperature a sharp threshold field is found in the crystallographic *ac* plane with a minimum value of 6500 ϕ; at higher temperature its value increases somewhat.

Specific heat measurements reveal the existence of a short-range order tail above the sharp Néel temperature at which antiferromagnetism vanishes.

In the investigations on proton magnetic resonance a sharp transition is found between a nonsymmetrical paramagnetic resonance diagram and a symmetrical resonance diagram characteristic for antiferromagnetism. In this way it is found that the Néel temperature depends on the direction of the magnetizations.

It is possible to follow the turn-over of the magnetizations near the threshold field. The position of the protons and the nature of the sublattices have been determined. The sublattices do not exchange position within 10^{-4} sec. Microwave resonances have been observed at 9400 and at 4000 megacycles/sec. The absorption bands are confined to the neighborhood of the turn-over fields. General agreement with Ubbink's theoretical treatment is found.

INTRODUCTORY REMARKS

IN this review paper the chief results are given of four different kinds of investigations carried out by four teams of workers in the Kamerlingh Onnes Laboratory. On the whole the results are in agreement with the phenomenological theory described in another review paper.[1]

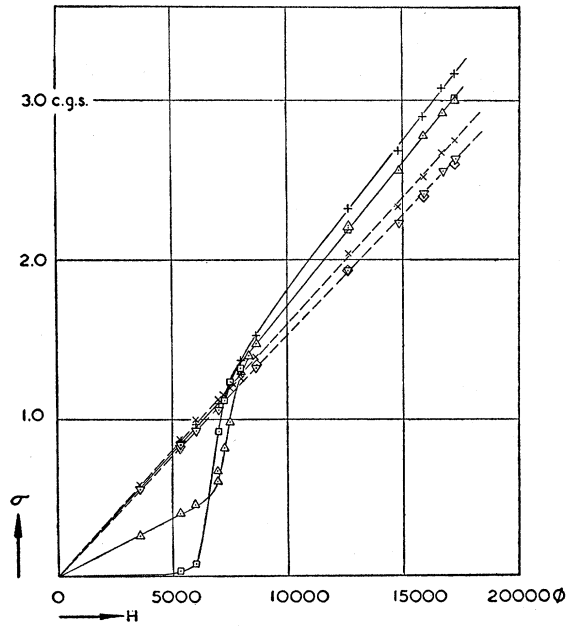

FIG. 1. Magnetization σ as a function of the field H. +4.1° K; field in the direction of the a axis. × 4.1°K; field in the direction of the b axis. △ 3.02°K; field in the direction of the a axis. ▽3.02°K; field in the direction of the b axis. ⊡ 1.57°K; field in the direction of the a axis. ◊ .57°K; field in the direction of the b axis.

They are presented as tests and confirmations of that theory which is presumed to be known. The historical order, however, was different: Many of the essential results had been collected before the theory in its present form had been set up, although at a later phase it was helpful in the classification of the data. For full details I refer to the original papers, which appeared in the Communications from the Kamerlingh Onnes Laboratory and in *Physica*.

MAGNETIZATION

By the usual Faraday method for the measurements of the magnetization parallel to a magnetic field,

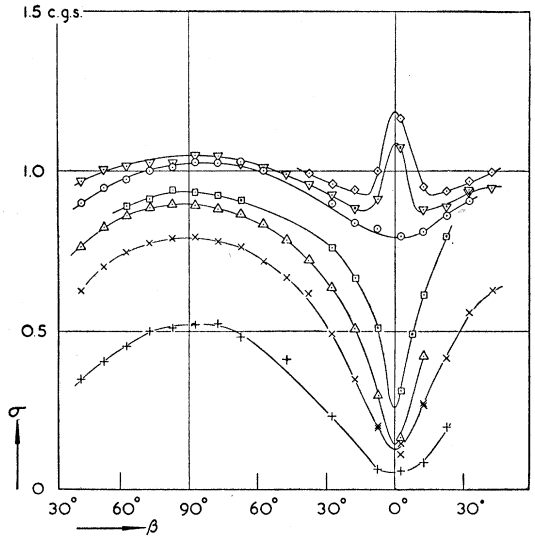

FIG. 2. Magnetization σ when the field H lies in the ab plane as a function of the angle between H and the a axis. Temperature 2.1°K. + $H=3600\ \phi$. × $H=5300\ \phi$. △ $H=6000\ \phi$. ⊡ $H=6300\ \phi$. ⊙ $H=7000\ \phi$. ▽ $H=7250\ \phi$. ◊ $H=7450\ \phi$.

[1] C. J. Gorter, Revs. Modern Phys. **25**, 277 (1953).

Handel, Gijsman, and Poulis[2] investigated the hydrated copper chloride in the crystallographic *ab*, *ac*, and *bc* planes.[1] Between room temperature and the lowest liquid hydrogen temperatures the susceptibility χ follows the Curie-Weiss law,

$$\chi=\sigma/H=Ng^2\mu_B^2/k(T-\theta),$$

where μ_B is the Bohr magneton and k is Boltzmann's constant. g is found to be 2.19, 2.05, and 2.25 in the crystallographic *a*, *b*, and *c* directions, respectively, while $\theta=5°$K.

At the lowest liquid helium temperatures (1.57°K), however, the magnetization remains very small when a field in the *a* direction up to 6500 ϕ is applied (Fig. 1). Then, in an interval of a few hundred oersted, the magnetization increases steeply. At still stronger fields the magnetization is simply proportional to the field strength. In the *b* and *c* directions the magnetization is proportional to the field at all field strengths used.

The three field independent susceptibilities are found to be approximately proportional to the squares of the three *g* factors just mentioned. This indicates that the antiferromagnetic exchange energy ($-\frac{1}{2}\alpha\mu^2$) is about 5×10^{-16} erg/ion and that its anisotropy is not higher than 1 percent.

It is clear that the threshold field at 6500 ϕ can be identified with the turn-over field discussed in reference 1. This leads to the result that the exchange energy, when the magnetizations in the sublattices are in the $\pm a$ directions, is 0.2 percent lower than in the $\pm b$ directions. When a constant field is rotated in the *ab* plane (Fig. 2), the susceptibility has a sharp minimum in the *a* direction, which, in agreement with the theoretical formulas, goes over into a narrow and small maximum at the threshold field strength. In the *ac* plane (Fig. 3), however, the corresponding curves at fields above 6500 ϕ consist of two clearly distinct parts. Near the *a* axis a platform develops which is separated by a steep fall from a region where the magnetization behaves as if the threshold field had not yet been reached. Obviously the steep fall indicates the position of the hyperbola in the field space which separates the regions where the magnetizations in the sublattices remain in the *ac* plane from those where they have been turned over into the $\pm b$ directions. The shape of the hyperbola

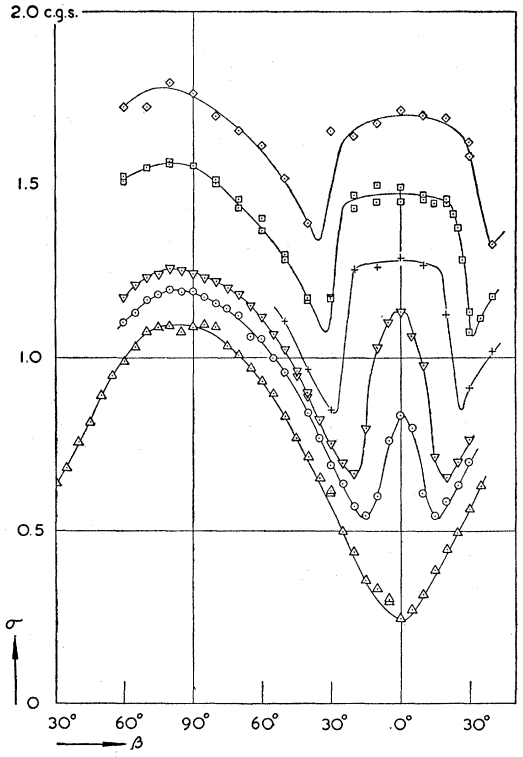

FIG. 3. Magnetization σ when the field H lies in the *ac* plane as a function of the angle between H and the *a* axis. Temperature 2.1°K. △ $H=5660\ \phi$. ⊙ $H=6640\ \phi$. ▽ $H=6880\ \phi$. + $H=7560\ \phi$. ⊡ $H=8175\ \phi$. ◇ $H=9225\ \phi$.

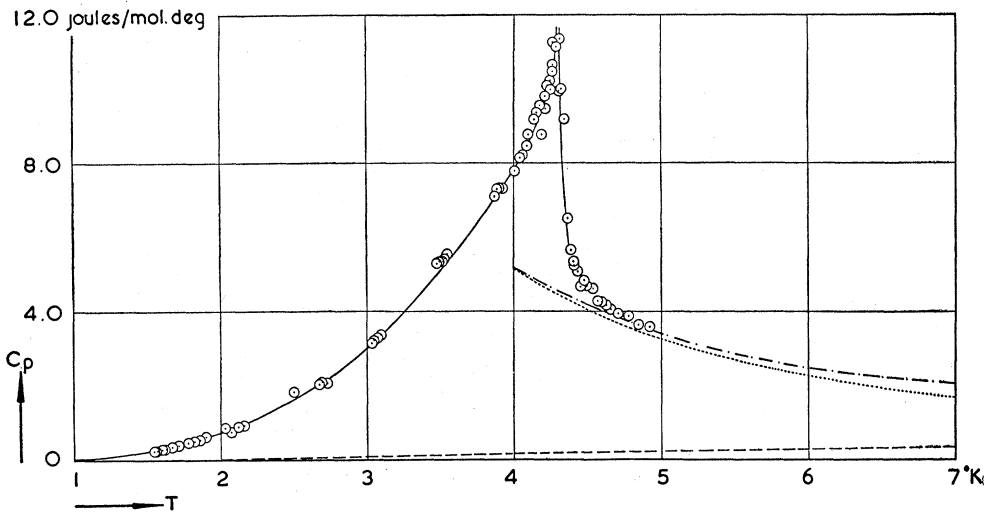

FIG. 4. Specific heat C_p as a function of temperature T. — — — specific heat caused by lattice waves. · · · · · tail caused by disappearing short-range order. —·—·—·sum of tail and lattice specific heat.

[2] Handel, Gijsman, and Poulis, Leiden Comm. 290c.

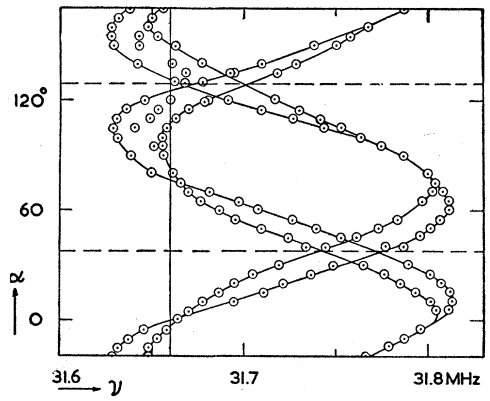

FIG. 5. Resonance diagram in the paramagnetic state. Proton magnetic resonance frequencies as a function of the angle in the *ab* plane. $T=14.3°K$; $H=7460$ ϕ.

indicates that the exchange in the $\pm c$ directions is again 0.8 percent higher than that in the $\pm b$ directions.

When the temperature increases, the low-field susceptibility in the *a* direction varies in the way predicted by Van Vleck.[3] The threshold field increases somewhat.

SPECIFIC HEAT

Dr. S. A. Friedberg has measured the specific heat.[4] It shows a lambda-anomaly with a steep fall at 4.3°K (Fig. 4) marking the Néel temperature θ_n. It is noteworthy that $-\frac{1}{2}k\theta_n$ is only about $\frac{2}{3}$ of the exchange energy as determined from the susceptibilities. At the high temperature side the specific heat has a tail which is approximately proportional to T^{-2}. In this tail apparently the short-range order disappears gradually. Below θ_n an entropy of about $0.40R$ is contained, while it is evaluated that the tail contains $0.25R$. Thus, the sum is not much smaller than the theoretical entropy value $R\ln 2=0.69R$.

According to Van Vleck's theoretical treatment, the exchange specific heat at high temperatures should be $3\alpha^2\mu^4/2zRT^2$, where z indicates the number of interacting antiferromagnetic neighbors.[5] This would lead to $z=3$ or $z=7$ depending on whether $\alpha\mu^2$ is deduced from θ_n and θ or from the susceptibilities in the antiferromagnetic region.

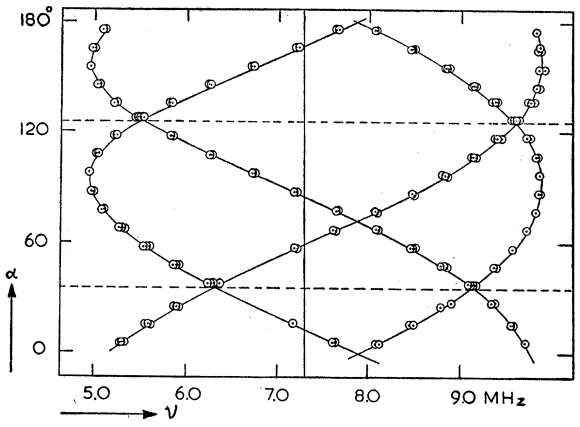

FIG. 6. Resonance diagram in the antiferromagnetic state below the threshold field H_c. *ab* plane; $T=3.03°K$; $H=1705$ ϕ.

PROTON MAGNETIC RESONANCE

Poulis, Hardeman, and Bölger[6] have carried out elaborate investigations on the proton magnetic resonance. The observation of the frequency at which the nuclear magnetic resonance occurs gives a very accurate determination of the average local magnetic field at the spot where the nucleus happens to be located. Bloembergen discovered in the paramagneiic $CuSO_4\cdot 5H_2O$ that, when at low temperatures the average magnetization of the copper ions in the external field becomes large, the average local field may differ considerably from the external field. The observed splittings of the proton line are proportional to the external field and approximately inversely proportional to the temperature.

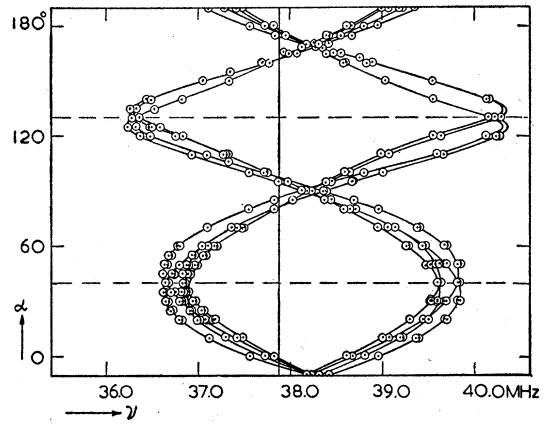

FIG. 7. Resonance diagram in the antiferromagnetic state above the threshold field H_c. *ab* plane; $T=3.02°K$; $H=8920$ ϕ.

$CuCl_2\cdot 2H_2O$ behaves similarly in the liquid hydrogen region, but at the lowest helium temperatures Poulis *et al.* found a very different kind of resonance diagram. The general width of the structure is independent of the temperature and of the external field, and a marked symmetry in the resonance diagram indicates that to every proton experiencing a certain field due to the copper ions there is another proton that feels an exactly opposite field. It was this observation which constituted the starting point of all the other observations on $CuCl_2\cdot 2H_2O$.

[3] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).
[4] S. A. Friedberg, Leiden Comm. 289[d].
[5] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).
[6] N. J. Poulis and G. E. G. Hardeman. Leiden Comm. 287[a], Physica **18**, 201 (1952); Leiden Comm. 288[b], Physica **18**, 315 (1952). Poulis, Hardeman, and Bölger, Leiden Comm. 289[a], Physica **18**, 429 (1952).

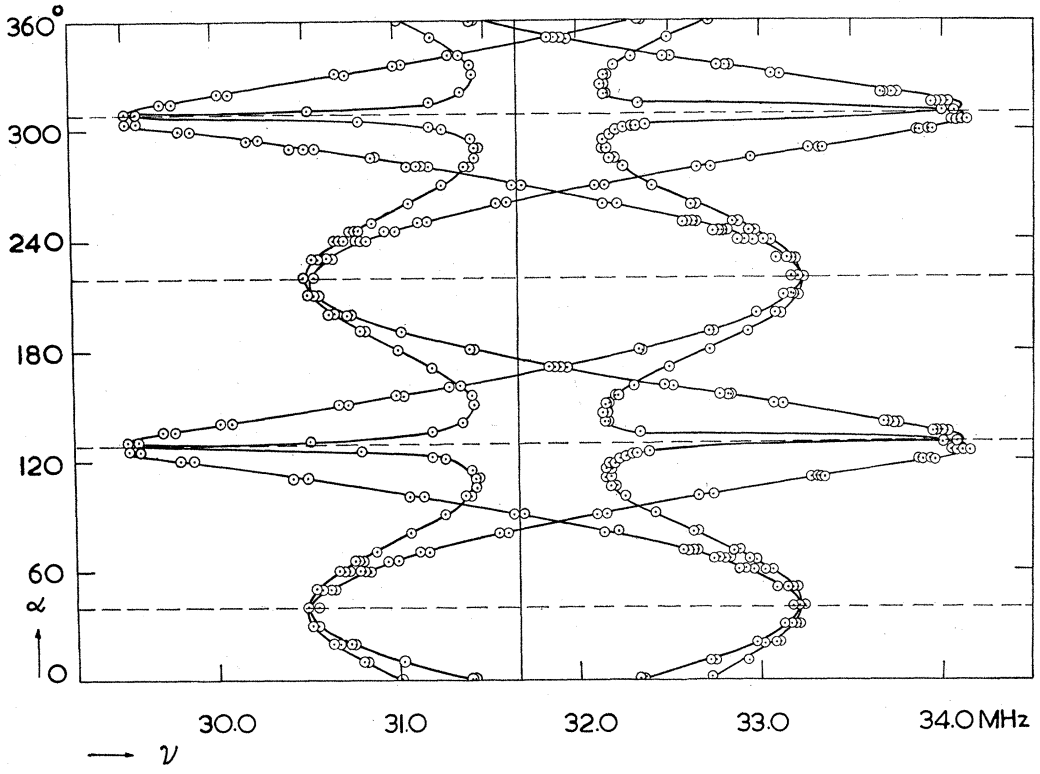

FIG. 8. Resonance diagram in antiferromagnetic state just blow the threshold field H_c. ab plane, $T=3.47°K$; $H=7460\ \phi$.

Below the threshold field the resonance diagram has a period of 360°, since the magnetizations in the two sublattices then remain in the neighborhood of the $\pm a$ directions. Above the threshold field, however, the magnetizations remain approximately perpendicular to the field.

After a rotation of 180° the magnetizations have also rotated over 180°, thus the relative orientation is the same; hence, the period of 180° in the diagram (Fig. 5).

Near the threshold field the resonance diagrams are complicated, and it is possible to follow the turning over of the magnetizations in detail.

It was not easy to find satisfactory locations for the protons and to divide the crystalline lattice in sublattices in a way that accounts for the many data in the paramagnetic as well as in the antiferromagnetic state. By trial and error a satisfactory arrangement was finally

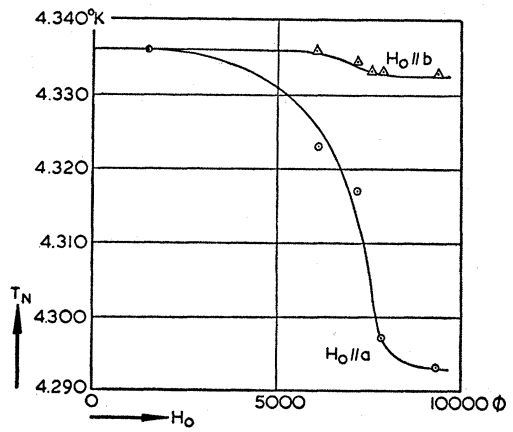

FIG. 9. Temperature at which the antiferromagnetic diagram is transformed into a paramagnetic resonance diagram as a function of a field in the a direction (⊙) and in the b direction (△).

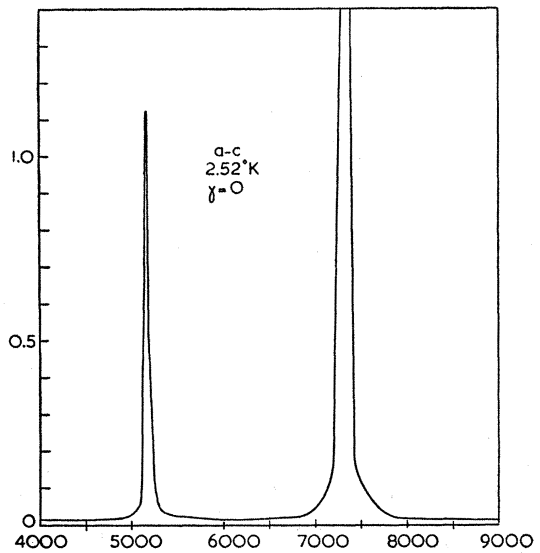

FIG. 10. Antiferromagnetic resonance absorption in arbitrary units as a function of a field in the a direction. $T=2.52°K$; 9400 megacycles/sec.

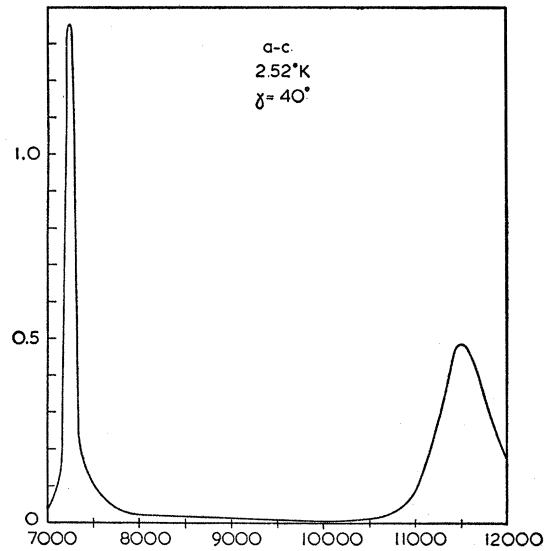

FIG. 11. Antiferromagnetic resonance absorption in arbitrary units as a function of a field making an angle of 40° in the *ac* plane with the *a* direction. 9400 megacycles/sec.

found in which successive copper layers parallel to the crystallographic *ab* plane have alternating spin-orientations. The narrowness of the resonance lines proves that the sublattices cannot exchange positions within 10^{-4} sec.

When the temperature increases, the width of the pattern of splittings decreases. This is obviously due to a decrease of the spontaneous magnetization on the sublattices. The dependence of this spontaneous magnetization, thus found, agrees up to about 4°K with that to be expected from Néel's theory with $S=\frac{1}{2}$ and $\theta_n=4.5$°K. Above 4°K, however, the spontaneous magnetization decreases much more rapidly. This behavior is rather similar to that of ferromagnetics.

The change from the antiferromagnetic to the paramagnetic pattern is quite abrupt. In a small external field, which leaves the magnetization near the favorable $\pm a$ direction, the change occurs at 4.33°C.

When, however, a field above the threshold field is applied in the *a* direction which turns the magnetizations over to the $\pm b$ directions, this Néel temperature decreases to 4.29°K.

The ratio of the width of the pattern at 4.4°K and at 15°K is only about 1.4, while theoretically $(15+5)/(4.4+5)=2.13$ should be expected. This, and the similar anomaly encountered in the susecptibilities, is connected with the two different values of the exchange energy.

ANTIFERROMAGNETIC RESONANCE

The antiferromagnetic resonance was studied at the frequency of 9400 MHz by Ubbink, Poulis, and Gerritsen.[7] A few experiments were also carried out at 4000 MHz. In general, it may be said that absorption has been observed in the neighborhood of the threshold hyperbola in the *ac* plane and that all results are in good agreement with Ubbink's theory (Figs. 6–12). When the constant field is situated in the *ac* plane, one absorption

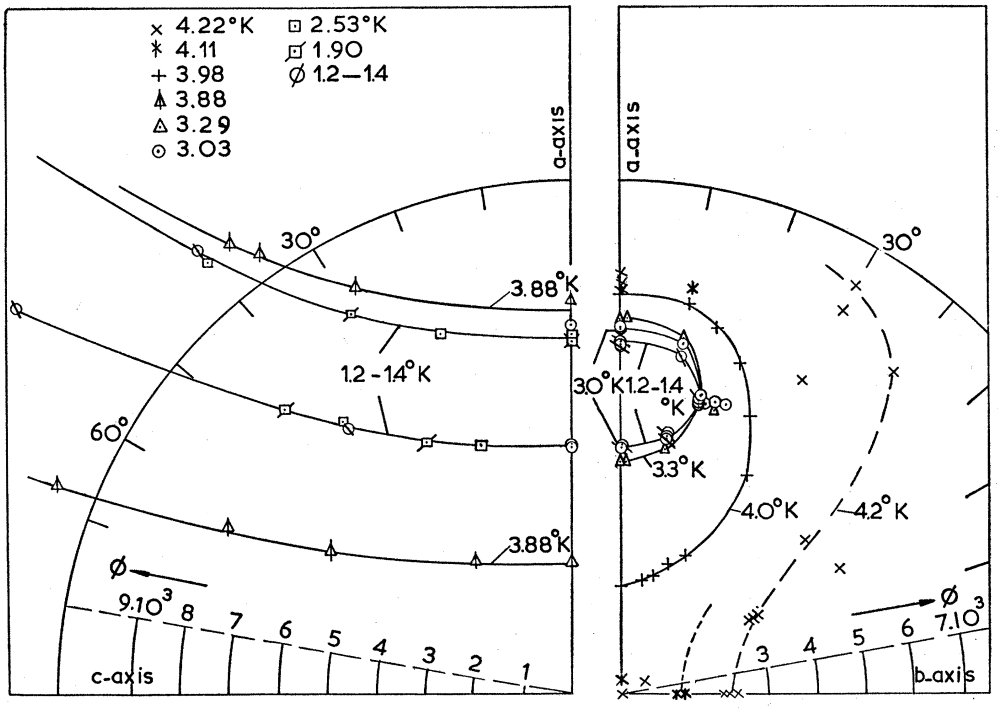

FIG. 12. Polar diagrams of the position of the resonance magnetic fields at 9400 megacycles/sec. Left-hand side: field in the *ac* plane. Right-hand side: field in the *ab* plane.

[7] Ubbink, Poulis, Gerritsen, and Gorter, Leiden Comm. 288[d], Physica 18, 361 (1952).

band is observed slightly below the threshold field and one slightly above it. When the constant field is situated in the *ab* plane, the two bands approach each other, merge, and vanish if the angle with the *a* axis increases.

The high frequency susceptibility increases anomalously at the low-field side of the lower band and not at the high-field side as it otherwise does. This is in agreement with the theoretical expectations.

DISCUSSION

M. LAX, *Syracuse University, Syracuse, New York:* It is not surprising, as Professor Gorter points out, that a deviation occurs from the Curie-Weiss law just above the Curie temperature, and that this deviation is not adequately explained by the classical molecular field theory. The deviation from the Curie-Weiss law originates in fluctuations of spin orientation that are neglected in the usual molecular field treatment. The spherical model which includes these fluctuations yields a molecular field coefficient that varies with temperature above the Curie temperature and thus can account qualitatively for the observed deviations.

F. KEFFER, *University of Pittsburgh, Pittsburgh, Pennsylvania.*

Mr. J. Kaplan has made an Ewald-Kornfeld calculation of the magnetic dipole field factors. By using these and anisotropy of the g factors, he finds a 1300-oersted anisotropic field between preferred and next-preferred axis, 12 oersted between preferred and third axis. This is clearly wrong.

Professor Kittel suggested using pseudo-dipole coupling between the exchange-coupled spins. This gives a dipole-like factor of order $J(g\text{-}2)^2$. By using this and the anisotropy of the g factors and adding to Kaplan's calculation, we find 500-oersted anisotropic field between preferred and next-preferred axis and 1000 oersted between preferred and third axis. This is in agreement as to order of size and direction as measured by Professor Gorter's group.