PHYSICAL REVIEW B VOLUME 7, NUMBER 3 1 FEBRUARY 1973

Hydrostatic-Pressure Study of Antiferromagnetic Resonance in $FeCl_2$[†]

K. C. Johnson* and A. J. Sievers
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 10 July 1972)

The magnetic behavior accompanying the structural phase change in $FeCl_2$ near 2 kbar has been studied by measurements of the frequency shift of the far-infrared-active antiferromagnetic-resonance mode as a function of applied pressure.

INTRODUCTION

The layered antiferromagnetic crystal $FeCl_2$ has attracted interest chiefly because it exhibits the property of metamagnetism[1]; that is, as an applied magnetic field exceeds a critical field H_c the total magnetization abruptly changes from the near-zero value of an antiferromagnet to the large value typical of a ferromagnetic crystal. $FeCl_2$ is also of interest to workers in the area of high-pressure magnetic studies because it undergoes a structural phase change at the easily attained pressure of 2 kbar.[2] The purpose of the present work has been to study the magnetic behavior of $FeCl_2$ as it realigns structurally by measuring the frequency shift of the far-infrared-active antiferromagnetic-resonance mode as a function of applied hydrostatic pressure.

$FeCl_2$ has a hexagonal layered structure of the $CdCl_2$ lattice type, which is equivalent to a cubic close packing of the layers. The structure may be viewed as a stacking along the trigonal axis of an NaCl-like structure which has alternate layers of cations removed; that is, successive layers of Fe^{2+} ions are separated by two layers of anions. Within a layer the Fe^{2+} ions are coupled ferromagnetically by an exchange constant $2J_1 = -5.5\ \mathrm{cm}^{-1}$, while successive layers are coupled by the much weaker intersublattice exchange term $2J_2 = 0.24\ \mathrm{cm}^{-1}$ (with the convention that antiferromagnetic exchange is positive).[3] In zero applied field the alternate layers align antiferromagnetically, with the preferred spin direction along the [0001] hexagonal axis.[4]

EXPERIMENTS

A far-infrared-active mode attributed to the antiferromagnetic resonance (AFMR) in $FeCl_2$ was observed by Jacobs, Roberts, and Lawrence at $16.5\ \mathrm{cm}^{-1}$ at 4.2 °K.[5] The resonance frequency has the form

$$\omega_{\mathrm{AFMR}} = [H_A(H_A + 2H_E)]^{1/2} ,$$

where H_A and H_E are effective anisotropy and exchange fields, and only J_2 (the intersublattice exchange) contributes to H_E. The significance of H_A will be discussed in more detail below. H_E can be determined quite accurately because it is just equal to the field H_c at which the metamagnetic phase transition occurs. Susceptibility measurements[2] have established that $H_c = H_E = 10.9$ Kg $= 2.1\ \mathrm{cm}^{-1}$ (where the energy equivalent is for $g_{\parallel} = 4.1$). Hence $H_A \gg H_E$ and

$$\omega_{\mathrm{AFMR}} \approx H_A + H_E ,$$

where $H_A \approx 15\ \mathrm{cm}^{-1}$.

Our measurements of the AFMR were made on a 0.75-mm thick pressed-powder sample of $FeCl_2$. The experiments were performed using far-infrared-transmission techniques with a lamellar interferometer and a He^3-cooled doped-germanium-bolometer detector.[6] The sample was compressed by applied pressures up to 7.1 kbar and was usually held at 4.2 °K, although temperature control up to 40 °K could be maintained.[7] Measurements were made at the highest pressure first, with pressures always decreased. In order to change pressures it was necessary to heat the sample cell above the melting temperature of the solid helium (to about 60 °K) and release gas through an external valve. Hence the sample was always heated above its magnetic ordering temperature during a pressure change. An additional zero-pressure point was obtained in a later run on a new sample of length 2 mm which had not been pressure cycled; no difference in the zero-pressure AFMR frequency was detected between cycled and uncycled samples.

The frequency of the AFMR at 4.2 °K as a function of pressure is given in Fig. 1. A distinct difference between the measured zero-pressure frequency and the value obtained by extrapolating from the high-pressure region is observed. The difference is attributed to the effect of the structural transition from $CdCl_2$ (cubic-close-packed) to CdI_2 (hexagonal-close-packed) structure on the magnetic properties of the crystal. This phase change was observed by Narath and Schirber at about 2 kbar[2]; our data are consistent with this value, although no points could be taken between 0 and 1.5 kbar owing to failure of the cell-window pressure seals.

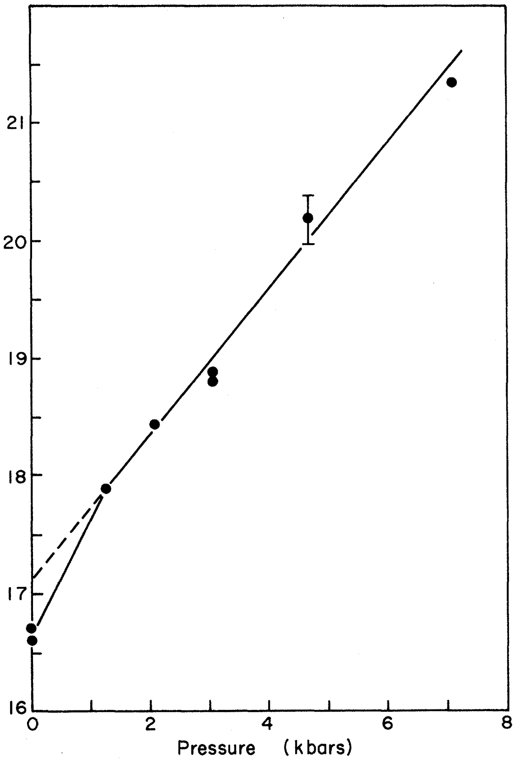

FIG. 1. Pressure dependence of the AFMR frequency in $FeCl_2$.

The pressure dependence of the AFMR frequency may be expressed in the form

$$\frac{d\omega_{AFMR}}{dP} = \frac{H_A}{\omega_{AFMR}} \frac{d\ln H_A}{dP} + \frac{H_E}{\omega_{AFMR}} \frac{d\ln H_E}{dP} .$$

The value of $d\ln H_E/dP$ was determined previously from critical-field measurements[2]; for $P > 2$ kbar, $d\ln H_E/dP = 0.069 \pm 0.005$ kbar^{-1}. By subtracting the critical-field results from the resonance data the behavior of the anisotropy field in the high-pressure phase can be extracted:

$$\frac{d\ln H_A}{dP} = (3.6 \pm 0.3)\times 10^{-2}\ \text{kbar}^{-1}\ \ (\text{CdI}_2\ \text{phase}) .$$

Also, the change in anisotropy due to the structural transition can be found by extrapolating the high-pressure curve to zero pressure, with results

$$\Delta H_A/H_A = (2.5 \pm 1)\times 10^{-2}\ \ (\text{CdCl}_2 \rightarrow \text{CdI}_2) .$$

This is, the change in H_A under a uniform compression of 1 kbar is greater than the change due to transition from cubic to hexagonal close packing.

The temperature dependence of the AFMR frequency was also determined at several pressures, and is shown in Fig. 2. By comparing equivalent points on the curves a rough estimate of the change in T_N with pressure can be made: $dT_N/dP \approx 0.7$ °K/kbar. A more intriguing result, however, is that at zero pressure the mode frequency does not go to zero at T_N as does the sublattice magnetization, but in fact may persist even for temperatures slightly above T_N.

DISCUSSION

Let us first consider the crystal field environment of the single Fe^{2+} ion. The ligand symmetry is nearly octahedral, with a trigonal distortion along the axis normal to the layers. The cubic component of the crystal field splits the free-ion ^5D state into an upper doublet and lower triplet. Mössbauer measurements[8] indicate that the trigonal distortion energy is close to that due to spin-orbit coupling, so the two effects must be considered simultaneously in determination of further

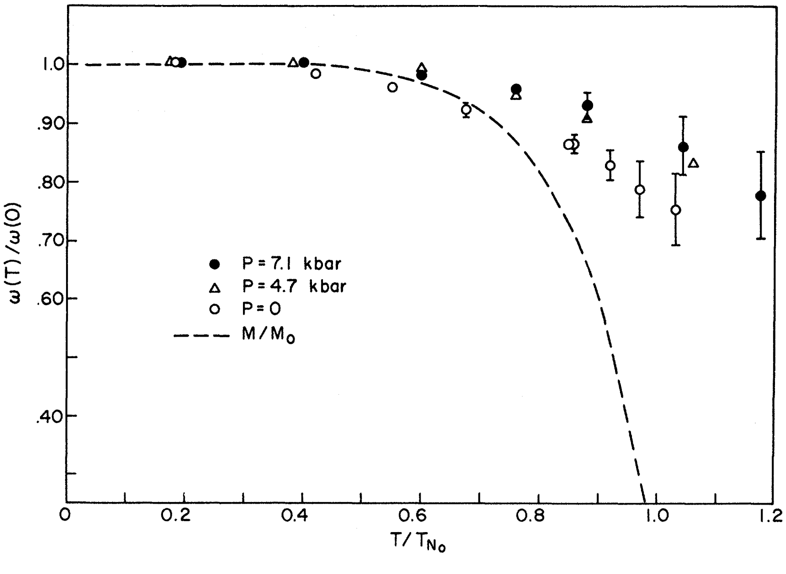

FIG. 2. Temperature dependence of the AFMR frequency in $FeCl_2$ for several applied pressures. The temperature scale is based on the zero-pressure Néel temperature T_{N0} (23.5 °K).

splittings. A Hamiltonian describing the lowest 15 states of the Fe^{2+} ion has been given by Ono *et al.*[8]

$$H_1 = \lambda \vec{l}_1 \cdot \vec{S}_1 + c l_{z_1}^2 + 2(J_1'\langle \vec{S}_1\rangle + J_2'\langle \vec{S}_2\rangle)\cdot \vec{S}_1 \ .$$

Here λ is the spin-orbit parameter, c is the trigonal term, $\vec{l}$ is a pseudo-orbital-moment of magnitude 1, $\langle\vec{S}_1\rangle$ and $\langle\vec{S}_2\rangle$ are averaged spin values in the same and opposite sublattices, and J_1' and J_2' are isotropic exchange constants between the "real" spins. Alben obtained best values of $\lambda = 67\ \text{cm}^{-1}$ and $c = -88\ \text{cm}^{-1}$.[9]

Alben[9] has analyzed H_1 in the strong spin-orbit approximation, in which the 15-fold-degenerate cubic level is split into levels based on $J = 1, 2,$ and 3 of multiplicity 3, 5, and 7. The $J = 1$ levels lie lowest and are separated from the $J = 2$ levels by $2\lambda \approx 135\ \text{cm}^{-1}$. Since the Néel temperature is 23.5 °K, only the effects of the low-lying triplet need be considered in analysis of the ordered magnetic behavior.

Birgeneau *et al.*[3] have described the behavior in the low-lying triplet by a spin Hamiltonian based on a pseudospin $s = 1$:

$$H = -\sum_i D[(s_i^z)^2 - \tfrac{2}{3}] + 2\sum_{i>j} K_{ij} s_i^z s_j^z + 2\sum_{i>j} J_{ij}\vec{s}_i\cdot\vec{s}_j \ .$$

The single-ion anisotropy term D is roughly proportional to the trigonal factor c, J_{ij} is the effective isotropic exchange between pseudospins, and K_{ij} incorporates exchange anisotropies arising from the real-spin to pseudospin transition and is proportional to J_{ij}. In this notation the anisotropy field H_A may be written

$$g\mu_B H_A \cong D(2s-1) + 2s\sum_{l'} K_{ll'} \ ,$$

where l' refers to intrasublattice terms, and the much weaker intersublattice terms have been ignored.

Therefore, the measured value of $d\ln H_A/dP$ in our experiment describes the behavior of a sum of trigonal anisotropy and in-plane exchange. Since the two terms are of roughly the same magnitude, their pressure behavior cannot be separated uniquely in the high-pressure region. On the other hand, the structural phase transition consists of planes sliding relative to each other, so that in-plane exchange should be little affected. Therefore the structural discontinuity term ΔH_A is a direct measure of the change in trigonal splitting due to the transition from cubic to hexagonal close packing. Since ΔH_A is so small, it appears that the change in magnetic energy is not sufficient to produce the phase change, and the trigonal distortion simply monitors the structural change. It is interesting that the atomic rearrangement can occur at temperatures below 60 °K. A more detailed analysis of our pressure results requires a determination of the compressibility of $FeCl_2$.

The temperature behavior of the AFMR at zero pressure measured here is quite similar to that reported previously by Jacobs, Roberts, and Lawrence,[5] although we report additional high-temperature points. In particular, the AFMR was clearly observable slightly above T_N at (24.2 ± 0.2 °K. At 28 °K the mode could no longer be seen. Birgeneau *et al.*[3] have reported the disappearance of zone-boundary magnons by 26 °K, although the mode is still barely observable at 23.55 °K. They concluded that the magnon spectrum collapses precipitously toward zero frequency as T_N is approached from below. Our results, on the other hand, indicate a much slower rolloff in the zero-wave-vector AFMR mode near T_N, with a slight persistence of the mode into the paramagnetic region. The region for the discrepancy between the two sets of measurements is not clear.

The existence of a second magnetic-dipole-active mode at a frequency below the AFMR was predicted by Alben,[9] who suggested that mutual repulsion between the two modes might explain the slow rolloff in ω_{AFMR} near T_N. We searched for such a second mode at temperatures between 4 and 30 °K for frequencies between 5 and 30 cm^{-1} and found no evidence for its existence. In light of this breakdown of Alben's theory and the conflict between our data and the neutron measurements, we must conclude that the temperature behavior of the spin waves in $FeCl_2$ near T_N is not yet understood.

---

†Work supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-3151, Technical Report No. COO-3151-5. Additional support was received from the Advanced Research Projects Agency through the Materials Science Center at Cornell University Report No. 1826.

*Lawrence Livermore Laboratory, Livermore, Calif. 94550.

[1] C. Starr, F. Bitter, and A. R. Kaufman, Phys. Rev. 58, 977 (1940).

[2] A. Narath and J. E. Schirber, J. Appl. Phys. 37, 1124 (1966).

[3] R. J. Birgeneau, W. B. Yelon, E. Cohen, and J. Makovsky, Phys. Rev. B 5, 2607 (1972).

[4] M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev. 113, 497 (1959).

[5] I. S. Jacobs, S. Roberts, and P. E. Lawrence, J. Appl. Phys. 36, 1197 (1965).

[6] A. J. Sievers, J. Appl. Phys. 41, 980 (1970).

[7] K. C. Johnson and A. J. Sievers (unpublished).

[8] K. Ono, A. Ito, and T. Fujita, J. Phys. Soc. Japan 19, 2119 (1964).

[9] R. Alben, J. Phys. Soc. Japan 26, 261 (1969).