Magnetic Properties of $FeCl_2$ in Zero Field. I. Excitations

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A detailed neutron-scattering investigation of the magnetic properties of the antiferromagnet $FeCl_2$ in zero field has been carried out. In this paper we report inelastic studies of the spin waves and magnetic excitons both at low temperatures and around the phase transition. The spin waves are found to simulate those of a two-dimensional ferromagnet with large anisotropy. The magnon dispersion relations at 5 °K may be accurately described by simple $S=1$ spin-wave theory with an anisotropy field $g\mu_B H_A = 2.0 \pm 0.1$ meV, in-plane isotropic exchange interactions of $2J_1 = 0.68 \pm 0.02$ meV, $2J_2 = -0.09 \pm 0.02$ meV, and an antiferromagnetic interplanar interaction of $2J_1' = -0.03 \pm 0.01$ meV. The temperature dependence of these magnons is quite unusual. Up to 21 °K there is no renormalization at all of the exchange part of the spin-wave energy. However, between 21 °K and $T_N = 23.55$ °K the entire magnon branch collapses precipitously into a continuum of scattering. Magnetic excitons originating in transitions between the spin-orbit-split $^5T_{2g}(J=1)$ and $(J=2)$ states have also been observed. However, these are complicated by coupling to the optical phonons so that only qualitative results are obtained.

I. INTRODUCTION

The unusual magnetic properties of $FeCl_2$ and the other iron-group dihalides have made these compounds a subject of considerable experimental and theoretical interest for many decades.[1-5] Briefly, $FeCl_2$ is composed of hexagonal sheets of ferromagnetically aligned Fe^{++} spins with strong anisotropy confining the spins to the hexagonal axis; successive planes are then weakly coupled antiferromagnetically to each other so that the over-all magnetic structure is antiferromagnetic[6] with a Néel temperature of 23.55 °K. At low temperatures the weak between-plane antiferromagnetic coupling may be overcome with a modest applied field (~11 kOe) causing a first-order transition from antiferromagnetic to ferromagnetic (paramagnetic) ordering of the spins.[4,6-8] This particular behavior is generally described as *metamagnetism*.

The magnetic properties of $FeCl_2$ have recently taken on renewed importance because of two distinct advances in our understanding of cooperative phenomena. First, the experiments of Jacobs and Lawrence[8] have shown that at $\sim 0.87T_N$ the metamagnetic phase transition in $FeCl_2$ goes over from being first order to second or higher order. Griffiths[9] has labeled this particular place on the phase diagram a *tricritical point* since it occurs at the intersection of three lines of critical points. He and others[10,11] have predicted that the thermodynamic behavior around the tricritical point may differ considerably from that at conventional second-order phase transition points. Second, recent experimental and theoretical work[12-15] has shown that *dimensionality* plays a central role in the dynamics of magnetic systems, particularly at elevated temperatures. $FeCl_2$ presents the interesting and hitherto unexamined case of a pseudo-two-dimensional ferromagnet with large anisotropy.

In this and the following paper[16] we report detailed elastic- and inelastic-neutron-scattering studies of the magnetic properties of $FeCl_2$ in zero field. These experiments were motivated partially by the desire to determine the suitability of $FeCl_2$ for tricritical-point studies. The work naturally subdivides itself into two parts. First, we have measured the excitation spectra at low temperatures and around the Néel point. These results are discussed in this paper. Second, a careful study of the critical behavior of the order parameter, that is, the sublattice magnetization, has been made;

in addition, the behavior of the wave-vector-dependent susceptibility $\chi^{\alpha\alpha}(\vec{Q})$ above T_N has been qualitatively surveyed. These latter results are reported in the following paper.[16]

The format of this paper is as follows: In Sec. II, we describe the crystal structure and magnetic ordering of $FeCl_2$. Section III gives the theory of the magnetic excitations. The experimental techniques are discussed in Sec. IV, and in Sec. V the experimental results and analysis are reported. Section VI contains a summary of the results and conclusions.

II. CRYSTAL AND MAGNETIC STRUCTURE

Single crystals of $FeCl_2$ may be grown relatively straightforwardly using standard Bridgman techniques.[17] The major difficulty in working with the material is its extreme softness and tendency to flake in sheets perpendicular to the c axis. As a result of this softness, crystals of $FeCl_2$ large enough for inelastic-neutron-scattering experiments tend to have rather unsatisfactory mosaics. The actual crystal used in this experiment was in the form of a platelet approximately $2\times1\times0.4$ cm with the c axis perpendicular to the flat face. The mosaic spread was typically $1^\circ-1\frac{1}{2}^\circ$ full width at half-maximum. Because of this rather large mosaic, care had to be taken in the types of inelastic scans employed in order to minimize any broadening.

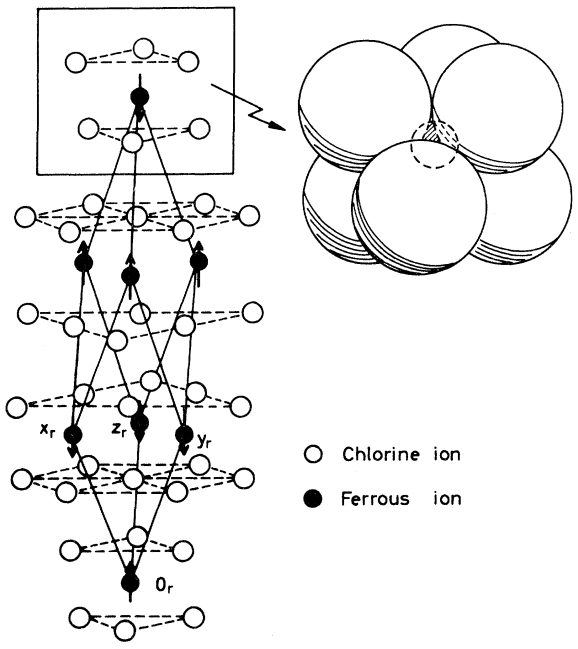

FIG. 1. Crystal and magnetic structure of $FeCl_2$. O_r, X_r, Y_r, Z_r define the rhombohedral primitive axes.

The crystal and magnetic structures of $FeCl_2$ are illustrated in Fig. 1. The primitive nuclear cell is rhombohedral, space group D_{3d}^5, with one molecule per unit cell. The rhombohedral axes $\vec{x}_r$, $\vec{y}_r$, $\vec{z}_r$ are displayed in the figure. The Fe^{++} ion sits at (0, 0, 0) and the Cl^- ions at $\pm(u, u, u)$, where $u=(0.2543\pm0.0005)a$.[6] This crystal structure may, in fact, be generated from the rock-salt structure by removing alternate sheets of metal atoms along the [111] axis. In the present investigation it has proven more convenient to use an enlarged hexagonal cell. The conventional principal hexagonal axes[18] may be generated from the rhombohedral axes by $\vec{x}_h=\vec{x}_r-\vec{y}_r$, $\vec{y}_h=\vec{y}_r-\vec{z}_r$, $\vec{z}_h=\vec{x}_r+\vec{y}_r+\vec{z}_r$, and this hexagonal cell then contains three formula units. However, in order to incorporate the effects of the antiferromagnetic ordering with its consequent doubling of the c axis from the beginning, we shall use a *double hexagonal cell* with $\vec{Z}_{2h}=2(\vec{x}_r+\vec{y}_r+\vec{z}_r)$. In this double hexagonal cell the Fe^{++} ions sit at (0, 0, 0), (0, 0, $\frac{1}{2}$), ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{3}$), ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{5}{6}$), ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{6}$), ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{2}{3}$), and the Cl^- ions are at each of these $\pm(0, 0, \frac{1}{2}u)$. The lattice constants for our sample at 4.2 °K are $a=3.583\pm0.004$ Å, $C_{2h}=34.89\pm0.06$ Å.

The magnetic structure was first determined by Wilkinson *et al.*,[6] and our own single-crystal measurements are consistent with their observations. As mentioned in the Introduction and displayed in Fig. 1, the spins order in ferromagnetic sheets along the c axis with successive sheets antiparallel to each other in zero field. In the double hexagonal cell, nuclear Bragg peaks occur at (h, k, l) with $-h+k+\frac{1}{2}l=3n$, where n is an integer. The magnetic reciprocal-lattice points are generated by $h-k+l=3n$, but only those with l odd have a non-vanishing structure factor. In addition, since the spins are aligned along the c axis no magnetic scattering is observed at the ($0\,0\,l$) positions. The ($h\,0\,l$) plane of the reciprocal lattice is displayed in Fig. 2. For illustrative purposes, a cross section of the magnetic Brillouin zone is drawn around the (1, 0, 5) reciprocal-lattice point. All measurements reported in this paper were carried out in this ($h\,0\,l$) plane.

III. THEORY

The Hamiltonian appropriate to the Fe^{++} ions in $FeCl_2$ has been discussed in some detail by Ono *et al.*[19] and by Alben.[20] The free-ion $3d^6\,{}^5D$ state of the Fe^{++} ion is split by the cubic component of the crystal field due to the surrounding chlorines (see Fig. 1) so that the orbital triplet ${}^5T_{2g}$ is lowest. This ${}^5T_{2g}$ state is then subject to much smaller perturbations from the spin-orbit coupling, a residual trigonal component of the crystal field, and the exchange interactions. Since all of these are appreciably weaker than the cubic-crystal field,

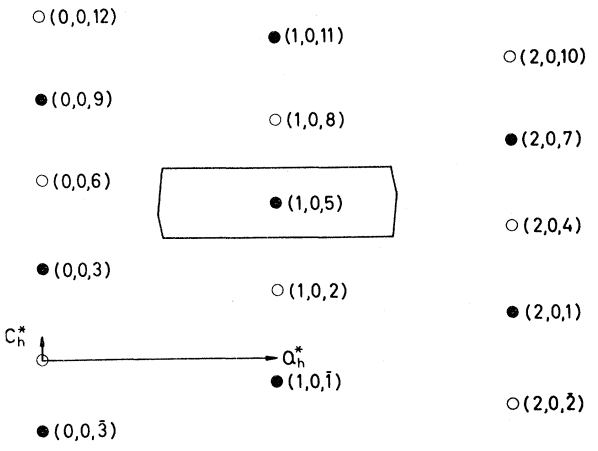

FIG. 2. (h 0 l) reciprocal-lattice plane for the double hexagonal unit cell. Filled dots are magnetic-reciprocal-lattice points where the magnetic structure factor is nonvanishing. Open dots are both nuclear- and magnetic-reciprocal-lattice points.

the T_{2g} orbital state may be treated as an effective angular momentum $l = 1$, that is, a ^5P state in the usual fashion.[21] Within this ^5P state the Hamiltonian is

$$\mathcal{H} = \sum_i \{\lambda \vec{L}_i \cdot \vec{S}_i + \delta[(L_i^z)^2 - \tfrac{2}{3}]\} - 2\sum_{i>j} \mathcal{J}_{ij} \vec{S}_i \cdot \vec{S}_j \,, \tag{1}$$

where we have assumed that the exchange is isotropic between the real spins. We shall discuss this latter assumption in more detail in Sec. V.

From the temperature dependence of the Fe^{++} nuclear-quadrupole splitting, Ono *et al.*[19] conclude that $\delta/\lambda \sim -1.25$ with $\lambda = 95$ cm^{-1} [22] (the free-ion value is 100 cm^{-1}). Alben,[20] from an analysis of susceptibility, resonance, and magnetization data, finds a similar value for δ/λ (−1.31) but with $\lambda = 67$ cm^{-1}. From a consideration of the crystal structure it is immediately evident that only the first-two-neighbor in-plane and the nearest-neighbor between-plane exchange constants are likely to be important. Reliable quantitative estimates are available only for the between-plane coupling. We shall defer a discussion of the actual exchange constants until later except to note that the exchange is weak compared to the spin-orbit coupling and the trigonal field.

In order to obtain the correct excitation spectra, including all possible magnetic excitons, it is necessary to treat the Hamiltonian (1) in its entirety from the beginning. This can be done most readily using the "effective-boson" approach of Trammell, Bozorth, and Van Vleck, and Grover[23] or, equivalently the "time-dependent–molecular-field" method espoused by Alben.[20] Such a calculation has, in fact, already been performed by Alben using the set of parameters which he deduced from the bulk properties and the resonance data. In this paper, however, our primary interest is in only the lowest-lying excitons, that is, the spin waves; for these excitations the more general approach is not necessary. We shall therefore diagonalize the single-ion part of Eq. (1) exactly and then treat the exchange as a perturbation using an effective-spin model. The error introduced by this approximation is probably less than that involved in assuming that the exchange is isotropic between the real spins in the first place.

For simplicity we shall use Alben's values $\lambda = 67$ cm^{-1}, $\delta = -88$ cm^{-1}. Although these values are certainly not exact, they should be a good first approximation. The consequent energy-level diagram is shown in Fig. 3. From the figure it may be seen that although δ is comparable with λ, the levels retain the $J = 1, 2, 3$ grouping appropriate to spin-orbit coupling alone. Thus we may validly treat the $J = 1$ manifold using an effective-spin $s = 1$ Hamiltonian, provided that the exchange is considerably less than $E(J=2) - E(J=1)$. This condition is reasonably well fulfilled.

It is interesting to note that in the absence of exchange transverse excitations between the ground state and the $J = 2$ levels would be observed at 113 and 163 cm^{-1} (14.0 and 20.2 meV) and a longitudinal exciton would be observed at 127 cm^{-1} (15.8 meV). These may be compared with Alben's[20] $q = 0$ values

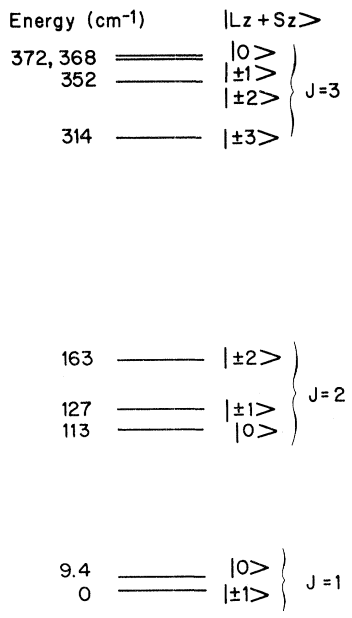

FIG. 3. Single-ion energy-level diagram for the $^5T_{2g}$ state of the Fe^{++} ion in $FeCl_2$; the Hamiltonian is as in Eq. (1) with $\lambda = 67$ cm^{-1}, $\delta = -88$ cm^{-1}, all $J_i = 0$ (1 cm^{-1} = 0.124 meV).

of 136, 162 cm^{-1} (16.9, 20.1 meV) for the transverse excitons and 141 cm^{-1} (17.5 meV) for the longitudinal excitation calculated using the full Hamiltonian including exchange. Thus the exciton energies are only shifted by about 10% by the exchange field.

Within the lowest effective-spin $s=1$ multiplet the spin Hamiltonian may be written

$$\mathcal{H}=\sum_i D[(s_i^z)^2-\tfrac{2}{3}]+\sum_{i>j}[-2\alpha_{\parallel}^2\mathcal{J}_{ij}s_i^z s_j^z - 2\alpha_{\perp}^2\mathcal{J}_{ij}(s_i^x s_j^x+s_i^y s_j^y)]. \quad (2)$$

Here $\alpha_{\parallel}$, $\alpha_{\perp}$ are proportionality factors connecting the matrix elements of real- and effective-spin operators. For $\delta/\lambda=-1.31$, $\alpha_{\parallel}=1.67$ and $\alpha_{\perp}=1.40$ For small δ, the operator equivalence of the trigonal-field term within the lowest $s=1$ multiplet is given by[20]

$$\delta[(L^z)^2-\tfrac{2}{3}]\simeq\tfrac{1}{10}\delta[(s^z)^2-\tfrac{2}{3}], \quad (3)$$

so that $D=\frac{1}{10}\delta$. However, for increasing δ this simple relationship breaks down.

The magnon dispersion relation corresponding to Eq. (2) may be simply obtained using standard techniques. In particular, since $FeCl_2$ corresponds to a simple two-sublattice antiferromagnet the well-known expression given by Keffer in his review article[24] may be used directly. In order to simplify the notation we rewrite Eq. (2):

$$\mathcal{H}=\sum_i D[(s_i^z)^2-\tfrac{2}{3}]-2\sum_{i>j}K_{ij}s_i^z s_j^z-2\sum_{i>j}J_{ij}\vec{\mathbf{s}}_i\cdot\vec{\mathbf{s}}_j. \quad (4)$$

We then make the identification

$$g\mu_B H_A=-2D(s-\tfrac{1}{2})-2s\textstyle\sum_m K_{lm}+2s\sum_{l'}K_{ll'}, \quad (5)$$

where the primes refer to intrasublattice terms.

Substituting directly into Eq. (38.14) of Keffer,[24] the dispersion relation for magnons in the $(h\,0\,l)$ plane in $FeCl_2$ is given by

$$E^2(h\,0\,l)=[g\mu_B H_A+8(J_1+J_2)(1-\cos2\pi h)+4J_2(1-\cos4\pi h)-12J_1']^2 - 16J_1'^2[\cos\tfrac{1}{3}\pi l(\cos\tfrac{4}{3}\pi h+2\cos\tfrac{2}{3}\pi h) - \sin\tfrac{1}{3}\pi l(\sin\tfrac{4}{3}\pi h-2\sin\tfrac{2}{3}\pi h)]^2, \quad (6)$$

where J_1 and J_2 are the nearest- and next-nearest-neighbor in-plane interaction constants and J_1' is the nearest-neighbor between-plane exchange constant.

Two of the parameters in Eq. (6) may be estimated from already measured quantities, viz., the antiferromagnetic resonance frequency[25] (2.0 meV, but see Sec. V) and the metamagnetic transition field at 4.2 °K (11 kOe).[8] The isotropic component of the intersublattice exchange is given by

$$-2ZJ_1'(\alpha_{\parallel}/\alpha_{\perp})^2=g_{\parallel}\mu_B H \quad \text{(metamagnetic)}, \quad (7)$$

where Z is the number of between-plane nearest neighbors. Using $\alpha_{\parallel}/\alpha_{\perp}=1.19$, $g_{\parallel}=4.1$, we find $2J_1'=-0.03$ meV. Substitution for $E(0\,0\,0)$ and $2J_1'$ in Eq. (6) then yields $g\mu_B H_A=1.8$ meV. Since $12J_1'\ll g\mu_B H_A$, the second term in Eq. (6) therefore is always negligible; hence the dispersion relation simplifies to

$$E(h\,0\,l)=g\mu_B H_A-12J_1'+8(J_1+J_2)(1-\cos2\pi h)+4J_2(1-\cos4\pi h). \quad (8)$$

The excitation spectrum thus reduces to that of a simple two-dimensional ferromagnet with large anisotropy.

There are two final points of note. First, the assumption of isotropic exchange between the real spins [Eq. (1)] yields an effective-spin Hamiltonian, Eq. (4), with uniaxial anisotropy. A more general exchange would allow, for example, $J_1^{xx}\neq J_1^{yy}$ in the effective-spin Hamiltonian. There could also be sizable biquadratic terms.[26] The effect of such terms in general is to remove the degeneracy between the two spin-wave branches while having little effect on the mean energy at a particular q. Order-of-magnitude considerations, however, indicate that such terms would have to be anomalously large in order to produce an observable splitting.[27] Second, the temperature dependence of the excitations should prove quite interesting, particularly since the gap energy is comparable with T_N. Both theory and recent experiments on lower-dimensional antiferromagnets indicate that there should be little renormalization of the exchange part of the magnon energy until very near T_N.[12-15] In addition, one might anticipate that magnonlike excitations would persist into the paramagnetic phase.

IV. EXPERIMENTAL TECHNIQUE

The experiments were carried out on the H-7 and H-8 triple-axis spectrometers at the Brookhaven high flux beam reactor. The experimental techniques used were the standard procedures for triple-axis spectrometry in this laboratory. The results reported in Sec. V A were carried out mainly using 14.8-meV incident neutrons. Pyrolytic graphite reflecting from the (0 0 2) plane was used for both monochromator and analyzer. The monochromator was bent about a horizontal axis to provide focusing of the incident neutrons.[28] A large-mosaic pyrolytic-graphite filter placed before the sample acted as a tunable $\frac{1}{2}\lambda$ filter.[29] All collimators were either 20 or 40 min depending on the comparative needs of intensity and resolution. The $J=1\leftrightarrow J=2$ excitons which occur at much higher energies were studied using incident neutrons of energies 50 and 60 meV. The monochromator was beryllium (1 1 0) and the analyzer

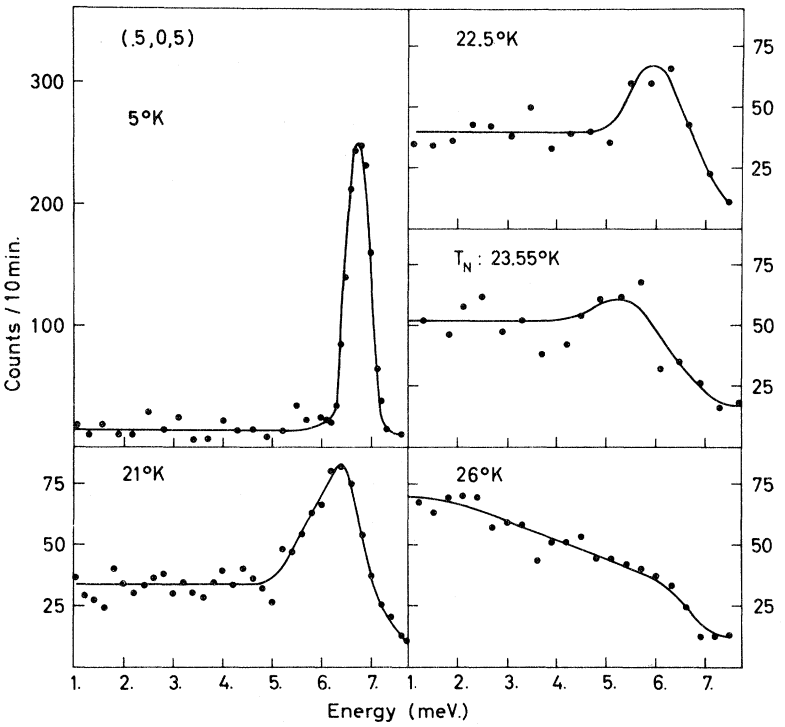

FIG. 4. $FeCl_2$ zone-boundary in-plane magnon scans as a function of temperature at the position (0.5, 0, 5), corresponding to a reduced wave vector of ($\frac{1}{2}$, 0, 0).

was beryllium (0 0 2).

The sample was mounted with its long axis, which corresponded to the $[1\bar{1}0]$ direction, vertical, so that wave vectors of the form $(h, 0, l)$ could be surveyed. The crystal was epoxied to an aluminum sample holder which was then sealed in an aluminum can in an atmosphere of helium gas. The epoxy and aluminum pedestal were carefully shielded with cadmium. The cans were mounted in a Cryogenics Associates Dewar, type CT 14. The temperature could be varied continuously from 4.8 °K upwards with a relative accuracy of 10^{-2} °K over limited temperature ranges but a somewhat larger absolute accuracy; the temperature was measured with a germanium resistance thermometer.

V. EXPERIMENTAL RESULTS AND ANALYSIS

A. Spin Waves

Typical experimental scans as a function of temperature are shown in Fig. 4. These measurements were made at (0.5, 0, 5) corresponding to a reduced wave vector of ($\frac{1}{2}$, 0, 0), that is, at effectively the in-plane zone-boundary position. We first discuss the data up to 21 °K. At each q value a single spin-wave peak is observed, in accordance with our expectations from the theory given in Sec. III. The dispersion relations for magnons propagating along the $[h\,0\,0]$ direction at each of 5, 18, 21 °K are shown in Fig. 5. The gap energy at 5 °K is 2.13 ± 0.05 meV (17.2 ± 0.4 cm^{-1}), in reasonable agreement with the antiferromagnetic-resonance values[25] of 2.02 ± 0.04 meV (16.3 ± 0.3 cm^{-1}) measured by Jacobs, Roberts, and Lawrence and 2.07 ± 0.06 meV (16.7 ± 0.5 cm^{-1}) measured by Cohen. Measurements of the dispersion relation along (0, 0, l) from the zone center to the zone boundary were made at 5 and 21 °K. In both cases the magnon energy was *independent of* l to within the experimental error. The magnetic excitations in $FeCl_2$, therefore, do indeed simulate those of an ideal two-dimensional ferromagnet.

The dispersion relations at each temperature may now be fitted to Eq. (8) in order to obtain the interaction constants in the effective-spin Hamiltonian. The best fit to the 5 °K data yields the values given in Table I. The error limits correspond to two-standard-deviation statistical errors. The solid line through the points in Fig. 5 is the dispersion relation calculated using these parameters; the fit is excellent.

Using the result $2J_1' = -0.03 \pm 0.01$ meV deduced from the metamagnetic transition field, we have *in toto* at 5 °K.

$$\begin{aligned} g\mu_B H_A &= 2.0 \pm 0.1 \text{ meV}, \\ 2J_1 &= 0.68 \pm 0.02 \text{ meV}, \\ 2J_2 &= -0.09 \pm 0.02 \text{ meV}, \\ 2J_1' &= -0.03 \pm 0.01 \text{ meV}. \end{aligned} \tag{9}$$

For isotropic exchange between the real spins, one has from Eqs. (2) and (5) for $s = 1$

$$g\mu_B H_A = -D + 6\left[(\alpha_{\parallel}^2 - \alpha_{\perp}^2)/\alpha_{\perp}^2\right](2J_1 + 2J_2 - 2J_1') \,. \tag{10}$$

Using the values for D, $\alpha_{\parallel}/\alpha_{\perp}$ given previously, we calculate from Eq. (10)

$$g\mu_B H_A(\text{calc}) = 2.7 \text{ meV} \,. \tag{11}$$

This is somewhat larger than the experimental value but considering the uncertainties in D, $\alpha_{\parallel}/\alpha_{\perp}$, and the oversimplified nature of the theory, the agreement is reasonable. This in turn necessitates that our assumption of isotropic exchange between the real spins is nearly, if not exactly, correct.

The results of fits to the 18 and 21 °K data are also given in Table I. We have tabulated $2J_1 + 2J_2$ rather than $2J_1$ since it is the former combination which is most accurately determined. From the parameters in Table I and indeed from the form of the dispersion relations themselves it is evident that up to 21 °K all of the temperature dependence originates in the anisotropy; there is no renormalization of the exchange to within experimental error. It should be noted that at 21 °K

$$\frac{E(q=0,\ 21\ ^\circ\text{K})}{E(q=0,\ 5\ ^\circ\text{K})} \sim \left(\frac{M(21\ ^\circ\text{K})}{M(5\ ^\circ\text{K})}\right)^{3/2} , \tag{12}$$

where $M(T)$ is the sublattice magnetization. From Eqs. (8) and (9) it may be seen that the gap energy is given mainly by $g\mu_B H_A$ which in turn arises from the bilinear anisotropic exchange and the second-order crystal field terms in Eq. (4). We would therefore expect the power in Eq. (12) to lie between 2 and 3.[30] Thus the temperature or, equivalently, sublattice-magnetization dependence of the anisotropy is somewhat weaker than that usually observed. It should also be noted that we observe neither the additional mode predicted by Alben[20] to occur around 1 meV nor any explicit effects from the two-magnon bound states discussed by Tonegawa.[31]

TABLE I. Effective-spin-Hamiltonian parameters determined from the magnon dispersion relations.

T (°K)	$g\mu_B H_A - 12J_1'$ (meV)	$2J_1 + 2J_2$ (meV)	$2J_2$ (meV)
5	2.16 ± 0.04	0.59 ± 0.01	-0.09 ± 0.01
18	1.72 ± 0.11	0.61 ± 0.02	-0.10 ± 0.04
21	1.46 ± 0.20	0.60 ± 0.03	-0.13 ± 0.07

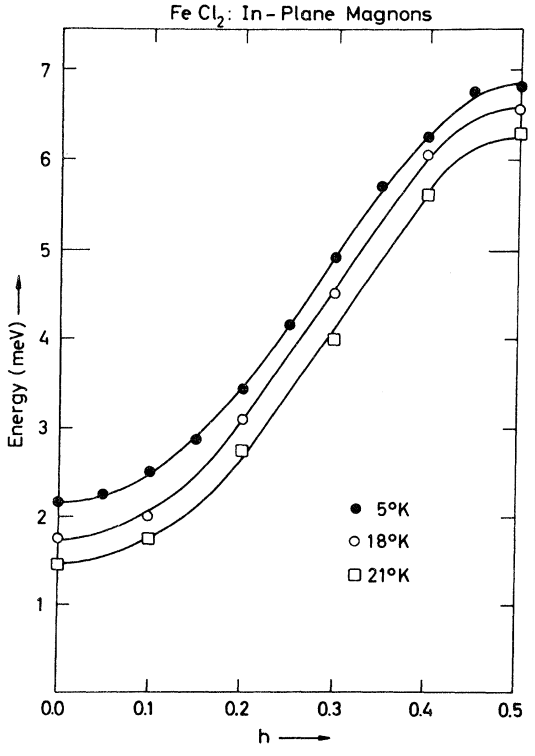

FIG. 5. Magnon dispersion curves in the $[h\,0\,0]$ direction at 5, 18, and 21 °K; magnons in the direction $[0\ 0\ l]$ are independent of l.

In summary, the spin-wave excitations at low temperatures can be adequately described by a simple effective-spin $s = 1$ Hamiltonian with reasonable values for the parameters. We note that the nearest-neighbor exchange J_1 is strong and ferromagnetic, whereas the second-neighbor in-plane and first-neighbor between-plane exchange constants, both of which involve *two* intervening chlorines, are weak and antiferromagnetic. The explicit values we obtain for the various exchange constants may change somewhat in a more exact theoretical treatment but such effects should be small; certainly the qualitative conclusions of our analysis will not be altered. Finally, the apparent absence of any renormalization of the exchange part of the spin-wave energies up to 21 °K is consistent with Dyson-type spin-wave theories.[32] The theory appropriate to $FeCl_2$ has been discussed by Narath and Davis[12] in the context of $CrCl_3$, an analogous system. Basically, there is no measurable change in the effective exchange at 21 °K because even at that temperature only long-wavelength in-plane magnons are appreciably populated; the consequent renormalization is then very small.

We now discuss the behavior of the excitations around T_N. It has been found recently in a number of antiferromagnets that intermediate- and short-wavelength magnons persist well into the paramagnetic phase. These effects are most marked in lower-dimensional systems such as the planar antiferromagnet K_2NiF_4 and the linear-chain system $(CD_3)_4NMnCl_3$. In these systems it has been suggested[33] that one may understand these "paramagnetic magnons" qualitatively by noting that kT_N is much less than the zone-boundary magnon energy,

so that few spin waves are thermally populated even very close to T_N. One then visualizes magnons propagating unimpeded within regions of statically correlated spins. However, no quantitative theory is yet available for these effects. On the above basis we had anticipated finding "paramagnetic magnons" in $FeCl_2$.

Typical scans at 22.5 °K, $T_N = 23.55$ °K, and at 26 °K at a reduced wave vector of $(\frac{1}{2}, 0, 0)$ are shown in Fig. 4. From the figure it may be seen that the above hypothesis is completely *incorrect*. Between 21 °K and T_N the magnons collapse quite precipitously and there are no propagating modes above the phase transition. Identical behavior is observed at all other q values. We thus have the rather surprising result that in $FeCl_2$ the magnons are barely renormalized up to $0.9\,T_N$ and then between $0.9T_N$ and T_N the entire magnon branch collapses into a continuum of scattering.

This result was most unexpected and indeed it illustrates clearly that in the many-body spin-dynamics problem intuition can be a very poor guide. It also highlights the fact that we still have no theory which enables us to predict in advance that, for example, K_2NiF_4 and $FeCl_2$, both of which are anisotropic planar antiferromagnets, would exhibit quite different behavior at elevated temperatures. The main physical difference between the two systems is that $FeCl_2$ mimics a two-dimensional ferromagnet with large anisotropy whereas K_2NiF_4 is a planar antiferromagnet with small anisotropy. A proper explanation of these results must rest in these differences.

B. $J = 1 \leftrightarrow J = 2$ Excitons

As mentioned previously, in addition to the spin waves there should also be transverse and longitudinal magnetic excitations originating in transitions between $J = 1$ and $J = 2$ manifolds. Such a transition has already apparently been observed at 21 ± 3 meV by Hautecler *et al.*[34] in $FeCl_2$ at room temperature. Since our primary interest in $FeCl_2$ was in the phase-transition properties and the magnons, no extensive investigation of these excitons was carried out. However, a cursory examination of the scattering around 20 meV was made.

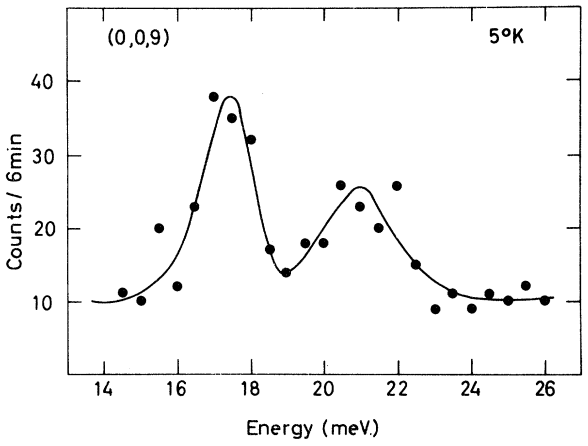

FIG. 6. Typical exciton scan at 5 °K at the position (0, 0, 9).

Even this brief survey proved more difficult than anticipated. The problems originated in the fact that a variety of peaks were observed at various positions in reciprocal space, and in general it proved quite difficult to characterize these peaks as being either purely magnetic or purely lattice vibrational. We find instead that the magnetic excitons and the optical phonons are strongly coupled.

Figure 6 shows a typical scan at the magnetic reciprocal-lattice point (0, 0, 9). At this position, two transverse excitons are anticipated and, indeed, the spectrum shows two dominant peaks. These peaks have intensities of ~10% of that of the spin waves. When the temperature is increased above T_N both peaks broaden and shift to lower energies, thus apparently confirming their identification as magnetic. However, the intensity variation of the 17-meV peak at various Q's is rather anomalous; in particular, it is observed at certain Q values where the form factor is vanishingly small so that the excitation cannot be purely magnetic. The peak at 21 meV, on the other hand, exhibits the correct form-factor dependence. Also, it has no measurable dispersion in the c^* direction and less than 1-meV dispersion in the a^* direction.

Alben calculates the energies of the two transverse excitons at $q = 0$ to be 17 and 20 meV, in excellent agreement with the observed values of 17 and 21 meV. However, this agreement may be somewhat fortuitous since he used an exchange field about a factor of 2 too low and, of course, his theory does not include any exciton-phonon coupling. Clearly a more complete explanation of this coupled exciton-phonon system would be of considerable interest. However, it is by no means a simple problem either experimentally or theoretically.

VI. SUMMARY AND CONCLUSIONS

In summary, we have studied the magnetic excitations in metamagnetic $FeCl_2$ in zero field. The low-lying excitons, the spin waves, are found to have the form predicted on the basis of previously available information; that is, they simulate the magnons in a true two-dimensional ferromagnet with large anisotropy. The temperature dependence of the spin-wave energies is consistent with the predictions of Dyson-type spin-wave theories. Up to $0.9T_N$ the gap renormalizes somewhat faster than the sublattice magnetization, whereas the exchange energy is essentially constant due to the fact that

even at $0.9T_N$ only long-wavelength magnons are appreciably populated. However, between $0.9T_N$ and T_N the entire spin-wave branch collapses uniformly into a continuum of scattering. This latter result was rather unexpected in light of results in other lower-dimensional antiferromagnets where long-lived magnons persist well into the paramagnetic regime. It should be noted, however, that results similar to ours in $FeCl_2$ have been found in the planar ferromagnet $CrBr_3$.[14]

A brief survey of the scattering in the 20-meV region, where the $J=1 \longleftrightarrow J=2$ excitations were anticipated, was also carried out. The spectra in this energy region were found to be rather complicated; from the anomalous intensity variation of several of the peaks, we conclude that the excitons and optical phonons are strongly coupled. Nevertheless, two transverse $q=0$ peaks at 17 and 21 meV could be identified as being primarily magnetic in origin and their energies are in good agreement with the theoretical predictions of Alben.

We conclude, therefore, that the magnetic interactions in $FeCl_2$ and the consequent excitations at low temperatures are now well understood. From the point of view of cooperative phenomena, $FeCl_2$ may be described as an $S=1$ antiferromagnet with large anisotropy. The critical behavior, and, in particular, the tricritical behavior, should be that appropriate to a three-dimensional $S=1$ Ising antiferromagnet.

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comes

$$E_q = [A_q^2 - (|B_q| \pm |D_q|)^2]^{1/2}.$$

Here A_q and D_q are just the first and second parts of our Eq. (6), and B_q is an intrasublattice anisotropic exchange term of the form

$$J^{xx}(q) - J^{yy}(q) + i[J^{xy}(q) + J^{yx}(q)].$$

Since $|D_q|$ is very small, it is clear that $|B_q|$ would have to be anomalously large in order to produce an observable splitting.

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Magnetic Properties of $FeCl_2$ in Zero Field. II. Long-Range Order

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In Paper I it has been shown that the critical behavior of $FeCl_2$ in zero field should be that appropriate to the three-dimensional $S=1$ Ising model. This paper reports a detailed study of the critical behavior of the sublattice magnetization below T_N together with a qualitative survey of the wave-vector-dependent susceptibility above T_N. The sublattice magnetization is found to follow the power law $M_T/M_0 = D(1 - T/T_N)^{\beta}$, with $D = 1.47 \pm 0.02$, $T_N = 23.553 \pm 0.01$°K, $\beta = 0.29 \pm 0.01$, over the range 0.1 to < 0.001 in reduced temperature. The exponent β is in reasonable agreement with the rigid-lattice Ising value of 0.313 ± 0.003. The regular behavior of M_T together with the unusual metamagnetic properties of $FeCl_2$ make this an ideal system for a study of the critical behavior of the order parameter around a tricritical point. The wave-vector-dependent susceptibility $\chi^{\alpha\alpha}(\vec{Q})$ above T_N is found to exhibit typical behavior for a three-dimensional anisotropic antiferromagnet. Only $\chi^{zz}(\vec{\tau})$, the component along the anisotropy axis, diverges at the phase transition. Furthermore $\chi^{zz}(\vec{Q})$ is found to be fully three dimensional; that is, it has the form of a peak rather than a ridge, in spite of the fact that the spin waves are essentially two dimensional in form.

I. INTRODUCTION

The critical properties of $FeCl_2$ in zero field are of interest for two principal reasons. As we have seen in the previous paper, the spin waves have a pronounced two-dimensional character with the inter- and intraplanar interactions differing by about a factor of 20. $FeCl_2$ thus lies intermediate between such antiferromagnets as $KNiF_3$, which is fully three dimensional and[1] K_2NiF_4, which exhibits a "two-dimensional" phase transition. The behavior of both the order parameter in the antiferromagnetic regime and the correlations in the paramagnetic phase in such an intermediate-dimensional compound should be quite interesting. In particular, one anticipates that the critical behavior will be fully three dimensional in spite of the directional nature of the interactions.[2]

A second motivation for studying the critical behavior of $FeCl_2$ in zero field is, of course, to evaluate the suitability of $FeCl_2$ for detailed tricritical-point studies.[3] The critical behavior may be affected both by Fe^{3+} contamination and by spin-phonon effects. The latter could be particularly important in this case because of the extreme softness of the lattice and the large orbital contribution to the effective $S=1$ moment. Such effects could manifest themselves either through a smearing of the phase transition or renormalization of the critical exponents.