Optical investigation of the metamagnetic properties of $FeCl_2$

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(Received 25 March 1974)

Measurements of optical density and magnetic circular dichroism are reported for all magnetic phases of $FeCl_2$. A transparent magnetic circular dichroism is reported to exist only in the mixed-phase region of the phase diagram, and further verification of the spin-forbidden transition at 4270 Å is presented. These optical measurements are used to map the magnetic-phase boundary of $FeCl_2$. We report a Néel temperature of (23.7 ± 0.1) °K and a tricritical temperature of (21.5 ± 0.1) °K.

I. INTRODUCTION

The magnetic properties of magnetic insulators such as $FeCl_2$ have recently been the subject of much theoretical and experimental effort.[1-12] $FeCl_2$ is a layered compound having the crystal structure of $CdCl_2$. In the magnetically ordered state, which occurs at temperatures less than 23.7 °K, spins within each hexagonal layer are ferromagnetically coupled perpendicular to the planes and adjacent planes are antiferromagnetically coupled. The ratio of the intraplanar ferromagnetic coupling constant J_1 to the interplanar antiferromagnetic coupling constant J_2 is about 20. The application of a sufficiently large external magnetic field parallel to one sublattice magnetization and antiparallel to the other results in a phase transition from the antiferromagnetic (AF) state to a paramagnetic (P) or saturated paramagnetic (SP) state. This transition is first order below and second or higher order above the tricritical temperature T_T. It is the occurrence of this tricritical point (T_T, H_T) that is responsible for the recent interest in $FeCl_2$.

Schnatterly and Fontana[1] have performed the first optical study of $FeCl_2$. They observed a particularly interesting temperature dependence of a sharp absorption line at 4270 Å. The oscillator strength f of this line is zero at low temperatures and sharply increases with temperature before saturating at $T = 2T_N$; the slope of f with temperature shows an abrupt change at T_N. They interpreted this result by assuming that this spin-forbidden transition is partially allowed by spin disorder within the ferromagnetically coupled planes. According to this interpretation the oscillator strength is a measure of the nearest-neighbor two-spin correlation function.

In this paper we report the extension of such optical experiments. We report the results obtained from measurements of optical density (OD) and magnetic circular dichroism (MCD) in all regions of the magnetic-phase diagram of $FeCl_2$. We report a transparent magnetic circular dichroism (TMCD) that exists only in the mixed-phase region of the magnetic-phase diagram. We report further verification of the Schnatterly-Fontana interpretation of the spin-forbidden transition at 4270 Å by examining the field dependence of this absorption. Using both the TMCD and OD measurements we present a magnetic-phase diagram of $FeCl_2$. Finally, we report measurements of the MCD at 4270 Å.

II. EXPERIMENTAL TECHNIQUES

The samples of $FeCl_2$ used in these experiments were thin, flat plates typically 0.01 cm thick and 1.0 cm square.[13] They were oriented with their hexagonal axis parallel to the magnetic field and optical path, and were attached to a copper block in the vacuum chamber of the optical cryostat. This copper block was thermally connected to the liquid-helium reservoir of the cryostat via a small cylindrical chamber which could be evacuated for high-temperature measurements, backfilled with helium exchange gas for medium-temperature work, and filled with liquid helium for low-temperature measurements. Room-temperature radiation heating was reduced by placing the sample between two cold windows also thermally attached to the copper block. The measurement and control of sample temperature were accomplished with a germanium resistance thermometer and a carbon resistance heater. The temperature resolution by this method was 10 m °K, but due to the magnetoresistance of the thermometer and heater the temperature stability during a series of magnetic field scans was about 0.1 °K.

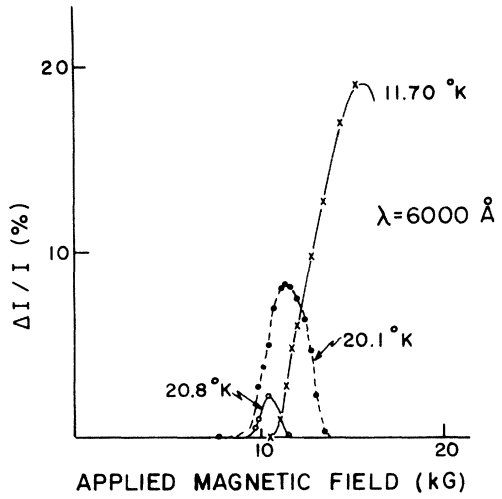

FIG. 1. Transparent magnetic circular dichroism at 6000 Å vs applied magnetic field measured at three temperatures.

The cryostat with the sample was then placed in a magnet ($H \leq 16$ kG) and the magnetic properties of $FeCl_2$ were monitored by measuring the magnetic circulation dichroism (MCD) and the optical density (OD) as a function of temperature and external magnetic field. Magnetic circular dichroism measurements were made using the polarization modulation technique of Jasperson and Schnatterly.[14] Briefly, this method involves a 50-kHz polarization modulation of a linearly polarized beam of light by a fused quartz block mechanically coupled to a piezoelectric transducer. The fundamental frequency component of the transmitted light is proportional to the amount of circular dichroism of the sample. Optical-density measurements were then accomplished by utilizing a property of the constant photomultiplier current mode. In this mode the voltage applied to the dynode chain is adjusted to maintain the average output current constant independent of the light intensity reaching the photomultiplier tube. Since the photomultiplier gain varies approximately exponentially with the voltage, the variation of the dynode voltage required to maintain a constant average current is proportional to the optical density of the sample. Calibration was accomplished with neutral density filters and the resultant accuracy in the optical density is estimated to be 5%–10%. The resolution of relative changes in optical density, however, was much better.

III. TRANSPARENT MAGNETIC CIRCULAR DICHROISM

A "magnetic circular dichroism" was found to exist in the mixed-phase region of the phase diagram at a wavelength at which $FeCl_2$ is transparent. We shall call this effect transparent magnetic circular dichroism (TMCD). In Fig. 1 the external magnetic field dependence of this effect at a wavelength of 6000 Å is reported for three typical temperatures. As the mixed-phase region was entered the transmission of the sample was observed to decrease, thus indicating that in this magnetic phase the incident light is scattered. Because the right and left circularly polarized lights are scattered unequally the sample appears to exhibit magnetic circular dichroism at a wavelength at which $FeCl_2$ is transparent. A simple coherent-light-scattering experiment has been performed with a He-Ne laser to directly confirm the existence of light scattering. The intensity distribution of the transmitted spot changed in the mixed phase. In addition, domains of saturated paramagnetic regions larger than 2000 Å in size have been predicted by Birgeneau based on neutron scattering data.[15] Such domains have been optically photographed by Dillon[8] using Faraday rotation.

The polarization dependent scattering is believed to be due to the domain structure of the mixed phase. Figure 1 indicates that there is no measureable TMCD in either the AF of the SP phases. The scattering is believed to be induced by the domain wall separating the two phases. The TMCD increases at first slowly and then rapidly with applied field, reaches a maximum, and decreases to zero. This behavior corresponds to first the formation of SP domains, then the increase in number of such domains, and finally the coalescing of SP domains as the SP phase boundary is approached.

The scattering itself is very probably due to den-

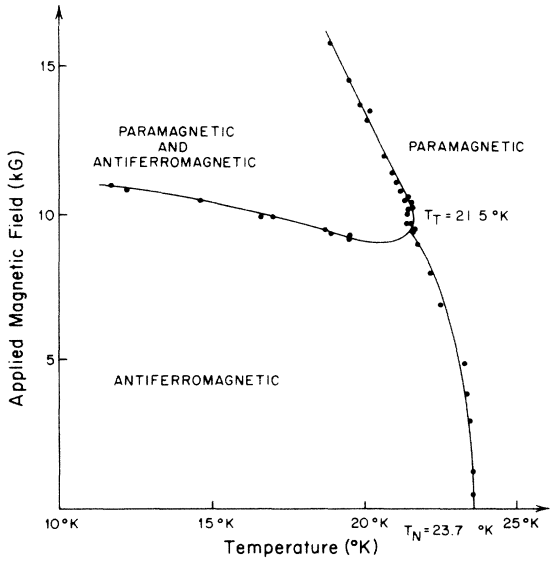

FIG. 2. Magnetic-phase diagram of $FeCl_2$.

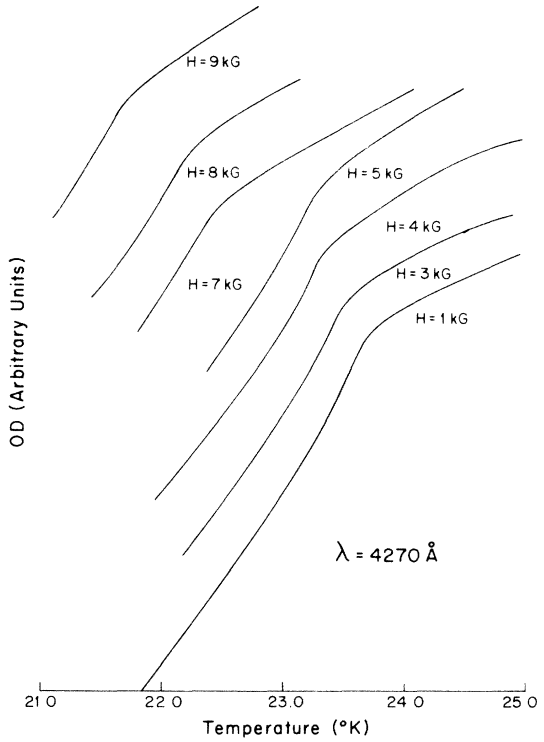

FIG. 3. Optical density at 4270 Å vs temperature at several constant applied magnetic fields.

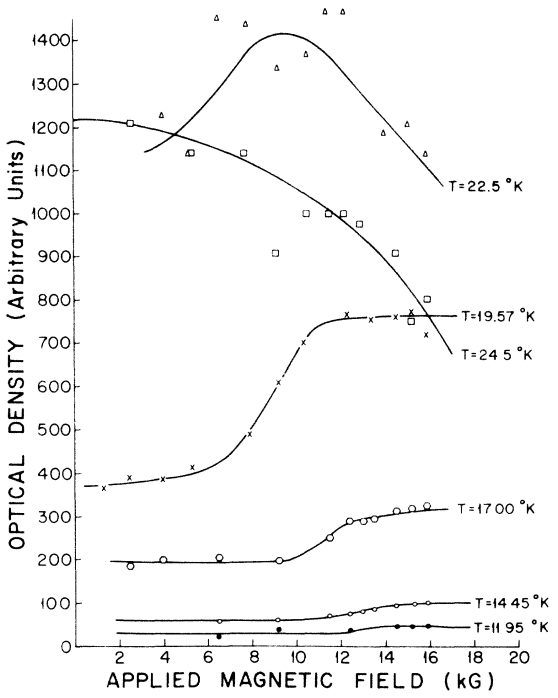

FIG. 4. Optical density at 4270 Å vs applied magnetic field at several constant temperatures.

sity variations (index of refraction variations) caused by magnetostriction at the domain boundaries.[16] The fact that the domain walls have a handedness indicates that the domain walls have finite thickness. If for example at the domain boundary, the sublattice magnetization changed from down to up suddenly, that is between nearest neighbors, there would be no reason for a spiral structure. On the other hand if the magnetization rotates slowly from down to up so it has a transverse component at a point within the wall, then there is some freedom of choice for the direction of this transverse magnetization. If all the boundaries had magnetizations pointing the same way then there would be a macroscopic transverse magnetization which costs energy. So the crystal can lower its energy by arranging that the fields from different domain walls cancel each other. This still allows an enormous number of arrangements. One solution which works for any size domain is for the wall orientation to vary periodically with position parallel to the magnetic field. Such a spiral form of long-range order is consistent with our results, since it would result in an optically active medium.

TABLE I. A comparison of results presented here with results of other experiments.

	Reported here	Birgeneau	Vettier
T_N (°K)	23.7 ± 0.1	23.55 ± 0.01	22.9 ± 0.1
T_T (°K)	21.5 ± 0.1	21.15	20.3 ± 0.1

If this light scattering is due to the mixed-phase state, as argued above, it can be used as a means of detecting the presence of this state; that is we can locate the boundaries of the mixed-phase region by measuring the TMCD. Figure 2 reports the locus of points at which the TMCD appears and disappears using the following convention: The lower field H_c^- and higher field H_c^+ are the applied fields at which the TMCD is 1% of its maximum value at that temperature. Measurements made at different wavelengths give the same shape phase diagram. This measurement provides a new way of determining the magnetic-phase diagram below the tricritical temperature.

IV. OPTICAL DENSITY

Previous experiments[1] indicated that in zero magnetic field the optical density of the absorption at 4270 Å increases sharply with temperature, exhibits an abrupt change in slope at T_N, and then saturates. The temperature dependence of the optical density at this wavelength for a series of applied magnetic fields is reported in Fig. 3. For each of these magnetic fields the optical density again exhibits a change in slope which we attribute

to the change in magnetic order. According to this interpretation it is possible to obtain $T_N(H)$, the critical temperature in the applied magnetic field H, and to locate the line of phase transition for $T_T \leq T \leq T_N$ which is also indicated on Fig. 2. Thus, with the data obtained by measuring the TMCD at 6000 Å and the optical density at 4270 Å we can report the entire phase diagram of $FeCl_2$. We are not able to provide measurements of the internal magnetic field since neither the TMCD nor the OD provides a measure of the magnetization that is needed to correct for shape-dependent demagnetizing fields. In Table I the measured values of T_N and T_T reported here can be compared with those measured by Birgeneau[17] and with those measured by Vettier.[9]

In Fig. 4 is reported the magnetic field dependence of the optical density at 4270 Å for a series of temperatures. At $T = 24.5$ °K, in the paramagnetic phase, the large optical density at zero field decreases as the magnetic field is increased. According to the model of Schnatterly and Fontana the zero-field value is due to the thermally induced nearest-neighbor spin disorder. The magnetic field serves to increase spin order in the paramagnetic phase and therefore reduce the optical density. At 22.4 °K the magnetic field behavior of the optical density is to first increase, reach a maximum at 9.5 kG, and then decrease. The zero-field optical density is again due to the thermal disorder and is reduced from that in the paramagnetic phase. The initial increase with field is most likely due to the spin disorder associated with the antiparallel planes since the applied field opposes the internal field which they experience. The subsequent decrease in optical density is again related to the spin order induced by the external field once the antiparallel planes have been reoriented. At 19.6 °K the field dependence of the optical density exhibits a small initial increase, a subsequent sharp increase, and finally becomes field independent. The zero-field value has again decreased. The sharp increase with field at this temperature is probably due to the appearance of domains in the mixed phase and the spin-disorder characteristic of the domain walls. Finally, at the lower temperatures reported in Fig. 4, the field dependence of the optical density is similar to that at 19.6 °K. The significant difference, however, is the reduction in magnitude of both the optical density and its change with field. Such a reduction is expected, for at low temperatures the thermally induced spin disorder is smaller, the AF domains are larger, and the disorder associated with realignment of the antiparallel sublattice is smaller.

The data reported in Fig. 4 does not exhibit the same behavior with temperature and field as magnetization measurements. For example, at T=19.6 °K the optical density begins to increase at $H = 6$ kG and begins to saturate at $H = 12$ kG, although the onset of magnetic domains occurs at $H = 9.5$ kG and the end occurs at $H = 16$ kG. At lower temperatures the optical density exhibits similar differences with magnetization measurements. The magnetic order associated with the optical density is not, therefore, the same as that responsible for the magnetization. Instead, the magnetic order responsible for the behavior of the optical density is nearest-neighbor ferromagnetic short-range order and is proportional to the two-dimensional magnetic internal energy. These optical experiments can, therefore, be used to measure the short-range magnetic order which contributes strongly to the specific heat. Moreover, by permitting the optical path to extend over only a small area in the center of the sample the inhomogeneity of the internal magnetic field can be kept relatively small. Such a technique is highly desirable in materials that cannot be easily machined to appropriate shapes.

V. MAGNETIC CIRCULAR DICHORISM AT 4270 Å

The entire spectral region investigated exhibits a complex and relatively large MCD with a complicated field and temperature dependence. In this paper we will concentrate only on the MCD at 4270 Å. Figure 5 illustrates typical experimental traces of the MCD of the 4270-Å line in the three magnetic phases.

In Fig. 5(a) one can see that in the paramagnetic phase, $T > T_N$, the MCD consists largely of a zero-moment change in the absorption band (MCD proportional to the absorption) with a small admixture of first-moment shape (MCD proportional to the first derivative of the absorption). Because the diamagnetic contribution to the MCD is expected to be small the MCD corrected for the temperature dependence of the optical density is proportional to the total magnetization, and in the magnetic field range available is linear in the applied magnetic field. The temperature dependence of the corrected MCD was also measured. In the range of 30 °K–130 °K it is approximately proportional to T^{-4}. Since the magnetization varies as $1/(T + T_N)$ in this range, this result suggests that at relatively high temperatures the complex nature of the Fe^{++} ground-state manifold must be considered in order to interpret the measurements. It was not possible to extend the MCD measurements to higher temperatures since the absorption line decreases rapidly because of the Debye-Waller factor.

For temperatures $T < T_T$ the MCD is illustrated in Figs. 5(b)–5(d) which exhibit graphically the evolution of the MCD as the lower boundary of the

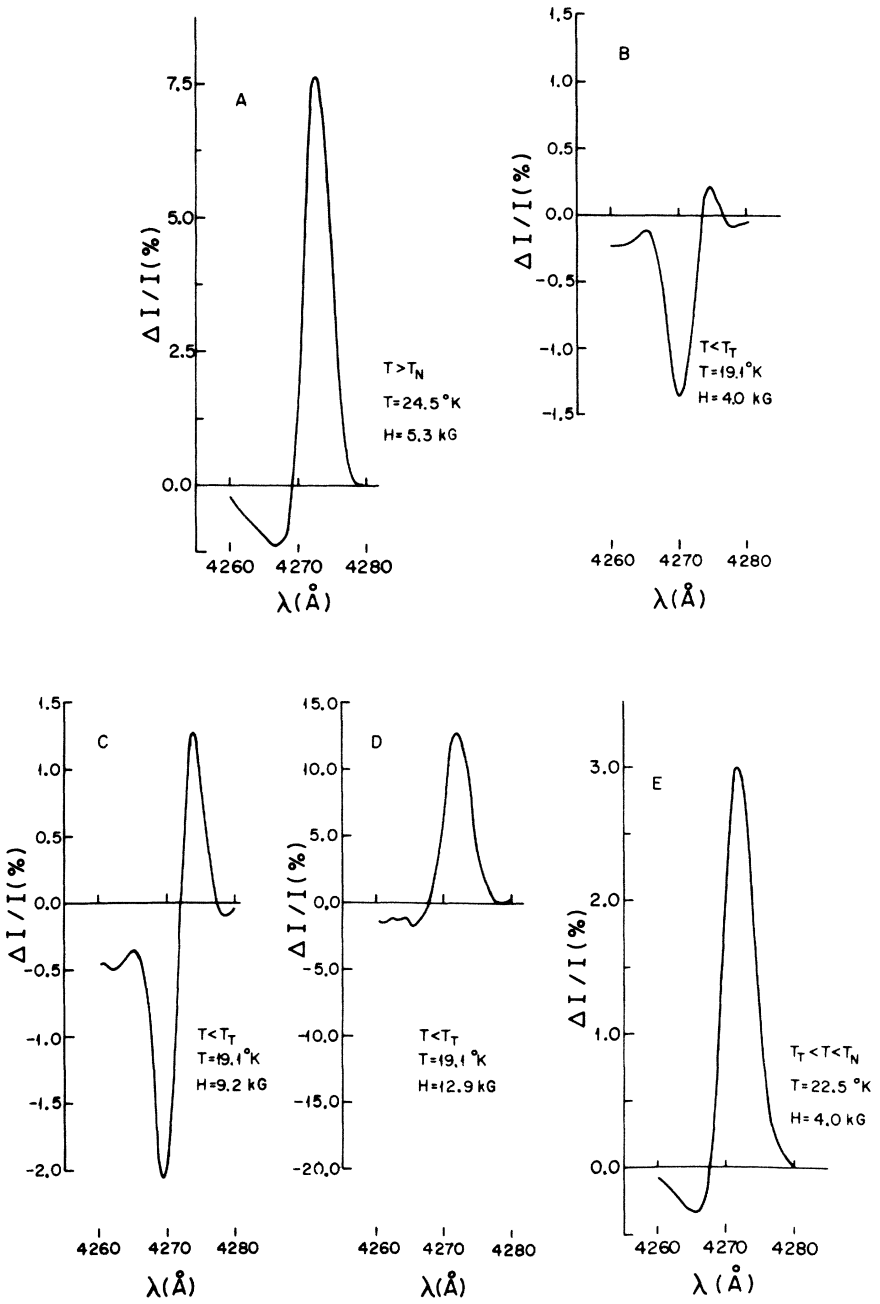

FIG. 5. Experimental traces of magnetic circular dichroism at five positions in the magnetic-phase diagram.

mixed-phase region is crossed at constant temperature from the AF phase. In magnetic fields $H < H_c^-$ the AF MCD illustrated in Fig. 5(b) consists of a zero-moment shape with the opposite sign and much smaller amplitude than the paramagnetic MCD. As the magnetic field is increased toward H_c^- this AF MCD increases in magnitude, and another zero-moment shape with the same sign as the paramagnetic MCD begins to appear. Figure 5(c) illustrates the simultaneous occurrence of these MCD components. The paramagnetic component, which is shifted to lower energies by 8 cm^{-1}, increases slowly with field at low field and then more rapidly with magnetic field as H_c^- is approached. Figure 5(d) illustrates the MCD of the mixed-phase region for $H_c^- < H < H_c^+$. In this region the MCD consists entirely of a zero-moment shape with the same sign as the paramagnetic MCD. For temperatures $T_T < T < T_N$ in the AF phase the MCD does not exhibit a negative MCD at low magnetic fields. Instead, as Fig. 5(e) indicates, the MCD at these temperatures consists of a zero-moment

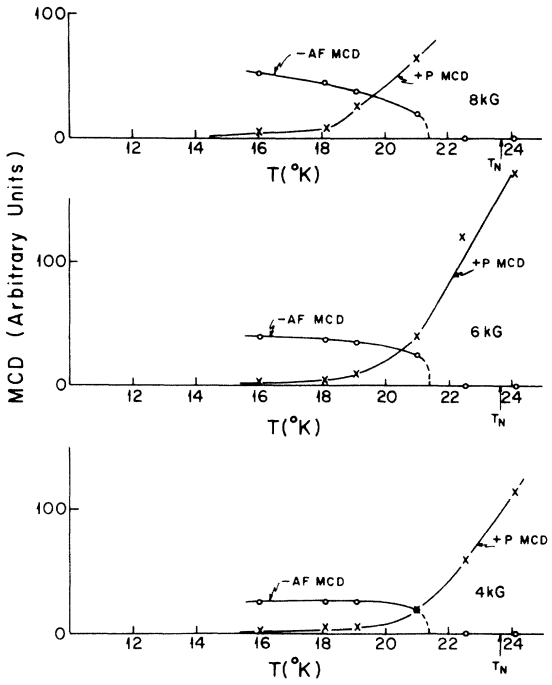

FIG. 6. Plot of the two components of magnetic circular dichroism vs temperature for several magnetic fields $H < H_c^-$.

shape with the same sign as the paramagnetic MCD. Figures 5(b) and 5(e) illustrate the evolution of the MCD as the temperature is increased at constant magnetic field. As the magnetic field is increased the field dependence of this MCD shows an abrupt change in slope at the higher-order phase boundary. In Fig. 6 the temperature dependence of the two components of the MCD is reported. This figure indicates that the negative MCD which disappears as the mixed-phase is reached at H_c^- also abruptly approaches zero with increasing temperature even in magnetic fields less than H_c^-.

The MCD in the magnetically ordered phases can be interpreted as the superposition of two zero-moment shape components. The existence of the negative MCD component for $T < T_T$ can be attributed to the spin-disorder induced optical absorption and the metamagnetic nature of $FeCl_2$. At low temperatures in zero applied magnetic field the two magnetic sublattices are aligned respectively parallel (sublattice A) and antiparallel (sublattice B) to the c axis. One sublattice exhibits a large ground-state spin polarization that is equal in magnitude but opposite in sign to that of the other sublattice, whereas the optical absorption on one sublattice is equal to that of the other sublattice. The MCD in zero magnetic field is therefore zero. The application of a small magnetic field has opposite effects on the two sublattices. In sublattice A the field tends to increase the spin order and to therefore decrease the optical absorption whereas in sublattice B the spin disorder is increased and the optical absorption is consequently increased. The MCD of sublattice B therefore will prevail over that of sublattice A. Thus the MCD is negative because the sublattice magnetization of B is opposed to the applied field.

As the temperature is increased, this negative MCD decreases and suddenly disappears at approximately 21.4 °K. It must be that above this temperature the net magnetization of sublattice B is no longer opposed to the applied field. There is still a staggered field in the sample, but the magnetization is positive on both sublattices. In the mixed-phase region the MCD is dominated by the volume of the saturated paramagnetic domains which are parallel to the applied magnetic field.

VI. CONCLUSIONS

We have reported the optical study of the metamagnetic properties of $FeCl_2$. The existence and explanation of the TMCD in the mixed-phase region of the magnetic-phase diagram have been reported, and the TMCD has been used to map the phase diagram below the tricritical point. The magnetic field dependence of the sharp, spin-forbidden transition reported by Schnatterly and Fontana has been investigated and used to plot the phase diagram above the tricritical point. We report a tricritical temperature of $T_T = (21.5 \pm 0.1)$ °K. We also have reported measurements of the MCD of this absorption line and have indicated the utility of optical studies to obtain measurements of both the short-range and long-range magnetic order. Based on the results presented here detailed optical investigation of the tricritical-point exponents of $FeCl_2$ and $FeBr_2$ are presently underway.

ACKNOWLEDGMENTS

The authors are indebted to R. J. Birgeneau, J. F. Dillon, E. Yi Chen, and Professor J. J. Hopfield for helpful discussions.

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