Metamagnetic Phase Transitions and Hysteresis in $FeCl_2$†

I. S. JACOBS AND P. E. LAWRENCE*
General Electric Research and Development Center, Schenectady, New York
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A reexamination and refinement of magnetization experiments on the prototypal metamagnetic antiferromagnet $FeCl_2$ is presented. From steady-field single-crystal measurements at 4.2°K, we find the abrupt (metamagnetic) transition at 10.6 kOe, from the low-moment antiferromagnetic state to the saturated configuration whose moment is 4.3±0.1 Bohr magnetons/Fe ion. This transition is of first order up to about 20.4°K, above which it is of higher order. Pulsed-field measurements reveal a marked hysteresis in the metamagnetic transition at 4.2°K. The latter two observations are tested against a critical review of theoretical treatments of the antiferro-paramagnetic transition. It is emphasized that, in order to retain the first-order transition above 0°K and to permit the occurrence of hysteresis, a ferromagnetic intrasublattice exchange is necessary (in addition to a significant anisotropy exceeding the antiferromagnetic intersublattice exchange). The experimental results on $FeCl_2$, along with those on several other metamagnets (i.e., $FeBr_2$, $CoCl_2 \cdot 2H_2O$), are successfully compared with predictions both for the upper-limit temperature (T^*) of the first-order transition (e.g., for $FeCl_2$; expt. $T^*/T_N=0.87$; calc. $T^*/T_N \approx 0.95$) and the variation of hysteresis as a function of T/T_N and of the ratio of intra- to intersublattice exchange. The temperature dependence of the normalized sublattice moment is shown to be reasonably described by an Ising model in the Bethe-Peierls approximation. Although the variation with temperature of the normalized transition field is in close correspondence with that of the sublattice moment, this result is in poor agreement with the model just cited and with all others presently available.

I. INTRODUCTION

FOR a number of decades the anhydrous dihalides of the iron-group elements have attracted interest. In particular, the field- and temperature-dependent magnetic properties of $FeCl_2$ have stimulated theoretical attention leading to models for antiferromagnetism[1] and for metamagnetism.[2] The latter name was proposed informally by Kramers[3] to apply to those substances which were unorthodox when viewed either as antiferromagnets or ferromagnets. In $FeCl_2$, this is manifested at low temperatures by a rather sharp transition[4] with increasing field (~10 kOe) from a state of low moment and low susceptibility to a state of high net moment and rather low differential susceptibility. It is this field-induced transition in an antiferromagnet which we call "metamagnetic," although this definition is more restrictive than originally used. The transition is thereby distinguished from the other magnetization processes[5] in a simple uniaxial antiferromagnet, i.e., the "spin-flop" phenomenon and the transverse magnetization.

The structure of $FeCl_2$ is isomorphous with $CdCl_2$ and can be imagined as deriving from the rocksalt lattice type by removal of alternate close-packed layers of cations. While the resulting structure is properly rhombohedral, it may be considered in a larger hexagonal cell. The ordering temperature[6] (T_N) is 23.5°K, and neutron diffraction[7] has confirmed the earlier conjecture[1] of intralayer (0001) parallel alignment and interlayer antiparallel alignment. The moment direction is perpendicular to the layer plane, i.e., along [0001].

For three-dimensional order, there must be cation-anion–anion-cation interlayer interactions, in addition to intralayer interactions of a more direct type. From a number of analyses it has been concluded that the intralayer exchange is strongly ferromagnetic while the interlayer exchange is antiferromagnetic and weak. An explanation in the spirit of the molecular field model was presented by Néel.[2] He concluded that a strong anisotropy, comparable to, or exceeding, the antiferromagnetic interlayer exchange must be present in order to obtain the sharp metamagnetic transition observed. In the simple version of this model, as in all concurrent or subsequent ones, the equilibrium field at which the transition occurs, at 0°K, depends only on the antiferromagnetic exchange and the sublattice moment. Extended calculations were given by Gorter and Van Peski-Tinbergen[8] and by Kanamori, Motizuki, and Yosida.[9] However, not all theoretical treatments of the antiferro-paramagnetic transition are appropriate

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* Present address: General Electric Company, Phoenix, Arizona.
[1] L. Landau, Physik. Z. Sowejetunion, **4**, 675 (1933).
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[3] See J. Becquerel, *Le Magnétisme* (Institut International de Cooperation Intellectuelle, CNRS, Paris, 1940), p. 97.
[4] C. Starr, F. Bitter, and A. R. Kaufmann, Phys. Rev. **58**, 977 (1940).
[5] T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. **4**, 1 (1955).
[6] O. Trapeznikowa and L. Schubnikow, Physik. Z. Sowjetunion **7**, 66 (1935); E. F. Westrum, Jr. quoted in J. W. Stout, Pure Appl. Chem. **2**, 287 (1961).
[7] M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev. **113**, 497 (1959); A. Herpin and P. Meriel, *Colloque National de Magnétisme, Strasbourg, 1957* (CNRS, Paris, 1958), p. 105.
[8] C. J. Gorter and T. van Peski-Tinbergen, Physica **22**, 273 (1956); see also O. P. van Wier, T. van Peski-Tinbergen, and C. J. Gorter, *ibid* **25**, 116 (1959).
[9] J. Kanamori, K. Motizuki, and K. Yosida, Buseiron-Kenkyu **63**, 28 (1953) (in Japanese); this paper was not available to us, see Sec. IVA herein.

to describe typical experimental observations on $FeCl_2$ and related substances. The discrepancies become particularly apparent as soon as the temperature is raised above 0°K. A discussion of the required features is one of our goals in this work.

Kanamori[10] investigated the microscopic origin of the anisotropy energy in $FeCl_2$ and concluded that, at low temperatures, a good approximation is an Ising model in which the transverse spin components are completely quenched. Both Yomosa[11] and Heap[12] adopted this model and applied the Bethe-Peierls statistical method to calculate a number of properties. Quite recently, Ôno *et al.*[13] and Stout[14] have reexamined the origin of the anisotropy and they conclude that the Ising model is an oversimplification of the energy-level structure.

Weighed against these theoretical efforts, the published experimental information has been relatively inadequate. The earliest studies were on polycrystalline material and were confined to low fields. The higher-field work of Starr *et al.*,[4] showing the full transition, opened a new era, although still on polycrystalline material. In retrospect, their $FeCl_2$ material must have had considerable preferred orientation, as several workers have noted. Most of the theories have been tested against Starr's work and the single crystal study of Bizette *et al.*[15] Unfortunately the latter work raised a number of problems in that it exhibited an apparently impossible magnitude of the magnetization above the transition field, a marked failure to saturate, and a persistence of the field-induced transition considerably above the ordering temperature.[16] The neutron diffraction study[7] gave some data on the magnitude of the sublattice moment, but with a moderately large experimental uncertainty. Quite recently, the low-field susceptibility measurements have been repeated,[17] some chlorine nuclear-magnetic-resonance data have been obtained,[18] and a Mössbauer study of the ferrous ion has been reported.[13]

With this background we undertook several experiments to make more precise the parameters describing the metamagnetic behavior of $FeCl_2$. From steady-field magnetization measurements on a single-crystal sample at low temperature we obtain the saturation moment after the abrupt transition and the critical (equilibrium) field for the transition, H_c. The transition is further characterized by its temperature dependence $H_c(T)$ and the temperature marking an upper limit to the occurrence of the abrupt transition. We also look for antiferromagnetic short-range order effects near or above the Néel point. Employing pulsed high fields we observe a small differential susceptibility after saturation and a marked hysteresis in the transition. The latter was initially surprising, for there had been very few reports of such behavior, despite several predictions thereof, hitherto ignored. These results confirm the supposition that the metamagnetic transition is of first order. Comparisons are made with calculations of the saturation moment, the upper-limit temperature for the first-order transition, the hysteresis, as well as the temperature dependences of the transition field and of the sublattice moment. In addition these comparisons are extended to observations on other metamagnetic antiferromagnets.

Preliminary reports on some of the results have been given earlier.[19,20] During this work a single-crystal magnetization curve through the transition at 4.2°K was published by Ito and Ôno.[21] Our present results are in good agreement with theirs, but cover a wider range of observation. Also there appeared a repeat measurement of magnetization by Bizette *et al.*[22] which removed the earlier objections. We are in general agreement with their new results, apart from a few details. A variety of far-infrared absorption measurements has been carried out,[19] the details of which will be reported at another time.

II. EXPERIMENTAL TECHNIQUES

All measurements were made on single-crystal samples cut from a boule section of anhydrous ferrous chloride generously provided by Dr. J. W. Cable of the Oak Ridge National Laboratory. This material is identical to that used in the neutron diffraction study [Wilkinson *et al.* (Ref. 7)]. For magnetization measurements, samples were cut into right circular cylinders with the cylinder axis perpendicular to the easily identifiable (0001) basal plane. To avoid hydration, for which there is a strong tendency, manipulations were carried out in dry atmospheres. Samples were coated with mineral oil for protection and mounted in tight plastic capsules. Despite the precautions, some cracking along basal planes occurred. These "cracks"

[10] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **20,** 890 (1958).
[11] S. Yomosa, J. Phys. Soc. Japan **15,** 1068 (1960).
[12] B. R. Heap, Proc. Phys. Soc. (London) **80,** 248 (1962).
[13] K. Ôno, A. Ito, and T. Fujita, J. Phys. Soc. Japan **19,** 2119 (1964).
[14] (a) J. W. Stout (private communication); (b) J. W. Stout, C. L. Brandt, and C. Trapp, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 887.
[15] H. Bizette, C. Terrier, and B. Tsai, Compt. Rend. **243,** 895 (1956).
[16] This feature was subsequently retracted. See H. Bizette, C. Terrier, and B. Tsai, *Colloque National de Magnétisme, Strasbourg 1957* (CNRS, Paris, 1958), p. 97.
[17] $\chi_{\parallel}$: C. L. W. Brandt, thesis, University of Chicago, 1960 (unpublished); $\chi_{\perp}$: C. Trapp, thesis, University of Chicago, 1963 (unpublished); see also Ref. 14.
[18] W. H. Jones, Jr., and S. L. Segel, Phys. Rev. Letters **13,** 528 (1964).
[19] I. S. Jacobs, S. Roberts, and P. E. Lawrence, J. Appl. Phys. **36,** 1197 (1965).
[20] I. S. Jacobs, Bull. Am. Phys. Soc. **12,** 285 (1967).
[21] A. Ito and K. Ôno, J. Phys. Soc. Japan **20,** 784 (1965).
[22] H. Bizette, C. Terrier, and B. Tsai, Compt. Rend. **261,** 653 (1965).

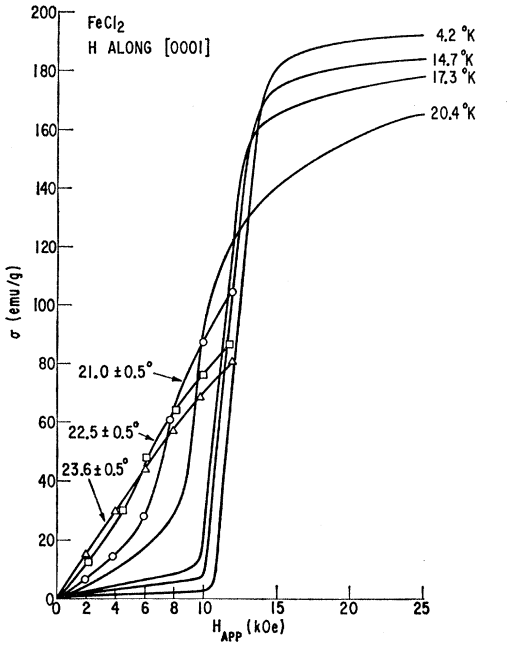

FIG. 1. Magnetization isotherms, σ versus H, (steady field) for single-crystal $FeCl_2$ (H||[0001]).

resulted in cylinder lengths greater than would be predicted by x-ray density calculations, i.e., lower apparent densities. If such lengths are kept constant during the experiments, e.g., by capsule confinement, no serious calibration problems arise. (Calibration is accomplished by comparison with nickel cylinders of similar dimensions.)

The steady-field magnetization measurements were carried out by a sample-motion method using a Grassot-type fluxmeter for detection. A description of this has been given,[23] except that the field range presently extends to 25 kOe. Both helium and hydrogen were used as cryogenic fluids. In such constant-temperature boiling fluids, data points were obtained at close field intervals. Above 20.4°K, the specimen is permitted to warm slowly, so that the drift in temperature limits the density of data readings within an "isotherm."

The pulsed-field measurements ranged up to 200 kOe and were carried out at 4.2°K only. Observations were made both of the moment σ and of its time derivative $d\sigma/dt$. The system[24] and techniques[24,25] have been described earlier. We note that these data are displayed on the oscilloscope as a function of (external) field. This method is particularly useful for detecting and measuring hysteresis effects. Employing only one magnet coil, the rate of change of field at the transition field was variable by a factor of three, from 2.5 to 7.5×10^7 Oe/sec. An apparent transition field is located very easily from the position of the spike in $d\sigma/dt$ versus H, but, because this includes the rise of magnetization against the demagnetizing field, it tends to locate the midpoint of the transition. A judgment of the initiation field for the transition, determined from the σ-versus-H curve, will always be lower. In our data, this difference as typically ~500 Oe.

III. RESULTS

The steady-field magnetization curves to fields of 25 kOe applied along the [0001] direction are shown in Fig. 1 for various temperatures from 4.2°K to the Néel temperature. For those isotherms in constant temperature baths, no hysteresis could be detected on retracing the curves in the reverse direction, within the magnet-calibration uncertainty. (Data points are very close and are omitted for clarity.) At 4.2°K, the low-field data yield a rather low susceptibility, but one which is several times larger than that measured by Brandt[17] in his careful study. While the present equipment is not very sensitive in this range, an enhanced susceptibility could readily appear if a small fraction of the sample were misoriented inasmuch as $\chi_\perp$ is 15 times greater at this temperature.[17] From this 4.2°K curve, we note a strong tendency to "saturation" above the transition. The moment above the transition (i.e., at 25 kOe) is about 4.3 ± 0.1 Bohr magnetons (β) per Fe ion. Its magnitude is in very good agreement with that recently reported by Ito and Ôno[21] [$(4.4\pm0.2)\beta$], and with the repeat measurement by Bizette *et al.*,[22] who report 4.29β at 17.5 kOe. It is also consistent with the less precise neutron diffraction results [Wilkinson *et al.* (Ref. 7)] [$(4.5\pm0.7)\ \beta$, $(4.35\pm0.4)\ \beta$].

The accord among all these determinations can be used to support the two recent microscopic calculations on the ground-state atomic moment. These considered the cubic and trigonal components of the crystalline field, the spin-orbit coupling and the exchange (as a molecular field). Stout[14] obtained his parameters by comparison with the susceptibility results of Trapp and Brandt, and calculated an atomic moment of 4.04β. Ôno, Ito, and Fujita[13] employed their results on the Mössbauer spectra to fix the parameters, resulting in a calculated moment of 4.14β. While the agreement is rather good, a discrepancy of about 5% remains between this observation and theory. One should note that in the preliminary far-infrared absorption study,[19] the g value of the antiferromagnetic resonance was 4.1 ± 0.1 (stated there as 4.0 ± 0.1). This rather better agreement with theory suggests a slight difference between the microscopic parameters of the antiferromagnetic state and those of the saturated configuration as measured herein. These two observations, the marked tendency toward saturation and the reasonable magni-

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[24] I. S. Jacobs and P. E. Lawrence, Rev. Sci. Instr. **29**, 713 (1958), improved by substitution of electronic integrators (Tektronix type O).
[25] S. Foner and S. L. Hou, J. Appl. Phys. **33**, 1289 (1962).

tude of moment, remove some of the problems presented in the prior single-crystal study.[15]

The remaining possible problem with the earlier study was the original report of a persistence of the field-induced transition up to $\sim 2T_N$.[15,16] This observation of an initial upwardly concave curve *above* T_N has also been reported for dysprosium aluminum garnet[26] and for ferrous bromide.[27] An exact calculation by Fisher[28] predicts such behavior from residual intermediate range *antiferromagnetic* order up to several tens of percent above T_N. From our data in Fig. 1, however, the curve at 23.6 ± 0.5°K which is closest to the Néel point fails to show any upward concavity, nor do other isotherms a few degrees higher (not shown). Equivalent behavior is reported in the repeat measurement by Bizette *et al.*[22] Although detailed criteria for the presence or absence of this behavior do not seem to have been worked out in detail, one generalization is easily made. While each of these compounds is highly anisotropic, the effect of residual antiferromagnetic order above T_N is present only for those with antiferromagnetic interactions which are comparable to or greater than their ferromagnetic ones. $FeCl_2$ does not meet this criterion.

Support for this generalization can be found by noting that this magnetization behavior manifesting a short- or intermediate-range *antiferromagnetic* order above T_N occurs in cases where the susceptibility maximum is at a temperature above T_N. Apart from the calculation of Fisher,[28] we cite that of Nagai[29] showing that the susceptibility maximum occurs at a temperature which decreases toward T_N as the strength of the ferromagnetic interaction increases toward equality with that of the antiferromagnetic one.

From the lowest temperature measured, up to 20.4°K ($0.87T_N$), and possibly slightly higher, the σ-versus-H curves have a transition region which is linear within the experimental accuracy. The differential susceptibility in this region (with respect to the applied field) is independent of temperature. We shall take this slope as the reciprocal of the effective demagnetizing factor. Determined in this way, the factor for different cylinder samples was about $1\frac{1}{2}$ to $2\frac{1}{2}$ times that calculated from their external dimensions. We attribute this to the basal plane cracking, as noted above, which invalidates the direct calculation of the demagnetizing factor. (As a simple example, assuming an internal differential susceptibility of 10 or more within the transition region, a crack causing a 1% apparent length change would cause a doubling of the magnetic reluctance.) With these assumptions, the transition is being considered as one of first order, i.e., the magnetization is discontinuous as a function of the *internal* field, persisting so up to 20.4°K. By extrapolating to zero magnetization from the linear transition region, we determine the internal critical transition field H_c at various temperatures. At 4.2°K, we obtain $H_c=10.6\pm0.1$ kOe. The other data on $H_c(T)$ are presented in Fig. 2, where the point for $T=(22.5°\pm0.5)$°K describes an inflection in the curve (higher-order transition) and that for $(21.0°\pm0.5)$°K locates a transition which probably is of a order higher than first. The low-temperature critical fields found in this work are 0.4 to 1.5 kOe lower than reported elsewhere.[4,15,21,22] In the work of Ito and Ôno, the external-field data were corrected using a demagnetizing factor calculated from the over-all dimensions of the sample. Despite the correction, their transition region retains a residual breadth in field, and the critical field was *chosen* as the midpoint of this region, 11.6 kOe at 4.2°K. Their sample, however, also had a less than ideal apparent density suggesting that an effective empirical demagnetizing factor would have been more appropriate. Extrapolation of their data to zero magnetization gives a value of 10.9 kOe, in closer agreement with the present work. The recent value obtained by Bizette *et al.* for $H_c(0)$ is 11.5 kOe. We have no explanation for this discrepancy.

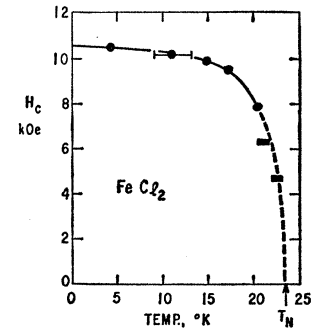

FIG. 2. Critical transition field H_c versus temperature T for $FeCl_2$. Solid line—first-order transition; dashed line—higher-order transition.

The pulsed-field magnetization measurements at 4.2°K (H parallel to [0001]) revealed two features. In the field range from 50 to 200 kOe, the $FeCl_2$ exhibits a residual differential susceptibility of $\chi_{||}=1.1\pm0.3\times10^{-2}$ emu/mole. Although our measurement is much less precise, this value agrees with Brandt's[17] value for the *low*-field susceptibility, $\chi_{||}(4.2°K)=1.16\times10^{-2}$ emu/mole. This has been quantitively calculated by Stout[14] as the single-ion Van Vleck susceptibility following from the ligand field theory energy-level diagram.[30] He obtained $\chi_{||}=1.11\times10^{-2}$ emu/mole, in comparison with Brandt's measured $\chi_{||}(\sim0°K)=1.05\times10^{-2}$ emu/mole.

[26] M. Ball, W. P. Wolf, and A. F. G. Wyatt, Phys. Letters **10**, 7 (1964); B. Schneider and W. P. Wolf, Bull. Am. Phys. Soc. **11**, 109 (1966).
[27] I. S. Jacobs and P. E. Lawrence, J. Appl. Phys. **35**, 996 (1964).
[28] M. E. Fisher, Proc. Roy. Soc. (London) **A254**, 66 (1960).
[29] O. Nagai, J. Phys. Soc. Japan **18**, 510 (1963).
[30] For other examples of this type of low-field calculations, see e.g., S. D. Silverstein and I. S. Jacobs, Phys. Rev. Letters **12**, 670 (1964). The connection between this mechanism and the high-field susceptibility was noted earlier. See W. P. Wolf, Rept. Progr. Phys. **24**, 212 (1961).

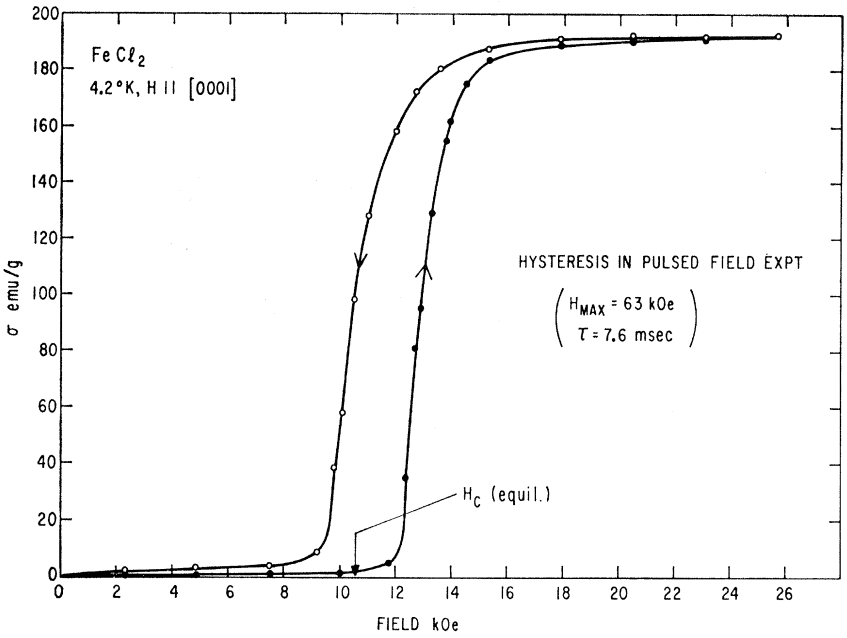

FIG. 3. Magnetization versus field at 4.2°K, (pulsed field, $H_{max}=63$ kOe, half-period=7.6 msec), for single-crystal $FeCl_2$ ($H||[0001]$).

Similar examples of such high-field residual susceptibilities (after saturation) have been noted for $FeBr_2$ [27] and $CoCl_2$.[31]

The second and more striking feature of the pulsed-field experiment is the appearance of a considerable hysteresis in the metamagnetic transition in contrast to the measurements in continuous fields. This was observed on several samples, varying in its magnitude among them. A typical result for the σ-versus-H mode of observation is shown in Fig. 3. The rising and falling field branches are roughly similar, but displaced asymmetrically with respect to the equilibrium transition field. Typical behavior was $\Delta H_c \sim 3$ kOe at $dH/dt = 2.5\times10^7$ Oe/sec (65 kOe, H_{max}), increasing to $\Delta H_c \sim 4$ kOe at $dH/dt = 7.5\times10^7$ Oe/sec (200 kOe, H_{max}). These separations are measured most easily in the $d\sigma/dt$-versus-H mode of observation. The rising field transition $H_c(+)$ occurred about $\frac{2}{3}\Delta H_c$ above the equilibrium value and that for falling field, $H_c(-)$, about $\frac{1}{3}\Delta H_c$ below. The magnitude of the hysteresis for a 65-kOe pulse was not affected by prior pulsing to 200 kOe. It may be roughly characterized as $\Delta H_c/H_c \approx 0.3$. It is interesting to note that $H_c(+)$, determined in the $d\sigma/dt$ mode, is very close to 13 kOe, in exact accord with the report of Foner and Hou,[25] who also used pulsed fields. It also exceeds the equilibrium H_c at 0°K, thus removing from consideration a magnetocaloric origin.

While hysteresis has been observed in the field-induced transitions of a number of compounds which exhibit first-order transitions with temperature in zero field, the present result might come as a surprise. This follows from the absence or near absence of previous reports for simple metamagnetic antiferromagnets. In $FeBr_2$,[27] a sharp metamagnetic transition in pulsed fields was observed at 4.2°K with no detectable hysteresis. Similarly, in $FeCO_3$,[32] no hysteresis was originally reported, although the transition was less sharp and experimental conditions tended to mask any hysteresis. For another view, however, Ozhogin[33] reported some hysteresis in $FeCO_3$. Of particular interest is the work of Motokawa and Date,[34] who recently observed pulsed-field hysteresis ($d\sigma/dt$ versus H) at the lower of the two magnetization discontinuities in $CoCl_2\cdot 2H_2O$ measured previously in steady fields, but *not* at the upper one.

Prompted by this background, we reexamined our results on $FeBr_2$, whose metamagnetic transition we reported at 31.5 kOe. Hysteresis at 4.2°K, if present at all, is very small ($\Delta H_c < 100$ Oe). By contrast, all curves recorded at 2°K exhibit a small but definite hysteresis ($\Delta H_c \approx 500$ Oe, $\Delta H_c/H_c = 0.016$) of a character closely resembling that in $FeCl_2$. Also, in a new investigation on a $FeCO_3$ crystal, we have confirmed Ozhogin's observation. For this compound, however, the character of the hysteresis is quite different from that in $FeCl_2$ or $FeBr_2$, in that it is confined to a low-field "tail" on the decreasing field branch. Thus the observation of hystersis in a metamagnetic transition appears to be quite general, provided, apparently, that some conditions on rapid sweep rates and sufficiently low temperatures relative to T_N are met. From a ther-

[31] I. S. Jacobs, P. E. Lawrence, and S. D. Silverstein, Bull. Am. Phys. Soc. **10**, 351 (1965).

[32] I. S. Jacobs, J. Appl. Phys. **34**, 1106 (1963).

[33] V. I. Ozhogin, Zh. Eksperim. i Teor. Fiz. **45**, 1687 (1963) [English transl.: Soviet Phys.—JETP **18**, 1156 (1964)]; (private communication).

[34] M. Motokawa and M. Date, J. Phys. Soc. Japan **20**, 465 (1965).

modynamic viewpoint, if the metamagnetic transitions of the type we are considering are truly of first order, as has often been stated, the possibility of metastable states and resulting hysteresis should be a natural consequence. Conversely, the existence of hysteresis in $FeCl_2$ is one of several proofs that the rather sharp transition is one of first order.

IV. DISCUSSION

A. Historical Review

In this section we discuss aspects of the metamagnetic behavior as revealed in the magnetization measurements. A molecular-field model will be adequate for most of this discussion. Thus, in the familiar fashion,[5] we introduce the following effective field acting on the spin of the positive and negative sublattices:

$$\mathbf{H}_{\text{eff}}{}^{\pm}=\mathbf{H}-A\mathbf{M}^{\mp}+\Gamma\mathbf{M}^{\pm}, \tag{1}$$

where $\mathbf{H}$ is the external field applied along the easy axis of the spins (z axis), $\mathbf{M}^{\pm}$ are the sublattice magnetizations (positive when they are parallel to the applied field, negative when antiparallel) and A and Γ are the molecular-field coefficients. The signs preceding A and Γ are chosen so that when these coefficients are positive, the exchange between sublattices (A) is antiferromagnetic and that within a sublattice (Γ) is ferromagnetic. We also employ anisotropy energy in the simplest form for a uniaxial system:

$$E_a=\tfrac{1}{2}K(\gamma_+{}^2+\gamma_-{}^2), \tag{2}$$

where γ_+, γ_- are the direction cosines of $\mathbf{M}^+$, $\mathbf{M}^-$ with respect to the easy (z) axis. This is also often expressed as an "anisotropy magnetic field,"

$$\mathbf{H}_a{}^{\pm}=(K/M^{\pm})\,(0,\,0,\,\gamma_{\pm})=(K/M_0{}^2)\,(0,\,0,\,M_z{}^{\pm}), \tag{3}$$

where M_0 is the value of $M^{\pm}$ for vanishing external field.

This model of two isotropic exchange coefficients and a uniaxial anisotropy of the form chosen is equivalent to a choice of an anisotropic exchange within a sublattice and an isotropic one between the sublattices. Anisotropic exchange between the sublattices does not appear to be required for the present work.

The development of theoretical treatments of metamagnetic transitions such as that in $FeCl_2$ is closely linked to the history of descriptions of how an antiferromagnet undergoes a phase transition to a paramagnetic state when subjected to a large external field. Starr[35] considered a model based on ordering of small groups of moments leading to an S-shaped curve, except at the absolute zero where it predicts an abrupt transition. Later, more realistic two-sublattice systems were considered. Motivated by different experiments, Garrett[36] employed the molecular-field model, restricted the spins to a particular direction, and considered, mainly, an antiferromagnetic interaction between the sublattices. When he did introduce intrasublattice interactions, they were also antiferromagnetic ($\Gamma<0$). Under these assumptions, the predicted magnetization curves are again S shaped (of order higher than first), except at the absolute zero. At the same time Ziman,[37] restricting himself to an antiferromagnetic interaction ($\Gamma=0$) between sublattices, invoked an Ising model ($K=\infty$) and applied the improved statistical approximation of the Bethe-Peierls method. Apart from some sharpening of the transition, the results are qualitatively similar. The most rigorous treatment in this vein is that of Fisher,[28] who solved exactly a two-dimensional Ising model. Here again the transitions above 0°K are of higher order, but the solution displays many features of interest, two of which we have noted above.

Only when we come to calculations in which one invokes a ferromagnetic intrasublattice interaction ($\Gamma>0$) do we find results with promise of application to $FeCl_2$. Perhaps the first of these was a particular case treated by Sauer and Temperley[38] in which the interaction of Ising spins was taken as approximately dipolar, and Bragg–Williams (or molecular-field) approximations invoked. Of particular interest is the fact that this model predicts a first-order transition at all temperatures below $2T_N/3$, and one of second order above that point. At the same time, and without knowledge of the experiments of Starr *et al.*,[4] Schultz[39] extended Landau's[1] early model to consider a molecular-field theory with two interactions. He was able to predict the possibility of abrupt transitions, tending toward saturation, that might also be accompanied by hysteresis. Undoubtedly, the interposition of the war prevented both a fuller development of this work and a normal distribution of the article. Over a decade elapsed before the problem was taken up again, more or less simultaneously in several places, and almost without knowledge of the earlier progress.

Néel[2] considered the case where $\Gamma/A\gg1$, and restricted himself to low temperatures. The resulting behavior depends on the ratio of anisotropy to antiferromagnetic exchange, i.e., the value of $K/AM_0{}^2$. For small values of this ratio, one observes the spin-flop transition which he had predicted much earlier.[40] When, however, the ratio equals or exceeds unity, there appears an abrupt (first-order) transition between the antiferromagnetic state and the ferromagnetic or saturated paramagnetic one. (At 0°K, the same sequence of events would occur with increasing K, even if $\Gamma=0$.) He noted the possibility of metastable states and accompanying

[35] C. Starr, Phys. Rev. **58,** 984 (1940).

[36] C. G. B. Garrett, J. Chem. Phys. **19,** 1154 (1951).
[37] J. M. Ziman, Proc. Phys. Soc. (London) **64A,** 1108 (1951).
[38] J. A. Sauer and H. N. V. Temperley, Proc. Roy. Soc. (London) **A176,** 203 (1940).
[39] B. H. Schultz, Physica **7,** 413 (1940).
[40] L. Néel, Ann. Phys. (Paris) **5,** 232 (1936).

hysteresis, but his remarks on this point dealt mainly with the spin-flop transition.

Gorter and Van Peski-Tinbergen[8] considered the molecular-field model in fuller detail for an orthorhombic symmetry, allowing anisotropic exchange and anisotropic moment values. Graphical methods for the solution of any case are presented, irrespective of the ratio of intra- to intersublattice exchange or of the relative magnitude of the anisotropy in the exchange coefficients (Γ/A and K/AM_0^2, respectively, in our simplified case). Also, these solutions are obtainable, in principle, at any temperature. If K/AM_0^2 equals or exceeds unity, then for all values of $\Gamma>0$, a first-order transition is obtained at low temperatures but above 0°K. (A certain minimal value of Γ is required, for this transition to resemble completely the antiferro-ferro transition just described.) At higher temperatures but below T_N, this first-order transition goes over into one of second order. (This recalls the predictions of Sauer and Temperley.[38]) In the region where the transition is of first order, hysteresis may be present, as is described in Sec. IVD below. It is possible to calculate its maximum value as a function of temperature for a given ratio of Γ/A. We present below results of such calculations along with other results obtained using the methods of these authors.

Meanwhile, an extensive treatment was developed by Kanamori, Motizuki, and Yosida.[9] Unfortunately, their work was not widely available, until certain parts of it were summarized in later papers by Kanamori[10] and by Motizuki.[41] This group adopted a molecular-field Ising model ($K=\infty$) in which the behavior is determined solely by Γ/A. Again, the first-order transition is preserved above 0°K, only if $\Gamma>0$. Although recent investigations[13,14] of the $FeCl_2$ crystal field have indicated some limitations to the Ising model, it remains rather useful. One advantage of their treatment is the derivation of a simple relation determining the upper limit temperature between transitions of first order at low temperature and those of higher order (second order in their model). This temperature, $\tau^*=T^*/T_N$, is given as

$$\tau^*=1-(A/3\Gamma), \tag{4}$$

valid in the region $0.6<\Gamma/A<\infty$. For smaller values of Γ/A, the boundary temperature occurs at τ slightly greater than the τ^* given in Eq. (4), (for details see Motizuki[41]). A second advantage inherent in the use of the Ising model is the possibility of invoking improved statistical calculations, such as the Bethe-Peierls method. Both Yomosa[11] and Heap[12] have done this with specific reference to $FeCl_2$. While their methods of treating the problem are similar, Heap avoids certain approximations used by Yomosa. Both find the first-order transition, giving way to one of second order at elevated temperatures, but below the Néel point.

[41] K. Motizuki, J. Phys. Soc. Japan **14**, 759 (1959).

B. Estimation of Exchange Parameters

Following this historical outline, we shall turn to a comparison of the predictions of these calculations with the improved experimental data on $FeCl_2$ and several other metamagnetic antiferromagnets, the data for which have become available only recently. In keeping with the phenomenological character of most of the models just described, we employ the parameters A, Γ, and K defined earlier. Some estimate of their relative magnitudes is needed in order to proceed. At this point, only a lower limit can be obtained for K, i.e., $K>AM_0^2$, deduced[2,8] from the existence of a discontinuous transition at $T=0$. In this K range then, there is no basic difference between those models which start with $K=\infty$ and those which allow smaller values. For evaluating A, *all* theories are identical, i.e., at $T=0$, a simple energy balance at the transition field H_c between the antiferromagnetic and the ferromagnetic states yields $H_c=AM_0$. On a microscopic view, $M_0=(N/2)\mu$, where μ is the moment per atom and $A=2z_{AF}J_{AF}/N$, where z_{AF} is the number of neighbors participating, each with an antiferromagnetic exchange of strength J_{AF}.

For evaluating Γ, the situation is less simple. The extrapolated Weiss temperature from high-temperature susceptibility data is very difficult to use in compounds that are so highly anisotropic and whose excited states are so easily populated at moderate temperatures. Thus we rely on the Néel point T_N and this choice brings us to the problem of statistical approximations. The easiest model to use is the molecular-field approximation which is well known for its limitations. For arbitrary spin S, one has

$$\Gamma/A=(kT_N/\mu H_c)(3S/S+1)-1, \tag{5a}$$

where k is Boltzmann's constant. In keeping with the calculations cited, and in a view suggested by the Ising model,[10] we shall tentatively pick an effective $S=\frac{1}{2}$. Thus from Eq. (5a) one has

$$\Gamma/A=(kT_N/\mu H_c)-1. \tag{5b}$$

As with the evaluation of A, a more precise definition of Γ is possible, i.e., $\Gamma=2z_FJ_F/N$, to show the individual ferromagnetic exchange contribution J_F from each of z_F neighbors. In the molecular-field approximation this precision is not needed, but it is significant with more refined statistics. In calculating with the Bethe-Peierls method, both Yomosa[11] and Heap[12] have adopted $z_{AF}=z_F=6$ for $FeCl_2$. Considering the possible superexchange paths, one may have some reservation about the choice, but a better one is not readily at hand. We shall adhere to their choice for $FeCl_2$ and also for $FeBr_2$, which is similar in crystal structure but not identical. With this choice we have $\Gamma/A=J_F/J_{AF}$. Their expressions for T_N are (in our notation) as follows:

$$1=5\tanh(\mu^2J_F/kT_N)+6\tanh(\mu^2J_A/kT_N), \tag{6}$$

$$\tfrac{5}{3}=\exp(-2\mu^2J_F/kT_N)+\exp(-2\mu^2J_A/kT_N). \tag{7}$$

TABLE I. Ratio of intralayer (ferromagnetic exchange Γ to interlayer (antiferromagnetic) exchange A, calculated in several Ising-model approximations.

Compound	T_N °K	H_c kOe	μ β	Γ/A Eq. (5b)[a]	Γ/A Eq. (6)[b]	Γ/A Eq. (7)[c]
$FeCl_2$	23.5	10.6	4.3	6.7	8.1	7.8
$FeBr_2$	11	31.5	4.0_5	0.28	0.34	0.42
$CoCl_2 \cdot 2H_2O$ I	17.5	31.6	3.2	0.72	...	...
$CoCl_2 \cdot 2H_2O$ II		46.0		0.49		

[a] Molecular field ($S=\frac{1}{2}$). [b] Bethe-Peierls (Yomosa, Ref. 11). [c] Bethe-Peierls (Heap, Ref. 12).

(From Yomosa and Heap, respectively.) The difference between the two expressions is quite small when Γ/A is large, but becomes more noticeable at smaller values of the ratio.

In Table I we present values of Γ/A obtained from Eqs. (5)–(7) for the ferrous compounds just cited, each of which shows a metamagnetic transition. Added to the list are molecular-field Ising estimates for the *two* metamagnetic transitions in $CoCl_2 \cdot 2H_2O$. This compound is of special interest here because of the hysteresis observed in the transition.[34] For the two ratios needed, the A values were taken as proportional to the two transition fields, or more specifically to those combinations of competing exchange interactions with which Narath[42] fit the observations using a collinear 6-sublattice configuration. (See also Oguchi.[43]) One observes that the ratio Γ/A for these compounds covers a wide range, being much greater than unity for $FeCl_2$, and less than unity but appreciable for $FeBr_2$ and $CoCl_2 \cdot 2H_2O$.

We may make another comparison with the $FeCl_2$ ratios from the ligand-field energy-level calculation by Stout,[14] fitted to accurate susceptibility data. He invoked exchange as a molecular field but considered the effects of nearby excited states in the statistics. His result is $\Gamma/A=9.8$. The lowest states in his energy-level scheme may be approximated by an effective spin $S=1$ in the spin-Hamiltonian formalism. With this choice, we may use Eq. (5a) to obtain $\Gamma/A=10.5$.

C. Order of the Transition

In our historical resumé, we stated that each of the models that predicts an abrupt first-order transition to a nearly saturated configuration at low but nonzero temperatures, also predicts that this transition gives way to one of higher order at elevated temperatures approaching T_N. As is true for all first-order transitions, the full solution[8,9] at low temperature shows that the net magnetization is not a unique function of H, i.e., that the stable-solution branches are separated by a branch of unstable solutions and branch segments of metastable solutions. As the temperature is raised, the field range of the metastable solutions decreases, finally vanishing at the boundary temperature T^* (or τ^*), above which the field-induced transition is no longer of first order. We now consider the predictions for this upper-limit temperature, T^*, depending upon Γ and A, in the light of experimental observations. (See also Keen *et al.*[44] and Kreines.[45])

The theoretical predictions of τ^* take a closed form (Eq. 4 above) in the molecular-field Ising model[41] (at least for a certain range of Γ/A); a different closed form in the Bethe-Peierls calculation of Yomosa,[11] when certain approximations are made (his Eq. 37); and a specific prediction for $FeCl_2$ in Heap's[12] Bethe-Peierls calculation, not readily generalized to other compounds.

Thus for $FeCl_2$, using the exchange coefficients of Table I, we obtain $\tau^*=0.95$ (Eq. 4), $\tau^*=0.96$ (Yomosa) and $\tau^*=0.936$ from Heap's predicted $T^*=22$°K. The spread of these predictions is only 0.6°K. We compare this to our observation of $T^* \approx 20.4$°K ($\tau^* \approx 0.87$) and the slightly lower value claimed by Bizette *et al.*[22] In a rough way, the agreement is satisfactory. While any temperature-dependent effect which reduces Γ/A would bring the predictions closer to experiment, a big effect would be required.

For $FeBr_2$, the molecular-field ($S=\frac{1}{2}$) value of Γ/A falls in the range where Eq. 4 is not directly applicable. Rather than try to fix this, we take the estimate from Yomosa's criterion. This yields $T^*=6.6$°K ($\tau^*=0.60$), which we accept despite the fact that it falls outside his assumption of τ^* lying close to unity. The experimental observations of sharp, first-order transitions at 2 and 4.2°K are consistent with this prediction, but not very demanding of it.

Lastly, we consider $CoCl_2 \cdot 2H_2O$ for which we have two transitions and two "Γ/A" values obtained in the molecular-field approximation. For the lower-field transition, Eq. (4) yields $\tau_1^*=0.52$ ($T_1^*=9.1$°K). At the higher-field transition, the result is $\tau_2^*=0.32$ ($T_2^*=5.6$°K), but its Γ/A value is in the special region[41] where the true boundary is slightly higher than predicted by Eq. 4. Experimentally both transitions are

[42] A. Narath, Phys. Letters **13**, 12 (1964).
[43] T. Oguchi, J. Phys. Soc. Japan **20**, 2236 (1965).
[44] B. E. Keen, D. Landau, B. Schneider, and W. P. Wolf, J. Appl. Phys. **37**, 1120 (1966).
[45] N. M. Kreines, Zh. Eksperim. i Teor. Fiz. **40**, 762 (1961) [English transl.: Soviet Phys.—JETP **13**, 534 (1961)].

TABLE II. Limiting temperature for first-order transition and observations of metamagnetic hysteresis.

Compound	Upper limit of first-order transition Calc. τ^*	Calc. T^*°K	Obs. T^*°K	Hysteresis observed in *pulsed*-field expt. ΔH (kOe)	$\Delta H/H_c$	at T°K
$FeCl_2$	0.95	22.3	≈20.4	3	0.3	4.2
$FeBr_2$	0.60	6.6	>4.2	0	0	4.2
				0.5	0.016	2.0
$CoCl_2 \cdot 2H_2O$ I	0.52	9.1	>4.2	7	0.22	4.2
II	0.32	5.6	<14	0	0	

of first order[46,47] at 4.2°K, while at 14°K a merged transition of higher order[47] is all that remains. The molecular-field estimates are thus seen to be reasonably reliable.

These comparisons are summarized in Table II. Clearly it would be interesting to carry out additional experiments at intermediate temperatures on $FeBr_2$ and $CoCl_2 \cdot 2H_2O$ in order to sharpen the comparison with predicted behavior.

D. Metamagnetic Hysteresis

We return to the low-temperature, first-order-transition range of the full solution[8,9] described above. At a given low temperature, the upper-field limit of the metastable branch (for increasing field) is some $H_c(+) > H_c(\text{equilibrium})$. Similarly, in decreasing field there is a lower-field limit of the metastable branch, $H_c(-) < H_c(\text{equilibrium})$. At these limiting fields, the transition is "zero-barrier" in contrast to the free energy balance characterizing the transition at $H_c(\text{equilibrium})$. Between these zero-barrier fields, if the attainment of equilibrium is prevented or retarded (for a pulse experiment), hysteresis will be observed. The maximum possible hysteresis is defined by the field range of the metastable solutions, $\Delta H_c = H_c(+) - H_c(-)$. This depends upon the ratio Γ/A and is a function of temperature, vanishing as both $H_c(+)$ and $H_c(-)$ move toward $H_c(\text{equilibrium})$ at τ^* (Sec. IVC).

An oversimplified model at the absolute zero of temperature gives a complementary illustration to the more general one. If, with Néel[2] we take $\Gamma/A \gg 1$, (a good approximation for $FeCl_2$) then the ideal behavior in any field-induced transition consists of the rotation-in-unison of all the atomic moments in each sublattice that seeks a new position. When $K/AM_0^2 > 1$ the transition occurring is the metamagnetic one to a saturated (ferromagnetic) configuration, and only the unfavorably oriented sublattice participates. It is readily shown that the fields required for the "zero-barrier" transitions are

$$H_c(\pm) = AM_0 \pm K/M_0. \tag{8}$$

Recalling that $H_c(\text{equil}) = AM_0$, we see that the potential hysteresis, $\Delta H_c = H_c(+) - H_c(-) = 2K/M_0$, is at least equal to $2H_c(\text{equil})$. Strikingly, once this idealized substance has undergone its first metamagnetic transition, it remains in the saturated configuration at all positive or negative fields. Only an increase in temperature can destroy that configuration.

A more realistic view of the hysteresis and its temperature dependence is obtained following the graphical methods of Gorter and Van Peski-Tinbergen[8] for locating $H_c(\pm)$ from the metastable-states branch. They use the molecular-field model with $K/AM_0^2 > 1$. Two cases are shown in Fig. 4; $\Gamma/A = 9$ which approximates the behavior of $FeCl_2$, and $\Gamma/A = 0.6$ which approximates that of $FeBr_2$ or of $CoCl_2 \cdot 2H_2O$. We plot the ratio $H_c(\tau)/H_c(0°\text{K})$ both for the equilibrium transition and for the "zero-barrier" transitions $H_c(\pm)$. The general features of this figure are (a) that the maximum possible hysteresis $\Delta H_c/H_c(\text{equil})$ is proportional to Γ/A at 0°K (this can be shown analytically), (b) that it decreases rapidly with temperature, but more so for Γ/A small, and (c) that it disappears at τ^*, which [as given by Eq. (4) and discussed above] is nearly unity for large Γ/A but as small as 0.44 for $\Gamma/A = 0.6$.

There is an excellent qualitative accord between the existing hysteresis observations (Sec. III and Table II) and the features of the Gorter and Van Peski-Tinbergen model. Also, some interesting quantitative remarks are possible. We ignore, initially, the discrepancy between the magnitude of the hysteresis observed and that predicted. The observation that the relative hysteresis ($\Delta H/H_c$) in $FeCl_2$ is much larger than that for the nearly isomorphous $FeBr_2$, follows naturally with the model, from their very different Γ/A values. Also, the temperature dependence of the $FeBr_2$ hysteresis (observable at 2°K, nearly invisible at 4.2°K), agrees with the indicated curve in Fig. 4 for a small value of Γ/A, and the calculation that $T^* = 6.6$°K. Lastly, that Motokawa and Date observed hysteresis in $CoCl_2 \cdot 2H_2O$ at 4.2°K only at the lower of the two transitions is in accord with the behavior expected for $T_1^* = 9.1$°K and $T_2^* \gtrsim 5.6$°K.

On the quantitive side, with some graphical inter-

[46] A. Narath, J. Phys. Soc. Japan **19**, 2244 (1964).
[47] H. Kobayashi and T. Haseda, J. Phys. Soc. Japan **19**, 765 (1964).

polation, we note that the ratio of $\Delta H_c/H_c$(equil) predicted for $FeCl_2$ at 4.2°K is roughly 30 times larger than that observed, and that nearly the same number is found for $FeBr_2$ at 2°K. A coincidence perhaps, but a suggestive one. Turning to $CoCl_2 \cdot 2H_2O$ whose ferromagnetic coupling is in linear chains, rather than in the hexagonal layers of the two ferrous halides, we find that the amount of hysteresis observed is roughly $\frac{1}{3}$ to $\frac{1}{2}$ of the maximum predicted. Inasmuch as the experimental conditions were similar, i.e., approximately equal values of (dH/dt), this association to the structural difference may be significant.

Why is the hysteresis so small (in $FeCl_2$ and $FeBr_2$) relative to its potential maximum, and why is it found only with pulsed fields? Evidently mechanisms exist which allow the system to reach equilibrium relatively easily. In short times, however, one must wait for nucleation and/or propagation of the new phase. Thus, in pulsed fields, the nonequilibrium metastable states can be retained, while only equilibrium conditions prevail in the dc measurements. This suggests a path for further research in the examinations of these transitions at much faster sweep rates, such as developed by De Blois[48] in studying the first-order para-to-ferromagnetic transition in MnAs.[49] If limiting values could be attained, further insight might follow.

In calling attention to the possibility of hysteresis in the spin-flop transition, Néel considered possible reasons for its absence. In particular, he pointed to the possible presence of antiferromagnetic domain walls as natural nuclei for the spin-flop phase. The same consideration applies for the metamagnetic transition, i.e., that domain walls in an otherwise perfect antiferromagnet provide sites from which the saturated configuration may grow when the internal field reaches the equilibrium transition field. For the return transition, however, this mechanism ceases to exist. At this stage the problem is nearly identical to that of domain nucleation in a previously saturated ferromagnetic body.[50] In that case, the discrepancy between simple theory and common observation is known as "Brown's paradox,"[51] and attempts at its resolution have given rise to a research field termed "micromagnetics."[52] The prior-saturation condition of micromagnetics is reasonably assured by the application of fields up to 200 kOe, despite the unfavorable cylindrical shapes employed. The maximum demagnetizing field, apart from corner singularities,[53] $4\pi M_s = 7.6$ kOe is small compared to the theoretical $\Delta H_c/2$ but not negligible with respect to

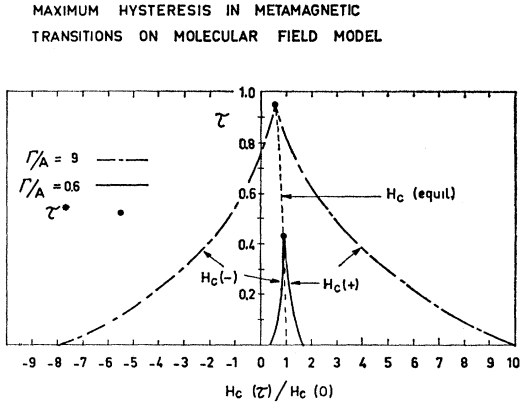

FIG. 4. Maximum hysteresis in metamagnetic transitions versus reduced temperature $\tau = T/T_N$, calculated on molecular-field model for two values of Γ/A, the ratio of intra- to intersublattice exchange. H_c (±) are the zero-barrier transition fields; τ^* is the upper-limit temperature for the first-order transition.

H_c(equil) or to the observed $\Delta H_c/2$. Thus, demagnetizing fields could play a role in reducing hysteresis during the return transition.

The role of structural imperfections in reducing hysteresis could be quite important. Thus the antiferromagnetic domain walls which exist in a perfect crystal,[54] are *required* in the presence of certain dislocations.[55] For the layer structure halides, screw dislocations with Burgers vector perpendicular to the layer are optimal for this effect and they would be likely in the crystal growth process. In addition, the core of the dislocation, or the site of other lattice defects, or the very crystal surface itself, are dissimilar structurally to the interior of a perfect crystal. These would considerably perturb the local crystalline electric fields from which the anisotropy derives its magnitude and direction. The same perturbation of local symmetry permits the antisymmetric spin coupling of the Dzialoshinskii-Moriya type which could enter to prevent complete alignment[56] in high fields. Thus there could be ions whose preferred magnetic axes are different from those of the bulk, and whose strengths of preference are weaker. When coupled ferromagnetically to other ions in the layer structure, they should be ideal nucleation sites to reduce the hysteresis. These remarks can be related back to the observation of a larger hysteresis (relative to the maximum predicted) in $CoCl_2 \cdot 2H_2O$, whose chain structure is less effective in coupling to nucleation sites.

Another path for further research relative to the transition and its hysteresis is to consider magneto-optical studies of the location of nucleation sites in slowly varying fields. Such information could support or destroy various of the foregoing speculations. The

[48] R. W. DeBlois, Rev. Sci. Instr. **32**, 816 (1961).
[49] R. W. DeBlois and D. S. Rodbell, Phys. Rev. **130**, 1347 (1963).
[50] A. Aharoni, Rev. Mod. Phys. **34**, 227 (1962).
[51] W. F. Brown, Jr., Rev. Mod. Phys. **17**, 15 (1945).
[52] S. Shtrikman and D. Treves, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 3, Chap. 8.
[53] S. Shtrikman and D. Treves, J. Appl. Phys. **31**, 72*S* (1960); see also Ref. 50.
[54] See Ref. 2; Y. Y. Li, Phys. Rev. **101**, 1450 (1956); J. F. Dillon, Jr., in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 3, Chap. 9.
[55] I. S. Jacobs and C. P. Bean, J. Appl. Phys. **29**, 537 (1958).
[56] A. Arrott, J. Appl. Phys. **34**, 1108 (1963).

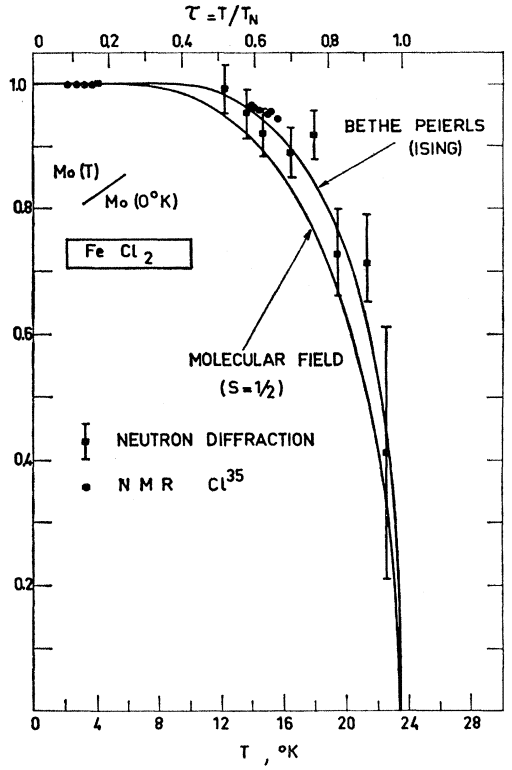

FIG. 5. Sublattice magnetization (normalized) versus temperature. Experiment (Refs. 18 and 60) and theory (Ref. 11), $FeCl_2$.

feasibility of such research on $FeCl_2$ is supported by certain observations of the resonance behavior,[19] and would resemble the Faraday-effect domain studies on $BaFe_{12}O_{19}$ by Kooy and Enz.[57]

We conclude that, contrary to our initial reaction, the appearance of hysteresis in metamagnetic transitions poses no problem, except that of explaining the reasons for its absence.

E. Sublattice Magnetization versus Temperature

Although measurements of sublattice magnetization as a function of temperature are not a direct outcome of the present experiments, our interest was aroused by two factors. Firstly, it has been customary[58] to compare the temperature dependence of the antiferromagnetic resonance frequency with that of the sublattice magnetization as a clue to understanding the anisotropy[59] in an antiferromagnet. Secondly, as we show below, there appears to be a rather good correspondence in $FeCl_2$ between the sublattice magnetization temperature dependence and that of the critical field for the first-order transition.

There are two experimental measurements of the temperature dependence of the sublattice magnetization of $FeCl_2$. One is from neutron diffraction, done in the original study [Wilkinson *et al.* (Ref. 7)] but not published.[60] The data are qualitatively similar to those shown in Fig. 2 of Wilkinson *et al.* (Ref. 7); the background of the neutron intensity must be subtracted, then the square root of the difference, normalized to the 0°K value, is the desired ratio $M_0(T)/M_0(0)$. This procedure leads to large uncertainties close to T_N, but our concern with that region is less. The second measurement is from the relative frequency, $\nu(T)/\nu(0)$, of the Cl^{35} nuclear magnetic resonance below T_N, obtained by Jones and Segel.[18] Although considerably more precise than the neutron diffraction data, measurements could not be obtained above $\frac{2}{3}T_N$ owing to line broadening. Both sets of data are shown in Fig. 5.

For comparison with theory we have an Ising-like ($S=\frac{1}{2}$) molecular-field model and a Bethe-Peierls model of an Ising system. Both are presented in Fig. 5. For the former, we use either the standard graphical method for a molecular-field model or the equivalent analytical expression, Eq. (29), in the paper of Yomosa.[11] (These are independent of Γ/A, when the expression for $T_N(\Gamma, A)$ is invoked.) For the latter model, we use Yomosa's Eq. (28) (recalculated with $\Gamma/A=8.1$), or the almost equivalent data given by Heap[12] (calculated by him with $\Gamma/A=12.4$).

The Bethe-Peierls model is a much better representation of the NMR data than is the molecular-field model. The less precise neutron diffraction data do not permit a clear choice between the models, but are in slightly better accord with the Bethe-Peierls model. Jones and Segel[18] had inferred an apparent ordering temperature of 30°K by fitting the molecular-field model to their NMR data. Had they tried the Bethe-Peierls model, the resulting temperature would have come rather close to the observed T_N, but still slightly above it. On balance at this stage, the Bethe-Peierls treatment of $FeCl_2$ as an Ising system appears very promising.

F. Temperature Dependence of the Transition Field

Until the current work (Fig. 2), and the simultaneous work of Bizette *et al.*,[22] there were no adequate data on the temperature dependence of the $FeCl_2$ transition field. In fact, apart from the recent careful work on dysprosium aluminum garnet[26,44] and the measurements on β-$CoSO_4$,[45] similar information has not existed for any other antiferromagnet exhibiting a relatively abrupt transition to a nearly saturated state. (We exclude those materials which exhibit thermally induced first-order transitions between such states in zero field.) In Fig. 6 we present the relative values, $H_c(T)/H_c(0)$,

[57] C. Kooy and U. Enz, Philips Res. Repts. **15**, 7 (1960).
[58] See, e.g., S. Foner, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, Chap. 9.
[59] See, e.g., J. Kanamori, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, Chap. 4; but see also H. B. Callen and E. Callen, J. Phys. Chem. Solids **27**, 1271 (1966).
[60] J. W. Cable (private communication).

from both studies on $FeCl_2$. Only those transitions considered as first order are included, which is to say those up to 20.4°K in our work, and those up to 20°K in the other work.[22] (That group feels their 20°K isotherm is no longer first order, but this seems open to discussion.) Despite the nearly 1 kOe discrepancy in $H_c(0)$ noted earlier, the *relative* behaviors are identical.

By contrast with the comparison to theory for the sublattice magnetization, that for the transition field is relatively poor. We show the predictions from the Bethe-Peierls calculations (Yomosa,[11] using $\Gamma/A=10$; Heap,[12] using $\Gamma/A=12.4$) and several points calculated graphically with $\Gamma/A=9$ using the Gorter and van Peski–Tinbergen[8] molecular-field model.

In the light of this weak agreement, it comes as a surprise to observe the relatively close experimental correspondence between $H_c(T)/H_c(0)$ and $M_0(T)/M_0(0)$. This is shown in Fig. 7, where the solid line gives the transition-field data from Fig. 6, drawn amidst the data points of Fig. 5. For the *second-order* transition between the spin-flop configuration and the saturated one (at $K/AM_0^2<1$) similar correspondence is expected on a molecular-field model[8] and only slightly modified with a better statistical model.[61] An improved theoretical model is needed.

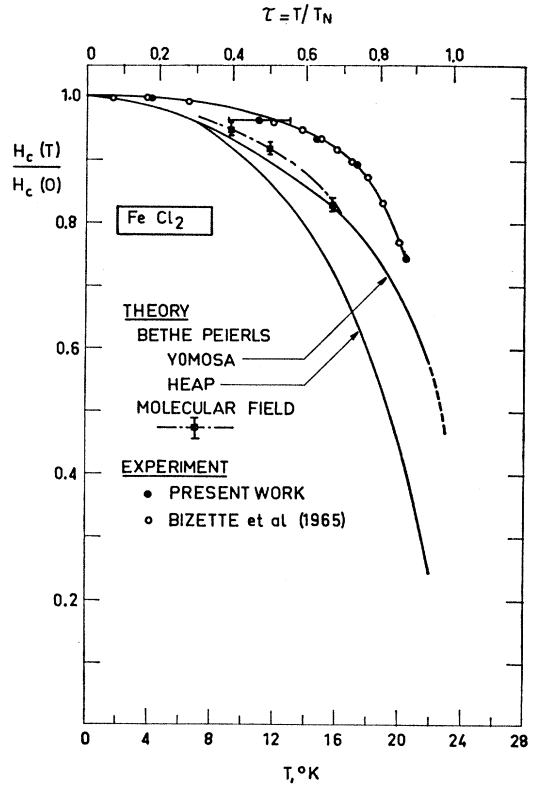

FIG. 6. Critical transition field (normalized) versus temperature. Experiment and theory, $FeCl_2$.

[61] F. B. Anderson and H. B. Callen, Phys. Rev. 136, A1068 (1964).

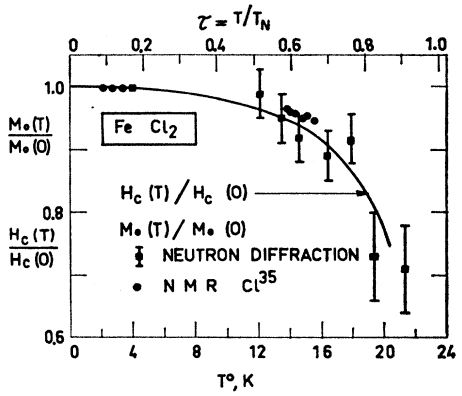

FIG. 7. Comparison of observed temperature dependence of critical transition field with that of sublattice magnetization, $FeCl_2$.

V. SUMMARY

In this work we study the metamagnetic transition in antiferromagnetic $FeCl_2$ both from the point of view of obtaining a quantitative improvement in the parameters measurable from magnetization curves and from that of obtaining a deeper qualitative understanding of the theoretical description of metamagnetism. The saturation moment, after the first-order transition at low temperature, agrees well with other measured values published during the course of this work and reasonably well with recent theoretical calculations thereof. By characterizing the transition through the temperature dependence of the transition field, we bring attention to the observation that the transition remains of first order for a significant range of temperature above 0°K, but gives way to one of higher order at a certain temperature T^* below the Néel point. From results obtained by pulsed-field measurements, we find a marked hysteresis in the transition at low temperature.

A critical and historical review of theoretical treatments of the antiferro-paramagnetic transition shows the necessity of a ferromagnetic intrasublattice exchange, as well as a significant anisotropy, in order that the first-order transition be retained above 0°K. These same conditions apply to the occurrence of hysteresis. The observations on $FeCl_2$ together with those of several other metamagnets are successfully compared with predictions for T^* and for the variation of hysteresis as a function of T/T_N and of the ratio of intra- to intersublattice exchange. The dependence upon temperature of the normalized sublattice moment (measured elsewhere) is shown to be reasonably described by an Ising model in the Bethe-Peierls approximation. Although the temperature dependence of the normalized transition field (below T^*) is in close correspondence with that of the sublattice moment, this result is in poor accord with the model just noted and with all others presently available.

The general success of the comparisons attempted herein suggests the desirability of more refined magnetic-phase-diagram studies (experimental and theoretical) on metamagnetic antiferromagnets.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge helpful discussions with Professor J. W. Stout of the University of Chicago, Professor W. P. Wolf of Yale University, and Dr. J. S. Kouvel and Dr. F. S. Ham of our institution. Professor Stout was also most generous in making available the details of his unpublished calculations. We also wish to thank Dr. J. W. Cable of the Oak Ridge National Laboratory for providing the single-crystal boule and unpublished neutron diffraction data. For one of the authors (I.S.J.), a significant part of this study was carried out during a research leave from the General Electric Research and Development Center. He wishes to thank the management of the Center for making the leave possible as well as to thank Professor L. Néel, Director, and Professor R. Pauthenet for their gracious hospitality in accepting him as a guest scientist at the Laboratoire d'Electrostatique et de Physique du Métal, CNRS, Grenoble.

Errata

Effect of Low-Temperature Structural Transformation on V^{51} Knight Shifts and Electric Field Gradients in V_3Si, A. C. GOSSARD [Phys. Rev. **149**, 246 (1966)]. In the last paragraph of Sec. IV, the third, fourth, and fifth sentences should be altered as follows: "The Γ_{12}^+ distortion may also be eliminated, since the symmetric third-order product of this representation with itself contains the identity.[14] (Γ_{15}^+ has an antisymmetric third-order invariant, the scalar triple product of *three* axial vectors, but this does not matter.) Thus the Γ_{15}^-, Γ_{25}^-, and Γ_{15}^+ distortions remain and satisfy the tetragonality and second-order transition requirements." In the next to last sentence of the same paragraph, "and Γ_{15}^+" should be omitted.

Ultraviolet Absorption Spectra of Pr^{3+} in Alkaline-Earth Fluorides, EUGENE LOH [Phys. Rev. **158**, 273 (1967)].

(1) The last sentence of the second paragraph on p. 274 should read "···from $4f$ to (i) $|\, 2z^2-x^2-y^2\rangle$, (ii) $|\, xy\rangle$, and (iii) $|\, yz\rangle$ and $|\, zx\rangle$···."

(2) Footnote 7 should read "··· in Refs. 1 and 6."

(3) In the first row of Table III: omit the second "Pr^{3+}" in column 2. Add a long horizontal bar between "(Free-ion Pr^{3+})" and "(single-ion Pr^{3+} in CaF_2)" in column 4.

Measurement of the Laser Transition Cross Section for Nd^{+3} in Yttrium Aluminum Garnet, J. K. NEELAND AND V. EVTUHOV [Phys. Rev. **156**, 244 (1967)]. We wish to thank Dr. W. R. Sooy of Hughes Aircraft Company for calling to our attention the following error:

Equation (1) should read $\sigma=\lambda^2/4\pi^2\epsilon\tau_l\Delta\nu$.

Therefore, the cross section calculated from the lifetime as measured by method 1 should be 7.0×10^{-19} cm^2. Similarly, the lifetime calculated from the cross section as measured by method 2 should be 1516 μsec. Therefore, nonradiative transitions plus transitions to the $^4I_{15/2}$ and $^4I_{13/2}$ multiplets make up $\sim$60% of the total drain from the $^4F_{3/2}$ levels.