Metamagnetism of Ni(NO$_3$)$_2$·2H$_2$O†

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Magnetization isotherms have been measured for single-crystal Ni(NO$_3$)$_2$·2H$_2$O between 1.4 and 4.2°K with fields up to 16 kOe applied along the a axis. These isotherms exhibit the metamagnetic threshold phenomenon anticipated on the basis of earlier zero-field susceptibility measurements. The locus of the metamagnetic transition points in the (H,T) plane forms a smooth phase boundary separating antiferromagnetic and ferro- or paramagnetic regions. The extremities of this boundary occur at T_N $(H=0) \approx 4.2$°K and H_c $(T=0) \approx 3.4$ kOe. The thermodynamic character of the transition, as indicated by the shape of the isotherms, changes at $T_c \approx 3.85$°K. Below T_c, the transitions appear to be of first order, while between T_c and T_N (0) they are of higher order or perhaps λ-like. It has been possible to reproduce many features of the magnetization curves as well as the (H,T) and (M,T) phase diagrams of Ni(NO$_3$)$_2$·2H$_2$O with $\mathbf{H}\|a$ by means of the same two-sublattice molecular-field model used to describe the zero-field susceptibilities. Spins on a given sublattice lie on alternate sheets of this layered structure. Intrasublattice (intrasheet) spin coupling is ferromagnetic and about 7 times larger in magnitude than the antiferromagnetic intersublattice (interlayer) interaction. Two variants of the model are considered, as are possible improvements to account for the consequences of the inequivalence of the two Ni^{++} ions per unit cell.

I. INTRODUCTION

ON the basis of their study of the magnetic susceptibilities of single-crystal Ni(NO$_3$)$_2$·2H$_2$O in approximately zero field, Berger and Friedberg[1] concluded that this substance contains layers of Ni^{++} ions with ferromagnetic intralayer exchange interaction and weaker antiferromagnetic interlayer coupling. They found it possible to fit the data above and below the Néel point, $T_N \approx 4.2$°K, with a simplified two-sublattice model of an antiferromagnet in which all spins on a given sublattice occupy all sites on alternate layers. The approximate uniaxial character of the susceptibilities about the a axis of this monoclinic crystal is incorporated into the model by taking as the spin Hamiltonian for the ground state of a Ni^{++} ion on either sublattice

$$\mathcal{3C} = DS_z^2 + g\mu_B \mathbf{S} \cdot \mathbf{H}_{eff}, \qquad (1)$$

where the z axis coincides with the a direction, $S=1$, and the spectroscopic splitting factor g is assumed isotropic. The effective fields $\mathbf{H}_{eff}$ at ions on sublattices A and B have the form

$$\mathbf{H}_A = \mathbf{H}_0 - n_1 \mathbf{M}_B(H_B,T) - n_2 \mathbf{M}_A(H_A,T),$$

$$\mathbf{H}_B = \mathbf{H}_0 - n_1 \mathbf{M}_A(H_A,T) - n_2 \mathbf{M}_B(H_B,T), \qquad (2)$$

where H_0 is the applied magnetic field; $\mathbf{M}_A$ and $\mathbf{M}_B$ are the magnetizations of sublattices A and B, respectively. The values of the parameters obtained in the fit of the zero-field susceptibilities are $n_1 = +0.321$ mole/cgs, $n_2 = -2.122$ mole/cgs, $D/k = -6.50$°K, and $g=2.25$.

We note the ferromagnetic sign of n_2, the intralayer molecular-field constant, and the fact that its magnitude is almost 7 times that of the interlayer constant n_1.

The negative sign of the coefficient D indicates, of course, that the energy of a Ni^{++} ion is minimized when its spin points along the positive or negative a direction. Of particular interest is the magnitude of D which measures the single-ion anisotropy energy. In this case it is found to be comparable with or larger than the exchange energy.

An antiferromagnet having the properties ascribed to this model may be expected to respond to a magnetic field applied along the preferred direction of spin alignment well below its zero-field Néel temperature $T_N(0)$ in a characteristic manner.[2,3] Initially, isothermal increase of the applied field causes only a small bulk magnetization $\mathbf{M} = \frac{1}{2}(\mathbf{M}_A + \mathbf{M}_B)$ to be induced in the specimen, since if $\mathbf{M}_A$ is parallel to $\mathbf{H}_{app}$ it will be nearly compensated by $\mathbf{M}_B$ which is antiparallel. At some "threshold" value of H, however, M_B will abruptly switch to a parallel orientation and M will rise rapidly, achieving ferromagnetic saturation upon further isothermal increase of H_{app}. The magnitude of the threshold field is a function of temperature [4,5] and vanishes at $T_N(0)$. A distinct thermodynamic phase change occurs at the threshold field, the locus of these transitions constituting a phase boundary dividing the H,T plane into two regions, one antiferromagnetic, the other ferro- or paramagnetic. The term metamagnet[6] has been used to describe an antiferromagnet which behaves in this manner.

It should be noted, by way of contrast, that an

[1] L. Berger and S. A. Friedberg, Phys. Rev. 136, A158 (1964).

[2] L. D. Landau, Phys. Z. Sowjetunion 4, 675 (1933).

[3] L. Néel, Nuovo Cimento Suppl. 6, 942 (1957), and earlier references cited there.

[4] J. Kanamori, K. Motizuki, and K. Yosida, Busseiron-Kenkyu 63, 28 (1953) (in Japanese). A summary of these results in English appears as an appendix to K. Motizuki, J. Phys. Soc. Japan 14, 759 (1959).

[5] C. J. Gorter and T. van Peski-Tinbergen, Physica 22, 273 (1956); C. J. Gorter, Nuovo Cimento Suppl. 6, 923 (1957).

[6] The history of the problem, with particular reference to FeCl$_2$, is reviewed by I. S. Jacobs and P. E. Lawernce, Phys. Rev. 164, 866 (1967).

antiferromagnet with relatively weak anisotropy can, in a parallel field at sufficiently low temperatures, exhibit a third phase in which M_A and M_B are roughly antiparallel to one another but perpendicular to H. This is the so-called "spin-flopped" phase and lies between the antiferro- and paramagnetic phase.

Figure 1 is a schematic phase diagram for a metamagnet. The theory of the two-sublattice metamagnet has been studied in some detail by a number of workers,[6] and several interesting features of the phase diagram[4,5,7] have been noted. In the case of concern to us in which the intrasublattice exchange is ferromagnetic ($n_2 < 0$) it is found that the threshold field at 0°K is simply related to the intersublattice exchange constant n_1 as follows:

$$H_c(0) = n_1 M_0, \tag{3}$$

where $M_0 = N g \mu_B S$ is the fully saturated value of either M_A or M_B. The metamagnetic transition proves to be of first order in the Ehrenfest[8] sense not only at 0°K but also at temperatures up to some value, say, $T_c < T_N$. Kanamori et al.,[4] working in a molecular-field–infinite-anisotropy approximation, find that for $0.6 < |n_2/n_1| < \infty$,

$$T_c = T_N[1 + \tfrac{1}{3}(n_1/n_2)]. \tag{4}$$

It is also possible to write T_c in terms of directly measured quantities if n_1 and n_2 are estimated in Eq. (4) with the help of appropriate expressions for T_N and θ, the Weiss constant[7]:

$$T_c = \tfrac{2}{3} \frac{T_N(T_N + 2\theta)}{T_N + \theta}. \tag{5}$$

Since the antiferro- and paramagnetic phases are of different symmetry, the phase boundary cannot simply terminate at T_c with $H > 0$.[9] Molecular-field calculations indicate, in fact, that between T_c and T_N the boundary continues as a line of second-order transition points. It is quite possible that more exact treatments would show the transitions in this range not to be strictly classifiable according to the Ehrenfest scheme but rather to be lambda-like.

Landau[2] first developed the theory of a metamagnet with ferromagnetic intrasublattice coupling to explain the magnetic and thermal behavior of such anhydrous halides as FeCl₂ (Ref. 6) and CoCl₂. Most of the substances positively identified as being metamagnets have been anhydrous compounds. The exceptions are CoCl₂·2H₂O,[10] CoBr₂·2H₂O,[11] and FeCl₂·2H₂O,[12] which
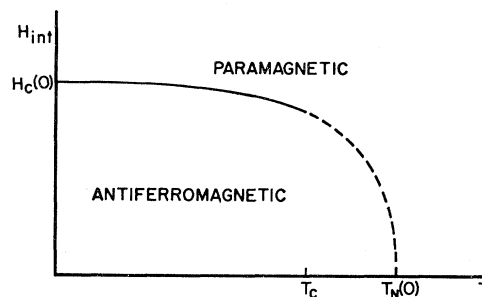

FIG. 1. Schematic H,T phase diagram for a metamagnet with strong anisotropy and ferromagnetic intrasublattice coupling.

are somewhat atypical in that they exhibit two successive field-induced phase transitions. With very few exceptions, the best known of which is dysprosium aluminum garnet[13] ($T_N(0) = 2.53$°K), most other known metamagnets have Néel points above liquid-helium temperatures. We have felt it to be a matter of some interest, therefore, to verify by direct measurement of magnetization at elevated fields the inference from low-field susceptibility data that Ni(NO₃)₂·2H₂O is metamagnetic with $T_N(0) = 4.2$°K. Having previously determined the parameters of a two-sublattice model by fitting the susceptibility data,[1] we are able to make a number of predictions about the anticipated metamagnetic transitions and phase diagram of Ni(NO₃)₂·2H₂O. Substituting the appropriate quantities in Eqs. (3) and (4), for example, we obtain $H_c(0) \approx 4$ kOe and $T_c \approx 3.97$°K. A slightly different estimate of T_c, namely 3.86°K is obtained upon substitution of $T_N = 4.2$°K and $\theta = 2.5$°K into Eq. (5). Thus, in fields and at temperatures readily accessible in the laboratory, it should be possible to study a major portion of the anticipated metamagnetic phase boundary for this material. This has been done in the present work. The extent to which the theory of the simple two-sublattice model gives agreement with magnetization data is considered after a short description of the relevant experimental details and a summary of the observations.

II. EXPERIMENTAL METHODS AND SPECIMENS

We have measured magnetization isotherms for single-crystal specimens of Ni(NO₃)₂·2H₂O in fields up to ~16 kOe at temperatures between 1.4 and 4.2°K. The isotherms were obtained quasistatically using a continuously recording pick-up-coil–flux-integrator technique which we have described in detail elsewhere.[14] Most of these measurements were made on a rod-shaped crystal of rhombic cross section about 2 mm on a side and 1 cm long. The crystallographic a axis coincided

[7] R. Bidaux, P. Carrara, and B. Vinet, J. Phys. Chem. Solids **28,** 2453 (1967).

[8] P. Ehrenfest, Proc. Koninkl. Akad. Wetenschap. Amsterdam **36,** 153 (1933); also Leiden Comm. Suppl. No. 75b.

[9] L. D. Landau, Phys. Z. Sowjetunion **11,** 26 (1937).

[10] H. Kobayashi and T. Haseda, J. Phys. Soc. Japan **19,** 765 (1964); A. Narath, Phys. Rev. **136,** A766 (1964).

[11] A. Narath, J. Phys. Soc. Japan **19,** 2244 (1964).

[12] A. Narath, Phys. Rev. **139,** A1221 (1964).

[13] B. E. Keen, D. Landau, B. Schneider, and W. P. Wolf, J. Appl. Phys. **37,** 1120 (1966).

[14] V. A. Schmidt and S. A. Friedberg, J. Appl. Phys. **38,** 5319 (1967).

with the specimen axis and the applied-field direction. The small specimen size necessitated the winding of a new pair of pick-up coils, each of 1000 turns. Calibration of the apparatus was determined, in this case, directly from the sample and coil geometry together with the calibration of the integrator. This procedure was practical because the demagnetization factor D for the long rod-shaped sample was rather small. Small errors in estimating D did not seriously affect the calibration.

Single crystals of $Ni(NO_3)_2 \cdot 2H_2O$ were grown from saturated aqueous solution of Fisher Certified Reagent grade nickel nitrate at a temperature of 103°C. According to Sieverts and Schreiner,[15] this procedure should yield the dihydrate. Slow growth was found to be essential, the sample used in the final experiments requiring nearly two months to form. These crystals displayed the interfacial angles characteristic of the dihydrate. According to Baughman and Jeffrey,[16] they belong to the monoclinic space group $P2_1/c$. The unit cell dimensions are $a=5.79\pm0.02$ Å; $b=5.90\pm0.02$ Å; $c=8.51 \pm0.04$ Å, with $\beta=91.1°\pm0.2°$. The normal needlelike growth habit, with the a direction and needle axis coincident, proves particularly convenient since the a axis is the apparent direction of preferred spin alignment in the ordered state and it is desirable to minimize demagnetizing effects.

III. DISCUSSION OF THE RESULTS

Four typical magnetization isotherms for $Ni(NO_3)_2 \cdot 2H_2O$ with the magnetic field applied along the a axis (preferred direction) are shown in Fig. 2. Successive curves have been displaced vertically for clarity. The same magnetization scale, in units of Bohr magnetons per Ni^{++} ion, applies to all curves. The horizontal axis is labeled H_{int} to indicate that the applied field has been corrected for demagnetizing effects to that value it would have inside an infinitely long needle. This correction has been performed by computer, using a digitizing procedure which preserves the detail of the continuously recorded isothermal curves.

Several features of the data are immediately apparent. Looking first at the isotherm for 1.42°K, the lowest temperature achieved in these measurements, we see an abrupt, nearly discontinuous rise in M at about 3.4 kOe. When H_{int} has reached 15 kOe, M is effectively saturated at a value of $2.22 \mu_B/Ni^{++}$ ion. This is quite close to the value expected for full ferromagnetic alignment of all Ni^{++}-ion moments if, as Berger and Friedberg[1] concluded, $S=1$ and $g=2.25$. The field-induced transition at 1.42°K and 3.4 kOe is thus rather clearly a metamagnetic one. The essentially discontinuous rise in M at the threshold field is what would be expected if the transition were of first order. The
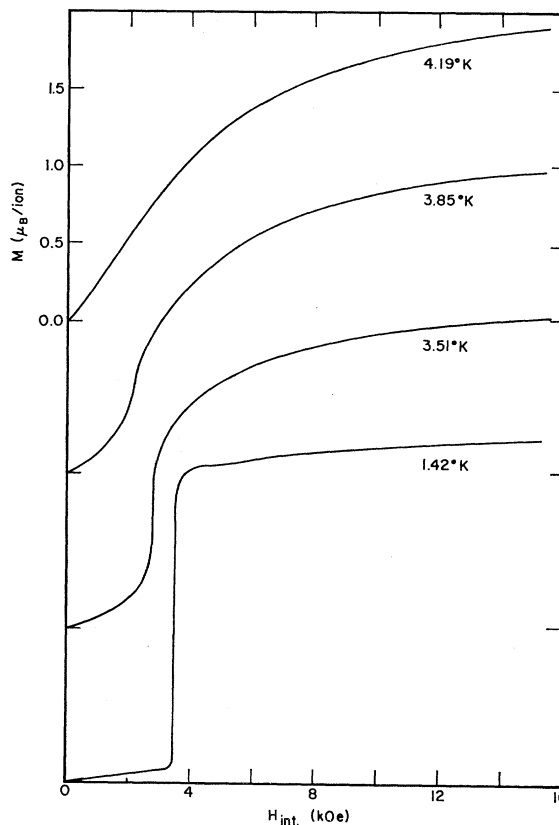
[15] A. Sieverts and L. Schreiner, Z. Anorg. Allgem. Chem. **219**, 105 (1934).
[16] R. Baughman and G. A. Jeffrey (unpublished work cited in Ref. 1).

FIG. 2. Typical magnetization isotherms for $Ni(NO_3)_2 \cdot 2H_2O$ with the magnetic field applied along the a axis. Note that the curves are displaced vertically and that all are drawn to the same scale.

isotherm was found to be completely reversible. It should be emphasized that this curve was recorded slowly enough (over periods of about 5 min) to maintain equilibrium conditions. The absence of hysteresis is thus not surprising nor inconsistent with the conclusion that the transition is actually of first order.

At higher temperatures, the isotherms exhibit more rounding above and below the threshold field, the value of which falls smoothly as T rises. At the threshold field M continues to show a nearly discontinuous rise whose magnitude, however, also falls with increasing T. In Fig. 2 we see that the 3.51°K isotherm still contains an apparent (near) discontinuity suggesting that the metamagnetic transition at this temperature is still of first order. At 3.85°K, however, the discontinuity seems to have disappeared, only a point of inflection evidently remaining to mark the threshold field. The inflection point persists in the isotherms taken at higher temperatures and may still be seen at 4.19°K, just below the zero-field Néel point at ~4.20°K.

Above ~3.85°K, the metamagnetic transitions are evidently no longer of first order. To the resolution of our experiments, the isotherms in this region do not show the slope discontinuity expected of a simple

second-order transition. Instead, an inflection point occurs with very large slope. This suggests that the transitions between ~ 3.85 and $T_N(0) \approx 4.20°$K are probably λ-like. If this is so, then it may be shown[14] that the transition point and the point of inflection of the isotherm, i.e., the maximum in $(\partial M/\partial H)_T$, are coincident.

Identifying the threshold field for the metamagnetic transition either from the (near) discontinuity or the inflection point in the magnetization isotherm, we may construct a portion of the magnetic (H,T) phase diagram for Ni(NO₃)₂·2H₂O. Such a diagram is presented in Fig. 3 and contains experimental points from all our measured isotherms including those given in Fig. 2. We note that at the lowest temperature for which data are available (1.42°K), the threshold field appears to be approaching an asymptotic value of about 3.4 kOe. This is in quite reasonable agreement with the value 4 kOe predicted for $T=0°$K with Eq. (3) using the value of n_1 obtained by fitting zero-field susceptibility data at and above $T_N(0)$.

The change in the thermodynamic character of the metamagnetic transition in Ni(NO₃)₂·2H₂O occurs at about 3.85°K and is indicated in Fig. 3 by a change in the interpolated phase boundary from a solid to a dashed line. We may compare the empirical value of T_c, namely, 3.85°K, with the theoretical estimates 3.97 and 3.86°K given by Eqs. (4) and (5), respectively. Again the agreement is rather good, especially when we note that the calculations yielding Eq. (4) and the fitted values of n_1 and n_2 involve somewhat different approximations.

Encouraged by the reasonable agreement between observations on Ni(NO₃)₂·2H₂O in elevated fields and these simple estimates for a two-sublattice model metamagnet, we have felt it to be worthwhile to calculate some representative magnetization isotherms in detail. This has been done treating two variants of the model in the molecular-field approximation. It should be emphasized that both of these models neglect the fact that the unit cell of Ni(NO₃)₂·2HO contains two nonequivalent Ni^{++} ions. We shall refer later to some inadequacies of the theory which perhaps arise from this approximation.

The first model is the one employed by Berger and Friedberg[1] and summarized in Eqs. (1) and (2) of the Introduction. A uniaxial single-ion anisotropy expressing some average property of the two inequivalent Ni^{++} per unit cell is incorporated directly into the Hamiltonian [Eq. (1)]. From Eq. (1) we can obtain the partition function and then the magnetization of sublattices A and B:

$$M_A = M_0 \left(\frac{2 \sinh(\mu_B H_A/kT)}{e^{D/kT} + 2 \cosh(\mu_B H_A/kT)} \right),$$

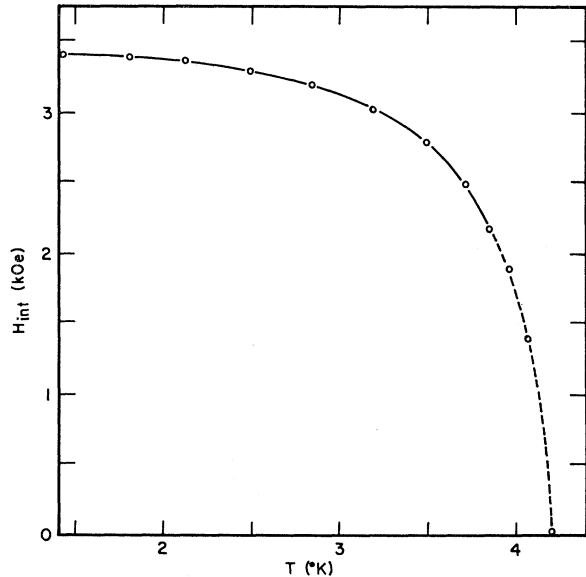$$M_B = M_0 \left(\frac{2 \sinh(\mu_B H_B/kT)}{e^{D/kT} + 2 \cosh(\mu_B H_B/kT)} \right). \tag{6}$$

FIG. 3. Experimental (H,T) phase diagram for Ni(NO₃)₂·2H₂O with $\mathbf{H}\|a$ axis.

These equations, together with Eqs. (2) which relate H_A and H_B to M_A and M_B, can be solved for M_A and M_B to yield the total magnetization $M = \frac{1}{2}(M_A + M_B)$. We take the constants to be those obtained by fitting the zero-field susceptibilities, namely $n_1 = 0.321$ mole/cgs, $n_2 = -2.12$ mole/cgs, $D/k = -6.5°$K, and $g = 2.25$. We refer to this version as model I.

The second model is perhaps the more conventional in that it simply assumes the existence of anisotropy sufficiently large to prevent spin flopping at any temperature and lets

$$M_A = M_0 B_S(\mu_B H_A/kT),$$
$$M_B = M_0 B_S(\mu_B H_B/kT). \tag{7}$$

In this case $B_S(X)$ is the Brillouin function of argument $X = \mu_B H_{\text{eff}}/kT$ for $S=1$. Equations (7) together with Eqs. (2) must be solved to obtain M_A and M_B, and thus M. The constants in this model, which we call model II, are n_1, n_2, and g. We assume $g = 2.25$ and determine n_1 and n_2 from Eq. (3) and the expression for $T_N(0)$ of model II, namely,

$$T_N(0) = [(S+1)/3S][(n_1 - n_2)/k]\mu_B^2. \tag{8}$$

Substituting $H_c(0) = 3.4$ kOe and $T_N(0) = 4.20°$K, one obtains $n_1 = 0.377$ mole/cgs and $n_2 = -2.94$ mole/cgs.

We have solved Eqs. (2) and (6) (model I) and Eqs. (2) and (7) (model II) by an iterative method using a digital computer. From the work of Gorter and van Peski-Tinbergen[5] and Kanamori et al.,[4] we expect the isotherm at some temperature less than but near T_c to have the form shown schematically in Fig. 4. The discontinuous rise in M marking the first-order phase transition occurs at that field for which the shaded
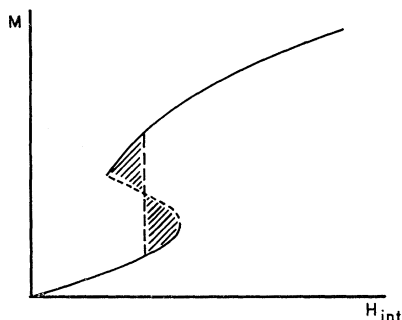
FIG. 4. Schematic magnetization isotherm for two sublattice metamagnet at T less than but near T_c.

areas to the left and right of the vertical line are equalized, according to Maxwell's rule.[17]

Our iterative procedure could not give the unstable (dashed) portion of an isotherm such as that in Fig. 4. However, it was possible to obtain all of the upper and lower solutions in the region where the isotherm is multivalued as well as the solutions for single-valued segments. Thus all stable and metastable solutions, as indicated by the solid lines in Fig. 4, could be calculated. This proved to be enough information to permit a rather unambigious interpolation of the dashed line and thus to locate the transition within reasonably small limits, so long as T was not too far below T_c. The iterative procedure gave the whole single-valued isotherm for any temperature above T_c without difficulty.

The results of these computations are compared with the experimental isotherms for 3.97 and 3.51°K in Figs. 5 and 6, respectively. Qualitatively the agreement
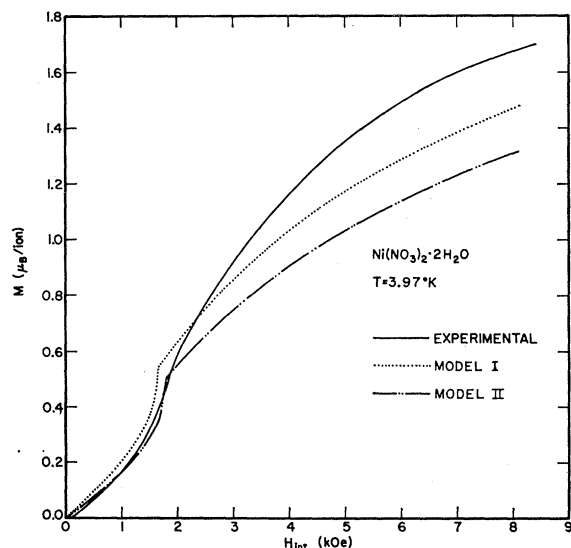

FIG. 5. Comparison of observed and calculated isotherms at 3.97°K for Ni(NO₃)₂·2H₂O with H∥a axis. Models I and II are described in the text.

[17] J. C. Maxwell, Nature 11, 357 (1875).

is quite striking in both cases. At 3.97°K, the two calculated curves clearly exhibit the discontinuity of slope expected at a second-order transition point, while the observed isotherm shows the inflection point with steep tangent suggestive of a λ transition. At 3.51°K, both calculated curves clearly show the discontinuity associated with a first-order phase change, as does the experimental isotherm. The change in thermodynamic character of the metamagnetic transition at T_c inferred from the observations is thus reproduced by the simple theories. Both models predict T_c to be within about 0.1°K of our estimated value $T_c \approx 3.85°$K.

We note in Figs. 5 and 6 that model II yields values of the threshold field in closest agreement with the observed values. This is probably reasonable since, unlike model I, it employs parameters fitted at the
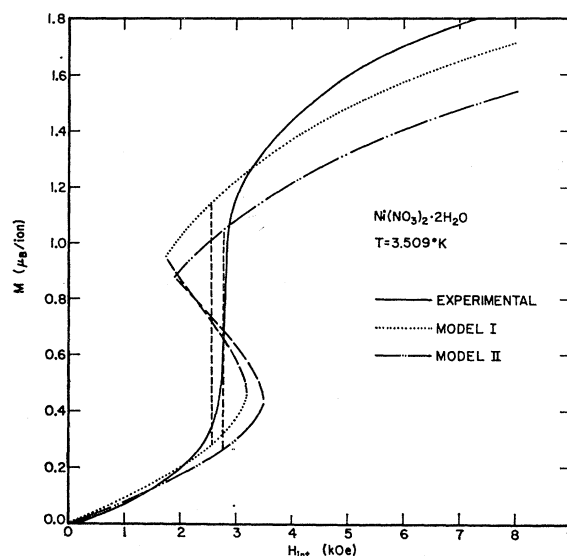

FIG. 6. Comparison of observed and calculated isotherms at 3.15°K for Ni(NO₃)₂·2H₂O with H∥a axis. Models I and II are described in the text.

extremes of the actual phase diagram, i.e., at 0°K and $T_N(0)$. Neither model reproduces very well the rapid rise in M above the threshold field, although, at sufficiently high fields, the isotherms which they yield do extrapolate to the expected saturation value. The isotherms computed with model I are much closer to the experimental ones in this region. However, this may be due in part simply to the fact that model I also gives generally lower threshold fields for the present choice of parameters.

As Gorter[5] has pointed out, the portions of the isotherms given by molecular-field models which correspond to the paramagnetic phase will extrapolate back to $H=0$ at $M=0$. This is certainly apparent for the calculated curves of Fig. 5, for example. This is clearly not true, however, for the experimental isotherms of Figs. 5 and 6. Instead, the portion above the

threshold field is more steeply sloped and extrapolates to a positive intercept on the H axis at $M=0$. Similar behavior has been noted earlier[14] for the antiferromagnets $CoCl_2 \cdot 6H_2O$ and $MnBr_2 \cdot 4H_2O$.

Another useful comparison with earlier observations on $MnBr_2 \cdot 4H_2O$ may also be made. It was noted[14] that the observed isotherms for $MnBr_2 \cdot 4H_2O$ consistently fell below those calculated with a molecular-field model (equivalent to model II) at fields above the antiferroparamagnetic transition. It was suggested that this effect might be due to the persistence into the paramagnetic phase of short-range ordering not incorporated into the model. Since the dominant interaction in $MnBr_2 \cdot 4H_2O$ is antiferromagnetic, persistent short-range order should tend to depress the total magnetization, as is observed. In $Ni(NO_3)_2 \cdot 2H_2O$, however, ferromagnetic interaction predominates so that short-range ordering would be expected to enhance the magnetization above the threshold field. Referring to Figs. 5 and 6, we see that this is actually what happens. The observed isotherms for $Ni(NO_3)_2 \cdot 2H_2O$ lie above the calculated ones in the paramagnetic phase and approach saturation more rapidly.

At temperatures below $\sim 3°K$, the initial slopes of the theoretical isotherms are much smaller than the observed values. This discrepancy was noted in the original calculations of zero-field susceptibilities and several possible causes were considered.[1] Among them was the inequivalence of the two types of Ni^{++}-ion sites occurring in the unit cell and thus in the layers parallel to the bc planes normal to which we have assumed simple ferromagnetic alignment to occur. If the local anisotropy fields at the the two kinds of sites have different orientations, some canting of the spins can result and with it a nonzero initial slope even for the magnetization isotherm at $0°K$.

Such canting might also account for another feature found in all isotherms recorded below $2.1°K$ and easily seen in the bottom curve of Fig. 2. Just above the threshold field, the magnetization levels off over a short interval before resuming its rise with field toward saturation. Presumably slight canting away from the a axis could prevent the spins from achieving complete parallelism until fields well above the threshold value are reached even at $0°K$.

The point in the (H,T) plane at which the line of first-order phase transitions terminates and beyond which a line of higher-order phase transitions extends has been referred to as a critical point.[7] While adopting this convenient designation, we must bear in mind that this point differs significantly from the critical points occurring in the phase diagrams of simple fluids or their mixtures. The (H,T) representation is not a particularly revealing way of exhibiting the behavior of the system at or near the critical point. An (M,T) diagram, however, exposes interesting details in this region. We have constructed such a diagram for $Ni(NO_3)_2 \cdot 2H_2O$ from

information contained in the magnetization isotherms. It is shown in Fig. 7 and consists of three curves which meet at the critical point (M_c, T_c). The upper curve below T_c gives the value of the magnetization at each temperature just as the system enters the ferro- or paramagnetic phase, i.e., just above the discontinuity in the isotherm. The lower curve represents the magnetization values just before the system leaves the antiferromagnetic phase, i.e., just below the discontinuity. The curve for $T > T_c$ gives the value of the magnetization at the inflection point of each isotherm and thus represents the line of higher-order phase transitions.

In view of the rounding of the observed curves (see Fig. 2) it is difficult to specify very precisely the upper and lower limits of the discontinuity we attribute to an isotherm at $T < T_c$. Estimated uncertainties in these magnetization values are shown in Fig. 7 by means of vertical bars. Note that the phase diagram of Fig. 7 is displayed with both reduced and direct coordinate scales. The reduced variables are $m \equiv M/M_0$ and $t \equiv T/T_N(0)$.

The theoretical M,T phase diagram for model I has been constructed using numerous isotherms computed essentially as were those of Figs. 5 and 6. It appears in Fig. 7 as solid lines and is seen to reproduce qualitatively most of the features of the data. In some regions the agreement is semiquantitative. This diagram is essentially the same as the one obtained by Bidaux et al.[7] for the two-sublattice metamagnet in the extreme Ising limit.

The discrepancies between the observations and the calculated phase diagram in Fig. 7 deserve comment. Note that the calculated critical point, i.e., the intersection of the three solid lines, occurs at $3.97°K$ whereas the data suggest $T_c \approx 3.85°K$. As was noted above, this difference probably reflects the fact that the parameters used with model I were determined from data obtained in zero field at and above $T_N(0)$. Presumably, other choices of parameters could be made which would remove this discrepancy. They would not, however, alter the differences existing at reduced temperatures below $t \sim 0.6$ between the data and the upper and lower boundaries. We believe that these differences are probably due to the relative canting of spins on the two types of sites within the unit cell. As has already been emphasized, our model ignores this possibility. In principle, at least, it should not be too difficult to incorporate canting into the theory. If, as appears likely, canting produces no net moment in zero field, a more realistic model would involve at least four sublattices with a corresponding increase in the number of fitted parameters. Eventually, we hope to carry out such calculations.

As Bidaux et al.[7] have emphasized, molecular-field analysis of the behavior of metamagnetic models in applied fields gives results consistent with Landau's theory of phase transitions. One prediction of this
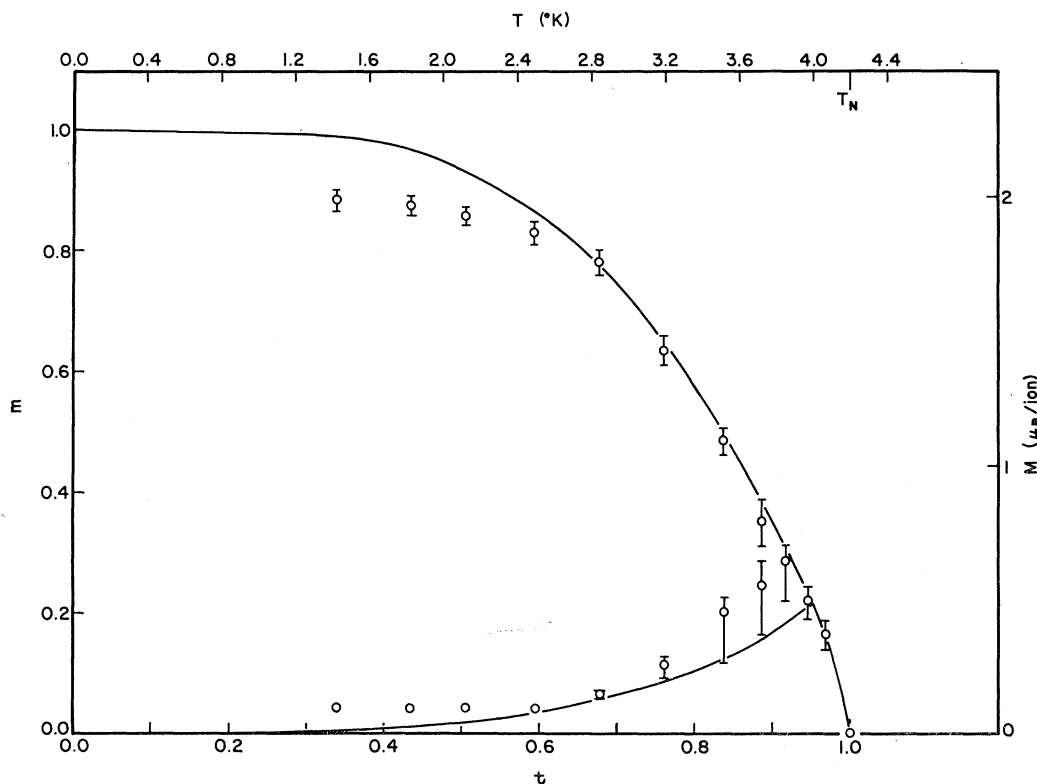
FIG. 7. M,T (m,t) phase diagram for $Ni(NO_3)_2 \cdot 2H_2O$ with $H \| a$ axis. Solid lines are calculated with model I of text. Reduced variables are $m \equiv M/M_0$ and $t \equiv T/T_N$.

theory is that in the M,T phase diagram the upper phase boundary for the region of first-order transitions and the single boundary for the region of second-order transitions join smoothly with common slope at T_c. This is found to be true for the calculated phase diagram of Fig. 7. The experimental data are not obviously inconsistent with this rule. Whether this would be true if the critical region were examined with high resolution is an interesting question. There is an analogous physical system for which this prediction of Landau's theory appears not to hold. Griffiths[18] has pointed out that the M,T diagram of a metamagnet with ferromagnetic intrasublattice spin coupling is the analog of the composition-temperature (X,T) diagram for He^3-He^4 mixtures. T_c becomes the temperature below which phase separation takes place. For $T < T_c$, the upper and lower branches of the X,T diagram give the temperature variation of the composition of the He^3-rich and He^4-rich phases, respectively. For $T > T_c$, only a single phase occurs whose λ point as a function of composition defines the curve which completes the diagram.

Graf et al.[19] have performed a detailed experimental study of the X,T diagram for He^3-He^4 solutions in the critical region. The λ line is found to join the upper branch of the phase separation region of the diagram with a discontinuity of slope. Landau's rule is derived for systems exhibiting second-order phase transitions above T_c. It is quite possible that failure of the rule in the case of He^3-He^4 mixtures is associated with the difference between transitions of the λ type and those of second order. As was noted earlier, the metamagnetic transitions in $Ni(NO_3)_2 \cdot 2H_2O$ above T_c may be of the λ type. This suggests that under sufficiently high resolution the critical region of the M,T diagram of this substance might show departures from the Landau rule. Experiments to test this possibility are planned.

ACKNOWLEDGMENTS

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