

## Mechanism of the Ferrimagnetic to Antiferromagnetic Transition in $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$

H. S. JARRETT

*E. I. du Pont de Nemours and Company, Central Research Department,\* Wilmington, Delaware*

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The mechanism of the first-order ferrimagnetic to antiferromagnetic transition (exchange inversion) in  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$ ,  $x < 0.41$ , was investigated by exchange magnetostriction. A second-order term has been included in the strain energy which gives an effective elastic constant dependent on magnetization and magnetic ordering. It also introduces a discontinuous change in the magnetization at the transition and hence a contribution to the entropy change in addition to that caused by the change of lattice dimension. For  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$ , the effect of this term is small but necessary to obtain the qualitative behavior of the discontinuous change in lattice dimension and the shift in the Curie temperature with composition. The anisotropy behavior of  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$  was investigated for various values of  $x$ , and it is shown that an anisotropy in the critical lattice dimension of only  $4 \times 10^{-4} \text{ \AA}$  accounts for the observed change in magnetic anisotropy with exchange inversion that occurs for transition temperatures between 200 and 350°K. For transition temperatures above 350°K, anisotropy is positive, and spin-flopping measurements can be made on the antiferromagnetic state. An expression for the critical field in the presence of exchange inversion is obtained and compared with experiment.

### INTRODUCTION

THE basic features of exchange inversion have been investigated theoretically by Kittel.<sup>1</sup> In this paper Kittel's theory is extended to include Curie-point shifts, magnetization, entropy, and magnetic anisotropy and is applied to Cr-modified  $\text{Mn}_2\text{Sb}$ . Kittel proposes that a transformation from ferromagnetic (F) to anti-ferromagnetic (AF) spin ordering will take place by a first-order process when there is, during normal thermal contraction, a critical lattice dimension  $c_c$  at which the sign of the exchange interaction changes from F to AF. Accompanying the first-order transition is a discontinuous change in dimension of the crystalline unit cell. The magnitude of the discontinuous change, as Kittel has pointed out, is equal to the difference between the magnetoelastic expansion of the ferromagnetically ordered lattice and the contraction of the antiferromagnetically ordered lattice. Experimental data that have been obtained support qualitatively the essential features of this theory.

The ternary composition  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$  is an ideal magnetic material on which to check semiquantitatively the features of an exchange-inversion theory.  $\text{Mn}_2\text{Sb}$  forms sets of 3-layer sheets<sup>2</sup> of strongly coupled spins ( $J/k \sim 450^\circ\text{K}$ ); the spins between sets are only weakly coupled by exchange forces ( $J/k \sim 80^\circ\text{K}$  at the Curie temperature). The net saturation moment of this 3-layer set is approximately 0.9 Bohr magneton.<sup>3</sup> We shall assume that detailed knowledge of the interatomic exchange forces is not needed and that this 3-layer set may be replaced with a single plane of spins strongly coupled ferromagnetically. Effects of magnetoelastic energy within this plane will also be neglected.

Thus, the model representing  $\text{Mn}_2\text{Sb}$  is a stack of weakly coupled ferromagnetic planes, the interplanar

exchange changing sign at some accessible lattice dimension. A main function of the Cr modifier is to provide an initial lattice contraction so that, depending on the amount present, the critical lattice dimension for exchange inversion occurs at some temperature below the Curie temperature.

### FREE ENERGY

In order to account for the exchange energy dependence on lattice dimension, the exchange energy is expanded in a Taylor series to quadratic terms about the critical lattice dimension  $c_c$  at which the exchange energy vanishes:

$$J(c) = \rho(c - c_c) + (\rho'/2)(c - c_c)^2. \quad (1)$$

Here  $\rho$  and  $\rho'$  are the first and second derivatives of the exchange interaction evaluated at  $c_c$ . This expansion for the exchange energy is identical to that used by Kittel except that he considered only the linear dependence of  $J$  on lattice parameter.

When the elastic energy  $\frac{1}{2}R(c - c_T)^2$  is included, the interplanar free energy per unit volume becomes

$$F/V = \frac{1}{2}R(c - c_T)^2 - [\rho(c - c_c) + (\rho'/2)(c - c_c)^2]m_1m_2 \cos\phi. \quad (2)$$

Here,  $R$  represents the elastic constant divided by the square of the average lattice dimension, and  $c_T$  is the lattice dimension in the absence of magnetic forces. The parameter  $m_i$  is the reduced sublattice magnetization obtained by normalizing the magnetization to the saturation value  $M_0$  at absolute zero.

The equilibrium value of  $c$  is given by  $\partial F/\partial c = 0$ , which yields

$$c = c_T + \left[ 1 - \frac{\rho' m_1 m_2}{R} \cos\phi \right]^{-1} \times \left[ \frac{\rho m_1 m_2}{R} \cos\phi + (c_T - c_c) \frac{\rho' m_1 m_2}{R} \cos\phi \right] \quad (3)$$

\* Contribution No. 830.

<sup>1</sup> C. Kittel, Phys. Rev. **120**, 335 (1960).

<sup>2</sup> L. Heaton and N. S. Gingrich, Acta Cryst. **8**, 207 (1955).

<sup>3</sup> C. Guillaud, thesis, University of Strasbourg, 1943 (unpublished). L. Néel, Ann. Phys. **3**, 137 (1948).

and, upon substitution into the free energy, Eq. (2), we obtain

$$\frac{F}{VR} = \left\{ -\frac{1}{2} \left( \frac{\rho m_1 m_2}{R} \right)^2 \cos^2 \phi - \frac{\rho}{R} m_1 m_2 (c_T - c_c) \right. \\ \left. \times \left[ 1 + \frac{\rho'}{2\rho} (c_T - c_c) \right] \cos \phi \right\} \left[ 1 - \frac{\rho' m_1 m_2}{R} \cos \phi \right]^{-1}. \quad (4)$$

Both the elastic energy and the second term in the exchange energy appear quadratically. A quadratic term in the exchange produces an effective elastic constant that is dependent on the spin orientation.

The condition for a transition to occur between  $F$  and AF spin configurations is no longer  $c_T = c_c$  of the Kittel theory but is readily obtained by equating the free energy for  $F$  ordering to the free energy for AF ordering to give

$$c_T - c_c = \frac{\rho}{\rho'} \left\{ -1 + \left[ 1 - \left( \frac{\rho' m_1 m_2}{R} \right)^2 \right]^{1/2} \right\}. \quad (5)$$

This expression reduces to the Kittel condition when  $\rho' = 0$ , and approaches the Kittel condition as the exchange-inversion temperature approaches the Curie point, where the sublattice magnetization is small. We now obtain from Eq. (3) the difference in interplanar spacing  $\Delta c$  between the  $F$  and AF states,

$$\Delta c = c^F - c^{AF} = \frac{2\rho m_1 m_2}{R \left[ 1 - (\rho' m_1 m_2 / R)^2 \right]} \left[ 1 + \frac{\rho'}{\rho} (c_T - c_c) \right]. \quad (6)$$

Substitution of Eq. (5) for the transition condition gives the discontinuous change in lattice dimension at the transition

$$\Delta c_s = \frac{2\rho m_1 m_2}{R} \left[ 1 - \left( \frac{\rho' m_1 m_2}{R} \right)^2 \right]^{-1/2}, \quad (7)$$

which is similar to the Kittel theory but is modified by the quadratic exchange term.

So far, this development has paralleled that of Kittel, but the results given demonstrate how the quadratic exchange term alters related conditions of the linear exchange theory. These expressions will also be necessary when attempting a fit to the experimental data using  $\rho/R$  and  $\rho'/R$  as adjustable parameters.

The free-energy expression, Eq. (4), is not complete, since the intraplanar exchange energy  $Jm^2$  and magnetic ordering entropy  $S$  have not been taken into account. Therefore, the following terms must be added to Eq. (4):

$$- (J_1/2) m_1^2 - (J_2/2) m_2^2 - kTS_1 - kTS_2, \quad (8)$$

where the classical entropy for  $N$  spins<sup>4</sup> with reduced

moment  $m$  is given by

$$\sigma = -\frac{N}{2} \left[ \left( \frac{1+m}{2} \right) \ln \left( \frac{1+m}{2} \right) + \left( \frac{1-m}{2} \right) \ln \left( \frac{1-m}{2} \right) \right]$$

for each sublattice.

### ENTROPY CHANGE

Addition of the terms (7) to Eq. (4) gives the total free-energy expression of the system including, in a rather disguised form, the lattice entropy. This fact may be demonstrated by differentiating the free energy with respect to temperature and taking the difference between the total entropy for  $F$  ordering and AF ordering. At the transition, given by the condition of Eq. (5), we obtain

$$\Delta S = -R \Delta c \left[ \frac{\rho'}{R} \frac{1}{m} \frac{\partial m}{\partial T} \frac{\Delta c}{2} + \frac{\partial c_T}{\partial T} \right]. \quad (9)$$

Thus, the change in entropy of the lattice at the transition is included in the dimension  $c_T$ . The first term in the bracket of Eq. (9) is of interest as it represents the magnetic contribution of the effective elastic energy to the change in entropy. Magnetization terms do not enter otherwise in Eq. (9) because the sublattice magnetization is assumed to be unchanged at the transition.<sup>5</sup> The magnitude of the first term of Eq. (9) at room temperature is of the order

$$\frac{1}{2} \frac{\rho'}{R} \frac{1}{m} \frac{\partial m}{\partial T} \frac{\Delta c}{c} \approx \frac{0.3}{2} (0.0015) \left( \frac{0.03}{6.5} \right) \approx 10^{-6} / ^\circ\text{K}$$

for  $\text{Mn}_2\text{Sb}$ , while

$$\frac{1}{c} \frac{\partial c_T}{\partial T} \approx 20 \times 10^{-6} / ^\circ\text{K},$$

and hence the first term is negligible. Therefore, the change in entropy at the  $F/AF$  phase transition arises largely from the lattice distortion and becomes

$$\Delta S \approx -C \left( \frac{\Delta c}{c} \right) \left( \frac{1}{c} \frac{\partial c_T}{\partial T} \right), \quad (10)$$

where  $C$  is the appropriate elastic constant in the direction of the strain  $\Delta c/c$ .

### MAGNETIZATION

Minimization of the free energy, Eq. (4) plus (8), with respect to the sublattice magnetization and rearrangement of terms gives

$$m = \tanh \left\{ \frac{m M_0}{kT} H_w \right\}, \quad (11)$$

<sup>4</sup> J. S. Smart, Phys. Rev. **90**, 55 (1953).

<sup>5</sup> A. E. Austin, E. Adelson, and W. H. Cloud, Phys. Rev. **131**, 1511 (1963).

where

$$H_w = \frac{2R}{NM_0} \left( \frac{J}{R} + \left\{ \left( \frac{\rho m}{R} \right)^2 \left( 1 - \frac{\rho' m^2}{2R} \cos\phi \right) + (c_T - c_c) \left[ \rho + \frac{\rho'}{2} (c_T - c_c) \right] \cos\phi \right\} \times \left[ 1 - \frac{\rho' m^2}{R} \cos\phi \right]^2 \right). \quad (12)$$

It has been assumed in Eq. (12) that the two sublattices are equivalent and that  $J_1 = J_2$ . The magnetization given by Eq. (11) is actually the Brillouin function for spin  $\frac{1}{2}$ . This form arises because the entropy expression assumes only two spin orientations. The first term of Eq. (12) represents the Weiss field due to intraplanar exchange, while the second term is due to interplanar exchange and, it is important to note, is dependent on the spin configuration through the  $\cos\phi$  term. If the  $\rho'$  term were not included, the  $\cos\phi$  dependence disappears, and there is no difference in the Weiss fields for F and AF ordering at the transition.

Thus, the magnetization is discontinuous at the transition because of the second-order  $\rho'$  term. However, even for fairly large values of  $\rho'/R \sim \frac{1}{2}$ , the discontinuous change of sublattice magnetization is of the order of a few percent and would be difficult to detect by neutron diffraction, for example. A large change in sublattice magnetization would alter all previously derived expressions, but for practical purposes we may ignore the small change in magnetization as long as  $\rho'/R < \frac{1}{2}$ . This restriction is no stronger than the initial assumption that the exchange energy dependence on lattice dimension can be represented by Eq. (1).

#### CURIE TEMPERATURE

Also contained in Eq. (11) is the unusual effect of a temperature-dependent Weiss field. In most molecular field treatments it is assumed that exchange interactions are constant over the entire temperature range below the Curie temperature. In exchange inversion, however, the exchange interaction is dependent on temperature through lattice contraction. Such effects should, therefore, influence the Curie temperature.

The Curie temperature for the magnetization expressed by Eq. (11) is

$$T_c = \frac{R}{Nk} \left\{ (c_{T_c} - c_c) \left[ \frac{\rho}{R} + \frac{\rho'}{2R} (c_{T_c} - c_c) \right] \cos\phi \right\} + \frac{J}{Nk}, \quad (13)$$

where  $(c_{T_c} - c_c)$  indicates that  $(c_T - c_c)$  is to be evaluated at  $T_c$ . We thus have a self-consistent equation in which  $T_c$  is contained explicitly on the left-hand side and implicitly on the right-hand side of Eq. (13). The second term  $J/Nk$  in Eq. (13) represents the Curie temperature

of the ferrimagnetically ordered 3-layer set of planes, while the first term is the interplanar Curie temperature. The Curie temperature is dependent on  $\cos\phi$ . For positive  $\rho$  the Curie temperature for F ordering is higher than the Curie temperature for AF ordering by twice the interplanar exchange energy. Thus, as temperature is decreased, ferromagnetic ordering first occurs and is the most stable configuration.

#### APPLICATION TO $Mn_2Sb$

In this section, the foregoing model is applied to Cr-modified  $Mn_2Sb$ .<sup>6</sup> It should be emphasized that the foregoing expressions represent a single composition whose F/AF transition occurs at a temperature  $T_s$ . In applying such a model to  $Mn_{2-x}Cr_xSb$  for various values of  $x$ , in which  $T_s$  varies with chromium content, one must investigate whether the behavior of all compositions can be represented by a model whose parameters are independent of composition, and yet whose thermodynamic quantities exhibit the observed functional dependence on composition.

Compositional changes are introduced into the function  $(c_T - c_c)$  by assuming that the temperature dependence of  $c_T$  remains the same as that of  $Mn_2Sb$ , but that the modifying element (chromium) reduces the absolute value of  $c_T$ . Thus, the requirement on the modifying element is that the lattice contraction introduced by it is just the amount required to satisfy Eq. (5) at the transition temperature  $T_s$ .

There are probably some deviations from this assumption at high chromium content, but the theory is not quantitative enough to warrant consideration of such deviations. At this point, we must mention a metallurgical property of this material. An increase in the value of  $x$  does not represent a proportional decrease in the value of  $c_T$ . It has been found that the chromium tends to segregate into an ever-present  $MnSb$  Widmanstätten precipitate,<sup>7</sup> and there is not a corresponding increase of chromium content in the  $Mn_2Sb$  phase proportional to the amount introduced into the melt. It must therefore be assumed that the transition temperature  $T_s$  occurs when Eq. (5) is satisfied and that the chromium in  $Mn_{2-x}Cr_xSb$  has introduced just the reduction in  $c_T$  required to satisfy Eq. (5) at  $T_s$ .

We shall also assume that  $c_c$  is constant throughout the entire range of transition temperatures. The value of  $c_c$  is critical only when calculating the F and AF lattice parameters for a given transition temperature. Otherwise  $c_c$  always appears in the expression  $(c_T - c_c)$  and, if this difference can be obtained,  $c_c$  needs to be known only approximately. A third assumption is that the magnetization of the sublattice of our model is given by the measured magnetization rather than by Eq. (11). As has already been discussed,<sup>5</sup> the spins of the 3-layer

<sup>6</sup> F. J. Darnell, W. H. Cloud, and H. S. Jarrett, Phys. Rev. **130**, 647 (1963).

<sup>7</sup> J. D. Wolf and J. E. Hanlon, J. Appl. Phys. **32**, 2584 (1961).

sets of atomic planes remain ordered antiparallel and appear to be strongly coupled by exchange forces. We assume, therefore, that the details of the magnetization behavior of Mn I and Mn II ions within this plane do not contribute to exchange inversion except through the temperature dependence of the magnetization of the entire 3-layer set. One would not expect that Eq. (11) should represent the magnetization of Mn<sub>2</sub>Sb. On the other hand, the conclusions drawn from Eq. (11) by use of the Weiss field is semiquantitatively correct even though the functional form is not. This functional dependence arose because we have used classical statistics in the magnetic entropy and assumed only a single sublattice.

To obtain the parameters  $\rho/R$  and  $\rho'/R$ , consider the discontinuous change in the  $c$  lattice parameter given by Eq. (7). The elastic constant  $R$  does not need to be known until absolute energy comparisons are made. The best fit to  $\Delta c_s$  is given by  $\rho/R=0.02 \text{ \AA}$  and  $\rho'/R=0.4$ .

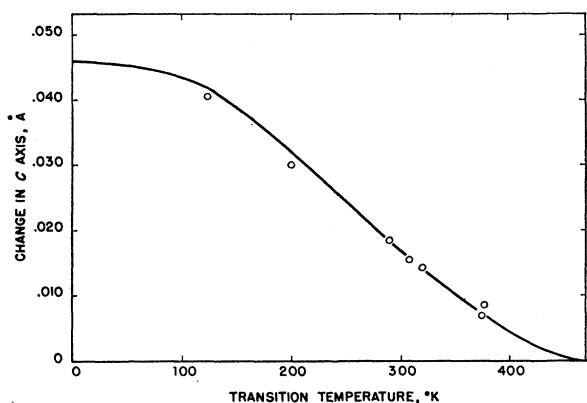


FIG. 1. Discontinuity in  $c$  axis as a function of transition temperature  $T_s$ . Experimental results (Ref. 6) are shown by the open circles.

Within the limits of experimental error, the value of  $\rho'/R$  is not too critical. For example, a 0.1 variation in  $\rho'/R$  can be tolerated and still obtain a fit with the experimental data. The value of  $\rho/R$  is more critical for only 0.001 Å variation can be tolerated here. This fit of experimental data to the theoretical equation is shown in Fig. 1. Since the introduction of chromium reduces both  $T_c$  and the saturation moment, the magnetization of Mn<sub>2</sub>Sb cannot be used in Eq. (7). Instead, the magnetization measured at  $T=T_s$  of that composition whose F/AF transition temperature is  $T_s$  is used. This magnetization is lower than the magnetization of Mn<sub>2</sub>Sb at the corresponding temperature.

We may now obtain the temperature dependence of  $(c_T - c_e)$  for unmodified Mn<sub>2</sub>Sb. From Eq. (3) we obtain  $c_F$ , the dimension of the unit cell for ferromagnetic ordering at  $\phi=0$ . Rearrangement of terms gives

$$(c_T - c_e) = (c_F - c_e)[1 - (\rho'/R)m^2] - (\rho/R)m^2, \quad (14)$$

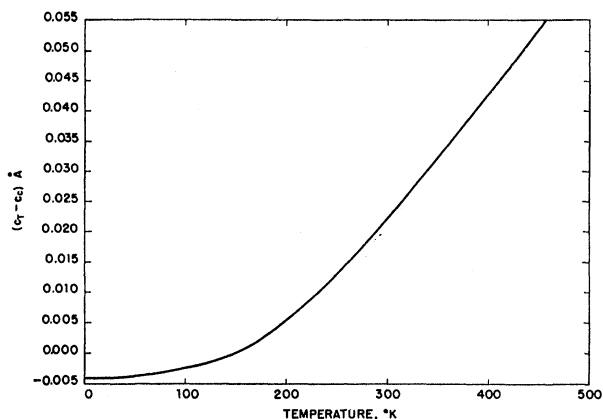


FIG. 2. Dimension  $(c_T - c_e)$  as a function of temperature calculated from the thermal contraction of Mn<sub>2</sub>Sb.

where the values of the magnetization to be used in Eq. (15) are those of Mn<sub>2</sub>Sb. It is seen in Eq. (14) that  $c_e$  must be known. The experimentally measured lattice dimension of Mn<sub>2</sub>Sb is  $c_F$ . The value of  $c_e$  within reasonable limits does not affect appreciably the empirically determined temperature dependence of  $(c_T - c_e)$ . Selection of the value of  $c_e = 6.506 \text{ \AA}$  is discussed later in the paper. Figure 2 shows the temperature dependence of  $(c_T - c_e)$  obtained from Eq. (14).

The change in entropy may now be calculated by use of Fig. 2 and Eq. (10). The value of the entropy is dependent only on the rate of change of  $c_T$  with temperature. The calculated change in entropy is shown in Fig. 3 in units of the elastic constant. Agreement with the experimentally measured  $\Delta S$  given by the open circles is good, if it is assumed that the elastic constant  $C$  is  $4.7 \times 10^{12} \text{ ergs/cm}^3$ . Some experimental values<sup>8</sup> of  $\Delta S$  in units of the elastic constant are shown for comparison. Such agreement is also indicative of the validity of the assumption that the temperature dependence of  $c_T$  is nearly independent of chromium content. We have been unable to measure an elastic constant along the  $c$

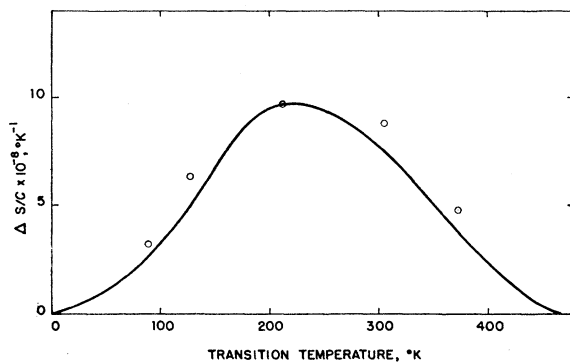


FIG. 3. Entropy change versus transition temperature. The data of Flippen (Ref. 9) are shown for comparison.

<sup>8</sup> R. B. Flippen and F. J. Darnell, J. Appl. Phys. **34**, 1094 (1963); W. A. Doerner and R. B. Flippen (to be published).

axis because of the severe cracking normal to the  $c$  direction that always accompanies samples large enough for ultrasonic measurements. The value required for  $C$  is comparable to  $C_{11}$  of tungsten, which is large compared to that of most materials, but not improbable. The few measurements that have been taken to determine the elastic constant by ultrasonic methods have indicated that the elastic constant is greater than  $3 \times 10^{12}$  ergs/cm<sup>3</sup>, which is, at least, consistent with the required value from the entropy data.

The Curie temperature is obtained from Eq. (13) as a function of  $T_s$ . It must be remembered that a different  $(c_T - c_c)$  curve is required for each chromium composition. The new  $(c_T - c_c)$  is found by reducing  $c_T$  by the contraction of the Mn<sub>2</sub>Sb lattice introduced by the chromium. The temperature which satisfies the equality in Eq. (13) is the Curie temperature for the composition. The Curie temperatures for various ternary compositions were thus calculated from the experimentally determined lattice contractions and the results are shown in Fig. 4 plotted against the associated F/AF transition temperature  $T_s$ . The measured Curie temperatures are included for comparison.

For the foregoing calculation the intraplanar exchange energy must be known. From the measured Mn<sub>2</sub>Sb Curie temperature  $J/Nk$  is found to be 470°K by subtracting the value of the first term for Mn<sub>2</sub>Sb on the right-hand side of Eq. (13). Actually an unknown parameter is introduced by the scale factor  $R/Nk$ , which converts elastic energy to temperature units. Our model compresses the 3-layer set of planes into a single layer. Therefore, the effective density  $N$  of the magnetic ions is not known, and the value we select for  $N$  influences the value of the intraplanar Curie temperature. However,  $N$  cannot be varied widely because the  $T_c$  calculated for the modified Mn<sub>2</sub>Sb materials would deviate widely from the experimentally measured values. There is no real advantage gained in making a least-squares

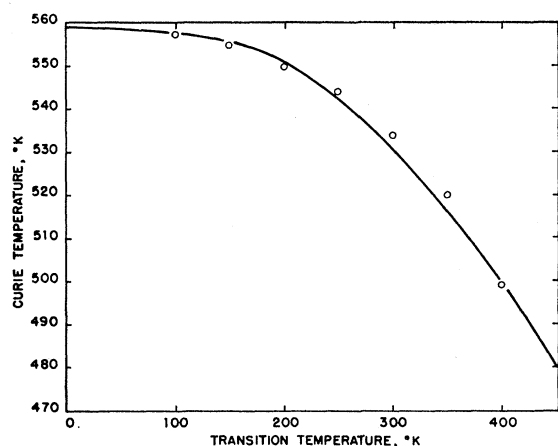


FIG. 4. Dependence of Curie temperature on F/AF transition temperature. Experimental results (Doerner and Flippen, to be submitted) are shown for comparison.

fit, so the density of magnetic ions in the 3-layer set,  $6.2 \times 10^{22}$ /cm<sup>3</sup>, is selected as the density  $N$  of ions for the model. The effective value of  $R$  is obtained from the change in entropy, Eq. (9), and the scale factor is  $R/Nk = 1.5 \times 10^4$  °K/Å<sup>2</sup>.

The parameters which have been evaluated allow calculation of the sublattice magnetization from Eq. (11). The sublattice magnetization for  $(c_T - c_c)$  given in Fig. 2, which would correspond to unmodified Mn<sub>2</sub>Sb, is essentially a Brillouin function with  $J = \frac{1}{2}$ . For  $(c_T - c_c)$  modified to give  $T_s > 0$ °K, the sublattice magnetization differs slightly from the unmodified  $(c_T - c_c)$  because of the reduction of Curie temperature, but the shape is still essentially a Brillouin function. The calculated discontinuity in  $M$  for  $T_s = 300$ °K is only 0.8%. There is little agreement between the experimental and the theoretical magnetization compared to the rather remarkable agreement in the foregoing calculations. This result is to be expected, of

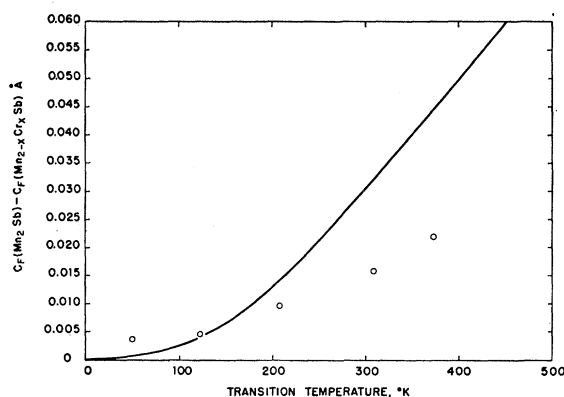


FIG. 5. Reduction of the ferromagnetic lattice dimension with increasing  $T_s$ .

course, since the functional form of the magnetic entropy is based on a molecular field model of a single sublattice.

A value for  $c_c$  has been used in the foregoing calculations, but its derivation has not been established. The expression for  $c_F$  is obtained from Eq. (3) for  $\phi = 0$  and  $m = m_s$ , the measured value of the magnetization at  $T_s$ . The lattice contraction in the F state due to the introduction of chromium is then given by

$$\Delta c_F = \frac{c_T - c_c + (\rho/R)m_s^2}{1 - (\rho'/R)m_s^2} + c_c - c_F(\text{Mn}_2\text{Sb})$$

and is shown in Fig. 5 with the experimental points obtained from Fig. 1 of Darnell *et al.*<sup>6</sup>

The value of  $c_c$  was selected to fit the low  $T_s$  materials. It is seen that deviations by a factor of 2 occur for high  $T_s$  materials, which indicates that our initial assumptions about the passive role of the chromium may not be entirely valid. Either  $c_c$  is not constant over

the range of transition temperatures or the temperature dependence of  $c_T$  changes at high chromium content. However, in view of the success of the theory which assumes the functional form of  $c_T$  is not changed with the addition of chromium, it seems more probable that  $c_c$  is not constant.

### ANISOTROPY

The anisotropy energy has not been taken into account in the foregoing treatment. On the whole, the anisotropy energy is 1 to 2 orders of magnitude smaller than the smallest exchange interaction, and its inclusion has not been necessary. There is however, an effect of anisotropy which is quite apparent. Consider Fig. 10 of Darnell *et al.*<sup>6</sup> It is seen that the temperature  $T_A$  at which the anisotropy changes sign for F ordering is not continuous across the  $T_s$  boundary into the AF region, but lies on this boundary from 200 to 350°K before entering the AF region. This effect is ascribed to an anisotropy in the interplanar exchange energy. In Fig. 6 the free energy is represented schematically as a linear function of temperature. Although the actual functional dependence is more complex, this representation serves this discussion. The anisotropy contribution is also exaggerated in proportion to the free energy so that it can be seen in the figure. The curves are labeled according to the orientation of the spins with respect to the crystallographic axis, parallel or perpendicular to  $c$ , and according to F or AF ordering.

It has been shown by Darnell *et al.*<sup>6</sup> that the anisotropy energies for F and AF ordering, which arise from dipole-dipole and crystal-field effects, are so nearly the same that the small differences can be ignored. Thus, the first-order contribution to the magnetic anisotropy energy to be added to the free energy is the same for F and AF ordering, and anisotropy is continuous across the F/AF transition. However, in second order, the anisotropy mixes with the exchange energy producing an anisotropic exchange. The effect of an anisotropic exchange is shown in Fig. 6 by the difference in the temperature at which  $F_{AF^\perp}$  and  $F_{F^\perp}$  intersect and  $F_{AF^\parallel}$  and  $F_{F^\parallel}$  intersect. The free energy at the intersection for parallel ordering is lower than that for perpendicular ordering by the anisotropy energy. For transition temperatures between the  $F_{AF^\perp}$  and  $F_{F^\perp}$  intersection and the  $F_{AF^\parallel}$  and  $F_{F^\parallel}$  intersection, Fig. 6(a) results. Since the magnetic system follows the lowest free energy, the F/AF transition takes place with a concomitant transition from positive to negative anisotropy. This situation is the condition for a transition between 200 and 350°K.

Figure 6(b) represents the free-energy relations for F/AF transition temperatures  $T_s > 350^\circ\text{K}$ . Here the  $F_{AF^\parallel}$  and  $F_{F^\perp}$  intersection is at a temperature lower than the F/AF transition temperature  $T_s$ , and the anisotropy remains positive at  $T_s$ . Figure 6(c) shows the situation for a low F/AF transition temperature,

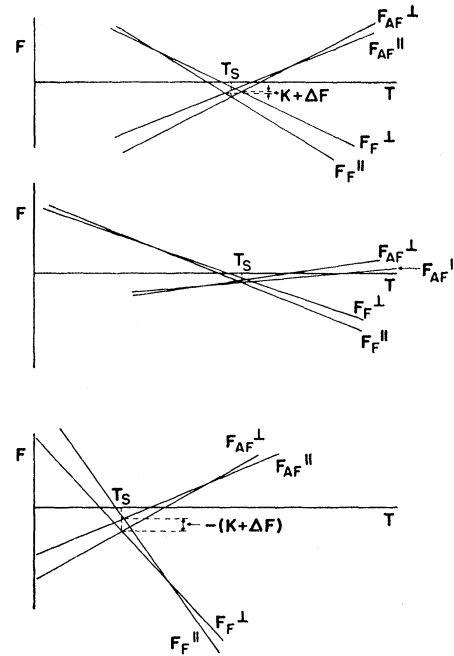


FIG. 6. Schematic representation of the effect of anisotropic exchange on magnetocrystalline anisotropy: (a)  $200^\circ\text{K} < T_s < 350^\circ\text{K}$ , (b)  $T_s > 350^\circ\text{K}$ , (c)  $T_s < 200^\circ\text{K}$ .

$T_s < 200^\circ\text{K}$ . Here the  $F_{F^\parallel}$  and  $F_{F^\perp}$  intersection is at a temperature higher than  $T_s$  and the anisotropy changes from positive to negative before the F/AF transition occurs.

Relative to the free energy for parallel orientation of spins, the free energy for perpendicular orientation is

$$F_{AF,F^\perp} = F_{AF,F^\parallel} + \Delta F_{AF,F} + K^0.$$

The differences between the  $F^\perp$  and  $F^\parallel$  curves of Fig. 6 are due to the temperature dependence of the  $(\Delta F + K)$  terms. Thus, the anisotropy of  $\text{Mn}_2\text{Sb}$  must contain not only terms of the type described by Darnell *et al.* and designated here by  $K^0$  but also an anisotropic exchange  $\Delta F$  whose contribution cannot be distinguished experimentally in a given composition.

These effects may be described more quantitatively by considering the variation of the free energy with the interplanar exchange  $\rho(c - c_c)$ . If it is assumed that only  $\rho$  is anisotropic, and that its anisotropy  $\Delta\rho = \rho_\parallel - \rho_\perp$  is small, the first-order deviation in the free energy is obtained by differentiation with respect to  $\rho$ , giving

$$\Delta\left(\frac{F}{R}\right) = - \left[ 1 - \left(\frac{\rho'}{R}\right) m^2 \cos\phi \right]^{-1} \times \left[ \left(\frac{\rho m^2}{R}\right)^2 \cos^2\phi + \left(\frac{\rho}{R}\right) m^2 (c_T - c_c) \cos\phi \right] \frac{\Delta\rho}{\rho}. \quad (15)$$

From Eq. (15), the magnitude of the anisotropy in the free energy  $\Delta F$  depends on the spin ordering through

$\cos\phi$ . In the Kittel approximation,  $\rho'=0$ . At the F/AF transition ( $c_T-c_c=0$ ), and  $\Delta F$  becomes independent of spin ordering for the F and AF configurations. Without the second-order exchange term  $\rho'$ , the shift in the free energy is the same for both F and AF ordering, and behavior of the type described by Fig. 6(a) does not arise. Explicit calculation of  $\Delta(F/R)$  from Eq. (15) shows that this contribution to the anisotropy of the AF state is smallest near  $T_s$ . Therefore, although there may be a second-order contribution to the temperature dependence of the anisotropy from an anisotropic  $\rho/R$ , no significant difference in the temperature at which the anisotropy changes sign in the F and AF states occurs. Similarly, an anisotropic  $\rho'/R$  suffers the same deficiencies.

The most reasonable additional source of anisotropy is a variation  $\Delta c_c=c_c^+-c_c^-$  of the critical lattice dimension with spin orientation,

$$\Delta\left(\frac{F}{R}\right)=\left[1-\left(\frac{\rho'}{R}\right)m^2\cos\phi\right]^{-1} \times \left[\frac{\rho}{R}+\frac{\rho'}{R}(c_T-c_c)\right]m^2\cos\phi\Delta c_c. \quad (16)$$

Here, in the Kittel approximation  $\rho'=0$ , the incremental changes in the free energy are in opposite direction for the F and AF states, i.e., this contribution to the anisotropy from Eq. (16) changes sign at  $T_s$ . Such behavior is just that which is necessary to account for the qualitative arguments summarized by Fig. 6. Thus, the first-order anisotropy constant may be expressed as

$$K=K^0+\rho m^2\Delta c_c\cos\phi, \quad (17)$$

where  $K^0$  contains all other contributions to the anisotropy that are predominately independent of spin ordering, e.g., crystal-field anisotropy and contributions such as expressed by Eq. (15).

In order to show that the additional contribution to the anisotropy in Eq. (17) is plausible, we compare the temperatures at which the anisotropy changes sign for the F and AF states. For the situation described by Fig. 6(a), anisotropy changes sign when exchange inversion occurs for a range in  $T_s$  of  $150^\circ$ . By use of the value of  $\rho/R$  found previously,  $\Delta c_c$  must be  $4\times 10^{-4}$  Å. Such a value for  $\Delta c_c$  is reasonable, unfortunately however, it is difficult to detect directly. It is significant, however, that such a small anisotropy in the exchange can play a dominant role in the magnetic anisotropy whenever magnetoelastic effects are present.

#### SPIN FLOPPING

The appearance of positive anisotropy in the antiferromagnetic state suggests that spin-flopping experiments can be performed on the high-chromium  $\text{Mn}_2\text{Sb}$  compositions. Such experiments have been reported by

Flippen.<sup>9</sup> Spin flopping has not been treated in an exchange-inversion material, and we outline briefly here the derivation of the spin-flopping conditions. Exchange inversion and spin flopping are quite different phenomena and should not be confused. Besides the obvious fact that exchange inversion can take place in the absence of an externally applied field, the most important feature is that the F/AF transition can be induced by an external field applied along any crystallographic direction. Spin flopping, however, can occur only when the anisotropy of the antiferromagnetic state is positive and when the external field is applied parallel to the anisotropy field. The spin configuration in the "spin flopped" state is canted, and this state is stable only in the presence of the applied magnetic field. The state is not stabilized when the external field is applied perpendicular to the anisotropy field or when the anisotropy is negative.

The condition for an exchange-inversion transition has been treated thus far in the absence of external fields. However, an F/AF transition can be induced at temperatures below  $T_s$  by application of a sufficiently strong magnetic field. The condition for an F/AF transition in the presence of an applied field is given by equating the free energies for F and AF ordering, including the magnetic energy of the applied field,

$$F(\pi)=F(0)+2\mathbf{H}\cdot\mathbf{M} \quad (18)$$

from which is obtained the critical field for the F/AF transition

$$H_c^{\text{AF/F}}=\frac{m}{M_0}\left\{\left(\frac{\rho m^2}{R}\right)\rho'+(c_T-c_c)\right. \\ \left.\times\left[\rho+\frac{\rho'}{2}(c_T-c_c)\right]\right\}\left[1-\left(\frac{\rho' m^2}{R}\right)^2\right]^{-1}. \quad (19)$$

It can be verified that the derivative of Eq. (19) with respect to temperature and application of the magnetic form of the Clausius-Clapeyron equation gives Eq. (8). Also, it can be seen by direct substitution that the critical field vanishes when Eq. (5) is satisfied.

The anisotropy has been ignored in Eq. (18). Anisotropic exchange introduces anisotropy in the critical field for the F/AF transition. If this were the only contribution to the anisotropy, the calculated value of  $\Delta c_c$  gives a critical field perpendicular to the  $c$  axis about 2000 G larger than the field applied parallel for a given temperature. When all sources of anisotropy are included, one would expect the anisotropy of the critical field to be proportional to the magnetocrystalline anisotropy field. Such anisotropy in the critical field is mentioned by Bierstedt<sup>10</sup> in connection with his resis-

<sup>9</sup> R. B. Flippen, J. Appl. Phys. **34**, 2026 (1963).

<sup>10</sup> P. E. Bierstedt, Phys. Rev. **132**, 669 (1963).

tivity measurements. More detailed unpublished data of Bierstedt show that the lower critical field is parallel to the easy direction of the anisotropy. Thus, the lower critical field changes from parallel to perpendicular to the  $c$  axis for compositions with  $T_s < 200^\circ\text{K}$ , the temperature below which the anisotropy changes sign before the exchange inversion occurs.

The second-order quantity  $\rho'/R$  is small, and its inclusion contributes only additional complications. We shall neglect it in the succeeding calculation of spin flopping. Eq. (19) becomes

$$H_c^{AF/F} = \frac{m}{M_0} \rho (c_T - c_c). \quad (20)$$

To obtain the spin-flopping conditions we again equate the free energies

$$F(\pi) = F(\theta) + 2\mathbf{H} \cdot \mathbf{M} + 2K \sin^2\theta. \quad (21)$$

Here the solution of Eq. (21) is anticipated by assuming that  $H$  is directed along the anisotropy field of the antiferromagnetic state and that the "spin-flopped" state is canted with the moments of the two sublattices making the same angle  $\theta$  with respect to the applied field. Equation (21) may be rearranged to give

$$\cos\theta \left[ \cos^3\theta + \left( \frac{m^2 \rho (c_T - c_c) + K}{\rho^2 m^4} R - 1 \right) \times \cos\theta + R \frac{H_c^{AF/C} M}{\rho^2 m^4} \right] - \frac{KR}{\rho^2 m^4} = 0, \quad (22)$$

where  $K$  is the anisotropy energy of the canted state. In order to obtain the critical field  $H_c^{AF/C}$  for spin flopping, the equilibrium value of  $\theta$  must be determined by setting the torque equal to zero,  $\partial F/\partial\theta = 0$ , where  $F$  is understood to contain the anisotropy and magnetic energies. Thus, the equilibrium condition

$$\cos^3\theta - \frac{1}{2} \left[ 1 - \frac{K + 2\rho(c_T - c_c)m^2}{2\rho^2 m} R \right] \times \cos\theta + \frac{H_c^{AF/C} M}{\rho^2 m^4} - \frac{KR}{\rho^2 m^4} R = 0 \quad (23)$$

must be satisfied simultaneously with Eq. (22).

General solution of Eqs. (22) and (23) are complex, however, the essential features may be obtained by an approximate solution applicable to the experimental conditions of Flippen. Substitution of the field dependence of the F/AF transition and the observed critical field for spin flopping in Eq. (23) indicate that  $\theta \cong 90^\circ$ , and  $\cos^3\theta$  can be neglected. Therefore, by solving Eq. (23) for  $\cos\theta$  and substituting into Eq. (22), the

spin-flopping condition is obtained

$$H_c^{AF/C} = \frac{1}{M} \left( 2 \left\{ K \left[ \frac{\rho^2 m^4}{R} - \rho(c_T - c_c)m^2 \right] \right\}^{1/2} - K \left\{ K \left[ \frac{\rho^2 m^4}{R} - \rho(c_T - c_c)m^2 \right] \right\}^{1/2} \right). \quad (24)$$

When  $K$  is small compared to the magnetic strain  $\rho^2 m^4/R$ , the second term of Eq. (24) may be neglected for any value of  $(c_T - c_c)$ . Substitution of Eq. (20) gives the relation between the spin-flopping field and the field for exchange inversion

$$H_c^{AF/C} = \frac{2}{M} \left\{ K \left[ \left( \frac{\rho^2 m^4}{R} \right) + H_c^{F/AF} M \right] \right\}^{1/2}. \quad (25)$$

The anisotropy field of the canted state is found to be of the order of 1000 Oe or  $2 \times 10^5$  erg/cm<sup>3</sup> from analysis of the data of Flippen.

#### INTERMEDIATE STATE

Darnell *et al.*<sup>6</sup> and Austin *et al.*<sup>5</sup> show that at low transition temperatures a third magnetic state appears as an interruption in the F/AF transition. The foregoing model does not account for such behavior principally for two reasons: First, effectively only nearest-neighbor interactions are contained in the model, and there is no competition between exchange interactions for spin direction that might give rise to a helical structure. Second, the model assumes a Bravais lattice and even if the details of the exchange interactions were included, only proper helical structures would result. The spin configuration of the intermediate state must be represented by a mixture of two configurations,

$$\mathbf{S}_n = \mathbf{D} + \mathbf{U} \cos(\mathbf{k} \cdot \mathbf{r}_n) + \mathbf{V} \sin(\mathbf{k} \cdot \mathbf{r}_n), \quad (26)$$

a  $k=0$  ferromagnetic component and a helical component commensurate with the lattice periodicity given by  $k_z = 2\pi/3c$ . For  $x < 0.022$  in the composition  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$  the intermediate state is stable at absolute zero. In order to account for such a spin configuration, one must treat the actual crystal structure of  $\text{Mn}_2\text{Sb}$  by the generalized Luttinger-Tisza method proposed by Lyons and Kaplan<sup>11</sup> and Lyons *et al.*<sup>12</sup> Preliminary calculations indicate that the spin eigenfunction given in Eq. (26) can lower the energy eigenvalues below the ferromagnetic and antiferromagnetic states. Details of this calculation will be published in a forthcoming paper.

#### DISCUSSION

The foregoing theory based on a highly simplified model of  $\text{Mn}_2\text{Sb}$  demonstrates considerable success in accounting for the behavior of the F/AF transition in

<sup>11</sup> D. H. Lyons and T. A. Kaplan, *Phys. Rev.* **120**, 1580 (1960).  
<sup>12</sup> D. H. Lyons, T. A. Kaplan, K. Dwight, and N. Menyuk, *Phys. Rev.* **126**, 540 (1960).



$\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$ . As pointed out by Bierstedt,<sup>10</sup> this transition is accompanied by hysteresis. For transitions near room temperature, the hysteresis is less than 1 deg of temperature. However, below about 200°K, hysteresis begins increasing sharply and reaches a value of about 20° for a transition occurring near the temperature of liquid nitrogen. First-order transitions to the ferromagnetic state in MnAs and the associated hysteresis have been investigated by Bean and Rodbell.<sup>13</sup> They point out that the maximum hysteresis arises when the spin system remains at the initial minimum of the free energy, even though it is not the lowest minimum, until the free energy is "down-hill-all-the-way." The measured hysteresis in MnAs is about 2/3 of this maximum value.

<sup>13</sup> C. P. Bean and D. S. Rodbell, *Phys. Rev.* **126**, 104 (1962).

This situation does not hold for the F/AF transition in  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$ . Kittel has shown that the maximum hysteresis in  $a_T$  is  $\Delta a_T = 2\rho m^2/R$ . The free energy used in this treatment does not alter appreciably this expression. At room temperature, therefore, the expected hysteresis in  $\Delta a_T$  using  $\rho/R$  obtained previously is of the order of  $10^{-2}$  Å, which may be transformed to a thermal hysteresis of about 50° by use of Fig. 2. This large discrepancy with the observed hysteresis indicates some very efficient mechanism nucleates the new state so that for transitions near room temperature the most stable state is nearly the equilibrium state. At low temperatures this nucleation mechanism must become less efficient, since the thermal hysteresis increases rapidly. A satisfactory model has not been obtained.

## Magnetic Susceptibilities of Transition Elements in Host Crystals. II. $\text{Ni}^{2+}$ in ZnO and CdS†

WILLIAM H. BRUMAGE AND CHUN C. LIN\*

*Department of Physics, University of Oklahoma, Norman, Oklahoma*

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The magnetic susceptibilities of  $\text{Ni}^{2+}$ -doped ZnO and CdS crystals have been measured along and perpendicular to the trigonal crystalline axes over the temperature range of 28–500°K. The magnetic susceptibilities of both crystals approach constant values at low temperature and decrease more rapidly with increasing temperature at  $T > 60^\circ\text{K}$ . An unusually large magnetic anisotropy is observed for  $\text{Ni}^{2+}:\text{ZnO}$ . The non-Curie behavior can be explained on the basis that the ground state of  $\text{Ni}^{2+}$  is nonmagnetic ( $A_1$ ) and the temperature-dependent susceptibility arises mainly from the ions in the first two excited states ( $A_2$  and  $E$ ). By fitting the theoretical susceptibilities to the experimental values, the spin-orbit coupling constant of  $\text{Ni}^{2+}:\text{ZnO}$  is obtained as  $-175 \pm 25 \text{ cm}^{-1}$  and the trigonal field splitting of the  $T_1[{}^3T(F)]$  state (the lowest  $T_1$  state) as  $100 \pm 10 \text{ cm}^{-1}$ . The corresponding quantities for  $\text{Ni}^{2+}:\text{CdS}$  are  $-170 \pm 10 \text{ cm}^{-1}$  and  $10 \pm 4 \text{ cm}^{-1}$ . In both crystals the  $A_2$  component of the  $T_1[{}^3T(F)]$  state lies below the  $E$  level. The large reduction of the spin-orbit coupling constant from the free-ion value indicates a rather strong covalency between the  $\text{Ni}^{2+}$  ion and the ligands. Combination of the trigonal splittings of the  $T_1[{}^3T_1(F)]$  state with those of  $T_2[{}^3T_1(P)]$  observed in the optical spectra leads to a determination of the trigonal field parameters. The experimental values of the trigonal parameters are consistent with those calculated by using the point-charge model and assuming a local contraction of the lattice with a slightly larger contraction for the three anions off the trigonal axis than for the one on the axis.

### I. INTRODUCTION

IN a previous paper we have pointed out that the magnetic susceptibilities of  $\text{V}^{3+}$ -doped corundum may be used quite effectively for determining certain structural parameters of the crystals.<sup>1</sup> For example, the trigonal field splitting of the lowest  ${}^3T_1$  level of  $\text{V}^{3+}:\text{Al}_2\text{O}_3$  was determined from the Van Vleck temperature-independent susceptibility which was evaluated from the magnetic data in the temperature interval of 77–295°K, and the zero-field splitting of the ground state was obtained from the susceptibilities at low tempera-

tures. By combining these results with those of electron spin resonance experiments and optical spectra,<sup>2</sup> the two trigonal field parameters and the spin-orbit coupling constant were estimated. The trigonal field parameters were found to be in reasonable agreement with the ones calculated from the empirical point-charge model. In this paper we shall report some magnetic measurements of  $\text{Ni}^{2+}:\text{CdS}$  and  $\text{Ni}^{2+}:\text{ZnO}$ . The susceptibility data make it possible to locate the first two excited states which hitherto have not been determined accurately.<sup>3</sup>

<sup>2</sup> D. S. McClure, *J. Chem. Phys.* **36**, 2757 (1962).

<sup>3</sup> An estimation of the energy of the first excited state of  $\text{Ni}^{2+}:\text{ZnO}$  has been made by intensity measurements. See R. Pappalardo, D. L. Wood, and R. C. Linares, Jr., *J. Chem. Phys.* **35**, 1471 (1961).

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<sup>1</sup> W. H. Brumage, C. R. Quade, and C. C. Lin, *Phys. Rev.* **131**, 949 (1963).