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Magnetic Disorder as a First-Order Phase Transformation

C. P. BEAN AND D. S. RODBELL
General Electric Research Laboratory, Schenectady, New York

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The exchange interaction that gives rise to ordered magnetic states depends upon interatomic spacing. If the lattice is deformable, then a spontaneous distortion of the lattice will occur in the ordered state. We have calculated, in the molecular field approximation, the properties of a system in which the exchange energy dependence is given by $T_c=T_0[1+\beta(v-v_0)/v_0]$. T_c is the Curie temperature appropriate to a lattice volume v while v_0 is the equilibrium volume in the absence of magnetic interactions. The course of the magnetization with temperature of such a system depends upon the steepness β of the exchange interaction dependence on interatomic distance, the compressibility K, and T_0. The behavior may be the usual second-order transition to paramagnetism, but it can in fact become a first-order transition with the properties usually associated thereto, e.g., latent heat and discontinuous density change. In the absence of an externally applied pressure, the transition will be of the first order if $\eta\equiv 40NkKT_0\beta^2[j(j+1)]^2/[(2j+1)^4-1]>1$. In this inequality, N is the number per unit volume of magnetic ions of angular momentum $j\hbar$ while k is the Boltzmann constant.

We have reviewed the experimental evidence on the nature of the first-order magnetic transition in MnAs. We find that this evidence indicates the transition to be one from ferromagnetism to paramagnetism rather than ferromagnetism to antiferromagnetism as has been generally assumed. Application of the theory noted above gives $\eta=2$ for this transition. In addition, we derive a value for the volume strain sensitivity, $\beta=19$ and infer the compressibility to be 2.2×10^{-12} cm^2/d.

INTRODUCTION

As a ferromagnet is heated, the magnetization usually decreases in a continuous manner and vanishes at the Curie temperature. This behavior indicates that the change of phase from ferromagnetism to paramagnetism at the Curie temperature is not a first-order phase transition in as much as the entropy (which is monotonically and continuously related to the magnetization) suffers no discontinuous change. Indeed the Weiss molecular field theory of ferromagnetism gave the first analytic treatment of a second-order phase transition.

It is of interest to inquire whether or not it is possible for this transition to be one of first order. Our interest in this question arose from some experiments on the stoichiometric compound MnAs. As has been known for many years,[1–8] this compound exhibits a discontinuous loss of ferromagnetism just above room temperature (see Fig. 1), and associated with this transition there is a latent heat of 1.79 cal/gm.[3] Early examination[5–7] had concluded that there was no change of crystal symmetry at this transition[9] although there is the discontinuous change of lattice parameter (i.e., density) that is associated with a first-order phase change. This transition has been generally ascribed to a transition from ferromagnetism to antiferromagnetism, but in the earlier treatments—prior to the recognition of antiferromagnetism as a possible state—it was supposed that the high temperature state was a paramagnetic one.[8] We shall review the experimental evidence in order to decide what magnetic state is a proper description of this compound. In view of the inconclusive nature of the published experimental evidence on this point we have been moved to examine

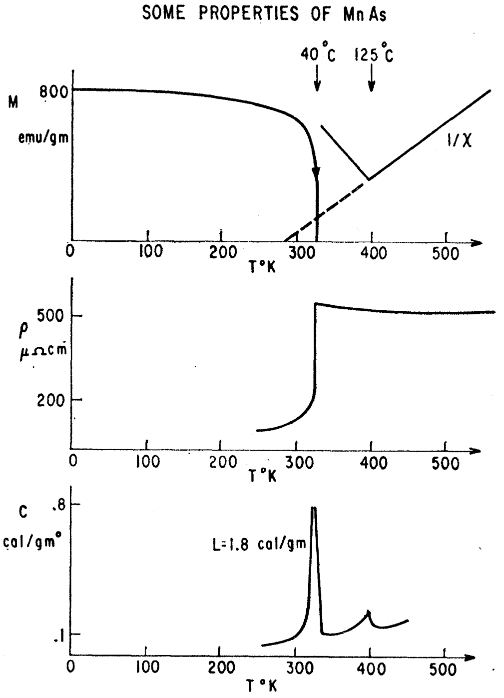

FIG. 1. Some features of the first-order phase transition exhibited by the compound MnAs.

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[1] F. Heusler, Z. angew. Chem. **1**, 260 (1904).

[2] S. Hilpert and T. Dieckmann, Ber. deut. chem. Ges. **44**, 2378, 2831 (1911).

[3] L. F. Bates, Proc. Roy. Soc. (London) **A117**, 680 (1928).

[4] L. F. Bates, Phil. Mag. **8**, 714 (1929).

[5] C. Guillaud, thesis, University of Strasbourg, 1943 (unpublished); also J. phys. radium **12**, 223 (1951).

[6] B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. (London) **B67**, 290 (1954).

[7] Z. S. Basinski and W. B. Pearson, Can. J. Phys. **36**, 1017 (1958).

[8] A. Smits, H. Gerding, and F. VerMast, Z. physik. Chem. 357 (1931).

[9] A current x-ray study by R. H. Wilson and J. S. Kasper of this Laboratory on single crystals has shown that above 40°C the structure of MnAs is not of the hexagonal NiAs type but of the orthorhombic MnP type. There are significant deviations of atomic coordinates from the NiAs arrangement, but the orthorhombic unit cell is of such dimensions as to allow a good approximation (within 0.15%) by a hexagonal cell.

the theoretical possibility of a first-order phase change from ferromagnetism to paramagnetism. We find that such a transition exists if the exchange interaction is a sufficiently strong function of lattice spacing and the lattice is compressible. This prediction, coupled with the properties of manganese arsenide and homologous compounds, indicates that the transition in manganese arsenide is probably of this type. Moreover, recent unpublished neutron and x-ray diffraction measurements by Kasper and Wilson, reviewed later, show this state to be paramagnetic. The generality of our treatment suggests that this phenomenon may not be unique to this compound.

In addition to the magnetic interest of this investigation, we have found in it a convenient model to elucidate the nature of first- and second-order phase transitions and, in particular, it points out the close relationship between them—a relationship that Wannier[10] has recently emphasized.

PHYSICS OF THE MODEL

Before proceeding to a detailed calculation, it may be helpful to give a feeling for the physics of our treatment. First, let us consider the usual method of treating magnetic disorder in which there is assumed to be a ferromagnetic interaction between the magnetic moments localized on each atom site and further, usually implicitly, that this interaction is not a function of lattice spacing. At low temperatures there exists substantially complete magnetization or perfect long range order. As the temperature is raised, the thermal randomization tends to destroy this order and the magnetization falls. The course of the magnetization is described more or less by the Brillouin function and at the Curie temperature, T_c, the spontaneous magnetization becomes zero without discontinuity. This transformation is of second order and the cooperative nature of the system is reflected by a discontinuity in the specific heat at T_c; there is not, however, the latent heat or discontinuous density change that characterizes a first-order transition.

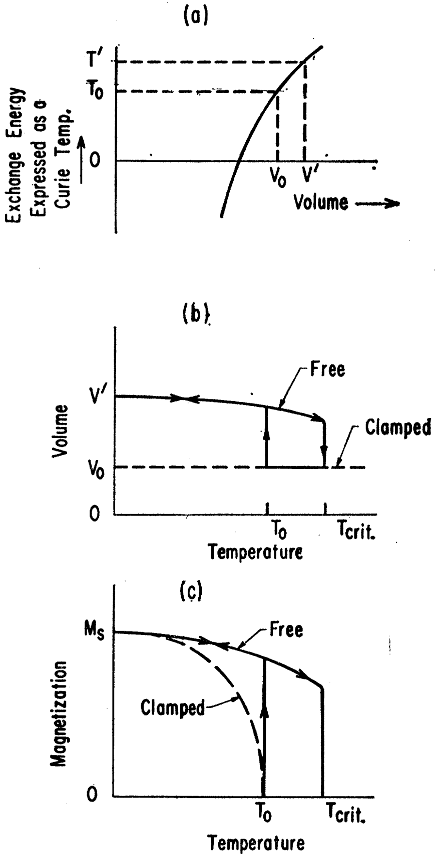

FIG. 2. A schematic representation of the volume-dependent exchange interaction (a) and some effects that result in (b) the sample volume and (c) the magnetization.

Now let us consider what results if we assume that the exchange energy (or Curie temperature) is a strong function of interatomic spacing. We show such a dependence in Fig. 2(a) in the form of an exchange that depends on atomic volume. At absolute zero the system's free energy may be lowered by a distortion of the lattice in the direction of increasing the Curie temperature. The distortion will introduce to the free energy a term in strain energy which will increase the free energy, and thus a compromise between distortion and exchange may be found that minimizes the free energy. This volume is indicated in Fig. 2(a) as v'. If we compare the course of the magnetization with temperature of such a system that is free to distort (free system) with that of a system whose volume is fixed (clamped system), we find the behavior sketched in Fig. 2(c), which omits the usual thermal expansion in order to focus upon magnetic effects. At low temperatures the free system will lose less of its magnetization than the clamped system because its effective Curie temperature (close to T') is greater than that of the clamped system, e.g., Fig. 2(c). If this change in apparent Curie temperature is large enough, then as the temperature is raised it is possible for the free system to have magnetization at temperatures greater than the Curie temperature, T_0, of the clamped system. Since the driving force to lattice expansion is caused by the ordered magnetic spins, the loss in magnetic moment or order at higher temperatures causes a diminution of the lattice strain as indicated in Fig. 2(b). Upon further elevation of temperature the magnetization will decrease, but there is no way for it to decrease smoothly to zero since its existence at these temperatures is due to the distortion which in turn is caused by the magnetization. This situation can only be resolved by a discontinuous loss of magnetization, i.e., a first-order phase transition. The situation is like that of a man who has run beyond the brink of a cliff; there is no gentle way down. There is a change in

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[10] G. H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, New York, 1959), Chap. 4.

volume at this transition that is caused by the loss of magnetic distortion, and a change in entropy that is occasioned by the loss of magnetic order as well as any change in lattice entropy associated with the volume change. Thermal hysteresis appears because, on cooling, the magnetization is not re-established until a temperature close to the "true" Curie point is reached. The fact that the transition may be first order depends upon the conditions of examination, i.e., in this treatment we allow the crystal to be "unclamped." A rigid (undeformable) crystal will not exhibit these features. Rice[11] has made this point explicitly in a theoretical treatment of the magnetic transformation in a two-dimensional Ising lattice.

DETAILED MODEL

The model that we consider is of a collection of interacting magnetic dipoles and we assume that their interaction may be approximated by the molecular field model. The central assumption of the model is given in Eq. (1) which is that

$$T_c = T_0[1+\beta(v-v_0)/v_0], \qquad (1)$$

where T_c is the Curie temperature, while T_0 would be the Curie temperature if the lattice were not compressible, v is the volume, and v_0 would be the volume in the absence of exchange interactions. β is the slope of the dependence of T_c on volume, and may be positive or negative. Let us now consider the case of particles of spin $\frac{1}{2}$ and we shall later generalize the results to arbitrary spin. The Gibbs free energy per unit volume is, within the molecular field approximation,

$$\begin{aligned} G_v = -HM_s\sigma - NkT_c\sigma^2/2 + (1/2K)[(v-v_0)/v_0]^2 \\ +P(v-v_0)/v_0 - TNk[\ln 2 - \tfrac{1}{2}\ln(1-\sigma^2) \\ -\sigma \tanh^{-1}\sigma], \qquad (2) \end{aligned}$$

where the first term on the right is the field term; the second, exchange; the third, distortion; the fourth, pressure; and the last, entropy. In (2), H is the applied magnetic field, M_s the saturation magnetization, σ the relative magnetization, N the number of particles per unit volume for volume v_0, k is the Boltzmann constant, and K is the compressibility. P and T are the pressure and temperature, respectively. The entropy of the spin system is obtained by the straightforward application of the Boltzmann definition of entropy.[12] We neglect other terms, in particular the entropy of the lattice, since the main conclusions may be drawn from this simplified form while in a later section we shall examine the contribution of the lattice entropy. We now minimize the free energy with respect to the volume by inserting expression (1) into (2) above, taking the partial derivative with respect to v, and equating the resulting expression to zero. The volume that minimizes the free energy satisfies the condition that

$$(v-v_0)/v_0 = NKkT_0\beta\sigma^2/2 - PK. \qquad (3)$$

This result shows that the volume change is due to a simple sum of the effects of magnetization and pressure.

By substitution of (3) into (2) above, minimizing the resulting expression with respect to σ, and setting the applied field H equal to zero, we determine the course of the normalized spontaneous magnetization. The result may be expressed conveniently as the implicit dependence

$$T/T_0 = (\sigma/\tanh^{-1}\sigma)(1+\eta\sigma^2/3 - PK\beta), \qquad (4)$$

with $\eta \equiv \frac{3}{2}NkKT_0\beta^2$. Expression 4, with the applied pressure set equal to zero, is plotted in Fig. 3 for various values of the parameter η. The maximum temperature, that for $\eta > 1$ corresponds to the discontinuous change in magnetization, is properly the beginning of a reentrant branch (drawn in dash for $\eta = 4$). Since this branch is not energetically the stable one, we have omitted it here and drawn instead the abrupt transition to paramagnetism. We shall shortly examine the energetics of this transition in more detail. Notice that for $\eta < 1$ the transition is of second order ($\eta = 0$ gives the usual function for $j = \frac{1}{2}$), while for $\eta > 1$ the transition is of first order. In expression 4 the term $PK\beta$ accounts for our primary statement (1) that the Curie temperature changes with unit cell volume. We may see this point by examining (4) for the temperature at which $\sigma = 0$. Since

$$\lim_{\sigma\to 0} \sigma/\tanh^{-1}\sigma = 1,$$

we have

$$T_c = T_0(1-PK\beta) \qquad (5)$$

as we must by our initial assumption. This critical temperature T_c is the paramagnetic Curie temperature that is the intercept on the T axis of a plot of reciprocal susceptibility vs temperature.

It is instructive to examine the free energy in more detail. Let us return to the Gibbs free energy obtained by substitution of (3) into (2). We expand the entropy into a power series of σ and after collecting terms in like powers of σ we obtain

$$\begin{aligned} (2G_v/NkT_0)_{\min} = -P^2K/NkT_0 \\ -(2T/T_0)\ln 2 - 2HM_s\sigma/NkT_0 \\ +[T/T_0 - 1 + PK\beta]\sigma^2 + \tfrac{1}{6}[T/T_0 - \eta]\sigma^4 \\ +(T/15T_0)\sigma^6 + (T/28T_0)\sigma^8 + (T/45T_0)\sigma^{10} + \cdots. \qquad (6) \end{aligned}$$

Neglecting terms independent of σ and in the absence of a magnetic field let us examine the dependence of the free energy on σ for various temperatures. For $T/T_0 < 1$ and σ small the free energy is dominated by the σ^2 term and is decreasing because of that term's negative coefficient. At larger σ's the σ^4, σ^6 etc., take over and the energy increases as a result of their positive

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[11] O. K. Rice, J. Chem. Phys. **22**, 1535 (1954).

[12] J. S. Smart, Phys. Rev. **90**, 55 (1953). Smart's paper contains an omission in its Eq. (5) which should contain a factor of $\frac{1}{2}$ in each factorial term of its denominator and will then yield the Eq. (6) given there.

contributions. The minimum in free energy occurs at the stable value of σ for the temperature of the evaluation. We have previously calculated the trajectory of σ with T (Fig. 3). The paramagnetic Curie point, as found previously (and again here), corresponds to the coefficient of the σ^2 term becoming zero, i.e., Eq. (5). The transition will occur at this temperature and be second order provided that the coefficient of the σ^4 term is positive, i.e.,

$$T_c/T_0 > \eta. \qquad (7)$$

This last condition is necessary because otherwise at temperatures above T_c the negative σ^4 contribution leads to a minimum energy at $\sigma \neq 0$ and gives rise to the first-order transition indicated previously. We may generalize our previous result (that in the absence of an externally applied pressure $\eta = 1$ separates the first- and second-order transitions) by the more general requirement that if

$$PK\beta > 1 - \eta, \qquad (8)$$

then the transition is of first order. Thus for β positive it appears possible to change a transition of the kind envisioned here from second to first order by application of sufficient external pressure. If β is negative, the reverse is true, i.e., sufficient pressure will change a first to a second-order transition. We shall subsequently examine the usual effect of pressure on a first-order transition.

We may illustrate further some of the features of the free energy of a first-order transition by plotting the free energy isotherms in the vicinity of the critical temperature. Figure 4 is such a plot appropriate to $\eta = 1.2$, ($P = 0$), and $j = \frac{1}{2}$.

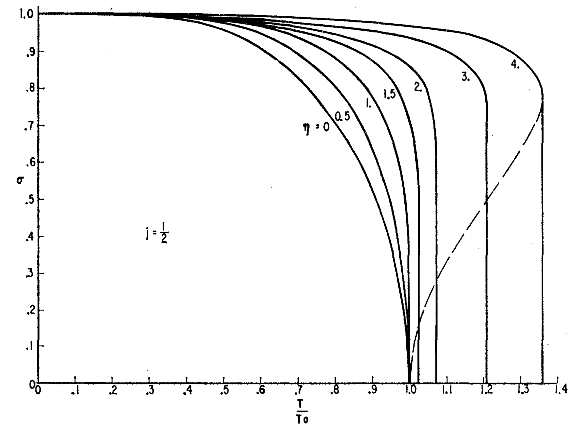

FIG. 3. The reduced spontaneous magnetization, σ, versus the reduced temperature for different values of the parameter η as obtained by evaluating expression 4 in the text. If $\eta > 1$, the transition to paramagnetism is of first order, and the magnetization is lost abruptly at the maximum temperatures indicated for the different η values.

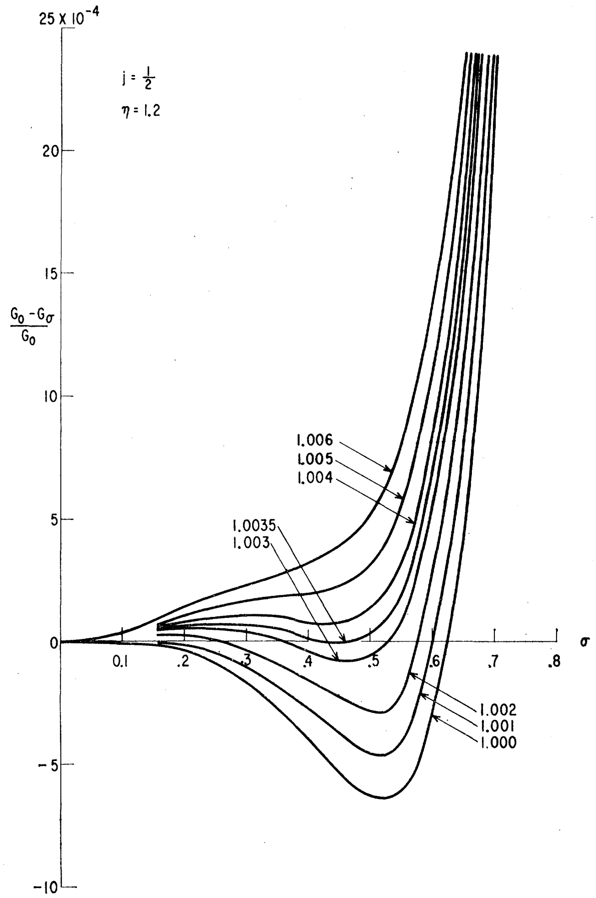

FIG. 4. The free energy isotherms in the vicinity of T_0 for a spin $\frac{1}{2}$ system characterized by $\eta = 1.2$; the curve indices are the ratio T/T_0.

Notice that the free energy minima that determine the spontaneous magnetization are a sensitive function of the temperature. The numbers associated with each curve are the reduced temperature T/T_0. With increasing temperature the free energy minimum moves to lower values of σ while becoming less and less pronounced. Eventually the minimum is degenerate in energy with that corresponding to $\sigma = 0$, and in sufficient time the magnetization will go to zero via a fluctuation. In the absence of nucleation processes, it may require long times, and we note that this "equilibrium" value, T_{equil}/T_0, is not necessarily the one observed in finite times. The maximum temperature that can retain $\sigma > 0$ corresponds in the plot (Fig. 4) to the isotherm that just attains a zero slope in free energy vs σ plot, thus giving a "down-hill-all-the-way" picture. In the case plotted in Fig. 4 this corresponds to a value $T_{\mathrm{max}}/T_0 = 1.005$. On cooling, i.e., starting from a state of $\sigma = 0$, we notice a somewhat similar situation in that the equilibrium temperature, T_{equil}/T_0, has the same value, but one must now decrease the temperature below this value to remove the barrier. The energy barrier in this case goes to zero at $T_{\mathrm{min}} = T_0$ and allows supercooling as compared to superheating in the previous cycle. The maximum thermal hysteresis that is expected for this model thus derives from the energy

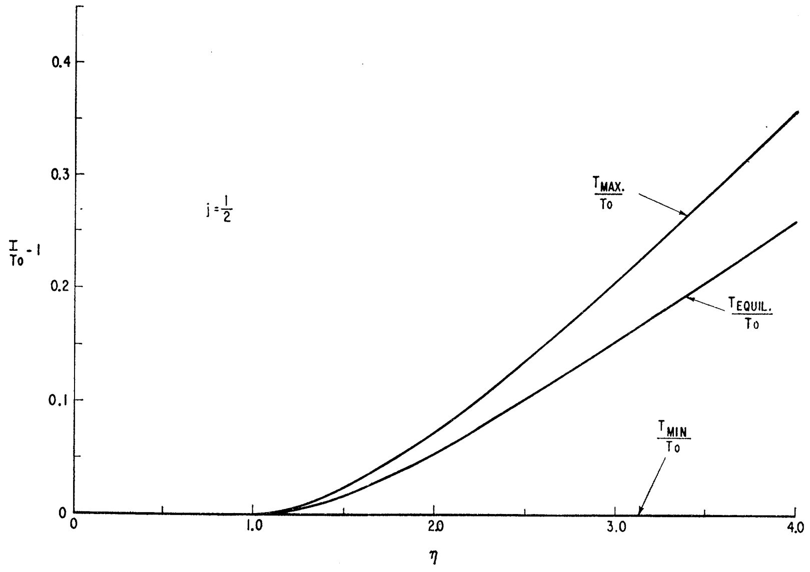

FIG. 5. The dependence upon η of the maximum and equilibrium temperatures of the magnetization determined from the free energy isotherms similar to Figure 4.

barriers between the local minima in free energy as a function of magnetization. We have plotted in Fig. 5 the critical and equilibrium temperatures as they depend upon η for the case $j=\frac{1}{2}$ and $P=0$. The maximum observable thermal hysteresis in the absence of nucleation will be dependent upon η and equal to the separation between $T_{\max}$ and $T_{\min}$. For cross reference we have evaluated the magnetization at these critical temperatures and have plotted these against η in Fig. 6. The critical magnetization is useful in estimating the latent heat of the transformation since the spin system entropy is conveniently expressed in terms of σ. The latent heat is

$$L=L_{\text{spin}}+L_{\text{lattice}}, \tag{9}$$

in which

$$L_{\text{spin}}=T\Delta S(\sigma). \tag{10}$$

The entropy change of the lattice may be either a positive or a negative contribution, depending upon the sign of β.

The magnetic contribution to the thermal expansion is contained in Eq. (3), which gives the volume that minimizes the system free energy. This is the contribution that must be added to the normal (i.e., nonmagnetic) thermal expansion to obtain the total thermal expansion. We have plotted this expression in Fig. 7 for $P=0$, $j=\frac{1}{2}$, and various values of η. For $\eta>1$ a discontinuous volume change occurs at the transition. In Fig. 8 there is plotted this discontinuous change in volume as a function of η. It is to be noted here that the magnetic contribution to the thermal expansion can yield a negative over-all thermal expansion even for continuous transitions, i.e., $\eta<1$, for sufficiently large compressibilities and sufficiently steep

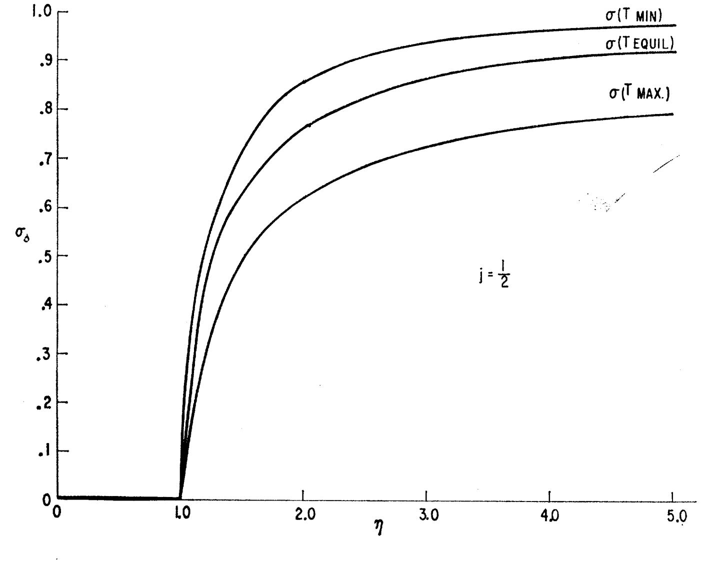

FIG. 6. The dependence upon η of the magnetization at the temperatures indicated.

Curie temperature dependence on specific volume. This is simply the Invar effect. He^3, a nuclear antiferromagnet, has been viewed in this framework.[13] The magnetic contribution to the thermal expansion coefficient is obtained from (3) by differentiating with respect to the temperature. By evaluating the limit of $\sigma d\sigma/dT$ (i.e., from the Brillouin function for $j=\frac{1}{2}$) we find[14] that the lower bound of the magnetic contribution to thermal expansion is $|\alpha_{\text{mag}}| \geqslant |\frac{3}{2}NkK\beta|$. Thus if $|\alpha_{\text{mag}}| > |\alpha_{\text{normal}}|$, a negative thermal expansion will be observed provided that the sign of $T_0\beta$ is positive. In Fig. 9 are displayed the qualitative features of this behavior.

COMPARISON WITH EXPERIMENT

We now examine the experimental observations made on manganese-arsenide. These observations initiated our interest in the kind of phase transition that we have been discussing; and although we discuss this compound in most detail, we believe that the treatment is more general and applies to other materials—we shall mention one of these later.

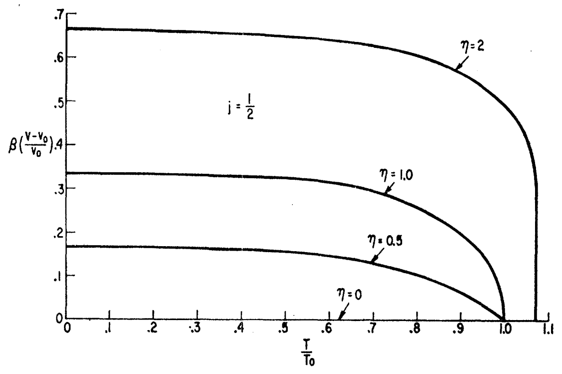

FIG. 7. The magnetic contribution to thermal expansion (or contraction) for several different η values.

The magnetic properties of MnAs were studied in detail by Guillaud[5] following the initial studies of Bates,[3,4] Hilpert and Dieckmann,[2] and others. In Fig. 10 we have replotted Guillaud's data along with data from other samples. The data are plotted on normalized coordinates, the ordinate being the moment measured in a field of 20 koe at the temperature indicated and normalized to the moment measured in 20 koe at 77°K. The abscissa is the temperature divided by the paramagnetic Curie temperature, 285°K, as determined by Serres.[15] The results for measurements made in magnetic fields of 20 koe or less show the abrupt drop of the magnetization at a critical temperature. Rodbell and Lawrence,[16] extending the work of Guillaud[5] and of Meyer and Taglang,[17] have shown that in very large magnetic fields it is possible to accomplish the phase transition by field alone and also to observe the dilatation resulting from the density change (an effect that eluded earlier attempts[8] with fields less than 25 koe). The course of the magnetization vs applied magnetic field is given in Fig. 11 for one of the samples examined. It is noteworthy that the critical field at which large magnetization changes appear depends upon temperature. The values of this H_{crit} for H increasing are plotted in Fig. 12. The experimental conditions of these observations are more closely adiabatic than isothermal. The isothermal observations made by Meyer and Taglang are reproduced in Fig. 13. The behavior may be understood as a consequence of the first-order nature of the transition as originally pointed out by Meyer and Taglang. In such a case, the Clausius-Clapeyron relation takes the form $\Delta T/T=-H\Delta M/L$. ΔT is the shift of the transition temperature, T, under the in-

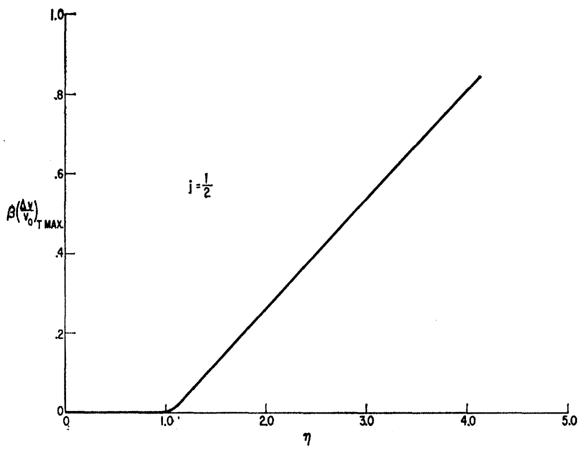

FIG. 8. The discontinuous change in volume to be expected at the first-order transition ($\eta>1$).

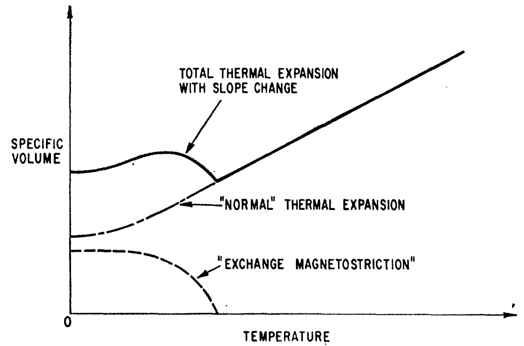

FIG. 9. A representation of magnetic effects upon thermal expansion, specifically indicating a "negative thermal expansion" situation.

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[13] D. S. Rodbell, Phys. Rev. Letters **7**, 1 (1961).

[14] The $\lim_{\sigma\to 0}(\sigma d/dT)=-3/2T_0$ for the Brillouin function of $j=\frac{1}{2}$. This value is the maximum expected for the undistorted Brillouin function.

[15] A. Serres, J. phys. radium **8**, 146 (1947).

[16] D. S. Rodbell and P. E. Lawrence, Suppl. J. Appl. Phys. **31**, 275 (1960).

[17] A. J. P. Meyer and P. Taglang, J. phys. radium **14**, 82 (1953).

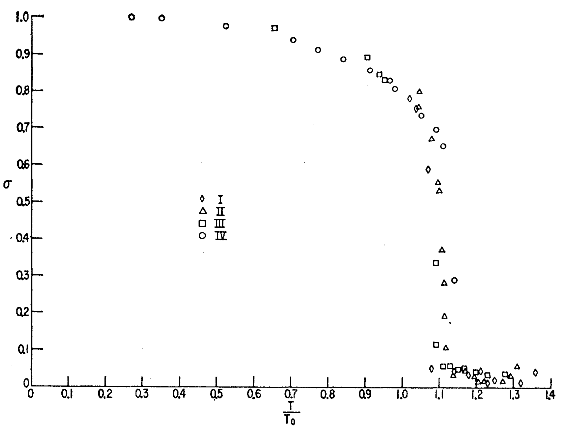

FIG. 10. The reduced magnetization vs reduced temperature for several MnAs samples. I–III are three different samples measured in this study. IV is a replot of Guillaud's data. The value of $T_0=285$°K is determined from data of Serres.

fluence of an applied field H and resulting magnetization change ΔM. The latent heat per unit volume is given by L. The observed values of ΔT, T, H and ΔM are in accord with the latent heat quoted in the literature, i.e., 1.79 cal/g, for this transition originally measured by Bates.[3] Similarly one may examine the shift of the transition temperature under a hydrostatic pressure and use the conventional Clausius-Clapeyron equation, where $H\Delta M$ in the expression above must be replaced by $-P\Delta v/v$; P is the pressure and $\Delta v/v$ is the relative change in volume at the transition. In this experiment the magnetization was determined as a function of the applied hydrostatic pressure for different temperatures. The observations are presented in Fig. 14. We plot in Fig. 15 the pressure at which the magnetization is half removed vs the temperature of observation and compare these data to that predicted by the Clapeyron relation. The solid line in Fig. 15 is drawn to a slope calculated from the Clapeyron relation and indicates that there is substantial agreement between these observations and the volume change and latent heat independently determined.

We now consider the magnetization data presented in Fig. 10 and compare these data with the theory that we have outlined in the previous section. As we have noted, the data of Fig. 10 are plotted to a temperature scale normalized to the paramagnetic Curie point (i.e., that temperature which corresponds to T_0 of our treatment, determined as the extrapolated intercept of the inverse paramagnetic susceptibility, $1/\chi$ vs temperature). Since the Curie constant obtained by Serres would imply a $j=\frac{3}{2}$ angular momentum state, we shall compare these data to the theory appropriate to $j=\frac{3}{2}$. The family of theoretical curves is shown in Fig. 16, and from inspection it would appear that $\eta=2$ would be a close representation for MnAs. We present in Fig. 17 the data for MnAs and the theory for $\eta=2$ with $j=\frac{3}{2}$. The plot for $j=\frac{1}{2}$ is also included for comparison. The agreement between experiment and theory is quite striking.

If we assume this description to be valid, we may determine the various parameters of manganese arsenide. From Eqs. (A6) and (A7) of the Appendix we have for $j=\frac{3}{2}$

$$\Delta v/v=0.90NkKT_0\beta\sigma_{\mathrm{crit}}^2, \qquad (11)$$

and

$$\eta=2.20NkKT_0\beta^2. \qquad (12)$$

In Eq. (11), $\Delta v/v$ is the fractional volume change at the transition and σ_{crit} is the fractional magnetization at the transition. If we take from experiment $\Delta v/v=1.8_4\times10^{-2}$, $N=2.9_5\times10^{22}$ cm^{-3}, $T_0=285$°K, $\sigma_{\mathrm{crit}}=0.65$, and $\eta=2$, we may deduce values for the compressibility, K, and the strain sensitivity of the exchange interaction, β. We find K to be 2.2×10^{-12} d^{-1}

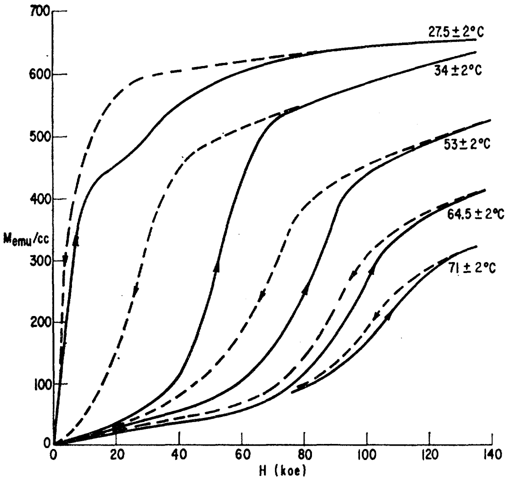

FIG. 11. Magnetization vs applied magnetic field for a sample of MnAs (Sample I of Fig. 10). These data illustrate the fact that the applied field shifts the transition temperature.

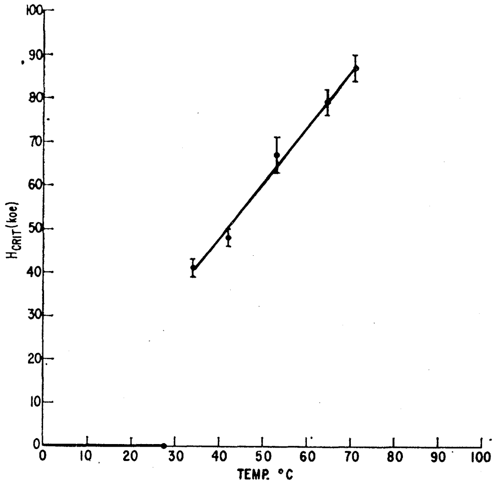

FIG. 12. The critical field vs the temperature as determined from Fig. 11. The critical field represented here is chosen as the onset of the increase in magnetic moment of the sample.

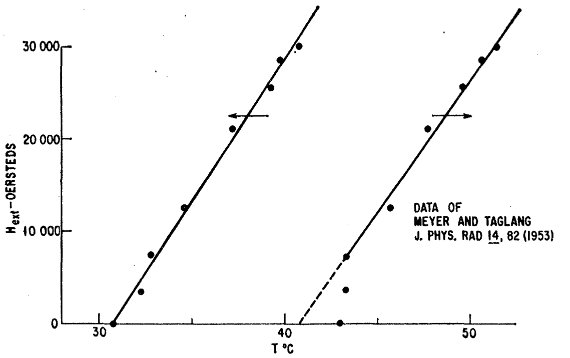

FIG. 13. A replot of the data of Meyer and Taglang who first measured the shift of transition temperature with applied field for MnAs.

cm^2 and β is 19. Unfortunately, there is no information on the compressibility of MnAs. Kittel,[15,18] on the basis of an alternate theory of the magnetic properties of MnAs, deduces the compressibility to be 2.4×10^{-13} d^{-1} cm^2. This theory, to be discussed in a later section, assumes the transition to be from ferromagnetism to antiferromagnetism. A direct measure of the compressibility would be a useful check on the validity of the two theories. The experimental value for β is also unknown but is in rough accord with the strong variation in Curie temperature for the compounds MnAs, MnSb, and MnBi.[19,20]

Let us now examine the latent heat of the transformation on the basis of the model that we propose. The latent heat arising from the spin disorder is $L_{\text{mag}}=T\Delta S_{\text{spin}}$. From the critical magnetization at the transition we may calculate the value of ΔS_{spin} on the assumption that the final state is one of complete spin disorder. For $\sigma_{\text{crit}}=0.65$ and $j=\frac{3}{2}$ we have[21] $\Delta S_{\text{spin}}/Nk=0.42$. From this we obtain $L_{\text{mag}}=2.05$ cal/g. This is in reasonable agreement with the observed latent heat of 1.8 cal/g. To the magnetic latent heat should be added the latent heat of the lattice, which we may expect to be a small negative number. The lattice latent heat is negative because the lattice shrinks upon heating at the transformation temperature.

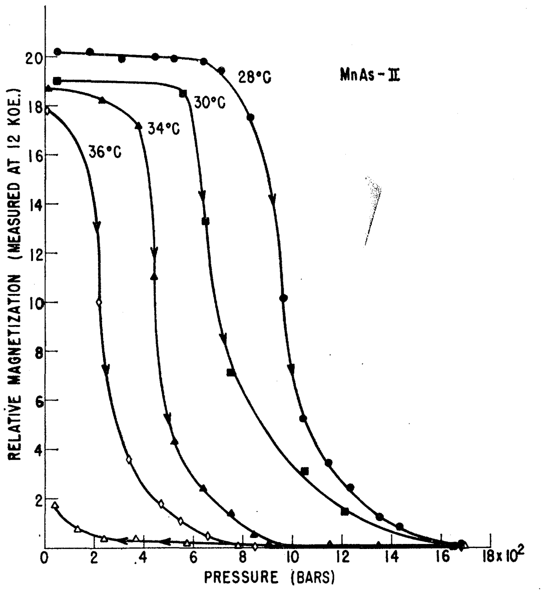

FIG. 14. The magnetization measured at 12 koe vs the applied hydrostatic pressure for a sample of MnAs at the various temperatures indicated.

Finally we note the negative thermal expansion behavior that has been observed[6] in the temperature region preceding that of the first-order transition. Recently these observations have been extended to below room temperature by Kornelsen.[22] We give Kornelsen's data in Fig. 18. The qualitative explanation of this behavior is given in Fig. 9. We have not attempted to give a quantitative explanation inasmuch as data over the full temperature range are not available.

In an interesting recent paper, Kittel[18] has made a simple model of exchange-inversion magnetization. The free energy function that he assumes is a truncated form of our Eq. (17) (below). The truncation consists of eliminating the entropy of the spin system. He concentrates upon the case in which thermal expansion

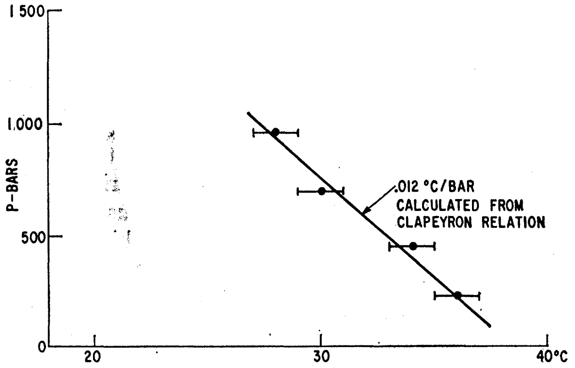

FIG. 15. The observed critical pressure vs the temperature compared to the prediction of the Clausius-Clapeyron relation.

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[18] C. Kittel, Phys. Rev. **120**, 335 (1960).

[19] A direct measure of the volume dependence of the magnetic ordering temperature for the compound CrTe has recently been reported by Grazhdankina, Gaidukov, Rodionov, Oleinik, and Shchipanov, J. Exptl. Theoret. Phys. (USSR) **40**, 433 (1961) [translation: Soviet Phys.—JETP **13**, 297 (1961)]. This material is similar to MnAs in that it is of the NiAs structure and has a comparable electrical resistivity ($\sim200\mu$ ohm). For this material $\beta\cong8$ is determined using the measured pressure dependence of the Curie temperature and a directly determined compressibility quoted by those authors to be $2.2\pm0.3\times10^{-12}$ cm^2/d. It is germane to consider here the fact that the transition in CrTe is observed to be of second order. We evaluate η for CrTe to be 0.34, a number less than one, and hence the second-order transition is in accord with the theory given here.

[20] A. J. P. Meyer and P. Taglang, Suppl. J. phys. radium **12**, 63 (1951).

[21] L. P. Schmid and J. S. Smart, Naval Ordnance Laboratory Report NAVORD 3640, 1954 (unpublished).

[22] R. O. Kornelsen (private communication).

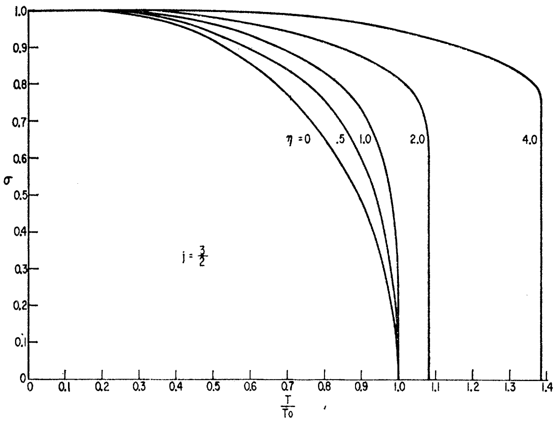

FIG. 16. The theoretical course of the magnetization vs the temperature for a $j=\frac{3}{2}$ spin system and evaluated for the indicated values of η.

(which arises from the change of lattice entropy with volume) carries the system from one fully magnetized state to another, e.g., from antiferromagnetism to ferromagnetism with increasing temperature. This is almost certainly the way to explain the properties of Cr-modified Mn_2Sb.[23] His tentative application of that theory to MnAs has, as he recognizes, several difficulties. First, it is hard to see how thermal expansion can drive the transition in MnAs since the lattice contracts at the transition point. Secondly, there is the question of the experimental evidence for antiferromagnetism above the transition point.

A fundamental experimental question is whether the state just above the transition point is paramagnetic, as we suggest, or antiferromagnetic, as most recent workers have postulated. The most direct measurement is that of neutron diffraction. This type of measurement was first made by Bacon and Street,[24] who found no evidence for antiferromagnetism. This experiment has been repeated by our colleagues Kasper and Wilson, who have been able, owing to higher neutron fluxes and greater resolution, to state that for simple models of the antiferromagnetic state the order indicated by their data must be less than a few percent of full order.

The question remains then as to the origin of the susceptibility maximum and specific heat anomaly near 125°C. These phenomena were the main evidence for the assignment of the antiferromagnetic state. Kasper and Wilson[25] have shown from a detailed single-crystal x-ray analysis that an interesting series of lattice changes takes place. They confirm pervious assignment of the ferromagnetic (i.e., <40°C) and high-temperature (>125°C) states as NiAs (hexagonal) structures. The intermediate state, however, is shown to be an orthorhombic distortion of the NiAs structure. Kornelsen[22] has found these distortions by powder x-ray methods of high resolution. Both Kornelsen and Kasper and Wilson find that the distortion disappears at 125°C. We may ascribe this distortion to the Jahn-Teller effect that is common for the Mn^{3+} ion. On this interpretation, the maxima in specific heat and susceptibility are only indications of the onset of this distortion and are not indicative of cooperative magnetic states.

Very recent work by Heeger, Beckman, and Portis[26] has established that the antiferromagnetic disorder in $KMnF_3$ at 88.3°K is a first-order transition. They have used the theory outlined above to understand this transition and derive the strain sensitivity of the exchange energy and an appropriate elastic constant of this material.

GENERALIZED FREE ENERGY[26a]

For completeness, we shall derive a free energy function that is generalized in two respects from the one considered previously. First, we shall include the possibility of either ferro- or antiferromagnetism. Secondly, we include explicitly the entropy of the lattice. Let ϕ be the angle between sublattice magnetizations ($\phi=0$ for ferromagnetism and π for antiferromagnetism). For spin $\frac{1}{2}$,[27] the Gibbs function per initial volume v_0 is

$$G_v=-HM_s\sigma\cos(\phi/2)-1/2NkT_c\sigma^2\cos\phi+\frac{1}{2K}[(v-v_0)/v_0]^2-T(S_{\text{spin}}+S_{\text{lattice}})+P(v-v_0)/v_0, \quad (13)$$

where the first term on the right is the field term; the second, exchange; the third, distortion; the fourth, entropy; and the last, pressure. The entropy for a spin-$\frac{1}{2}$ system we have already given in (2), while for the lattice term we have[28] for a volume v that contains N atoms,

$$S_{\text{lattice}}=3Nk[x/(e^x-1)-\ln(1-e^{-x})], \quad (14)$$

with $x\equiv h\nu/kT$ in the usual notation.

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[23] T. J. Swoboda, W. H. Cloud, T. A. Bither, M. S. Sadler, and H. S. Jarrett, Phys. Rev. Letters 4, 509 (1960).

[24] G. E. Bacon and R. Street, Nature 175, 518 (1955).

[25] R. H. Wilson and J. S. Kasper, American Crystallographic Association 1961 Annual Meeting, Abstract M-8.

[26] A. J. Heeger, O. Beckman, and A. M. Portis, Phys. Rev. 123, 1652 (1961).

[26a] *Note added in proof.* In a current study, R. W. DeBlois of this laboratory is extending the experiments on MnAs to include the effects of high pressures and high magnetic fields on a single crystal [Proceedings of International Conference on High Magnetic Fields, November 1–4, 1961, Massachusetts Institute of Technology (to be published)]. In addition, he is interpreting the data with the free energy function, discussed in this section, that includes lattice entropy. While the interpretation is qualitatively similar to that given above, there are numerical differences. For instance, he tentatively finds η to be 3.2 ± 0.3 and the compressibility, K, to be $(4.6\pm0.4)\times10^{-12}$ $d^{-1}cm^2$. He infers the volume dependence of the Curie temperature, β, to be 18.5 ± 2.0, and the volume thermal expansion coefficient to be $(5.5\pm1)\times10^{-5}$/°C.

[27] This may be generalized to arbitrary spin by the method provided in the Appendix.

[28] See, for instance, J. Lumsden, *Thermodynamics of Alloys* (Institute of Metals, London, 1952).

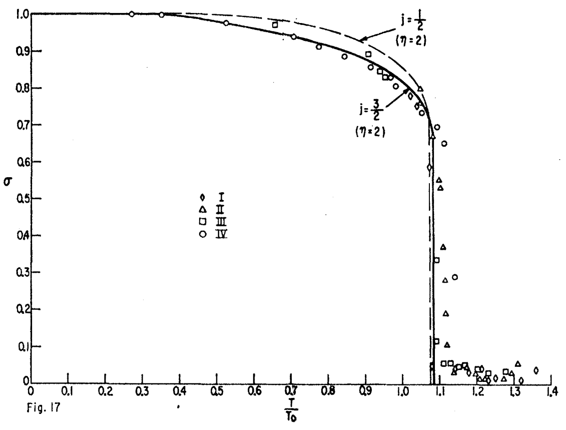

FIG. 17. A comparison of the observed data for MnAs (Fig. 10) with the theory for $j=\frac{3}{2}$; $\eta=2$ is estimated from the volume change at the transition. The $j=\frac{1}{2}$ prediction is indicated in dash.

Our concern shall be with elevated temperatures, i.e., temperatures comparable to the Debye characteristic temperature, θ. This enables us to simplify the entropy expression. Letting x be small and in the Debye approximation we use

$$S_{\text{lattice}}=Nk[4-3\ln\theta/T+(3/40)(\theta/T)^2+\cdots], \quad (15)$$

where $\theta\equiv h\nu_{\max}/k$. From (15) we have

$$\partial S_{\text{lattice}}/\partial v\cong-3Nkd\ln\nu_{\max}/dv=\alpha_1/K, \quad (16)$$

where $\alpha_1\equiv(1/v)(\partial v/\partial T)_P$ and $K\equiv-(1/v)(\partial v/\partial P)_T$. That is, the lattice entropy change with volume in this approximation is measured by the thermal expansion coefficient and the compressibility.[29]

We now minimize (13) with respect to volume and, introducing thermal expansion through (16), obtain

$$\begin{aligned}(G_v)_{\min}=&-HM_s\sigma\cos(\phi/2)-\tfrac{1}{2}NkT_0\sigma^2\\&\times\cos\phi[1-\beta(PK-\alpha_1T)]-P^2K/2-\alpha^2T^2/2K\\&+\alpha_1TP-(1/2K)(\tfrac{1}{2}NkT_0\sigma^2\beta\cos\phi)^2\\&-TNk[4+\ln2-\tfrac{1}{2}\ln(1-\sigma^2)-\sigma\tanh^{-1}\sigma]. \quad (17)\end{aligned}$$

By a minimization of (17) with respect to σ in the absence of any applied magnetic field we obtain the implicit dependence of σ on T for $j=\frac{1}{2}$ to be

$$\frac{T}{T_0\cos\phi}=\frac{\sigma}{\tanh^{-1}\sigma}\left[1-\beta(PK-\alpha_1T)+\frac{\eta\sigma^2}{3}\cos\phi\right]. \quad (18)$$

This result is analogous to our earlier illustrative example but now specifically contains the effect of thermal expansion.

The generalized free energy function given in Eq. (17) allows for transitions between antiferromagnetism, ferromagnetism, and paramagnetism as a function of field, temperature, and pressure. We hesitate to give specific examples of these phase diagrams because we feel that in real materials one must allow for two or more exchange interactions and their distance dependences. For instance, one must distinguish between nearest and next nearest magnetic neighbors in a cubic antiferromagnetic lattice. The generalization, so indicated, will be best made in specific cases for specific experimental situations.

SHORTCOMINGS OF THEORY

It is necessary to emphasize at this point the shortcomings of the theory that we have developed. In the first place, the long range interaction implicit in the molecular field theory is not in accord with experiment and theory that demonstrate the extreme local character of the exchange interactions that give rise to the ordered state. One consequence of this discrepancy is the prediction by the molecular field theory of no order above the Curie temperature of a normal ferromagnet or antiferromagnet, while experiment shows a significant short range order just above the Curie temperature. Another consequence is that the low temperature behavior, the excitation of spin waves, is not predicted by the molecular field model. For our purposes, the first discrepancy is potentially the most important since we purport to calculate the transition between the ordered and disordered state, and if our description of the disordered state is inadequate, then assuredly our calculations will be seriously in error. Fortunately, in the case of the first-order transition the transition is to a paramagnetic state well above its Curie temperature. In this case the short range order in the paramagnetic state will be very small and so approximate our assumption of no order in the paramagnetic state.

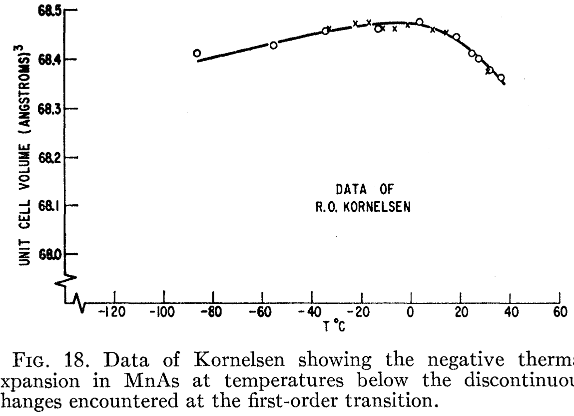

FIG. 18. Data of Kornelsen showing the negative thermal expansion in MnAs at temperatures below the discontinuous changes encountered at the first-order transition.

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[29] We can equally well consider the thermodynamic relation $C_p-C_v=\alpha_1{}^2VT/K$, in which C_p and C_v are the specific heats for the lattice of a volume v at constant pressure and volume, respectively. The entropy of the lattice

$$S_1\equiv\int_0^T(C_p/T)dT=\int_0^T(C_v/T)dT+\int_0^T(\alpha_1{}^2V/K)dT.$$

In the approximation that α_1 is a constant, we obtain the entropy of a volume v to be:

$$S_1=C_v\ln T+\alpha_1(v-v_0)/K.$$

In the same approximation, C_v is a constant; hence

$$\partial S_1/\partial v=\alpha_1/K.$$

As indicated in the previous section, even within the framework of the molecular field treatment, our assumptions are quite specialized. We assume, for instance, that the exchange interaction is a function only of lattice volume, and in addition we assume isotropy of the elastic properties of the material. In general these assumptions are incorrect, and in particular they are not true for MnAs. Indication of this lack of validity is given by the observation that the contraction at the critical temperature is not isotropic.[6] The *c*-axis spacing is barely affected, if at all. Again, as indicated in the previous section, one may extend this theory to more than one interaction by considering sublattices within the magnetic structure of the material in the same way as has been done in the conventional molecular field theory of antiferromagnets and ferromagnets. The net result of these extensions will be a rather formidable bit of algebra. Probably the most useful approach will be to make the minimum generalizing assumptions sufficient to treat the problem at hand.

DISCUSSION OF RELATED PROBLEMS

The first suggestion of a purely magnetic first-order phase transition was made by Rice.[11] It is well-known that one may calculate exactly the spontaneous magnetization of a two-dimensional square net of magnetic moments that interact with the Ising interactions,[30] i.e., an interaction between nearest neighbors that is a product of their z components of spin. It is tacitly assumed that these moments are on a rigid lattice and/or that the interaction does not depend on lattice spacing between nearest neighbors. The result of this calculation is a curve that is similar to our curves for $\eta=1$ in that the magnetization falls off very rapidly at the Curie temperature and the specific heat is infinite at this point. Rice pointed out that if one admits that the exchange interaction is a function of lattice spacing and that the lattice is deformable, then this transition will become one of first order with an associated latent heat and discontinuous volume change at the transformation point. In our picture this happens if the parameter η^* is greater than 1.[31]

Since our calculation is somewhat general, one would expect to see its analogs in other order-disorder transformations if one includes an interaction that depends on lattice spacing. Recently Ross and Ter Haar[32] have attempted to treat the case of alloy order and disorder in the quasi-chemical approximation including a volume-dependent interaction. They show the possibility of a first-order transformation as well as "anomalous" expansion near the critical temperature. There is not, however, a one-to-one correlation between the assumptions useful in treating alloy order-disorder and those we find useful for magnetic order-disorder.

It is well-known that many ferroelectric transitions are first-order transitions.[33] Devonshire[34] has proposed a phenomenological theory for $BaTiO_3$ in which he expands the free energy of this material in powers of the spontaneous polarization. The coefficients are fitted from experiment. As in our theory, the sign of the coefficient of the fourth power of the polarization determines the order of the transition. A necessary complication in Devonshire's theory is the inclusion of the elasticity tensor and direction of the polarization relative to the lattice. In addition, he found it necessary to include temperature-dependent coefficients.

CONCLUSION

This paper has two main conclusions: First, that it is theoretically possible for magnetic disorder to occur as a first-order phase transition if the exchange energy is a sufficiently sensitive function of lattice volume or distortion; secondly, that MnAs shows this behavior in its transition from ferromagnetism to paramagnetism. We believe that subsequent experimental work will reveal more examples of this type of transition. This belief is reinforced by the recent discovery of the antiferromagnetic-paramagnetic first-order transition in $KMnF_3$.

ACKNOWLEDGMENTS

Many of our colleagues have aided us by useful discussions and experimental assistance. Prominent among them are I. S. Jacobs, W. Känzig, J. S. Kasper, J. S. Kouvel, P. E. Lawrence, and R. H. Wilson. In addition, we have benefitted from interaction with A. J. Heeger, C. Kittel, and A. M. Portis of the University of California and R. O. Kornelsen of the Univesity of Ottawa.

APPENDIX

To generalize our results we must first derive the entropy expansion for arbitrary spin that corresponds to the spin entropy in Eq. (2) for spin $\frac{1}{2}$. This is easily done by expansion of the Brillouin function for angular momentum j

$$\sigma_j(\chi)=B_j(\chi)\equiv\frac{2j+1}{2j}\coth\left(\frac{2j+1}{2j}\chi\right)-\frac{1}{2j}\coth\left(\frac{1}{2j}\chi\right),$$

in powers of χ (where $\chi\equiv g\mu_b jH/kT$) to obtain

$$\sigma_j=\frac{(2j+1)^2-1}{(2j)^2}\frac{\chi}{3}-\frac{(2j+1)^4-1}{(2j)^4}\frac{\chi^3}{45}+\frac{(2j+1)^6-1}{(2j)^6}\frac{2\chi^5}{945}-\cdots. \quad \text{(A1)}$$

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[30] C. N. Yang, Phys. Rev. **85**, 809 (1952).

[31] $\eta^*\equiv\eta\cos\phi/[1-(PK-\alpha_1T)\beta]>1$ is the criterion that determines a first-order transition within the most general framework of our treatment.

[32] A. W. Ross and D. Ter Haar, Physica **25**, 343 (1959).

[33] See, e.g., W. Känzig in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 4, p. 1.

[34] A. F. Devonshire, Phil. Mag. [7] **40**, 1040 (1949); [7] **42**, 1065 (1951).

If we write the free energy for an assembly of *noninteracting* spins $G_j/NkT=-\chi\sigma_j-S(\sigma_j)$, setting $\partial G/\partial\sigma=0$ yields

$$\chi_j=-\partial S(\sigma_j)/\partial\sigma_j. \tag{A2}$$

If we express $S(\sigma_j)$ as a power series, we must exclude odd powers of σ_j since complete inversion can have no effect on the entropy, and thus

$$S(\sigma_j)=S_j(0)+a_j\sigma_j^2+b_j\sigma_j^4+c_j\sigma_j^6+\cdots.$$

We have from Eq. (A2) that

$$\chi_j=-2a_j\sigma_j-4b_j\sigma_j^3-6c_j\sigma_j^5-\cdots. \tag{A3}$$

If we substitute Eq. (A3) into Eq. (A1) and equate coefficients of powers of σ_j, we obtain the coefficients for the power series expansion of the entropy to be

$$a_j=-\frac{3}{2}\frac{j}{(j+1)}$$

$$b_j=-\frac{9}{20}\frac{[(2j+1)^4-1]}{[2(j+1)]^4}. \tag{A4}$$

We stop at the second term since this is the one that determines the nature of the transition, since as shown earlier the coefficient of σ^4 in the entropy expansion is of primary importance.

We may now write the free energy per unit volume including exchange interaction for arbitrary spin as

$$G=-\frac{3}{2}\left(\frac{j}{j+1}\right)NkT_c\sigma^2-HM_s\sigma+\frac{1}{2K}\left(\frac{v-v_0}{v_0}\right)^2 -NkT\left[\ln(2j+1)-\frac{3}{2}\left(\frac{j}{j+1}\right)\sigma^2 -\frac{9}{20}\frac{[(2j+1)^4-1]}{[2(j+1)]^4}\sigma^4-O(\sigma^6)+\cdots\right] +P\left(\frac{v-v_0}{v_0}\right). \tag{A5}$$

Inserting $T_c=T_0[1+\beta(v-v_0)/v_0]$ into (A5) and by minimizing that expression with respect to volume we obtain the equilibrium volume for spin j to be

$$\left(\frac{v-v_0}{v_0}\right)=\frac{3}{2}\frac{j^2}{j(j+1)}NkKT_0\beta\sigma^2-PK, \tag{A6}$$

which in turn leads to

$$\frac{G_{\min}}{NkT_0}=\frac{-P^2K}{2NkT_0}-\frac{g\mu_b jH}{kT_0}\sigma-\frac{T}{T_0}\ln(2j+1) +\frac{3}{2}\left(\frac{j}{j+1}\right)\left[\frac{T}{T_0}-1+PK\beta\right]\sigma^2 +\frac{9}{20}\frac{[(2j+1)^4-1]}{[2(j+1)]^4}\left[\frac{T}{T_0}-\eta_j\right]\sigma^4+O(\sigma^6)+\cdots, \tag{A7}$$

where

$$\eta_j\equiv\frac{5}{2}\frac{[4j(j+1)]^2}{[(2j+1)^4-1]}NkKT_0\beta^2.$$

We may also obtain the general result for the implicit dependence of the magnetization on the temperature by minimizing (A5) first with respect to volume then again with respect to σ. The result (for H, P both 0) is

$$\frac{T}{T_0}=\left[\frac{3j}{(j+1)}+\frac{9}{5}\frac{[(2j+1)^4-1]}{[2(j+1)]^4}\eta_j\sigma_j^2\right]\sigma_j\Big/ \left[-\frac{\partial}{\partial\sigma}(S_j/Nk)\right]. \tag{A8}$$