Coupled order parameters, lattice disorder, and magnetic phase transitions

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(Received 28 April 1975)

A mean-field theory is developed which describes the effects of lattice disorder on magnetic phase transitions. Depending on the parameter values, three types of renormalization effects on T_C can occur, i.e., weak, strong, or catastrophic; the last implies a first-order phase transition in both magnetic and lattice order parameter. Phase diagrams are obtained which show both the existence of critical triple points and the effects of phonon entropy in determining T_C. It is also shown that even in the weak-coupling limit, the lattice disordering process can be driven by magnetic entropy alone. The model is applied to MnBi, which undergoes a first-order magnetic phase transition well below its mean-field-value Curie temperature.

I. INTRODUCTION

Although the theory of phase transitions in single-order-parameter systems has been studied intensively for several decades, it is only recently that the more complicated case of interacting order parameters has been considered. Many-order-parameter systems are particularly interesting because even small interactions can lead to a strong renormalization of the critical temperature and in some cases change the character of the phase transition from second to first order or vice versa. Examples of such couplings between competing processes are found in mixed magnetic crystals with two types of magnetic ordering,[1] superfluid and crystalline ordering in solid ^{4}He,[2] magnetic-nonmagnetic metal insulator transitions,[3] and crystals which combine ferroelectric and ferromagnetic properties.[4]

In this paper we present a mean-field theory which describes the effects of lattice disorder on magnetic phase transitions.[5] As exemplified by the case of ferromagnetic MnBi, this type of interaction can be strong enough to change not only a second-order magnetic phase transition into a first-order one, but the character of the usual order-disorder process that takes place in nonmagnetic crystals as well.[6] The question we pose is the following: Given a crystalline magnetic system (antiferro, ferri, or ferromagnetic) which undergoes a second-order phase transition in the magnetization order parameter, what is the effect of the lattice structure which itself can disorder? Furthermore, will the effects of order-parameter coupling be readily observable?

In order to answer these questions a general, but well-defined model is derived in Sec. II. The thermodynamics of the model are derived using a mean-field approach in Sec. III and the results and phase diagrams obtained are discussed in Sec. IV. Finally, in Sec. V, MnBi is analyzed in some detail in the context of our theory.

Throughout this paper a mean-field approach is used, which neglects fluctuation effects. This is not a serious flaw, since in most cases the effects we are studying lead to first-order phase transitions well below T_C, so that fluctuations play a negligible role. However, in some cases our treatment may only be approximate. For example, the critical region for the magnetic order parameter for a ferromagnet is small, but the critical region in the lattice order parameter may be significant. In this case neglecting fluctuations might lead to errors in the description of weakly-first-order phase transitions in either order parameter.[7] Nevertheless, the qualitative behavior predicted by our theory will remain basically unchanged, and so we feel that a mean-field-theory approach throughout this paper is appropriate for our purposes.

II. MODEL

In order to analyze specifically the effects of lattice disorder on the properties of a magnetic system and conversely, we develop a simple but general model. We take the ground state of our thermodynamic system to be a perfectly ordered magnetic crystal with no defects. Furthermore, the ions are taken to be in a well defined spin state $|J\rangle$ coupled by a ferromagnetic exchange interaction. As the temperature increases, the system disorders either by promoting some of its ions into interstitial positions leaving a vacancy with no spin, or by disordering the spins at regular lattice sites. We assume that an ion in an interstitial site retains its spin multiplicity and that it is magnetically uncoupled to either the lattice or other interstitials. Although this assumption is restrictive, it does not affect the phase transition behavior and can be removed by introducing extra magnetic couplings between ions in interstitial sites or between ions in lattice sites and interstitial sites.

In the mean-field approximation the exchange Hamiltonian is written

$$H_{ex} = -2\sum_i \sum_{j\neq i} A_{ij} S_{iz} \langle S_{jz} \rangle , \tag{2.1}$$

where the summations are over all lattice sites, A_{ij} is the exchange interaction (J_{ij} is positive), and

S_{iz} is the z component of the spin operator at lattice site i. Since $\langle S_{jz}\rangle$ is independent of the lattice label Eq. (2.1) becomes

$$\bar{H}_{ex} = -2\sum_i \langle S_z\rangle \left(\sum_{j\neq i} A_{ij}\right) S_{iz} . \tag{2.2}$$

Furthermore, if the exchange coupling is nonzero for nearest neighbors only, then

$$\sum_{j\neq i} A_{ij} = A^0 z q J^2 , \tag{2.3}$$

where A^0 is the exchange constant, q is the lattice-site occupation probability, i.e., the probability that sites i and j are occupied simultaneously, z is the number of magnetic nearest neighbors for a given ion, and J is its spin eigenvalue. Next we define a lattice order parameter η in terms of the fractional number of occupied interstitials n_i as

$$\eta \equiv 1 - Qn_i , \tag{2.4}$$

where Q is the fractional number of interstitial sites which are occupied when $\eta = 0$. In terms of η, Eq. (2.3) becomes

$$\sum_{i\neq j} A_{ij} = A^0 z \eta^2 J^2 . \tag{2.5}$$

The total magnetization is given by

$$M = n_s 2\mu_B \langle S_z\rangle , \tag{2.6}$$

where n_s is the number of exchange-coupled sites per unit volume and μ_B is the Bohr magneton. Since an ion in an interstitial site is magnetically decoupled from all other ions, n_s is given by

$$n_s = N\eta , \tag{2.7}$$

where N is the total number of lattice ions plus interstitial sites. Upon substituting (2.5) and (2.7) in (2.2) the exchange Hamiltonian becomes

$$\bar{H}_{ex} = -A' M^2 , \tag{2.8}$$

where

$$A' = (-zA^0 J^2/2\mu_B^2 N)\eta . \tag{2.9}$$

An examination of Eqs. (2.8) and (2.9) indicates that lattice disorder produces a renormalization of the exchange energy. As shown below, the strength of the renormalization effects will depend on a subtle interplay of spin and lattice entropy. This interaction will in turn determine the temperature dependence of η and hence A'.

In order to completely specify the model, we must determine the lattice-disorder contribution to the internal energy. If U_i is the activation energy for promoting an ion into an interstitial site and no interaction is assumed between the occupied interstitial and the remaining vacancy, the total energy would be proportional to $U_i n_i$ (neglecting the kinetic energy of the ion). If, however, ion-ion or ion-lattice interactions are present, the total activation energy becomes excitation-number dependent and can be approximated by

$$\bar{H}_{lattice} = U_i n_i - U n_i^2 , \tag{2.10}$$

where U is a parameter which depends on the type of interaction one assumes. There are several mechanisms that can give rise to the second term in Eq. (2.10). The additional strain field induced by an ion in an interstitial site provides an interaction energy proportional to n_i^2; and so does the screened attractive interaction between an ion in an interstitial site and the vacancy it leaves behind.[8] Since the strain field of the populated interstitials is very small in very open lattice systems, we can safely assume that the screened interaction will produce the Un_i^2 term in crystals with large numbers of interstitial sites, such as MnBi.

The total internal energy is then

$$E = \bar{H} = zJ^2 A^0 \eta M^2 + U_i n_i - U n_i^2 , \tag{2.11}$$

which at $T = 0$ determines the equilibrium configuration of the system. For a perfectly ordered ($\eta = 1$) ferromagnetic crystal ($M = 1$), we must have

$$zJ^2 A^0 > U/Q - U_i/Q^2 , \tag{2.12}$$

whereas an ordered antiferromagnet requires

$$zJ^2 A^0 < U_i/Q^2 - U/Q . \tag{2.13}$$

III. THERMODYNAMICS

An expression for the entropy of the system is needed in order to write a trial Gibbs-free-energy density. In terms of E given by (2.11), the configurational entropy is

$$S = k_B \left[\ln\left(\sum_{\{n\}} e^{-\beta E(\{n\})} + \beta E\right)\right] , \tag{3.1}$$

where $\beta \equiv (k_B T)^{-1}$ and $E(\{n\})$ denotes all possible states of the system. An additional term is necessary to describe the change in force constants (and thereby vibrational frequency) that an ion undergoes as it is promoted into an interstitial site. For harmonic forces, the contribution to the partition function is given by

$$Z = \int\int_{-\infty}^{\infty} e^{-m(\dot{u}^2+\omega^2 u)/2k_B T}\, du\, d\dot{u} , \tag{3.2}$$

where m is the ionic mass and ω is its vibrational frequency in a regular lattice site. If the vibrational frequency in the interstitial site is ω_i, the total phonon contribution to the free energy is

$$G = -3n_i k_B T \ln\Gamma , \tag{3.3}$$

where $\Gamma \equiv \omega_i/\omega$ and the factor 3 arises from the allowed three vibrational modes. Finally, we obtain

$$G=(U_i-3k_BT\ln\Gamma)n_i-Un_i^2+A^0ZJ\eta M^2+k_BT[2n_i\ln n_i-n_i[\ln(2J+1)^Q]$$
$$+2(1-n_i)\ln(1-n_i)-(1-Qn_i)(\ln\{\sinh[(2J+1)BM/2J]\}-\ln[\sinh(BM/2J)])], \tag{3.4}$$

in which the exchange parameter B is defined by

$$B\equiv 2A^0zJ^2\eta/k_BT\ . \tag{3.5}$$

The equilibrium behavior of both the magnetic and lattice order parameters is determined by requiring the system to be in a state in which the Gibbs free energy is an absolute minimum at any given temperature. From $\partial G/\partial M=0$ we obtain

$$M=[(2J+1)/2J]\coth[(2J+1)BM/2J]-(1/2J)\coth(BM/2J), \tag{3.6}$$

which is the usual Brillouin equation modified by the temperature dependence of the exchange parameter as expressed directly in (3.5) and indirectly through η. The second minimization condition (i.e., $\partial G/\partial n_i=0$) yields

$$U_i+3k_BT\ln(\Gamma)-2Un_i=-A^0zJ^2QM^2+k_BT[2\ln(1-n_i)-2\ln(n_i)+\ln(2J+1)^Q$$
$$-Q(\ln\{\sinh[(2J+1)BM/2J]\}-\ln[\sinh(BM/2J)])]\ . \tag{3.7}$$

Equations (3.6) and (3.7), together with the requirement of providing an absolute free-energy minimum for G, determine the equilibrium configurations of the system. Before presenting and discussing the phase diagrams which result from solving (3.6) and (3.7), it is illuminating to consider some limiting cases. (i) As $T\to 0$, $\coth(BM/2J)\to 1$ and $M=1$ as expected. Moreover, the free energy becomes $G=-A^0zJ^2$. (ii) As $M\to 0$, Eq. (3.6) becomes

$$2MJ-[(2J+1)^2-1]BM/6J=0\ . \tag{3.8}$$

This equation, through the temperature dependence of B [Eq. (3.5)], gives the Curie temperature T_C,

$$T_C=2J(J+1)A^0z\eta/3k_B=T_C^0\eta\ . \tag{3.9}$$

As can be seen, Eq. (3.9) yields the usual mean-field value in the limit $\eta\to 1$. The lack of perfect lattice order causes T_C to be renormalized down by a factor $\eta=1-Qn_i$, with n_i determined by (3.7) at T_C. Furthermore, as $M\to 0$ the magnetic contribution to the free-energy density becomes

$$G=k_BT\ln(2J+1) \tag{3.10}$$

per ion. This result follows from small argument expansions of the hyperbolic functions. Thus regardless of the number of occupied interstitial sites we obtain the usual spin-multiplicity contribution to the entropy.

The entropy contribution to the free energy also provides insight into the role of coupled order parameters in determining not only the *degree*, but also the *character* of the phase transition. As noted above, the system entropy can increase in two ways with increasing temperature. First, by spin disorder at the lattice sites and second by promoting ions into paramagnetic interstitial sites. If both processes were totally uncoupled, the interstitial site population would be regulated solely by configurational and phonon entropy, whereas the magnetic disorder would be essentially determined by the value of the exchange constant and the spin multiplicity of the ions. However, because both degrees of freedom affect the transition, the disordering process can exhibit a rich variety of possible behaviors. In particular, the possibility exists that lattice disorder might be driven by magnetic entropy if the gain in spin entropy per ion promoted into an interstitial site becomes larger than the increase in phonon entropy resulting from the same process. If we assume $M\approx 1$, the condition for this magnetically driven lattice disorder process can be written

$$J>\tfrac{1}{2}(\Gamma^{-3/2}-1). \tag{3.11}$$

Thus even with no change in phonon frequency ($\Gamma=1$) an ion with spin as small as $\frac{1}{2}$ can drive a lattice order-disorder transition.

IV. NUMERICAL RESULTS

The large variety of phenomena described by the model is illustrated by solving Eqs. (3.6) and (3.7) for different values of the parameters. The technique used for solving these equations is quite straightforward. We set $n_i=0$ in η which appears in B of (3.6) and solve (3.6) numerically for M. This value of M is then used in (3.7) to determine n_i, which in turn is substituted in (3.6). Usually, one iteration is sufficient, but in rare cases a few have been necessary. The numerical procedure employed to solve (3.6) and (3.7) is the bisection technique, which works well in the vicinity of singularities of the type that occur in our equations. It should be noted that the free-energy minimum may not occur at the solutions of Eqs. (3.6) and (3.7). Rather, it may occur on the boundary, which is a rectangle in the (n_i, M) plane bounded by $n_i=0, 1/Q$ and $M=0, 1$. Thus we also seek minima on the

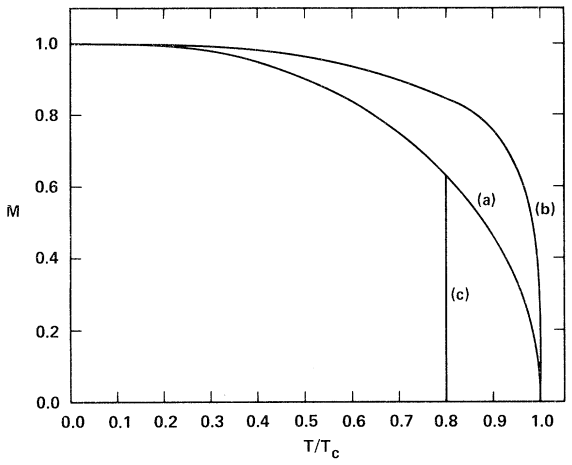

FIG. 1. Magnetization order parameter as a function of reduced temperature. Parameter values are $\Gamma = 1$, $Q = 2$, $J = 2$, and $z = 2$. Curve (a) corresponds to $A = 0.0077$ eV with $U_i/U = 1$, curve (b) to $A = 0.035$ eV with $U_i/U = 1$, and curve (c) to $A = 0.0077$ eV with $U_i/U = 0.6$.

boundary and compare values of the free energy to determine the absolute minimum.

The solutions we have obtained for the magnetic order parameter are of three distinct types, as illustrated in Fig. 1, where we plot the magnetization order parameter as a function of the reduced temperature for different sets of parameters.

(*a*) *Weak renormalization.* This case is characterized by a mean-field-type behavior for the magnetization with a perfectly ordered crystal. A second-order phase transition occurs at T_C [as given by (3.9) with $n \approx 1$] and with mean-field values for the critical exponents. In this situation, as found in most crystalline ferromagnets, the defect concentration is on the order of 10^{-7}–10^{-6}. Above T_C the material is an ordered paramagnet which undergoes a first-order phase transition in the lattice order parameter at some higher temperature than T_C.

(*b*) *Strong renormalization.* In this case there is a strong temperature variation of the lattice order parameter near T_C. The functional dependence of $M(T)$ changes drastically from a Brillouin-type solution with T_C strongly renormalized. This type of behavior, illustrated in Fig. 1(b), is the one in which fluctuation effects can significantly alter mean-field-theory predictions. Specifically, when the lattice order parameter undergoes a second-order phase transition near T_C, the critical exponents for both order parameters might even differ from those calculated by group renormalization techniques in the absence of any order parameter coupling.

(*c*) *Catastrophic renormalization.* This case is characterized by a lattice order parameter which undergoes a first-order phase transition at $T_0 < T_C$. Then the magnetization also undergoes a first-order phase transition to zero at T_0 as shown in Fig. 1(c). Above T_0 the system is totally disordered; it becomes a paramagnetic "liquid." There is a latent heat associated with this transition given by $L = T_0 \Delta S$, where ΔS is the entropy difference between the $M \approx 1, \eta \approx 1$ phase and the $M = 0, \eta = 0$ phase, i.e.,

$$L = T_0[S(1,1) - S(0,0)] , \tag{4.1}$$

where S is given by (3.4).

The total phase diagram in which the normalized temperature is plotted versus U/U_i for different parameter values is shown in Fig. 2. At a given temperature, depending on Γ and U/U_i, the system exists in one of three phases. One phase is the ordered ferromagnet in which both the spin and magnetization are ordered. A second phase is the ordered paramagnet in which the lattice is ordered, but the spin disordered. The third phase is the disordered paramagnetic in which both are disordered. The dashed lines delineate the second-order phase transition and the solid curves indicate the first-order transitions. As can be seen, Γ shifts the transition temperature but does not change the main features of the phase diagram. The solid curves terminate at critical points at both ends, but only

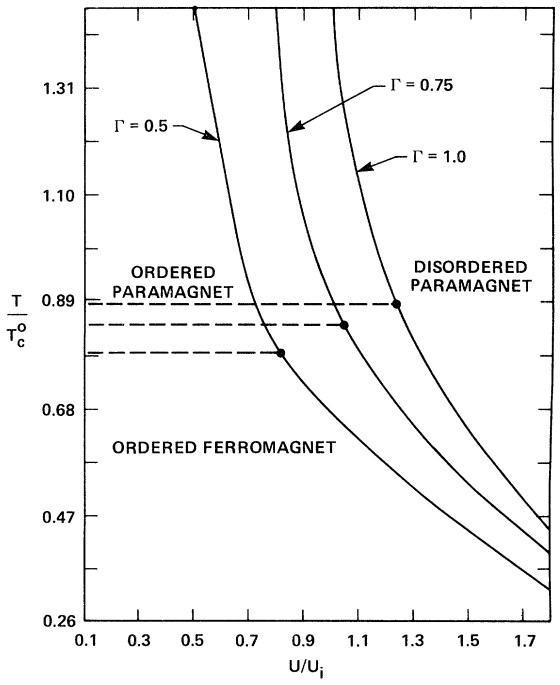

FIG. 2. Phase diagram of our model as a function of U/U_i for different values of the parameters. Solid lines denote first-order phase transitions; dashed lines denote second-order phase transitions. Small circles denote critical points; large circles correspond to critical triple points.

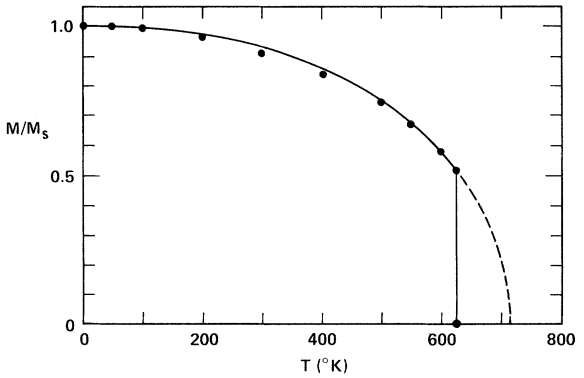

FIG. 3. Calculated magnetization for MnBi in the low-temperature phase. The solid line shows the calculated values; circles show the measured magnetization. The dashed line corresponds to the extension of Eq. (3.6) beyond T_0, the first-order phase transition. The defect concentration right below T_0 is of the order of 10^{-4}.

one critical point falls within the boundary of the figure. The intersections of the solid and dashed curves locate the *critical triple points* at the renormalized T_C.

V. MANGANESE BISMUTH

To illustrate some of the predictions of our model we consider manganese bismuth (MnBi), which is a room-temperature ferromagnet. Furthermore, MnBi has a large optical Faraday rotation, large anisotropy, and small domain size. These properties make it particularly useful for high-density magneto-optic holography. This stoichiometric compound has a low-temperature phase which has an open NiAs lattice structure. Its saturation magnatization at $T \to 0$ is approximately four Bohr magnetons which indicates that the Mn ions in the crystalline sites are in a Mn^{3+} configuration with $J = 2$.

The critical temperature T_C as given by Eq. (3.9) is 717 °K, well above the phase decomposition temperature of 625 °K. Thus one would expect that a catastrophic renormalization of the Curie temperature occurs. That this is indeed the case is illustrated by the first-order magnetic phase transition at 625 °K, which accompanies the lattice disordering process.

In terms of our model both phase transitions can be viewed as being caused by a delocalization of the Mn^{3+} ions which can occupy either a regular lattice site or an interstitial site. The latent heat accompanying this phase transition is 2.5 kcal/mole as calculated from (4.1) with $J = 2$. From (3.11) one concludes that the transitions are spin disorder driven for the following reason. Even if one assumes that the lattice constant changes by 25% upon promotion of an ion from a lattice to an interstitial site the right-hand side of (3.11) becomes 0.9, which is smaller than $J = 2$.

In Fig. 3, we plot the magnetization order parameter using known values appropriate to MnBi, viz., $J = 2$, $U_i = 1.0$ eV, $z = 2.0$, $Q = 2.0$ and $A^0 = 0.0077$ eV. Although U is not known *a priori*, the value $U = 1.7$ eV which yields $T_0 = 625$ °K, for $\Gamma = 1.0$, is quite reasonable. It should be noted that changing Γ and therefore U to retain $T_0 = 625$ °K does not significantly affect the magnetization curve below T_0. The solid curves in Fig. 3 were calculated using the free-energy minimization condition and the circles correspond to the measured magnetization in single crystal samples.[9] The agreement is quite good. This indicates that below 625 °K the magnetization closely follows mean-field-theory predictions for $J = 2$. The dashed curve is the extrapolation of the Brillouin-function solution in the case of uncoupled order parameters.

It has been recently reported by Chen[10] that the first-order magnetic phase transition is accompanied by a phase decomposition in which Bi is released. It is possible that the departure from stoichiometry is triggered by the interstitial occupation by Mn ions, which leave nucleation sites for Bi-rich areas on the surface.

VI. CONCLUSIONS

As we have shown, the coupling between the magnetization in a crystal and the lattice order parameter can lead to strong renormalization effects which influence not only the magnetic properties of the system but its lattice stability as well. In most cases magnetic phase transitions take place at temperatures much lower than that of the melting point of the crystal and therefore the effects of lattice disorder on T_C are negligible. However, there are crystals such as MnBi which undergo lattice order-disorder transitions at temperatures below T_C, and as we have shown, this leads to a first-order phase transition in the magnetization which in many instances accounts for all the observed latent heat. Equally important, the usual lattice order-disorder process can be driven by spin entropy if the entropy gain per spin [which is proportional to $\ln(2J+1)$] is larger than the phonon entropy gain, as we have shown in Sec. III. Since our treatment uses mean-field theory it only allows for qualitative predictions in the case where both lattice order parameter and magnetization tend to undergo a second-order phase transition simultaneously. Since the critical region for the lattice order parameter is much larger than that for the magnetization,[11] one expects the renormalization effects on $M(T)$ to be much stronger than those discussed above. Nevertheless, the qualitative features in this case will remain the same when fluctuation effects are considered.

Although we have only considered ferromagnetic coupling of the ions, the theory we have presented here is quite amenable to modifications which will make it very general. Besides describing the critical properties of systems with coupled order parameters, it can be used accurately for temperatures far below T_c and T_0 (where the usual Landau expansion of the free energy is not valid) and therefore yield into the nature of defect formation in complex situations.

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