Disorder-Induced Magnetic Phase Transitions

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A two-order-parameter model is presented for the effect of lattice disorder on the magnetic properties of a crystal. It takes into account the presence of defects in an open lattice and, among other things, predicts a first-order transition of the magnetization order parameter upon melting. It applies well to MnBi and is general enough to include different types of defects and interactions.

A theory of phase transitions that includes interacting order parameters gives rise to a range of interesting behaviors and unusual properties. In particular, if the order parameters satisfy different symmetry requirements, one expects that the order of the transition they undergo in the presence of coupling will be different from the one in the absence of any interaction.[1] Of special interest is the case when the lattice order parameter is coupled to an extensive variable such as magnetization or macroscopic polarization, for it may lead to a completely broken symmetry which forces a second-order phase transition to become first order. Such is the case, for example, if melting takes place in a ferromagnetic crystal below its Curie temperature or if a ferroelectric material undergoes a first-order transformation below its critical temperature.

We wish to present here a model for the effects of lattice disorder on the properties of a magnetic crystal. It accounts for the presence of lattice defects in an open lattice and among its many features predicts a first-order transition of the magnetization upon melting. It applies well to the stoichiometric compound MnBi and can be easily extended to include different types of defects and interactions.

In this model we take the ground state of the system as a perfectly ordered crystal with no defects present and with its atoms in a well-defined spin state $|J\rangle$, coupled by a ferromagnetic exchange interaction. As the temperature increases, it can disorder either by promoting some of its atoms into interstitial positions leaving a vacancy with no spin or by disordering the spins at the lattice sites. We shall assume that on moving into interstitial sites the atoms retain their spin multiplicity and are in a paramagnetic state[2]; and that in the spirit of a mean field theory the presence of a vacancy reduces the exchange interaction between the remaining atoms as $A\eta$, where A is the exchange energy and η the lattice order parameter which we define as

$$\eta = 1 - Qn_i \tag{1}$$

with n_i the fractional number of atoms in interstitial positions and Q the inverse of the number of interstitial sites that are occupied when the probabilities for an atom occupying a lattice site or an interstitial are the same.[3] With this definition it is clear that $0 \leq n_i Q \leq 1$.[4] If the activation energy for interstitial formation is taken to be excitation-number dependent, the lattice order parameter can undergo a first-order transition and the crystal will "melt" at a temperature T_0.[5] Whether or not this melting temperature T_0 is below or above the Curie temperature will determine the order of the transition for the magnetization order parameter.

In the mean field approximation, the internal energy density of the system can be written as

$$\mathcal{U} = U_i n_i - U n_i^2 - A\eta M^2, \tag{2}$$

where U_i is the activation energy for promoting an atom into an interstitial position, U is the attractive interaction between the interstitial and the vacancy, and M ($0 \leq M \leq 1$) is the magnetization order parameter. Equation (2) gives a perfectly ordered ferromagnet provided that $A > UQ^{-2} - U_i Q^{-1}$.

The lattice-disorder contribution to the entropy density arises from the configuration density of states associated with the number of ways n_i interstitials can be put into N sites, plus the paramagnetic and vacancy contributions. One then obtains

$$S(n_i) = -K_B[2n_i \ln(n_i) + 2(1-n_i)\ln(1-n_i) - (1-\eta)\ln(2J+1)]. \tag{3}$$

Equation (3) does not contain the entropy contribution from the localized phonon mode associated with

the interstitial. This term, which is equal to

$$S_{ph} = 3K_B n_i \ln\Gamma \tag{4}$$

with $\Gamma \equiv \omega'/\omega$ the ratio of the localized phonon frequency to the lattice phonon, acts as a temperature-dependent renormalization factor for the interstitial activation energy.

The magnetization entropy, which is proportional to the integral of the inverse Brillouin function of the spin J, can be cast in a convenient form by taking the one corresponding to $J=\frac{1}{2}$ but renormalized in such a way as to give a total number $2J+1$ of states. One then obtains

$$S(M) = -K_B\eta[\ln(2J+1)/\ln 2][\tfrac{1}{2}(1+M)\ln(1+M) + \tfrac{1}{2}(1-M)\ln(1-M) - \ln 2]. \tag{5}$$

Using Eqs. (1) and (3)–(5), we can write for the trial free energy density

$$F = U_i' n_i - U n_i^2 - A(1-Qn_i)M^2 + K_B T\{2n_i \ln n_i + 2(1-n_i)\ln(1-n_i) + Qn_i \ln(2J+1) + [(1-Qn_i)/\ln 2] \times \ln(2J+1)[\tfrac{1}{2}(1+M)\ln(1+M) + \tfrac{1}{2}(1-M)\ln(1-M) - \ln 2]\}, \tag{6}$$

where $U_i' \equiv U_i + 3K_B T \ln\Gamma$ is the temperature-dependent activation energy. By minimizing Eq. (6) with respect to n_i and M we find

$$U_i = 2Un_i + AQM(M-2) + K_B T\{\ln[n_i 2/(1-n_i)] - \ln[2J+1)^Q]\ln(1+M)/\ln 2\}, \tag{7}$$

$$M = \frac{K_B T}{4A}\,\frac{\ln(2J+1)}{\ln 2}\,\ln\left(\frac{1+M}{1-M}\right). \tag{8}$$

The thermodynamics of this model is then determined by Eq. (6), with n_i and M as given by Eqs. (7) and (8); and as usual the equilibrium configurations at a given temperature will be given by the absolute minima of the free energy. The important point to be stressed is that, depending on the values of U_i, U, and A, the system can display either a second-order phase transition in the magnetization at $T_c \simeq J(J+1)A/3K_B$ (with a negligible amount of interstitials present), or a first-order transition in both M and η at the melting point T_0. Although a detailed study of the phase diagrams will be published elsewhere,[6] we have chosen to illustrate its main bahavior for a given set of parameters in Fig. 1. We plot the free energy as a function of the magnetization and increasing temperature for $U = 1.7U_i$ and $A = 0.07U_i$ with $Q=2$ and $\Gamma = 1$. At low temperatures ($T < T_0$) two minima appear, the lowest one at $M \simeq 1$, $n_i = 0$. At $T = T_0$ the two minima have the same values, and a discontinuity in both M and η appears which signals the onset of a first-order phase transition into a paramagnetic liquid. For values of $T > T_0$ the system remains completely disordered, with $\eta = 0$ and $M = 0$. Associated with this first-order transition there is a latent heat $L = T \times \Delta S$, where ΔS denote the difference in entropies in the two phases [i.e., $S(M \simeq 1;\ n_i = 0) - S(M = 0;\ m_0 = Q^{-1})$].

Figure 2 shows the number of interstitials as a function of temperature for the parameter values used in Fig. 2. As can be seen, at low temperatures the number of interstitials increases in a modified exponential form, and at T_0 there is a discontinuity into a disordered state with half the atoms in interstitial positions.

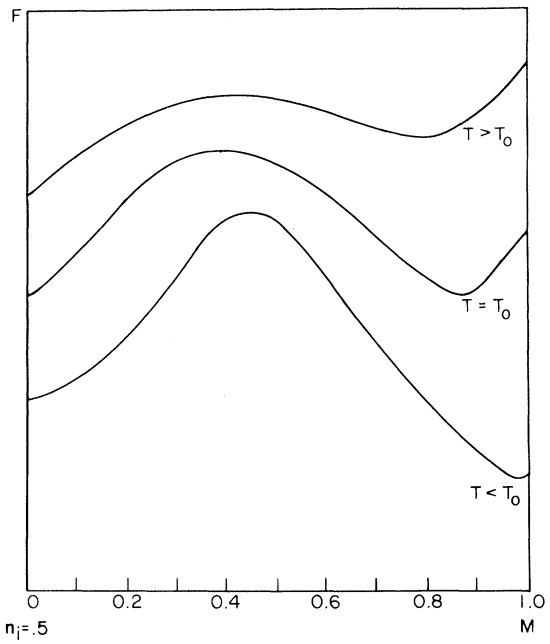

FIG. 1. The free energy, in arbitrary units, as a function of M and T, with M and η as given by Eqs. (7) and (8). We have taken $U_i = 1$ eV, $U = 1.7U_i$, $A = 0.07U_i$, $\Gamma = 1$, and $J = 2$. The value at the origin was computed for $M = 0$, $n_i = 0.5$. For these values of the parameters, $T_0 = 634$°K.

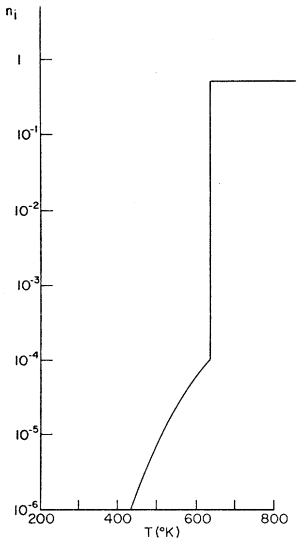

FIG. 2. The number of interstitials as a function of temperature for $A = 0.07$ eV, $U_i = 1$ eV, and $U = 1.7$ eV.

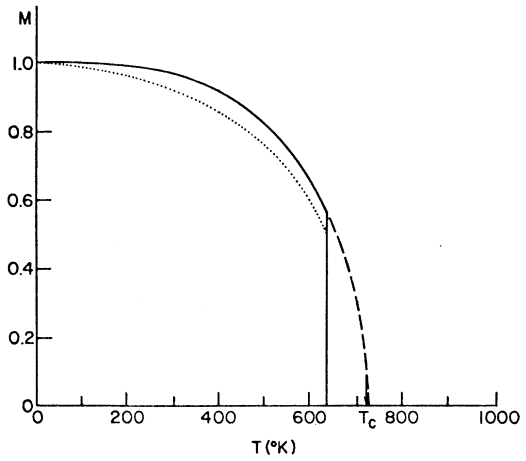

FIG. 3. The magnetization order parameter as a function of temperature for $U_i = 1$ eV, $U = 1.7U_i$, $A = 0.07U_i$, and $\Gamma = 2$. Solid line, calculated values; dashed line, extension of the modified Brillouin function in the absence of interactions; dotted line, experimental values for MnBi.

A striking example of this type of behavior is found in the stoichiometric compound MnBi, a very open lattice system with Mn^{3+} ions coupled ferromagnetically.[7] Unlike most ferromagnetic crystals, its melting point[8] lies below the Curie temperature, and as the temperature is increased the magnetization shows a first-order transition into a paramagnetic disordered state with a large fraction of the Mn atoms (~15%) occupying interstitial sites.[9]

In calculating the MnBi magnetization curve, we have chosen $A = 0.07$ eV and $U_i = 1$ eV with $U = 1.7$ eV. Since Γ is not known even in simple systems and only provides a "fine tuning" of the transition, we set it equal to zero. As shown in Fig. 3, where the solid line shows the calculated magnetization, the agreement is quite good. It should be mentioned that the difference between the calculated magnetization and the measured one for $T < T_0$ is due to the approximate character of the magnetization entropy for $J = 2$, which gives a modified Brillouin function.

For the parameter values chosen to fit MnBi, the latent-heat prediction of this model turns out to be $L = 2.2$ kcal/mole if total disorder ($\eta = 0$) is assumed. However, if the transition to a disordered state were to stop at $\eta = 0.7$ (15% interstitials present), then the latent heat would be $L = 205$ cal mole^{-1}. At the present time the experimental data are not conclusive enough as to the actual number of interstitial Mn ions present, although preliminary measurements give latent-heat values of the order of 1–3 kcal/mole.[10] It should be added that the fact that the first-order transition in MnBi does not occur at exactly the same temperature as the peritectic melting can be attributed to the heavy-mass Bi atoms which provide an extra stability to the lattice.

The effect of pressure on the thermodynamics of the model can be accounted for in a straightforward way if instead of the free energy we take the generalized thermodynamic potential

$$G = F + P\,\Delta V \tag{9}$$

with $\Delta V = n_i V_i$ the additional volume introduced by the interstitial. Equation (9) merely says that the effect of pressure renormalizes the activation energy, thus shifting the transition temperature.

In spite of its simplicity, this model accounts for a large variety of behaviors and provides a physical picture for the understanding of the effect of disorder on the magnetization properties of ferromagnets. It also gives a clue as to the effect of impurities and defects on the properties of such materials. The general approach used here suggests its applicability to other types of phase transitions where lattice disorder or an analogous order parameter play an important role.

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manuscript.

[1]A typical example is that of an antiferromagnetic insulator-to-paramagnetic metal transition; see, for example, D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Lett. 23, 1384 (1969).

[2]The possibility of having an exchange interaction between the interstitial atom and remaining atomic sites can be incorporated easily in this model and would lead to a different magnetic state in the disordered phase. For the sake of simplicity in this paper we will assume that no coupling of this nature exists.

[3]If x is the number of interstitials available per atom, then $Q = x + 1$.

[4]$n_i > Q^{-1}$ would imply the formation of a superlattice of correlated interstitials, i.e., the onset of a new type of order.

[5]By melting we mean a first-order transition into a quasicrystalline disordered state which characterizes the liquid state. See, for example, J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).

[6]B. A. Huberman and W. Streifer, to be published.

[7]C. Guillaud, J. Phys. Radium 12, 223 (1951); R. R. Heikes, Phys. Rev. 99, 446 (1955).

[8]The melting point in MnBi is of a peritectic character and takes place at 446°C.

[9]B. W. Roberts, Phys. Rev. 104, 607 (1956).

[10]T. Chen, private communication.

Molecular-Dynamics Investigation of Structural Phase Transitions

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We report on a molecular-dynamics study of a two-dimensional model system which is expected to exhibit antiferrodistortive structural phase transitions. The estimated values for the critical exponents β and γ are close to those of the two-dimensional Ising model. The origin of a central peak in the dynamic form factor is attributed to the formation and the dynamics of clusters.

Experimental and theoretical studies have emphasized the need of an anharmonic treatment of lattice dynamics in systems undergoing a structural phase transition.[1-4] The molecular-dynamics technique is a powerful way of examining the static and dynamic properties associated with these transitions, since anharmonicity is treated without approximation.[5]

In this note we report molecular-dynamics results performed on a two-dimensional model system which is expected to exhibit antiferrodistortive structural phase transitions. There exist two extreme cases: the order-disorder and displacive transitions.[1,6]

A prominent example of an antiferrodistortive displacive transition is $SrTiO_3$. A feature of this transition is that it exhibits nonclassical fluctuations as demonstrated by paramagnetic resonance studies.[7,8] A second attractive feature is the appearance of a central peak in addition to the conventional soft-mode resonance in the dynamic form factor of the density fluctuations at the R corner ($T \geq T_c$) and the Γ point ($T \leq T_c$) of the Brillouin zone, respectively.[9,10]

The unexpected appearance of the central peak gave rise to many theoretical speculations on the nature of this phenomenon.[11-15] From the presently available neutron-scattering data, however, the origin of the observed peak cannot be elucidated because of resolution limitations. This open question was one of the compelling reasons for making a molecular-dynamics study.

A model Hamiltonian, covering the whole range from the order-disorder limit to the displacive limit, reads[1,6]

$$\mathcal{H} = \sum_{l,\kappa} \left[\tfrac{1}{2} (\vec{P}_\kappa^{\,l})^2 + \tfrac{1}{2} A (\vec{U}_\kappa^{\,l})^2 + \tfrac{1}{4} B (\vec{U}_\kappa^{\,l})^4 \right] + C \sum_{l,\kappa} \sum_{l',\kappa'} \vec{U}_\kappa^{\,l} \cdot \vec{M}_{\kappa\kappa'}^{\,ll'} \vec{U}_{\kappa'}^{\,l'} \cdot \vec{M}_{\kappa\kappa'}^{\,ll'} . \quad (1)$$

$\vec{P}_\kappa^{\,l}$ is the momentum of the κth particle in the lth unit cell and $\vec{U}_\kappa^{\,l} = \vec{R}_\kappa^{\,l} - \vec{R}_{0\kappa}^{\,l}$ denotes the corresponding displacement from the reference position $\vec{R}_{0\kappa}^{\,l}$. The unit vector $\vec{M}_{\kappa\kappa'}^{\,ll'}$ equals $(\vec{R}_{0\kappa}^{\,l} - \vec{R}_{0\kappa'}^{\,l'}) / |\vec{R}_{0\kappa}^{\,l} - \vec{R}_{0\kappa'}^{\,l'}|$ for nearest neighbors and is zero otherwise. The arrangement of the particles and the constraints subjected to the displacements are shown in Fig. 1 for a two-dimensional system. These constraints imply that we consider only an antiferrodistortive transition,