

Theory of Magneto-thermomechanics

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We show that in both ferromagnetic and antiferromagnetic systems with weak magnetostrictive coupling the coefficient of thermal expansion gives a useful measure of the magnetic specific heat. We also analyze the strong coupling situation by means of our simplified, but soluble model, and find it possible to introduce an effective temperature T^* and an effective magnetic susceptibility. The exact pressure dependence of the thermodynamic functions can be found, and the pressure dependence of the Curie temperature is given explicitly. In strong coupling, a novel first-order thermodynamic phase transformation can occur which is manifested by a discontinuity in T^* as a function of T . An equal area rule for determining the transition is derived, which is reminiscent of the laws of condensation of nonideal gases. It is also shown that in its simple version the theory is not directly applicable to a one-dimensional chain, which is separately analyzed in an Appendix.

IN some ferromagnetic or antiferromagnetic substances, the measured lattice expansivity (coefficient of thermal expansion) displays anomalous behavior correlated to that of the magnetic specific heat. In materials with strong magnetostrictive coupling it has even been suggested that new thermodynamic phase transformations can occur as a result of this coupling.¹

In the present work we give an exact, but rather idealized interpretation of these phenomena, generalizing the theories of Rice,² Smart,³ Bean and Rodbell,¹ and earlier work in the theory of magnetostrictive coupling. Within the scope of our model it is even possible to introduce rigorously such concepts as "effective spin temperature" and "effective magnetic susceptibility," which are conceptually very valuable in establishing a correspondence among systems differing principally in the strength of the magnetomechanical coupling. The present method does not require being able to solve, even approximately, the problems associated with the interacting spins.

We discuss only so-called "volume magnetostriction,"⁴ in single-domain perfect cubic crystals. That is, we allow changes in the volume, but not in the shape. A certain selection in the class of allowed magnetic interactions is also made, as is fully explained in the following section. These are the minimum requirements for a soluble model. The results can, therefore, not be presumed to apply in substances for which the model Hamiltonian of Eq. (1) is not accurate, but nevertheless, we hope they are suggestive and have some qualitative merit in general.

We establish, as a first consequence of magnetostriction, that when the interacting spin system is at temperature T , it has the thermodynamic properties of an otherwise identical spin system situated on an incompressible lattice at an effective temperature T^* , and

it is seen that at zero pressure $T^* \leq T$. Although T^* is shown to be a monotonic function of T , we find that it is not always a continuous one.

In fact, when T^* is a discontinuous function of T , a first-order "magneto-thermomechanical" (MTM) transition occurs. This is a phase transition uniquely caused by the magnetostrictive coupling and which can only occur if this coupling exceeds a certain critical strength rather larger than in the usual materials. It is not at all necessary, however, that the same spin system on an incompressible lattice have any kind of phase transition, (such as a Curie, or Néel point), in order for the MTM transition to occur in the compressible system. The onset of an MTM transition will be related to an infinite expansivity, and the lattice constant changes discontinuously in such a transition.

The effects of pressure and of perturbations to the magnetic system are also considered. In this manner we can obtain a rigorous derivation of the effects of pressure on such critical temperatures as may exist in the magnetic substances under consideration, and a theory of the effective magnetic susceptibility. The reader interested in prior knowledge about such effects will find the effects of pressure and strain on magnetic properties, both experimental and theoretical, discussed in a recent book by Belov.⁵ But there too, the theoretical results were unnecessarily predicated on the validity of some approximation, i.e., the Landau theory of second-order phase transitions.⁶ In the spirit of the present analysis, many results of Belov's, such as the pressure dependence of magnetization, could be rederived almost by inspection, and their meaning further clarified. Other minor topics in thermodynamics are discussed where relevant. Finally, in the Appendix we discuss a one-dimensional

⁵ K. P. Belov, *Magnetic Transitions*, translated by W. H. Furry (Consultant's Bureau, New York, 1961). Cf. sections on "Effects of Stresses on Magnetisation," "Magnetostriction," "Displacement of Curie Point Under the Influence of Elastic Stresses," "Non-Magnetic Phenomena in Neighborhood of Antiferromagnet Transition Point," etc.

⁶ L. D. Landau and E. M. Lifshitz, *Statistical Physics*, translated by E. and R. F. Peierls (Pergamon Press, New York, 1958), Chap. XIV.

¹ C. P. Bean and D. S. Rodbell, *Phys. Rev.* **126**, 104, (1962).

² O. K. Rice, *J. Chem. Phys.* **22**, 1535, (1954).

³ J. S. Smart, *Phys. Rev.* **90**, 55 (1953).

⁴ R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), p. 641.

model. We neglect the temperature dependence of the compressibility and nonmagnetic contributions to the lattice expansion in our calculations.

[We have also found it convenient to modify the notation normal in this field, so as to retain the even more familiar definition of $\beta \equiv (kT)^{-1}$.]

GENERAL MODEL

First, consider all Hamiltonians of the form

$$H = (1/2K)\delta^2 + (1+\eta\delta)H_M^0, \quad (1)$$

where H_M^0 is the magnetic Hamiltonian appropriate to the spin-spin interaction in the unit volume v_0 , K is the lattice compressibility, η is the first-order magnetostrictive coefficient, and $\delta = (v - v_0)/v_0$ is the fractional change in volume. We postpone considerations of applied pressure and of perturbations on the magnetic system. H_M^0 may be quite arbitrary and need in no way be restricted to the usual Heisenberg or Ising models of magnetic interactions.

An accurate realization of this model (1) is a homogeneous cubic single crystal with nearest-neighbor spin interactions. Another example is a cubic magnetic model with Ruderman-Kittel indirect exchange interactions.⁷ In both cases a Taylor series expansion in the lattice constant gives a result which leads to Eq. (1). The first example is obvious, but let us examine the indirect exchange theory in somewhat more detail. The coupling between spins at R_i and R_j depends on a function $J(k_f r_{ij})$, where k_f is the radius of the Fermi surface, which is assumed to be spherical. The requirement that the number of electrons per atom remain fixed under homogeneous strain implies that $k_f v$ is a constant, and consequently, $k_f r_{ij}$ is also constant. This has previously been remarked⁸ by Liu. The effect of homogeneous strain can, therefore, only be to change the over-all coupling constant. Unfortunately, this analysis cannot be rigorously extended to materials of hexagonal structure, in which the simplest Fermi surface is an ellipsoid, the eccentricity of which affords an extra degree of freedom which can change value under strain. In that case, and in general, our results can only be considered suggestive.

STATISTICAL MECHANICS

One must first establish the thermodynamics of the ideal incompressible system described by H_M^0 . Its magnetic free energy $F_M(\beta)$ is defined by

$$F_M(\beta) = -\frac{1}{\beta} \ln \text{Tr}(e^{-\beta H_M^0}), \quad (2)$$

where $\beta = (kT)^{-1}$. The internal energy $U_M(\beta)$ is

$$U_M(\beta) = \frac{\partial}{\partial \beta} (\beta F_M) \leq 0. \quad (3)$$

Three general properties of U_M are considered in the following section. The magnetic specific heat $C_H(\beta)$ at

constant applied field is, as usual,

$$C_H = \partial U_M / \partial T \geq 0. \quad (4)$$

Within the present work we attempt to explain how experiments on a compressible system for which the Hamiltonian is given by Eq. (1) will yield information about the thermodynamic functions (2)–(4) of the ideal magnetic system, which are the functions usually given (or approximated) by theory.

Consider, therefore, the Gibbs free energy associated with Eq. (1), defined by

$$G(\beta, p) = -\frac{1}{\beta} \ln Z = -\frac{1}{\beta} \ln \text{Tr}(e^{-\beta(H+pv)}). \quad (5)$$

Strictly speaking, the trace includes an integration over all values of $v = v_0(1+\delta)$ and of the other variables characterizing the configuration and dynamics of the lattice. At present, we replace δ by its most probable value over the ensemble and neglect the other degrees of freedom. In a later section, we introduce a quantum-mechanical phase-space analysis of small deformations, which establishes the validity of the present approximation in two or three dimensions. The special case of one dimension is analyzed in more detail in the section on magnetic susceptibility, and is worked out in the Appendix.

Taking the trace over spin variables in (5) and treating δ as a parameter, we find

$$Z = \exp\{-\beta[\delta^2/2K + p(1+\delta) + (1+\eta\delta)F_M(\beta^*)]\}, \quad (6)$$

where

$$T^* \equiv T/(1+\eta\delta), \quad \beta^* \equiv (1+\eta\delta)\beta, \quad \delta \equiv (\beta^* - \beta)/\beta\eta. \quad (7)$$

We have taken v_0 to be the unit volume. The most probable value of δ is that which maximizes Z , and by straightforward differentiation we obtain

$$\delta = -K[p + \eta U_M(\beta^*)], \quad (8)$$

which is an implicit equation for δ .

Of the two relations (7) and (8) involving δ , the first should be considered the definition, and fundamental. The effects of neglected anharmonicities of the lattice must be absorbed into Eq. (8), but not Eq. (7), by adding a term independent of the spins $\delta_1(T)$ to the right-hand side, or by using an "effective pressure" to accomplish the same purpose. Nevertheless, Eq. (7) defining β^* is correct without modification in terms of the observed δ , and the calculation of the pressure dependence of β^* [which is in effect what we later do in Eq. (30)], does not require δ_1 to vanish or to have any particular value. Equations (7) and (8) are most conveniently considered as two parametric equations for δ in terms of β^* . In cases when they have more than one simultaneous solution the one which leads to largest Z , i.e., lowest Gibbs free energy, must be chosen to describe thermodynamic equilibrium. Other solutions, corresponding to higher free energies, are unstable or metastable and can give rise to irreversible effects such as *hysteresis* and *supercooling*. Still further metastable configurations of the magnetomechanical system are possible if F_M itself has metastable solutions. Further investigation of this point is left to the reader.

If we assume that K and η are independent of the temperature, then we can find the expansivity α and the observed compressibility K_{obs} by differentiating Eq. (8):

⁷ M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954). For a theory of ferromagnetism and antiferromagnetism based on this interaction, see also D. Mattis and W. Donath, *ibid.* **128**, 1618 (1962).

⁸ S. H. Liu (unpublished).

$$\left. \frac{\partial}{\partial T} \right|_p \equiv \alpha = \frac{-(T^*/T)\eta K C_H(\beta^*)}{1 - \eta^2 K [(T^*)^2/T] C_H(\beta^*)}$$

$$= \frac{-\eta K C_H(\beta^*)}{1 - \eta K \{p + \eta [U_M(\beta^*) + T^* C_H(\beta^*)]\}}, \quad (9a)$$

and

$$\left. \frac{-\partial}{\partial p} \right|_T \equiv K_{\text{obs}} = \frac{K}{1 - \eta^2 K [(T^*)^2/T] C_H(\beta^*)}$$

$$= \frac{(T/T^*)K}{1 - \eta K \{p + \eta [U_M(\beta^*) + T^* C_H(\beta^*)]\}}, \quad (9b)$$

or finally,

$$\alpha = -(T^*/T)\eta K_{\text{obs}} C_H(\beta^*). \quad (9c)$$

The expansivity has a sign opposite to η [cf. discussion following Eq. (20)]:

$$\eta\alpha < 0, \quad (10)$$

which may help determine the sign of η experimentally. Of course, we have neglected any nonmagnetic contributions to α which may, or may not, be substantial. We return to the problem of isolating magnetic effects in a later section.

In the weak-coupling limit, one retains only lowest order terms in η and Eq. (9c) reduces to

$$\lim_{\eta \rightarrow 0} (\alpha/\eta) = -K_{\text{obs}} C_H(\beta). \quad (11)$$

Thus, the expansivity becomes a direct measure of the magnetic specific heat. Its value as a "thermometer" is limited, however, to regions where (11) is not masked by nonmagnetic contributions to the expansivity.

Under zero applied pressure, we use Eq. (8) and the fact that the internal energy U_M is negative to deduce

$$\eta\delta > 0, \quad (12)$$

and therefore "the spins are cooler than the lattice," or more precisely,

$$T^* \leq T \quad \text{at } p=0. \quad (13)$$

Let us now turn to a graphical technique for solving Eqs. (7) and (8) at arbitrary coupling strength.

GRAPHICAL SOLUTION FOR ARBITRARY PRESSURE

Defining

$$\phi_1 \equiv (\beta - \beta^*)/\beta, \quad (14)$$

and

$$\phi_2 \equiv K[\eta p + \eta^2 U_M(\beta^*)], \quad (15)$$

the graphical solution of Eqs. (7) and (8) is given by the intersections of the linear "load line" ϕ_1 with the "magnetic characteristic," ϕ_2 , to use the terminology of circuit theory. The effect of pressure is to shift the origin of ϕ_2 . The latter is also limited by the following properties shared by all magnetic systems.

(a) The internal energy vanishes with increasing disorder as $T \rightarrow \infty$; therefore,

$$\phi_2(\beta^*=0) = K p \eta. \quad (16)$$

(b) The internal energy is bounded at all temperatures, increases monotonically with temperature, and is piecewise continuous. Thus,

$$-\infty \leq \partial \phi_2(\beta^*)/\partial \beta^* \leq 0, \quad \text{for all } \beta^*. \quad (17)$$

(c) From the third law of thermodynamics, the specific heat vanishes at the absolute zero and, therefore,

$$\lim_{\beta^* \rightarrow \infty} (\beta^*)^2 (\partial \phi_2/\partial \beta^*) = 0. \quad (18)$$

Two possible ϕ_2 curves are shown in the figures. In order for multiple intersections to occur (the analogy to "flip-flop" circuitry is striking), the slope of ϕ_2 is required to drop below a value $-1/\beta$; we deduce that there must exist at least one value of β for which

$$-\eta^2 K (\partial U_M/\partial \beta^*) = k (T^*)^2 \eta^2 K C_H(\beta^*) \geq T, \quad (19)$$

and finally we eliminate T by the condition $\phi_1 = \phi_2$. Thus, one can arrive at a condition both necessary and sufficient for an MTM transition to occur

$$\frac{T^* K \eta^2 C_H(\beta^*)}{1 - \eta K [p + \eta U_M(\beta^*)]} \geq 1 \quad \text{for some } \beta^*. \quad (20)$$

Evidently, the two-dimensional Ising model⁹

$$C_H(\beta_c^*) = \infty$$

will *always* have an MTM transition, as first remarked by Rice.²

This criterion generalizes that given by Bean and Rodbell¹ in a treatment based on the molecular field approximation. (This approximation, although probably accurate, destroyed, nevertheless, the basic symmetries of the problem.) Note that our criterion is closely related to the expression for the expansivity given in Eq. (9), and, in fact, is just the condition that $\alpha \rightarrow \infty$.

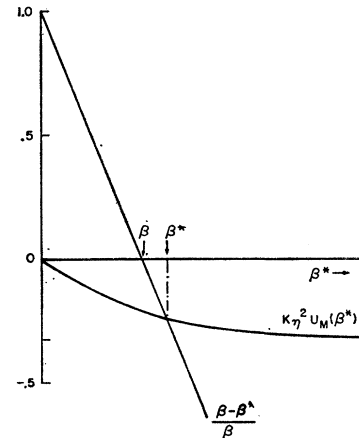


FIG. 1. Graphical solution of Eqs. (7) and (8) for the effective temperature $T^* = (k\beta^*)^{-1}$ as a function of $T = (k\beta)^{-1}$.

⁹ G. F. Newell and E. W. Montroll, *Revs. Modern Phys.* **25**, 353 (1953).

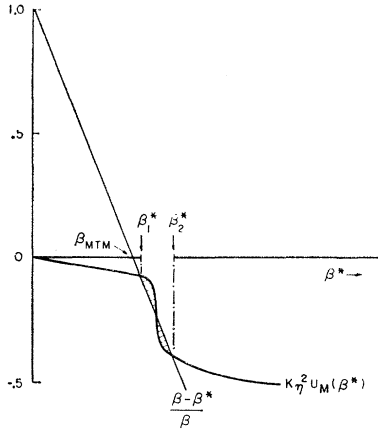


FIG. 2. First-order MTM transition occurs at β_{MTM} , and is marked by a discontinuous jump from β_1^* to β_2^* . Equality of shaded areas defines the transition, as shown in the text. Internal temperatures between β_1^* and β_2^* are, therefore, inaccessible in equilibrium thermodynamics.

When expression (20) becomes an equality, we have a critical point at the end of a two-phase boundary, in analogy with the liquid-gas critical point. The singular behavior of α is then expected.

In Fig. 1, we show a system in which the MTM transition is clearly impossible. This is the usual case. In Fig. 2, the simplest MTM transition is illustrated, for a system showing no magnetic transition at constant volume. It occurs at the value of β for which the two shaded areas are equal, as we prove below. We denote this point by β_{MTM} . It marks a discontinuity in β^* from β_1^* to β_2^* . The inaccessible region between β_1^* and β_2^* almost always will bracket the Curie (or Néel) point β_c , when there is one, so that when there is an MTM transition the magnetic system will never reach its internal critical temperature by any reversible path. Five or more intersections are also possible, and lead to multiple MTM transitions, for curves more "wiggly" than in Fig. 2.

The MTM transition is thus a new physical phenomenon. Although its likelihood of existing is increased by the existence of a transition in the magnetic system at constant volume [near which the slope of $\eta^2 K U_M(\beta^*)$ is likely to be large], this is in no way essential in principle. The transition can very well be between two states, *neither* of which shows any long-range magnetic order.

PROOF OF EQUAL AREA RULE

We have stated that an MTM transition occurs when the shaded areas in Fig. 2 are equal, and we now provide a proof.

The equality of the Gibbs free energies at β_1^* and β_2^* implies that

$$\begin{aligned} G(\beta_1^*) - G(\beta_2^*) &= \frac{1}{2K} \{ K^2 [p + \eta U_M(\beta_1^*)]^2 - K^2 [p + \eta U_M(\beta_2^*)]^2 \} \\ &\quad + p(-K\eta) [U_M(\beta_1^*) - U_M(\beta_2^*)] \\ &\quad + \frac{1}{\beta_{\text{MTM}}} [\beta_1^* F_M(\beta_1^*) - \beta_2^* F_M(\beta_2^*)] = 0. \end{aligned} \quad (21)$$

By Eq. (3),

$$\beta_1^* F_M(\beta_1^*) - \beta_2^* F_M(\beta_2^*) = \int_{\beta_1^*}^{\beta_2^*} dt U_M(t), \quad (22)$$

and by Eqs. (7) and (8),

$$-K\eta^2 [U_M(\beta_1^*) - U_M(\beta_2^*)] = (\beta_1^* - \beta_2^*) / \beta_{\text{MTM}}. \quad (23)$$

We use these relations to simplify Eq. (21), and thus find the desired result

$$(\beta_1^* - \beta_2^*) \left[\frac{U_M(\beta_1^*) - U_M(\beta_2^*)}{2} \right] = \int_{\beta_1^*}^{\beta_2^*} dt U_M(t). \quad (24)$$

EFFECTS OF PRESSURE

The effect of pressure is most easily seen in terms of the graphical construction already given. The pressure enters only in the function ϕ_2 , and there it enters linearly. Depending on the sign of η , an increase in pressure will either raise (if η is positive) or lower (if η is negative) the curve representing ϕ_2 without deforming it, and conversely for a lowering of the pressure. It thus becomes apparent that under some circumstances, a sufficient change of pressure can produce (or remove) an MTM transition that is normally absent (or present).

The effect of pressure on various thermodynamic quantities is readily calculated. As an example, in the present work, we consider the important case of a magnetic system exhibiting either a Curie or a Néel point at T_c^* when the system is at the volume v_0 , and showing no MTM transition when instead the pressure is held constant at $p=0$. We assume $\eta > 0$. At zero pressure, the system has a second-order transition at $T_c = 1/k\beta_c$. As the pressure is raised, β_c increases and T_c decreases (the opposite holds true if $\eta < 0$). It is easy to calculate the dependence of T_c on p because, the transition, *so long as it is still second order*, occurs at $\beta^* = \beta_c^*$, independent of pressure. As the pressure is varied, the observed critical temperature is obtained from the condition $\phi_1 = \phi_2$ which gives

$$T_c = [1 - Kp\eta - K\eta^2 U_M(\beta_c^*)] T_c^*, \quad (25)$$

and the change of critical temperature with pressure is, therefore,

$$\left. \frac{\partial T_c}{\partial p} \right|_{\beta^*} = -K\eta T_c^* = \frac{-K\eta T_c}{1 - Kp\eta - K\eta^2 U_M(\beta_c^*)}. \quad (26)$$

One may further use Eq. (9b) to express this in terms of the experimental compressibility, K_{obs} .

EXPERIMENTAL DETERMINATION

In the neighborhood of any magnetic or MTM transition, the contributions to specific heat, expansivity, etc., from other effects in the solid (such as lattice anharmonicities) should vary smoothly, in contrast to the contributions that are partly or wholly magnetic in origin.

This background can therefore be subtracted from measured values to give observed values for the magnetic contributions. One quantity that is observed is the specific heat. This is not the specific heat of an incompressible magnetic lattice, but rather it is the specific heat at constant pressure. By direct calculation, we find that it is given by

$$C_{p,H}(\beta) = \frac{\partial}{\partial T} \left[\frac{\partial}{\partial (1/T)} \left(\frac{G}{T} \right) \right] = C_H(\beta^*) (1 - \alpha \eta T^*), \quad (27)$$

where α is the expansivity previously calculated in Eq. (9). [Recalling that $\alpha \eta < 0$ this implies, incidentally, that $C_{p,H}(\beta) > C_H(\beta^*)$.]

An experimental test of the theory can now proceed along the following lines. The magnetostrictive coupling parameter η is measurable from (26), assuming it is small so that the term in $U_M(\beta^*)$ can be neglected. Measurement of $\alpha(T)$ allows a determination of $\delta(T)$ by integrating $\alpha \equiv (\partial \delta / \partial T)_p$, with the boundary condition $\delta(T = \infty) \rightarrow 0$. From $\delta(T)$ we have $\beta^*(\beta)$ according to Eq. (7). Equation (9) is also a differential equation for $U_M(\beta^*)$, which can be integrated with the boundary condition $U_M(T = \infty) \rightarrow 0$. All the quantities on the right side of Eq. (27) are then experimentally determined independently of a measurement of the specific heat on the left side of this equation. The validity of the idealizations we have made are therefore, experimentally verifiable as a check on this single equation.

MAGNETIC SUSCEPTIBILITY AND MAGNETIZATION

Here we investigate perturbations on the magnetic spin system. Our goal is first to find for the susceptibility an analog of Eq. (27), where we related the measured specific heat at the true temperature T , to the idealized one at T^* . In ferromagnetic systems the magnetization M is of foremost interest, so we study it first. It is given by

$$M(\beta, h) = -[\partial G(\beta, h) / \partial h], \quad (28)$$

where h is the applied magnetic field. We must first add to the Hamiltonian (1) a term independent of η and linear in h , hA . The calculation of thermodynamic quantities, such as F_M proceeds with this new augmented Hamiltonian, which includes the interaction of the system with this applied field. We shall express M in terms of the ideal magnetization M^* , which is by definition

$$M^*(\beta^*, h^*) \equiv -[\partial F_M(\beta^*, h^*) / \partial h^*]. \quad (29)$$

We have introduced the obvious notation,

$$h^* = h / (1 + \eta \delta). \quad (30)$$

After some straightforward manipulations, one finds

$$\delta = -K \{ p + \eta [U_M(\beta^*, h^*) + h^* M^*(\beta^*, h^*)] \}, \quad (31)$$

which gives the field and pressure dependence of the magnetostriction, when used in conjunction with (7).

Not surprisingly, we also find that the "internal" magnetization is actually what is observed,

$$M(\beta, h) = M^*(\beta^*, h^*). \quad (32)$$

This seemingly trivial result actually follows from Eq. (28), and the stationarity of G with respect to variations in δ . In systems without permanent magnetization, or in the case of the perpendicular ferromagnetic susceptibility, we use Eq. (32) to obtain further

$$\chi(\beta) \equiv \lim_{h \rightarrow 0} \left(\frac{M}{h} \right) = \frac{\beta}{\beta^*} \chi^*(\beta^*) \equiv \lim_{h^* \rightarrow 0} \left(\frac{M^*}{h^*} \right) \left(\frac{h^*}{h} \right), \quad (33)$$

which relates the observed susceptibility χ at β to the ideal one χ^* at β^* , and is valid for both the parallel and perpendicular susceptibilities.

Equations (32) and (33) suggest that deviations from idealized temperature dependence (i.e., the Bloch $T^{3/2}$ law for the low-temperature decrease in magnetization in a ferromagnet) *should* and *must* occur in the observed values in strongly magnetomechanical coupled system, because the well-known laws are obviously meant to govern the starred variables and not the unstarred ones, which are actually observed.

THE ASSUMPTION OF UNIFORM EXPANSION

From the beginning we have made an assumption which is standard in the literature, that the configuration of the lattice could be satisfactorily characterized by a single parameter δ , and that this parameter is to be chosen to minimize the free energy (or maximize the ensemble probability). While such an assumption is within the spirit of macroscopic thermodynamics, it might well be objected that it is crucial in the existence of MTM transitions, and that it should be further justified. On its face, it might even seem plausible that in a nearest-neighbor spin interaction model, the spacing between each pair of spins adjusts to the instantaneous relative orientation of the two spins of the pair. This would tend to strengthen the effective interaction of each pair of spins, and while changing the shape of the lattice, it would not change the character of the transition from second to first order. And in fact, for a one-dimensional Ising model, in which the coupling strength depends linearly on the spacing between spins, the exact solution (given in the Appendix) shows no MTM transition, whereas the theory as presented in previous sections allows for one in case of sufficiently strong magnetic or magnetostrictive coupling.

Our aim here is to explain on the basis of fluctuation theory why the theory, as developed in the text, is not valid in one dimension but is, nevertheless, valid in three. In the first place, neglecting all lattice configurations except the most probable one is really only a valid procedure for systems in which the distribution is

sharply peaked around the most probable. It is precisely in one dimension that the length of a chain (even omitting spin interactions) is not sharply defined, because a one-dimensional chain behaves more like a fluid than a solid. However, in *three* dimensions, long-wavelength fluctuations are strongly suppressed, as it is well known, because of a relative reduction in phase space. Let us investigate this in somewhat more detail.

Consider the dispersion in the probability distribution of the distance between two particles, ideally at \mathbf{R}_i and \mathbf{R}_j . Let the actual positions be

$$\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i \quad \text{and} \quad \mathbf{r}_j = \mathbf{R}_j + \mathbf{u}_j,$$

and calculate

$$\Delta_{ij} = \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle - \langle \mathbf{r}_i - \mathbf{r}_j \rangle^2 = \langle (\mathbf{u}_i - \mathbf{u}_j)^2 \rangle - \langle \mathbf{u}_i - \mathbf{u}_j \rangle^2. \quad (34)$$

Introducing normal modes,

$$\mathbf{u}_i = \left(\frac{2}{N}\right)^{1/2} \sum_{\mathbf{k}\sigma} \mathbf{e}_{\mathbf{k}\sigma} \begin{Bmatrix} \cos \mathbf{k} \cdot \mathbf{R}_i \\ \sin \mathbf{k} \cdot \mathbf{R}_i \end{Bmatrix} Q_{\mathbf{k}\sigma}, \quad (35)$$

and assuming inversion symmetry, we find

$$\Delta_{ij} \propto \frac{2}{N} \sum_{\mathbf{k}\sigma} \langle Q_{\mathbf{k}\sigma}^2 \rangle [1 - \cos \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \equiv \Delta^{(1)} - \Delta^{(2)}. \quad (36)$$

If $\mathbf{R}_i - \mathbf{R}_j$ is large, the second sum cannot be replaced by an integral, because successive contributions from $\cos \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)$ will oscillate rapidly. Thus, the $\cos \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)$ will not cancel the first term, except at $\mathbf{k} = 0$. Consider then, just the first term, which can be approximated by the integral,

$$\Delta^{(1)} \sim \frac{1}{N} \sum_{\sigma} \int d\mathbf{k} k^{n-1} \langle Q_{\mathbf{k}\sigma}^2 \rangle, \quad (37)$$

where n is the number of dimensions. Now in the quantum-mechanical ground state $\langle Q_{\mathbf{k}\sigma}^2 \rangle \sim 1/\omega_{\mathbf{k}\sigma}$ so, for long wavelengths at $T=0$,

$$\langle Q_{\mathbf{k}\sigma}^2 \rangle \sim 1/k. \quad (38a)$$

At high temperatures $\langle Q_{\mathbf{k}\sigma}^2 \rangle \sim 1/\omega_{\mathbf{k}\sigma}^2$ so, for sufficiently long wavelengths,

$$\langle Q_{\mathbf{k}\sigma}^2 \rangle \sim 1/k^2 \quad \text{if} \quad \hbar\omega_{\mathbf{k}\sigma} \ll kT. \quad (38b)$$

In either case, we see that $\Delta^{(1)}$ is divergent in one dimension and convergent in three. The two-dimensional case is delicate (but of less interest). If we had retained the summation in Eq. (36), we would have concluded that $\Delta^{(1)} = O(N)$ (or worse) in one dimension, whereas $\Delta^{(1)} = O(1)$ in three dimensions. The physical reason for the divergence is that long-wavelength fluctuations are not "damped" in one dimension as they are in three by the factor k^{n-1} . Closely related to this view of a free lattice are the conclusions to be drawn when one tries to include the deviations from uniform strain by some

kind of perturbation theory on the ground-state energy, or on the density matrix. If the elementary excitations of the lattice system are phonons with energies $\omega_k \sim k$, for small k , and if the elementary excitations of the spin system (in an ordered state) are some kind of spin waves with energies $\epsilon_k \sim k^2$ or k (corresponding to ferromagnetic and antiferromagnetic ordering, respectively), then we can consider perturbation corrections to the ground-state energy. They are of the form

$$\sum_k [|M_k|^2 / (\omega_k + \epsilon_k)]. \quad (39)$$

For $k \rightarrow 0$, $M_k \rightarrow \text{const}$, because for $k \equiv 0$, we have assumed a finite magnetostrictive interaction between the magnetic and elastic systems, and M_k is necessarily continuous. Converting to an integral in n dimensions, this gives

$$\int d\mathbf{k} k^{n-1} \frac{\text{const}}{k + O(k)}, \quad (40)$$

which also diverges in one dimension, because of the long-wavelength fluctuations, but not in three. Similar arguments hold justifying a perturbation theory of the *density matrix* in the *three*, but *not* in *one* dimension.

SUMMARY

We have considered a simple, but realistic, model for the interaction of the magnetic and elastic degrees of freedom in a magnetic solid, and have related the thermodynamic variables at constant pressure (such as T , C_p , χ , K_{obs} , M) to the ideal variables at constant volume (T^* , C_H , χ^* , K , M^*). We have also found a criterion for the existence of a magnetothermomechanical (MTM) first-order transition which can occur as a result of the strong magnetostrictive coupling, even in hypothetical magnetic systems with no magnetic transition. We have, however, neglected all nonmagnetic contributions to the lattice specific heat and the temperature dependence of the lattice compressibility. Also neglected were effects of interactions between phonons and elementary excitations of the magnetic system, except (see Appendix) in one dimension.

Our results can also be specifically applied by assuming a model for F_M (e.g., as is given by the internal field approximation). One can then calculate effects of strain on magnetization or on sublattice magnetization, and many other effects^{5,4} and compare the models with experiment. We have not done this in the present analysis, but we have suggested an "experimental determination" of the theory which relies neither on any specific magnetic model, nor even on the validity of the Landau theory of phase transitions.⁶

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APPENDIX

Consider in detail the one-dimensional Ising model with mobile spins, described by the Hamiltonian

$$H = \sum_i \left\{ \frac{p_i^2}{2m} + \frac{(x_{i+1} - x_i)^2}{2(K/N)} + [1 + \eta N(x_{i+1} - x_i)] J_i \sigma_i \sigma_{i+1} \right\}, \quad (\text{A1})$$

where p_i is the momentum of the i th atom, x_i is its displacement from equilibrium, K has the same meaning as in the text, and

$$\sigma_i = \pm 1, \quad \sigma_i^2 = 1. \quad (\text{A2})$$

It is instructive first to consider the problem in classical statistical mechanics, neglecting the lattice kinetic energy. The partition function can be evaluated exactly in a straightforward way, and is just

$$Z = Z_L Z_M = \prod_i \left\{ \frac{2\pi K}{\beta N} \right\}^{1/2} \times \exp\left(\frac{1}{2} N K^2 J_i\right) \prod_i (2 \cosh \beta J_i). \quad (\text{A3})$$

The magnetic internal energy at equilibrium ($x_i = 0$) is

$$U_M = -\frac{\partial}{\partial \beta} \ln Z_M = -\sum_i J_i \tanh \beta J_i. \quad (\text{A4})$$

The average deviation of the i th interparticle spacing from equilibrium at temperature T is $\bar{\rho}_i$,

$$\bar{\rho}_i \equiv \langle x_{i+1} - x_i \rangle = \eta K J_i \tanh \beta J_i, \quad (\text{A5})$$

so that the average fractional change in length of the

entire chain is

$$\delta = \sum_i \bar{\rho}_i = -\eta K U_M(\beta). \quad (\text{A6})$$

This is to be compared with Eq. (8).

$$\delta = \sum_i \hat{\rho}_i = -\eta K U_M(\beta^*), \quad (\text{A7})$$

where $\hat{\rho}_i$ is the most probable value of ρ_i . Although these expressions do agree to lowest order in η , Eq. (A7), but not Eq. (A6), can lead to an MTM transition. It is clear that the average of a sum of independent random variables is the sum of the averages, and the most probable value of the sum is also the sum of the most probable values. But when the distribution of the sum is not sharply peaked, the average and most probable value of the sum can differ in an important way, and it is then the average which corresponds to reality. In three dimensions the difference between the average and the most probable may be negligible, and the variables are not independent.

It is interesting to note that the exact quantum mechanical partition function can be found. For if we make the canonical transformation

$$x_i \rightarrow x_i - \eta K \sum_{j < i} J_j \sigma_j \sigma_{j+1}, \quad (\text{A8})$$

then

$$H \rightarrow \sum_i \left\{ \frac{p_i^2}{2m} + \frac{(x_{i+1} - x_i)^2}{2(K/N)} \right\} + \sum_i J_i \sigma_i \sigma_{i+1} + \text{const}, \quad (\text{A9})$$

where we have used Eq. (A2). The free energies of the decoupled spin and elastic systems can be simply added, and as is well known, neither has a phase transition in one dimension nor therefore, does the sum. The relation between expansivity and magnetic specific heat, (11) holds for all η in this one-dimensional case, and not just in weak coupling as in three dimensions.