New Fluctuation-Induced First-Order Antiferrodistortive Phase Transitions

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In a general Landau-Ginzburg-Wilson Hamiltonian, symmetry allows a term linear in the gradient and trilinear in the order parameter in many cases. General renormalization-group equations to $O(\epsilon)$ are given for such terms, and applied to the antiferrodistortive phase transition in calcite ($R\bar{3}c$). The commensurate transition is continuous in mean-field theory, but in the renormalization-group theory, this new term is relevant near all fixed points to $O(\epsilon^2)$ and causes a fluctuation-induced first-order transition.

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Previously[1] the authors introduced a general form for the effective Landau-Ginzburg-Wilson Hamiltonian for a structural phase transition. This Hamiltonian has been applied to the zone-boundary ($\vec{F}$ point) ferroelastic transition in calcite, which in the high-symmetry phase of interest [$CaCO_3$(I)] has space-group symmetry $R\bar{3}c$. Previously, calcite had been assigned to the hypercubic universality class with short-range interactions.[2] Thus, it was predicted to follow the stable Heisenberg fixed-point behavior.[3] The observed first-order transition (at room temperature and high pressure) to its lower-symmetry phase could at nonambient temperatures change to a continuous transition.

It is reported here, however, that a Hamiltonian term similar to that recently introduced in the literature for polar order parameters[4–8] will also be present in this and other antiferrodistortive structures. When the mean-field calculation is extended to include this term, the commensurate transition remains continuous if the new term is not too large. However, this term is relevant in an $O(\epsilon^2)$ renormalization-group (RG) calculation. Thus, in the case of calcite, there are no stable fixed points, and a first-order phase transition is predicted. In spite of some indication of critical phenomena from observed ESR data,[9] recent latent heat measurements on calcite confirm[10] that the transition indeed remains first order up to temperatures of 190 °C.

The free energy for a lattice dynamical system can be written[1]

$$F=-k_BT\ln\int Dc\, e^{-H(c)},$$

with

$$H(c)=\sum_{m=0}^{\infty}\frac{1}{m!}\int\cdots\int d\kappa_1\cdots d\kappa_m\, H^m_{I_m}(\vec{\kappa}_1,\ldots,\vec{\kappa}_m)\,\delta(\vec{\kappa}_1+\cdots+\vec{\kappa}_m)\,c_{i_1}(\vec{\kappa}_1)\cdots c_{i_m}(\vec{\kappa}_m). \qquad (1)$$

Here $\int Dc$ indicates a functional integration over the collection of $c_i(\vec{\kappa})$, where i refers to a basis vector of a physically irreducible representation D_{ij}. $\vec{\kappa}$ ranges continuously over the sphere $\kappa<\Lambda$ (Λ the cutoff parameter), corresponding to mode amplitudes about the element of the extended star (costar) $\vec{k}_l$ to which i corresponds. That is, $c_i(\vec{\kappa})$ is a linear combination of mode amplitudes at $\vec{k}_l+\vec{\kappa}$. Furthermore, $H(c)$ must be real, and invariant when $c_i(\vec{\kappa})$ is replaced by $D_{ij}(g)c_j(S^{-1}\vec{\kappa})$ for $g=(S|\vec{t}+\vec{\tau})$ a space-group element of G, the space group of the higher-symmetry phase. A summation convention on the components of the order parameter $i=1$ through l, where l is the dimension of $D(G)$, is used and I_m is the compound coefficient $i_1i_2\ldots i_m$. For simplicity factors of 2π have been absorbed in H^m.

Note that in Eq. (1) umklapp terms arise from the symmetry of $H(c)$ under crystal translations $(E|\vec{t})$ and are implicitly contained in the symmetry-restricted form of H^m. In essence we have taken Λ small enough so that $\sum_i\vec{\kappa}_i$ will always be smaller than any reciprocal-lattice vector for any set of $\vec{\kappa}_i$, at least up to any order in $H(c)$ that we deal with. This may be considered a slight refinement of the form used by Cowley and Bruce.[11] For further details see Ref. 1.

If we assume that the interaction is short ranged, then $H^m_{I_m}(\{\vec{\kappa}\})$ can be expanded in a Taylor series in the $\vec{\kappa}_i$. Now suppose that the unperturbed Hamiltonian is

$$H_0=\tfrac{1}{2}\int d\kappa\, a\kappa^2 c_i(\vec{\kappa})c_i(-\vec{\kappa}).$$

Then one can show that for linear scaling, where

$$c_i(\vec{\kappa})'=s^{(6-\epsilon-\eta)/2}c_i(s\vec{\kappa}), \qquad (2)$$

all the terms in $H(c)$ with $n+m>4$ will vanish in lowest order in ϵ. Here n is the order of $\vec{\kappa}$ (or the gradient, in direct space) in the Taylor series of H^m and m is, of course, the order of $c_i(\vec{\kappa})$. This indicates further, that if $H(c)$ (excluding H_0) is of $O(\epsilon)$, then terms with $n+m>4$ must necessarily have fixed-point values of $O(\epsilon^2)$ at least, since they arise from higher-order graphs. It then follows that in looking for fixed-point Hamiltonians to $O(\epsilon)$ in the vicinity of H_0, one need only consider the terms with $n+m\leqslant 4$.

There are then six such terms in Eq. (1) if the interactions are short ranged, and one considers the Hamiltonian[1]

$$\begin{aligned} H = \tfrac{1}{2}\int d\kappa\,[(r+a\kappa^2)\delta_{ij} + a_{ij,l}\kappa_l + a_{ij,lm}\kappa_l\kappa_m]\,c_i(\vec{\kappa})\,c_j(-\vec{\kappa}) \\ + \tfrac{1}{6}\int\int d\kappa\,d\kappa'\,(b_{ijl} + b_{j,il,m}\kappa_m + b_{i,jl,m}\kappa'_m)\,c_i(\vec{\kappa})\,c_j(\vec{\kappa}')\,c_l(-\vec{\kappa}-\vec{\kappa}') \\ + \tfrac{1}{24}\int\int\int d\kappa\,d\kappa'\,d\kappa''\,u_{ijlm}\,c_i(\vec{\kappa})\,c_j(\vec{\kappa}')\,c_l(\vec{\kappa}'')\,c_m(-\vec{\kappa}-\vec{\kappa}'-\vec{\kappa}''). \end{aligned} \tag{3}$$

We assume that only the appropriately symmetric parts have been kept in Eq. (3). The anisotropic terms corresponding to $a_{ij,lm}$ and $b_{j,il,m}$, which are usually omitted from $H(c)$, are of central interest in this Letter.

With use of Eq. (2), r, $a_{ij,l}$, and b_{ijl} scale to lowest order in ϵ as s^2, s^1, and s^1, respectively. These exponents will not change significantly because of $O(\epsilon)$ perturbations. The r term is always allowed by symmetry, and so always provides a relevant parameter. $a_{ij,l}$ and b_{ijl}, which transform according to the antisymmetric square-vector representation and the symmetric cube representation of G, respectively, then must vanish as a result of symmetry, since we want only one relevant parameter. This leads to the well-known conditions of Landau and Lifshitz for an active irreducible representation.[12]

Of the other parameters in Eq. (3), $a_{ij,lm}$ scales to lowest order in ϵ as s^0, $b_{j,ilm}$ as $s^{\epsilon/2}$, and u_{ijlm} as s^{ϵ}. Thus, around the Gaussian fixed point, these terms are marginal or relevant. Following the usual RG prescription one then looks for other, stable fixed points in the vicinity of the Gaussian fixed point using perturbation theory to $O(\epsilon^2)$. This procedure is well known for the terms corresponding to r and u_{ijlm},[13] particularly in isotropic and cubic systems.[3] However, no general treatment of $a_{ij,lm}$ and $b_{j,il,m}$ appears to have been given. In Refs. 4–8, they are treated (in mean-field theory) for a few cases of order parameters at $\vec{k}=0$, with a variational principle. Reference 6 also carries out RG calculations for several order-parameter forms at $\vec{k}=0$. In what follows, we will first give a general treatment of the $a_{ij,lm}$ and $b_{l,il,m}$ terms within the renormalization-group theory. Then we will give rigorous mean-field as well as RG results for the first case of an antiferrodistortive phase transition where such terms play an important role.

From the graphs shown in Fig. 1, to $O(\epsilon^2)$, one obtains the general RG equations for the nonzero terms in Eq. (3) as

$$a^s_{ij,pq} = a_{ij,pq} + \tfrac{1}{2}a^{-2}K_4 \ln s\,(b_{m,il,p}b_{m,jl,q} + b_{m,il,q}b_{m,jl,p} + \tfrac{1}{2}b_{m,il,t}b_{m,jl,t}\delta_{pq}), \tag{4}$$

$$b^s_{j,il,m} = (1+\tfrac{1}{2}\epsilon\ln s)\,b_{j,il,m} - \tfrac{1}{4}a^{-2}K_4\ln s\,(u_{rjtl}b_{r,it,m} - u_{rjti}b_{r,lt,m}), \tag{5}$$

and

$$u^s_{ijlm} = (1+\epsilon\ln s)\,u_{ijlm} - \tfrac{3}{2}u_{ijpq}u_{pqlm}a^{-2}K_4\ln s, \tag{6}$$

where $K_4=(8\pi^2)^{-1}=(2\pi)^{-d}\int d\Omega$ in $d=4$. Equations (4) and (5) are properly symmetric, but the last term in Eq. (6) must be symmetrized, e.g., by substitution in Eq. (3) and reading off of appropriate relations. The equations for r and a (from which one obtains η by requiring marginality) can also be given, but are of less interest here. One can then solve Eq. (6), then (5), and then (4).

From Eq. (4) and its extension to $O(\epsilon^3)$ one can show that $a_{ij,lm}$ is always irrelevant if $b_{j,il,m}$ is 0. This follows from the fact that spatially anisotropic terms can arise only from graphs with spatially anisotropic vertices. Then there are no $O(\epsilon^3)$ graphs contributing to $a_{ij,lm}$, and to second order in ϵ, it scales like $s^{-\eta}$, where $\eta<0$.

The specific case that we are considering, calcite, in the high-temperature, low-pressure phase has

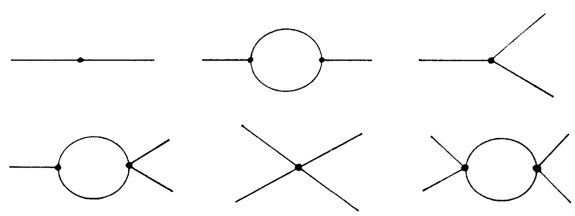

FIG. 1. Nonzero graphs contributing to Eqs. (4)–(6).

space-group symmetry $R\bar{3}c$, which changes to $P2_1/c$ on application of pressure at room temperature at about 14 kbar. X-ray data indicate that the transition is displacive, i.e., due to small shifts in the mean positions of the atoms. Furthermore, the pattern of shift can be matched to a zone-boundary soft mode[14] which transforms like the active irreducible representation of $R\bar{3}c$ denoted by $F\Gamma_2^-$ in the notation of Bradley and Cracknell.[15] None of the other active irreducible representations of $R\bar{3}c$ match the observed displacement.

With this, one finds that u_{ijlm} of Eq. (3) has the typical hypercubic form[2,3]

$$u_{ijlm}=\tfrac{1}{3}u(\delta_{ij}\delta_{lm}+\delta_{il}\delta_{jm}+\delta_{im}\delta_{jl})+v\delta_{ijlm}, \quad (7)$$

where δ_{ijlm} is 1 when $i=j=l=m$ and 0 otherwise. Substituting Eq. (7) into Eq. (6) one finds that the Heisenberg fixed point, with $u^*=6a^2\epsilon/(11K_4)$, $v^*=0$, is the only stable fixed point in the u-v plane.

From Ref. 1, we note that the coefficients $b_{j,il,m}$ correspond to occurrences of identity representations in $D^{(3E)}\times V$, where $D^{(3E)}$ is the nonsymmetric part of the third Kronecker power of D. Thus

$$b_{j,il,m}=-b_{j,li,m}=b_{i,jl,m}+b_{l,ij,m}$$

For $F\Gamma_2^-(R\bar{3}c)$ one finds one such invariant, which in a suitable basis leads to

$$b_{j,il,m}=ib\epsilon_{ijl}\epsilon_{imn}\delta_{nn}, \quad (8)$$

where b is a real parameter and ϵ_{ijl} is the completely antisymmetric tensor in three dimensions. Note that n is summed, but i is not, in Eq. (8).[16]

The general form for $a_{ij,lm}$, which transforms like $[D]^2\times[V]^2$, for the representation of interest in calcite can be written

$$a_{ij,lm}=\delta_{ij}(a_2\delta_{il}\delta_{im}+a_3\delta_{il}+a_3\delta_{im}+a_4), \quad (9)$$

where one supposes that $a_1=a$ in Eq. (3).

Unfortunately, it appears not to be possible to generalize the form of Eq. (8), found in $d=3$, to $d=4$, the form in which it appears in the ϵ expansion. This is a very real and significant problem with which one must deal, in general, any time that one studies anisotropic terms like $b_{j,il,m}$ and $a_{ij,lm}$ in the ϵ expansion. Here one does the best one can by applying the form of Eq. (5), obtained in $d=4$, to the $d=3$ forms. In essence, we assume a $d=4$ magnitude for $\vec{\kappa}$, but a $d=3$ angular dependence. When Eq. (8) is substituted into Eq. (5), with the use of Eq. (7), one finds that the parameter b satisfies

$$b^s=(1+\tfrac{1}{2}\epsilon\ln s)b-\tfrac{1}{4}a^{-2}K_4\ln s\, bu, \quad (10)$$

which leads to a scaling exponent of $4\epsilon/11$ around the Heisenberg fixed point. Thus b is a relevant parameter. On substitution of Eqs. (8)–(10) into Eq. (4), one easily sees that the a_i, $i=2$–4, of Eq. (9) are relevant about their fixed point of zero as well.

If we consider even the most general Gaussian propagator allowed by symmetry, i.e., we let the a_i of Eq. (9) be of $O(1)$, the results are not significantly changed. The "Heisenberg" fixed point may shift off the u axis, but is still stable in the u-v plane. The parameter b, when nonzero, again causes the fixed points to be unstable for any value of $a_{ij,lm}$. Thus, the transition is predicted to be first order. Details of this and other results reported here will be published elsewhere.

To interpret the meaning of the RG results we now look briefly at mean-field theory. We thus replace the free energy F of Eq. (1) by $H(c)$, also of Eq. (1), and then minimize this $H(c)$ with respect to c to obtain the minimum. Thus we require $\delta H/\delta c_i(\vec{\kappa})=0$, where $\delta/\delta c_i(\vec{\kappa})$ is the infinite volume limit of $\partial/\partial c_i(\vec{\kappa})$ and H is given by Eq. (3). Supposing, then, that solutions occur when $c_i(\vec{\kappa})=\sigma_i\delta(\vec{\kappa})$ leads to

$$r\sigma_i+\tfrac{1}{2}b_{ijl}\sigma_j\sigma_l+\tfrac{1}{6}u_{ijlm}\sigma_j\sigma_l\sigma_m=0. \quad (11)$$

For stability, or an absolute minimum, one requires that $\delta^2H/\delta c_i(\vec{\kappa})\delta c_j(\vec{\kappa}')$ be nonnegative definite. This condition will be satisfied if the Hermitian matrix

$$h_{ij}(\vec{\kappa})=(r+a\kappa^2)\delta_{ij}+a_{ij,l}\kappa_l+a_{ij,lm}\kappa_l\kappa_m+(b_{ijl}+b_{l,ij,m}\kappa_m)\sigma_l+\tfrac{1}{2}u_{ijlm}\sigma_l\sigma_m \quad (12)$$

has nonnegative eigenvalues for all $\vec{\kappa}$, $\kappa<\Lambda$, when the solutions of Eq. (11) are substituted for $\vec{\sigma}$. If the transition is to be continuous, even this more general form of the usual stability criteria requires that $a_{ij,l}$ and b_{ijl} vanish by symmetry. To keep the analysis of Eq. (12) tractable, we let $a_i=0$, $i=2$–4, in Eq. (9). There are two kinds of solutions to Eq. (11) for which $h(\vec{\kappa})$ will be positive semidefinite, namely, (a) $\vec{\sigma}\in\eta_1\langle 100\rangle$ and (b) $\vec{\sigma}\in\eta_3\langle 111\rangle$, where $\eta_1^2=-6r/(u+v)$ and $\eta_3^2=-6r/(3u+v)$. Another type of solution, $\eta_2\langle 110\rangle$, is not stable in Eq. (3). Examination of Eq. (12) shows that solutions (a) will be stable and associated with a continuous transition when

$$r<0, \quad u+v>0, \quad a>0, \quad \text{and} \quad v<3b^2/a, \quad (13a)$$

while solutions (b) will be stable when

$$r<0,\quad 3u+v>0,\quad v>0,\quad a>0,\ \text{and when}\ |u|<3b/a,\quad v>a(u-3b^2/a)^2/4b^2. \tag{13b}$$

In each set of conditions (13a) and (13b) the last condition was obtained from $\vec{\kappa}\neq 0$ parts of $h(\vec{\kappa})$ and are exact.

Since mean-field analysis predicts a continuous transition to a commensurate phase, while RG calculations indicate that such a transition must be first order, we predict a fluctuation-induced first-order commensurate phase transition for this system. However, the details of the stability calculation, combined with the RG results, Eq. (10), lead one to expect that the system may possess a continuous, incommensurate transition, as is seen in variational calculations in Refs. 4–8.

Many other systems possess nonzero $D^{(3E)}\times V$ invariants.[17] It is possible that a search for stable fixed points in such systems may yield new critical properties. Certainly such systems should be investigated experimentally and theoretically.

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[1]J. W. Felix and D. M. Hatch, to be published; J. W. Felix, "The Theory of Symmetry Breaking in Continuous Structural Phase Transitions," dissertation, Brigham Young University, 1984 (unpublished).

[2]D. M. Hatch and D. L. Decker, J. Chem. Phys. **74**, 2518 (1981).

[3]A. Aharony, in *Critical Phenomena and Phase Transitions,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, p. 357.

[4]T. A. Aslanyan and A. P. Levanyuk, Fiz. Tverd. Tela (Leningrad) **20**, 804 (1978) [Sov. Phys. Solid State **20**, 466 (1978)].

[5]E. B. Loginov, Kristallografiya **24**, 1109 (1979) [Sov. Phys. Crystallogr. **24**, 637 (1979)].

[6]A. L. Korzhenevskii, Zh. Eksp. Teor. Fiz. **81**, 1071 (1981) [Sov. Phys. JETP **54**, 568 (1981)].

[7]S. Alexander, R. M. Hornreich, and S. Shtrikman, in *Symmetries and Broken Symmetries in Condensed Matter Physics,* edited by N. Boccara (Institut pour le Développement de la Science, l'Education et le Technologie, Paris, 1981), p. 379.

[8]D. Blankschtein, E. Domany, and R. M. Hornreich, Phys. Rev. Lett. **49**, 1716 (1982).

[9]J. D. Barnett, Phys. Rev. B (to be published).

[10]D. L. Decker, private communication.

[11]R. A. Cowley and A. D. Bruce, J. Phys. C **11**, 3577 (1978).

[12]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1981).

[13]L. Michel, "Renormalization Group Fixed Points of General *n*-Vector Models" (to be published).

[14]D. M. Hatch and L. Merrill, Phys. Rev. B **23**, 3681 (1981).

[15]C. J. Bradley and A. P. Cracknell, *Mathematical Theory of Symmetry of Solids* (Oxford Univ. Press, London, 1972).

[16]Although here u_{ijlm} has the typical hypercubic form, the order parameter of $F\Gamma_2^-$ is not equivalent to a polar vector order parameter as in Ref. 8. This is manifested in the fact that our $b_{j,il,m}$ as given in Eq. (9) cannot be brought to the form of $b_{j,il,m}\sim(\delta_{im}\delta_{jl}-\delta_{lm}\delta_{ij})$, which is appropriate for the case of a polar vector.

[17]H. Stokes, private communication.