Lifshitz-Point Critical and Tricritical Behavior in Anisotropically Stressed Perovskites

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The antiferrodistortive phase transitions of some perovskite crystals, driven first order by strongly cubic order-parameter fluctuations, are shown to become continuous at finite anisotropic stresses favoring ordering of one order-parameter component. The associated critical and tricritical behavior will be that of one of a spectrum of uniaxial Lifshitz systems, its precise character reflecting the form of the anisotropy in the soft-mode dispersion. Our predictions are in substantial accord with recent experiments on $RbCaF_3$.

In a recent paper Domany, Mukamel, and Fisher[1] considered a variety of systems whose phase transitions, continuous within mean-field theory, are driven *first order* by *critical fluctuations.* They showed that, in certain cases, a continuous phase transition can be reestablished by inducing an appropriate *anisotropy,* which lowers the effective number n of components of the order parameter. In this Letter we show that particularly striking realizations of this process are to be found among those perovskite crystals (e.g., $KMnF_3$,[2] $RbCaF_3$,[3] $KCaF_3$,[4]...) which undergo a weakly first-order cubic-to-tetragonal phase transition, associated with the instability of an $n=3$-fold degenerate R_{25} (zone boundary) mode. The symmetry-breaking mechanism is realized as an appropriate anisotropic stress which lifts the degeneracy of the R_{25} mode, and promotes a phase transition whose effective order-parameter dimensionality is $n=1$. The particular richness of the associated phenomena resides in the *strongly cubic* character of the order-parameter fluctuations in these systems, as a result of which the *tricritical point* they will exhibit, at a critical value of the stress, and the *continuous phase transition,* occurring for larger stresses, should be those of a *uniaxial Lifshitz system.*[5] The associated exponents are quite different from those of the simple $d=3$, $n=1$ (Ising) system. In particular, expansion techniques[6] yield for the tricritical Lifshitz order-parameter exponent β_t a value in the range $\frac{1}{8}$ to $\frac{1}{6}$, in marked contrast to the Ising tricritical value $\beta_t=\frac{1}{4}$, and in good accord with recent measurements on anisotropically stressed $RbCaF_3$,[7] suggesting that anisotropically stressed perovskites may prove to be the first clear realizations of Lifshitz-type behavior.

Our analysis is based upon the $n=d$-dimensional Ginzburg-Landau-Wilson effective Hamiltonian of cubic symmetry,[8,9]

$$\mathcal{H}=\frac{1}{2}\sum_{\alpha=1}^{n}\int_{\vec{q}}U_{2,\alpha}(\vec{q})Q_\alpha(\vec{q})Q_\alpha(-\vec{q})+\sum_{\alpha,\beta=1}^{n}(u+v\delta_{\alpha\beta})\int_{\vec{q}_1}\int_{\vec{q}_2}\int_{\vec{q}_3}Q_\alpha(\vec{q}_1)Q_\alpha(\vec{q}_2)Q_\beta(\vec{q}_3)Q_\beta(-\vec{q}_1-\vec{q}_2-\vec{q}_3), \quad (1)$$

where $\int_{\vec{q}}\equiv(2\pi)^{-d}\int d^dq$ over the range $0<|\vec{q}|<\Lambda$. The strongly cubic character of the order-parameter fluctuations, manifested in the distinctive diffuse x-ray scattering streaks[10] observed in the perovskites cited above, is expressed in the coefficient $U_{2,\alpha}(\vec{q})$, describing the dispersion of the soft-mode branch associated with rotations of the perovskite octahedra about the α axis[11]:

$$U_{2,\alpha}(\vec{q})=r_\alpha+q_{\perp,\alpha}{}^2+aq_\alpha{}^{2L}, \quad (2)$$

with $r_\alpha=A(T-T_0)$, and $q_{\perp,\alpha}{}^2\equiv q^2-q_\alpha{}^2$. The extreme flatness[12] of the dispersion of the αth branch, along the α axis of reciprocal space, is reflected in the typically very small values of a [close to 0.01 for both $KMnF_3$ (Ref. 13) and $RbCaF_3$ (Ref. 14)] yielded by fitting the form (2)[11,15] to inelastic neutron-scattering data, with the *assumption* that the dispersion is predominantly *quadratic* in q_α (i.e., that $L=1$). However, it is quite conceivable that the dispersion is better modeled by the form (2) with a larger value of L—the results of experiments[7] on $RbCaF_3$ are immediately comprehensible if this is the case—and so we shall carry out our analysis for general $L\geq 2$.[16]

The critical behavior is exposed by a renormalization-group treatment, taking careful account of the parameter a which, in the language of Fisher,[17] constitutes a "dangerous irrelevant" variable: momentum-space integrals of the form

$\int_{\vec{q}}[U_{2,\alpha}(\vec{q})]^{-2}$ diverge (for r_α, $a\to 0$) as $a^{(d-5)/2}$, and one must construct recursion relations for the scaled variables $\tilde{u}\equiv ua^{(d-5)/2}$, $\tilde{v}\equiv va^{(d-5)/2}$. At leading order the results may be written in differential form, as

$$d\tilde{u}/dl = L\epsilon_c\tilde{u} - 4B[(n+4)\tilde{u}^2 + 6\tilde{u}\tilde{v}] + \dots, \qquad (3)$$

$$d\tilde{v}/dl = L\epsilon_c\tilde{v} - 4B(2\tilde{u}+3\tilde{v})^2 + \dots, \qquad (4)$$

where B is a constant, e^l is the renormalization-group rescaling factor, $\epsilon_c \equiv d_c - d$, and $d_c \equiv 5 - 1/L$ is the critical dimensionality for the problem. These equations have *no stable fixed point* for $n = d$, implying[18] a first-order transition, in accord with previous analyses[19,20] of the Hamiltonian (1), in the specific case $L=1$. The first-order character of the transition originates in the strongly anisotropic fluctuations, under whose influence the lines of Hamiltonian flow are driven into a regime [of large negative $v(l)$: cf. Eq. (4)] where the mean-field stability criterion $u(l)+v(l)>0$ is violated.[20,21] This behavior contrasts with that expected in systems (such as $SrTiO_3$) where the anisotropy is less pronounced,[22] producing only a very slowly decaying correction[8,19,20] to an $n=d$-component Heisenberg fixed-point behavior.

Consider now the effect of an applied stress, which couples through the elastic coordinates to the order-parameter degrees of freedom: A tensile uniaxial stress along the direction [100] (or, equivalently a compressive biaxial stress along [010] and [001]) lifts the degeneracy of the soft mode, making $r_1 < r_2 = r_3$ [Eq. (2)], and thus favoring fluctuations of the coordinates $Q_1(\vec{q})$ describing rotations of octahedra about the [100] axis.[23] For sufficiently large stresses ($r_1 \ll r_2$) the effects of the noncritical fluctuations (about the remaining axes) may be treated within perturbation theory[1,24]: their role is simply to dress the interactions among the critical coordinates $Q_1(\vec{q})$. The critical behavior of the system is then described by the $n=1$-component effective Hamiltonian

$$\mathcal{H} = \tfrac{1}{2}\int_{\vec{q}}(r_{\rm eff} + q_{\perp,1}^2 + aq_1^{2L})Q_1(\vec{q})Q_1(-\vec{q}) + u_{\rm eff}\int_{\vec{q}_1}\int_{\vec{q}_2}\int_{\vec{q}_3}Q_1(\vec{q}_1)Q_1(\vec{q}_2)Q_1(\vec{q}_3)Q_1(-\vec{q}_1-\vec{q}_2-\vec{q}_3) + O(Q_1^6), \qquad (5)$$

where the effective coupling constant $u_{\rm eff}$ is given by[1]

$$u_{\rm eff} \approx u + v - 8u^2\int_{\vec{q}}[U_{2,2}(\vec{q})]^{-2}, \qquad (6)$$

while its rescaled counterpart $\tilde{u}_{\rm eff} \equiv u_{\rm eff}a^{(d-5)/2}$ evolves, under the renormalization group, according to the single recursion relation to which Eqs. (3) and (4) reduce when $n=1$,

$$d\tilde{u}_{\rm eff}/dl = L\epsilon_c\tilde{u}_{\rm eff} - 36B\tilde{u}_{\rm eff}^2. \qquad (7)$$

Since the integral in Eq. (6) is a monotonically decreasing function of the mass r_2, and thence of the applied stress, the effective coupling constant $u_{\rm eff}$ will necessarily be positive at large stresses (we assume that the combination of bare coupling constants $u+v$ is positive[25]). Thus, for appropriate[26] large stresses the system will exhibit a continuous phase transition characterized by the single stable fixed point of (7), to which the lines of Hamiltonian flow have access when $\tilde{u}_{\rm eff}>0$. This fixed point will be of the uniaxial Lifshitz type with critical exponents whose expansions[5,6] in ϵ_c may be recovered from (7) (together with the linearized recursion relation for $\tilde{r}_{\rm eff} = r_{\rm eff}/a$). Specifically,

$$\beta_c = \tfrac{1}{2} - \tfrac{1}{6}\epsilon_c + O(\epsilon_c^2) = \frac{1}{2[1+\frac{1}{3}\epsilon_c]} + O(\epsilon_c^2). \qquad (8)$$

In the case of the simplest Lifshitz point[5] (for which $L=2$) extrapolation of the expressions (8) to $d=3$ (where $\epsilon_c = \frac{3}{2}$) yields values for β_c of $\frac{1}{4}$ or $\frac{1}{3}$, the difference reflecting the ambiguities inherent in all such expansions. For Lifshitz points of higher order ($L>2$) β_c will be even smaller, coinciding in the limit $L\to\infty$ with the $d=2$ Ising value $\beta_c = \frac{1}{8}$.[27]

For vanishing stress, then, the phase transition is first order; for large anisotropic stresses it is continuous, and characterized by an ordinary Lifshitz critical point. There will therefore exist a particular stress at which the transition becomes continuous: This stress thus locates a *tricritical Lifshitz point.* The borderline dimensionality in this case is $d_t = 4 - 1/L$, and expansions in $\epsilon_t \equiv d_t - d$ give[6]

$$\beta_t = \tfrac{1}{4} - \tfrac{1}{4}\epsilon_t + O(\epsilon_t^2) = \frac{1}{4(1+\epsilon_t)} + O(\epsilon_t^2). \qquad (9)$$

For the case $L=2$, extrapolation to $d=3$ (when $\epsilon_t = \frac{1}{2}$) gives $\beta_t = \frac{1}{8}$ or $\frac{1}{6}$. For large L, β_t will approach the $d=2$ tricritical Ising value $\beta_t \approx 0.04$.[28]

The value $\beta_t \approx \frac{1}{6}$ observed[7] in $RbCaF_3$ is in good accord with the $L=2$ tricritical Lifshitz result, although other interpretations of this observation are possible. A Lifshitz behavior of still higher order ($L>2$) cannot be ruled out, but seems less likely *a priori.* Alternatively, the value of β_t observed might reflect the intermediate behavior expected for a system exhibiting a crossover from a two-dimensional to a three-dimensional tricritical fixed point: Such a crossover would arise if the dispersion (2) is characterized by a *small* but still *dominant* term, *quadratic* in q_α ($L=1$, $a \ll 1$). However, the observations give no hint of crossover, suggesting that the behavior is dominated by a *single* fixed point, for which the $L=2$ uniaxial Lifshitz tricritical point seems the most plausible candidate. Nevertheless, this issue will be convincingly resolved only once the form of the soft phonon dispersion, in the relevant materials, is known with greater accuracy —a challenge to inelastic neutron and diffuse x-ray scattering techniques.

In summary, we have shown that a class of perovskite crystals should not only display the anisotropy-induced tricritical point predicted by Domany, Mukamel, and Fisher,[1] but also a variety of hitherto unobserved Lifshitz multicritical points.

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[25]It is in principle possible that this combination is in fact negative, and that the stress-induced tricritical point observed in $RbCaF_3$ (Ref. 7) actually reflects the pressure renormalization of the coupling parameters, through, e.g., the pressure dependence of elastic constants [ignored in Eq. (6)]. We consider this unlikely, since the phase transition in an unstressed system with $u+v \leq 0$ and with the degree of dispersion anisotropy characterizing $RbCaF_3$ would, according to Nattermann (Ref. 20), have a much more strongly first-order character than that observed. An experiment demonstrating the absence of a tricritical point in $RbCaF_3$ under *isotropic* stresses comparable with those employed in Ref. 7 would serve to substantiate this view.

[26]Under an anisotropic stress which leaves two critical components of the order parameter (e.g., a [100] compression) the phase transition will remain first order [for sufficiently anisotropic dispersion, (2)] since Eqs. (3) and (4) have no stable fixed point for $n=2$.

[27]Note that $d=3$ is rather far away from $d_c=4.5$, and so the estimates for β_c are quite ambiguous. Although expansions about the lower critical dimensionality d_l exist for $n>2$, when $d_l=2.5$ [G. S. Grest and J. Sak, Phys. Rev. B 17, 3607 (1978)], these are of no use for $n=1$. Similarly, $1/n$ expansions are also not expected to be of much help.

The main point to be stressed is that β_c for the Lifshitz point is farther away from the mean-field value, and therefore smaller, than its usual critical counterpart. A similar statement refers to the tricritical exponent β_t. We hope that this Letter will stimulate better numerical calculations of these exponents.

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Tricritical Behavior in Uniaxially Stressed $RbCaF_3$

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We have investigated the $O_h{}^1$ to $D_{4h}{}^{18}$ structural phase transition in $RbCaF_3$ under near-[100] stress σ, by monitoring the electron-paramagnetic resonance lines of Gd^{3+} ($S=\frac{7}{2}$) on a Ca^{2+} site. We find that the first-order transition at zero stress becomes second order at $\sigma_t = 1.9 \pm 0.3$ kg/mm^2 and $T_t = 195.3 \pm 0.1$ K. At this tricritical point, and up to $\sigma = 4.8 \pm 0.3$ kg/mm^2, the exponent of the temperature dependence of the rotational order parameter is $\beta = 0.18 \pm 0.02$.

The renormalization-group theory[1,2] has recently been used to investigate the topology of phase diagrams near complex multicritical points.[3] In structural phase transitions (SPT) such multicritical points result on application of external stresses.[4] Bicritical and tetracritical behavior is seen or predicted under uniaxial stresses σ if the transition is of second order at $\sigma = 0$. The prototypes of the latter topological variety are $SrTiO_3$ and $LaAlO_3$, which are of second order.[5] Other known transitions of the $SrTiO_3$-type $O_h{}^1$ to $D_{4h}{}^{18}$ are of first order as in $KMnF_3$ (Ref. 6) and $RbCaF_3$.[7] In these two crystals the dispersion of the soft antiferrodistortive R_{25} mode is flat and nearly the same from the R towards the M point of the Brillouin zone with $\alpha = \partial^2\omega_R{}^2/\partial q^2 \simeq 0.013 \pm 0.09$ as discussed by Rousseau, Nouet, and Almairac.[8] The discontinuities of the order parameter measured in these two cases are relatively small, i.e., the transition is almost second order. Thus, it has been conjectured[9] that such transitions are forced to become first order only, due to critical cubic fluctuations, the mean-field theory predicting a second-order transition. However, for fluctuation-induced first-order transitions to occur, α has to be quite small because $SrTiO_3$ is second order with $\alpha \simeq 0.036 \pm 0.012$.[8]

Recently Domany, Mukamel, and Fisher[10] derived theoretically that fluctuation-induced first-order transitions may be restored to a continuous transition on application of a symmetry-breaking uniaxial field. In this Letter we report on the first successful experiment bearing on this effect in a SPT. However, in contrast to magnetic cases[11] with isotropic dispersion, in the present case of $RbCaF_3$ with $\alpha = 0$ the situation is more complicated due to possible Lifshitz behavior.[12] Aharony and Bruce[13] (AB) have investigated the properties of an anisotropic cubic Hamiltonian with $\alpha \approx 0$ in detail. In our case of a tetragonal stable phase for $T < T_c$ at $\sigma = 0$, AB found that one can only reach a tricritical point if the symmetry-breaking stress induces a one-dimensional order parameter ($n = 1$). The system will then show Lifshitz tricritical $n = 1$ character if α is sufficiently close to 0, otherwise normal tricritical character. Our experiments cannot decide between the two.

Electron paramagnetic resonance (EPR) is known to be one of the most sensitive methods of investigating the order parameter in SPT. Thus,

