but are interrupted by the spatial disorder of the lattice and are "frozen in" at the ordering temperature with some finite mean correlation length, thus preventing the wavelength-dependent susceptibility from diverging.[6] These frozen-in fluctuations must in some manner be stabilized by the rare-earth–iron interaction, since in the absence of a magnetic rare earth the fluctuations are of much shorter range and never spontaneously order. We are undertaking experiments on other rare-earth–iron compositions to corroborate this model for the amorphous magnetic transition and determine whether the exchange or crystal field interactions are predominantly responsible for the anomalous behavior.

We are grateful for helpful discussions on these results with Dr. J. Cullen and Dr. A. Clark. The samples were fabricated by Battelle Northwest under ARPA support.

†Work supported by the Naval Ordnance Laboratory Independent Research Fund, Office of Naval Research, and Naval Air Systems Command.

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Polycritical Points and Floplike Displacive Transitions in Perovskites

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(Received 29 April 1974)

The critical behavior occurring at displacive phase transitions in anisotropically stressed perovskite crystals is examined. It is shown that, under various conditions, the asymptotic critical behavior may be of Ising, XY-model, or Heisenberg type. The existence of a "spin-flop"-like transition (at zero stress) between two differently ordered phases is predicted. An explanation of the discrepancy between the measured exponents and those predicted theoretically is proposed, and several new experiments are suggested.

It is well known that stressed crystals undergoing displacive phase transitions exhibit phase diagrams with interesting complexities.[1,2] In this Letter we show that, under different stress conditions, perovskite crystals may display a variety of types of critical behavior, including *tricritical and bicritical points, crossover phenomena,* and *floplike transitions* of the type proposed recently for anisotropic antiferromagnets.[3,4] The analysis raises the interesting possibility that the discrepancy between recent theoretical predictions[5-7] and measurements of the critical exponents characterizing the structural transitions in the perovskites $SrTiO_3$ and $LaAlO_3$[8] arises through the existence of systematic residual strains in the crystals studied. We show that these (conjectured) strains precipitate a crossover from the Heisenberg-like (or cubiclike) behavior, previously predicted,[5-7] to an Ising-like behavior. We use scaling theory to study this crossover, and propose several experiments which should elucidate the situation.

Our conclusions are based on an analysis of an effective Hamiltonian that is a natural extension of the Landau-type potential used in previous mean-field investigations of the 105°K phase transition in $SrTiO_3$.[2,9] The Hamiltonian embodies a coupling between the local rotational coordinates of the characteristic perovskite octahedra, $Q_\alpha(\vec{x})$ ($\alpha = 1, 2, 3$), in which the primary ordering occurs, and the elastic strain coordinates $e_i(\vec{x})$ ($i = 1, \ldots, 6$ in the Voigt notation). Allowing for an applied stress T_i ($i = 1, \ldots,$

6), we have[10]

$$\mathcal{H}=\int d^3x\{\tfrac{1}{2}[r_0\vec{Q}^2+(\nabla\cdot\vec{Q})^2]+u_0\vec{Q}^4+v_0\sum_{\alpha=1}^{3}Q_\alpha{}^4+\tfrac{1}{2}C_{11}\sum_{\alpha=1}^{3}e_\alpha{}^2+C_{12}\sum_{\alpha<\beta}e_\alpha e_\beta+\tfrac{1}{2}C_{44}\sum_{\alpha=4}^{6}e_\alpha{}^2-\sum_{\alpha=1}^{6}e_\alpha T_\alpha$$
$$-B_1\sum_{\alpha=1}^{3}e_\alpha Q_\alpha{}^2-B_2[e_1(Q_2{}^2+Q_3{}^2)+e_2(Q_1{}^2+Q_3{}^2)+e_3(Q_1{}^2+Q_2{}^2)]$$
$$-B_3(e_4Q_2Q_3+e_5Q_1Q_3+e_6Q_1Q_2)\}, \qquad (1)$$

where r_0 is proportional to $T-T_0$,[10] while the remaining coupling constants are assumed to depend only weakly upon temperature and pressure. The C_{ij} are to be regarded as "bare" elastic constants, appropriate in the absence of any coupling to the fluctuations in the Q_α. The effects of such fluctuations are represented by the term $[\nabla\cdot\vec{Q}(\vec{x})]^2$; terms of the form $[\nabla e_i(\vec{x})]^2$ have not been included in (1), however, since it is believed that they are irrelevant (in the renormalization-group sense),[11] so that the only source of divergent fluctuations in the strains lies in their coupling to the coordinates Q_α. In the absence of such terms the strain coordinates may be integrated out of the partition function defined by the Hamiltonian (1), yielding a reduced Hamiltonian of the form[12]

$$\bar{\mathcal{H}}=\int d^3x\{\tfrac{1}{2}[r_0\vec{Q}^2+(\nabla\cdot\vec{Q})^2]+\bar{u}_0\vec{Q}^4+\bar{v}_0\sum_{\alpha=1}^{3}Q_\alpha{}^4$$
$$-\sum_{\alpha=1}^{3}T_\alpha[(L_1-L_2)Q_\alpha{}^2+L_2\vec{Q}^2]-L_3(Q_1Q_2T_6+Q_2Q_3T_4+Q_3Q_1T_5)\}, \qquad (2)$$

where the new parameters are completely defined in terms of the parameters of the original Hamiltonian.

The primary effect of an *isotropic stress* ($T_i=-p$; $i=1,2,3$) is merely to renormalize the parameter r_0, and hence the transition temperature. In addition, however, although the symmetry of the Hamiltonian (2) remains the same as that of the stress-free crystal, an isotropic stress may lead to a change in the critical behavior, through the pressure dependence of the elastic constants which leads, in turn, to a pressure dependence of $\bar{u}_0$ and $\bar{v}_0$ in (2). A renormalization-group analysis shows that,[6] for $\bar{v}_0$ greater than some critical value v_c,[13] a second-order Heisenberg-like transition is to be expected[14]; for $\bar{v}_0=v_c$ one finds a cubiclike tricritical behavior; while for $\bar{v}_0<v_c$ a divergence of the renormalization-group equations is indicative of a first-order transition.[6] Note that the crossover exponent φ_c from the cubic tricritical behavior to the Heisenberg-like critical behavior is very small[6]; thus, cubic corrections to the Heisenberg scaling behavior may persist very close to the critical point.[15]

The application of an *anisotropic stress* leads, through Eq. (2), to a Hamiltonian with a *different symmetry* from that of the stress-free crystal; the changes in the critical behavior are striking. For *a stress along the* [100] *axis*, $T_i=-p\delta_{i1}$, the Hamiltonian (2) becomes

$$\bar{\mathcal{H}}^{[100]}=\int d^3x\{\tfrac{1}{2}[r_1Q_1{}^2+r_2(Q_2{}^2+Q_3{}^2)+(\nabla\cdot\vec{Q})^2]+\bar{u}_0\vec{Q}^4+\bar{v}_0\sum_{\alpha=1}^{3}Q_\alpha{}^4\}, \qquad (3)$$

with $r_1=r_0+2pL_1$ and $r_2=r_0+2pL_2$. Thus, the effects of such a stress are similar to those of an anisotropic exchange in magnetic systems. The latter have recently been extensively investigated, using renormalization-group and series-expansion techniques[16]; we thus use the results of these investigations in what follows.

Certain aspects of the p-T phase diagram for the Hamiltonian (3) depend upon the parameters in (3). We discuss first the case of $SrTiO_3$ (see Fig. 1), where studies of anharmonic properties have shown[17] that L_1 is positive, L_2 is negative, and $\bar{v}_0$ is small and negative (but $\bar{v}_0\gtrsim v_c$, since the transition seems to be of second order[18]). Thus, for $p<0$ we have $r_1<r_2$, so that the asymtotic critical behavior is dominated by the terms in (3) involving only Q_1. The transition is therefore Ising like, into a tetragonal phase with an ordering along [100]. For $p>0$ the critical behavior is XY-like, with an ordering perpendicular to the [100] direction. The ordered state asymptotically close to $T_c(p)$ has rotational invariance in the (100) plane; for finite $T_c(p)-T$, however, cubic corrections to scaling, associated with $\bar{v}_0$, will lead to predominantly [010] or [001] ordering.

The line $p=0$, separating the two ordered phases, locates a first-order phase boundary, at which the pseudospin order parameter $\langle\vec{Q}\rangle$ *flops* from the [100] direction to the (100) plane. This is strongly analogous to the spin-flop tran-

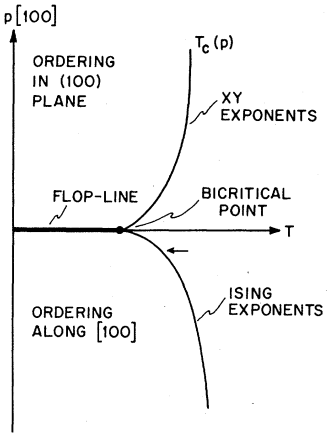

FIG. 1. Schematic phase diagram for a perovskite with a [100] stress, assuming $v_c < \bar{v}_0 < 0$ ($SrTiO_3$). The arrow locates qualitatively what we conjecture to be the position of the observed transition in monodomain $SrTiO_3$.

sition found in uniaxially anisotropic antiferromagnets.[3] The flop line terminates at $T = T_c(p = 0)$, in a *bicritical* point.[3,4]

The crossover (from Heisenberg to Ising or XY behavior), expected in the vicinity of the bicritical point, is displayed in the scaling form of the free energy, given by a renormalization-group analysis as[3,16]

$$G(T,p) \approx |t|^{2-\alpha_H} f(\hat{p}/|t|^{\varphi}). \quad (4)$$

Here we have introduced $t \equiv [T - T_c(p=0)]/k_B T$, and $\hat{p} \equiv p/k_B T$, while α_H is the Heisenberg specific-heat exponent ($\simeq -0.10$)[19] and φ the crossover exponent ($\simeq 1.25$).[16] Following Fisher and Nelson[3] we conclude the following from (4): (a) At the flop line ($p = 0$, $t < 0$) the thermodynamic conjugate to $T_1 = -p$, namely, the elastic strain e_1, exhibits a discontinuity which varies with t as $\Delta e_1 \sim |t|^{\tilde{\beta}}$, with $\tilde{\beta} = 2 - \alpha - \varphi \simeq 0.85$. (b) The components of the elastic compliance diverge, for $p = 0$, as $|t|^{-\tilde{\gamma}}$, with $\tilde{\gamma} = 2\varphi + \alpha - 2$ ($\simeq 0.4$). (c) At $t = 0$, $\hat{p} \sim |e_1|^{\tilde{\delta}}$, where $\tilde{\delta} \equiv \varphi/\tilde{\beta}$ ($\simeq 1.47$). (d) The phase boundary lines near the bicritical point vary as $\hat{p}(t) \approx \pm w_{\pm} t^{\varphi}$, where $w_{\pm}$ are constants.

To our knowledge, none of the experiments suggested by (a)–(d) has been performed, although investigations of the ultrasonic properties of $SrTiO_3$ have succeeded in demonstrating the existence of critical anomalies (in addition to the discontinuities expected from mean-field theory[9]) in the elastic constants.[20] Note that, in contrast to the system discussed in Ref. 3, the symmetry of our problem enables us to identify the scaling field causing the crossover as being purely the pressure $\hat{p}$: This should make experimental verification of the above predictions easier.

The nature of the XY-like transition ($p > 0$), and the resulting ordered state, may change with the value of $\bar{v}_0$: For $\bar{v}_0 < v_c$, we expect the transition to be of first order, into a tetragonal phase, with $\vec{Q}$ along [010] or [001]. For $\bar{v}_0 > 0$, as is appropriate in $LaAlO_3$,[9] the transition remains of second order, and the cubic corrections to scaling lead to an ordering along [011]. In this case, when the ordering tendency of $\bar{v}_0$ and of the applied stress are in competition, a further decrease in temperature may lead to additional phase transitions.

A similar analysis has also been applied for the case of a [111] stress, with similar results. For $SrTiO_3$ ($\bar{v}_0 < 0$), further first-order transitions may occur, as described above and as observed in Ref. 1. Such situations require further investigation.

We now turn to review the existing experimental results on the critical behavior of $SrTiO_3$. A striking feature of the EPR experiments[8] (regarded as the most accurate measurements of the critical exponents) is that, in the interests of accuracy, they were performed on samples shaped in such a way as to transform into a *monodomain* low-temperature phase.[8] Moreover, subsequent experiments on these samples have clearly demonstrated a strong *anisotropy* in the order-parameter fluctuations above T_c, these fluctuations being preferentially about the ordering axes of the monodomain sample.[21] We interject the remark that this anisotropy, which clearly shows the presence of an "orienting mechanism"[21] that breaks the cubic symmetry, is to be distinguished from the *cubic* anisotropic terms omitted from (1), but discussed elsewhere,[5,7] which give rise to "pancakelike" anisotropy in the correlations: *This* anisotropy should *not* affect the asymptotic critical behavior.[7] Although the existence of an "orienting" mechanism in these samples has been recognized,[21] the implications for the critical behavior have, to our knowledge, not been examined. In the light of the above analysis we conjecture that this mechanism is simply a systematic strain field which breaks the cubic symmetry, as discussed above, and leads to a *crossover* from the purely Heisenberg critical behavior expected for a strain-free sample to an *Ising-like behavior*, as indicated in Fig. 1.[22] We note that the experimental value[8] of $\beta = 0.33 \pm 0.02$ is quite consistent with this suggestion since we

must presume that the experiments were performed in the crossover region, in which the effective value of β changes from its Heisenberg value, $\beta_H \simeq 0.37$, to that appropriate for the Ising system, $\beta_I \simeq 0.31$.[19] A partial experimental check of this conjecture would be provided by a measurement of the exponent β in samples subjected to an external stress. Application of the appropriate stress (e.g., a tensile stress along [100] or, equivalently, a biaxial stress along [010] and [001] in $SrTiO_3$) should reveal that the asymptotic exponents are truly of Ising type in this situation. In addition, specific-heat experiments on such stressed samples should reveal a divergence ($\alpha_I \simeq 0.125$[19]) in contrast to the behavior of well annealed crystals (that transform into a polydomain) for which a cusp is to be expected ($\alpha_H \simeq -0.10$).[23] Finally, experiments to test the predictions (a)–(d), discussed above, would also provide a check on the overall picture that we have proposed.

The authors have benefited from stimulating discussions with D. R. Nelson and with Professor M. E. Fisher. Support by the National Science Foundation, in part through the Materials Science Center at Cornell University, a Fulbright-Hays scholarship (A.A.), and a British Science Research Council research fellowship (A.D.B.) are also acknowledged.

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[10]For a discussion of the Hamiltonian (1) see Ref. 5, in which, however, the coupling to elastic strain was ignored.

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[12]Here we have ignored the effects of the free surfaces of the sample; a similar procedure has been used, for an Ising system, by A. Aharony [Phys. Rev. B 8, 4314 (1973)]. Such effects were found in Ref. 11 to lead ultimately to a first-order transition. However, experiments suggest that the first-order character of such transitions may be quite small (C. W. Garland, private communication).

[13]The critical value v_c may depend on all the parameters in the system Hamiltonian.

[14]Expansions in $\epsilon = 4 - d$ and a Padé analysis indicate (A. Aharony, unpublished) that the n-component Heisenberg-type fixed point is stable against a cubic perturbation for $n < n_c = 4 - 2\epsilon + 2.59\epsilon^2 + O(\epsilon^3) \simeq 3.13$, and hence for $n = 3$.

[15]This results in interesting values of several tricritical exponents: A. Aharony, paper presented at the Conference on Critical Phenomena in Multicomponent Systems, Athens, Georgia, 15–17 April 1974 (unpublished).

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