$\Delta V_F^{stat})_{max} = 10^{-2}$ at 0°K. Silver and copper exhibit one of the smallest effects: about one-third of that for lithium.

Considering the fact that the uncertainty in the most precise measurement[5,6] of ΔV is $\sim 10^{-2}$, the contribution of both zero-point and thermal vibrations to the usual LS-calculated vacancy formation volume is indeed negligible. Thus, the usual formulation of LS suffices for the calculation of the vacancy formation volume at all temperatures.

The authors wish to express their deepest thanks to Dr. Roger Taylor of the Physics Division, National Research Council of Canada, for many helpful discussions and exchanges of scientific materials.

*Supported by the Centre National de la Recherche Scientifique, France.

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Trigonal-to-Tetragonal Transition in Stressed $SrTiO_3$: A Realization of the Three-State Potts Model

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(Received 18 October 1976)

The trigonal-to-pseudotetragonal structural first-order transition in [111]-stressed $SrTiO_3$ is shown to be a realization of the continuous three-state Potts model. The measured order-parameter discontinuity at the transition, $\langle \Delta \vec{\varphi} \rangle$, depends on the trigonal order parameter $\langle \varphi_{[111]} \rangle \propto M$ as $|\langle \Delta \vec{\varphi} \rangle| \propto |M|^{\delta^*}$, with $\delta^* = 0.62 \pm 0.10$ (mean-field theory predicts $\delta^* = 1$). This agrees with renormalization-group predictions, and proves that the model has a first-order transition even in the fluctuation-dominated region.

Multicritical points in stressed perovskite crystals undergoing displacive phase transitions have been the subject of much recent interest.[1-4] It has been shown[4] that stress p along the [100] axis leads to a bicritical point[5] in $SrTiO_3$[3] and to a tetracritical point in $LaAlO_3$. Stress p along the [111] diagonal in $SrTiO_3$ leads to a rather more complicated phase diagram, studied both experimentally and using mean-field theory in Refs. 1, 2, and 4 and shown in Fig. 1. At constant stress p (> 0), one first observes a second-order transition from the "pseudocubic" phase into a trigonal phase at temperature $T_1(p)$, and then, at $T_2(p)$, a first-order transition into a "pseudotetragonal" phase. For $p < 0$ there is a direct second-order pseudocubic-to-pseudotetragonal transition. The point $p = 0$, $T = T_1(0) = T_2(0)$ is thus bicritical.[4] However, it is not identical to the one discussed in Refs. 3 and 5. A renormalization-group study of this phase diagram showed[4] that the transition at $T_1(p)$ is Ising-like, while that at $T_1(0) = T_2(0)$

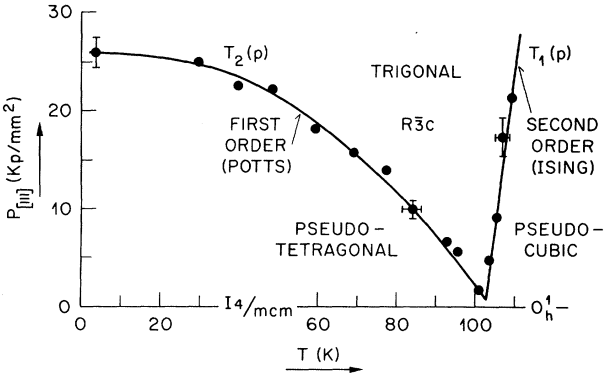

FIG. 1. Experimental phase diagram of $SrTiO_3$ for stress along the [111] diagonal, from Ref. 1.

is Heisenberg-like.[3] The former prediction is experimentally verified in the present work. However, the nature of transition at $T_2(p)$, when *critical fluctuations* are taken into account, remained unclear.

Following a recent idea by Mukamel, Fisher, and Domany,[6] who discussed the behavior of cubic ferromagnets in a magnetic field, we point out in this Letter that *the transition at $T_2(p)$ is actually described by the continuous version of the three-state Potts model.*[7] In the trigonal phase, the rotational order-parameter vector $\vec{\varphi}$ is along the [111] diagonal. However, the cubic symmetry of $SrTiO_3$ is such that ordering along cubic axes (e.g., [100]) is preferred. As the stress is lowered, one reaches a transition in which the components of the order parameter perpendicular to [111] order. In this (111) plane there is now a three-fold symmetry, corresponding to projections of the three $p=0$ preferred directions [100], [010], and [001]. This is exactly the Potts symmetry.[6,7] The magnitude of the coefficient of this symmetry-breaking term in the reduced Hamiltonian, w, is proportional both to the cubic anisotropy coefficient, v, and to the trigonal order parameter at $T_2(p)$, $\langle\varphi_{[111]}\rangle \propto M$. Thus, varying p along $T_2(p)$ allows us to vary M, and study the Potts transition at different values of w.

The order of the three-state Potts-model transition has been the subject of much dispute. Mean-field theory always predicts a first-order transition.[8] Series expansions[8] and exact results[9] at $d=2$ show that critical fluctuations make the transition continuous. Series at $d=3$ are inconclusive.[10,11] Renormalization-group studies, both using the approximate recursion relations[12] at $d=3$ and the exact ones at $d=4-\epsilon$,[13] indicate a first-order transition for any $w\neq 0$. Moreover, these studies also show that for small w the transition is not properly described by mean-field theory! Critical fluctuations due to the almost second-order XY-model transition (occurring at $w=0$) modify the mean-field behavior. For example, the order-parameter discontinuity $|\langle\Delta\vec{\varphi}\rangle|$ at the transition is given by $|\langle\Delta\vec{\varphi}\rangle| \propto |w|^{\delta^*} \propto |M|^{\delta^*}$, where $\delta^* \simeq 0.56$[12] or $\delta^* = 1 - \frac{2}{5}\epsilon + O(\epsilon^3)$ ($\simeq 0.6$ at $\epsilon = 1$).[13] These values are quite distinct from the mean-field result $\delta^* = 1$.[8]

Analyzing the experimental EPR measurements of the order parameter,[1] we find $\delta^* = 0.62 \pm 0.10$. The non-mean-field-like value of δ^*, which agrees remarkably well with renormalization-group predictions,[12,13] shows that we are indeed in the *fluctuation-dominated region.* In spite of these fluctuations, the transition remains *first order.* This is thus *the first experimental proof that the continuous three-state Potts model does indeed have a first-order transition, even in the fluctuation-dominated region.*

Our conclusions are based on the same effective Hamiltonian used for previous analyses of the structural transitions in perovskite crystals.[1-4] This Hamiltonian is a functional of the pseudocubic axial vector of the soft optic mode which lies at the [111] corner of the Brillouin zone, $\vec{Q}$, and of the elastic strain tensor $e_{\alpha\beta}$. The order parameter $\vec{\varphi}$ is nearly proportional to $\vec{Q}$. After the elimination of $e_{\alpha\beta}$, we end up with the reduced Hamiltonian[3,4]

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

Here $r_0 \propto (T - T_0)$, and T_i $(i = 1, \ldots, 6)$ are the components of the stress (in the Voigt notation). The other coefficients are practically constant near the transition. We concentrate here on the case of stress along the [111] diagonal, $T_i \equiv -p/3$, and $v < 0$, which is applicable to the experiments on $SrTiO_3$.[1]

As discussed in Refs. 4 and 6, it is now convenient to define the new coordinates $S_1 = (Q_1 + Q_2 + Q_3)/\sqrt{3}$, $S_2 = (Q_1 - Q_2)/\sqrt{2}$, and $S_3 = (Q_1 + Q_2 - 2Q_3)/\sqrt{6}$. This transforms (1) into

$$\mathcal{H} = \int d^d x \{\tfrac{1}{2}[r_1 S_1{}^2 + r_2(S_2{}^2 + S_3{}^3) + (\nabla\vec{S})^2] + u|\vec{S}|^4 + v[\tfrac{1}{3}S_1{}^4 + 2S_1{}^2(S_2{}^2 + S_3{}^2) + 2\sqrt{2}S_1S_3(S_2{}^2 - \tfrac{1}{3}S_3{}^2) + \tfrac{1}{2}(S_2{}^2 + S_3{}^2)^2]\}, \quad (2)$$

with $r_1 = r_0 + \frac{2}{3}(L_1 + 2L_2 + L_3)p$ and $r_2 = r_0 + \frac{1}{3}(2L_1 + 4L_2 - L_3)p$. $\mathcal{H}$ is of exactly the same form as that of Ref. 6. For $SrTiO_3$, $L_3 < 0$,[1,2] and therefore $r_1 < r_2$ for $p > 0$. Thus, as we lower the temperature at constant $p > 0$, the component S_1 will order first, with Ising-like critical exponents.[4] For $T < T_1(p)$ one thus has a trigonal ordering, with the order parameter $\langle\varphi_{[111]}\rangle \propto \langle S_1\rangle = M$. We reanalyzed the data of Fig. 2(b) in Ref. 1, giving M as a function of p for constant $T = 104$°K, and found that indeed, for $p(T_1) = 5$ kg/mm^2

$<p \lesssim 12$ kg/mm^2, it is consistent with $M \sim [p - p(T_1)]^\beta$, where $\beta = 0.32 \pm 0.02$ agrees with Ising-model predictions. This non-mean-field-like result explains the discrepancy between Eqs. (6) and (7) in Ref. 1.

In the trigonally ordered phase, it is convenient to replace S_1 by $S_1 + M$, so that $\langle S_1 \rangle = 0$. This leads to a shift in the parameters of (2), i.e., $r_1 \to \tilde{r}_1 = r_1 + 4(3u + v)M^2$, $r_2 \to \tilde{r}_2 = r_2 + 4(u + v)M^2$, and to the addition of the odd terms

$$\Delta\mathcal{H} = \int d^dx \{[r_1 + 4(u + \tfrac{1}{3}v)M^2]MS_1 + 4(u + v)MS_1(S_2^2 + S_3^2) + 4(u + \tfrac{1}{3}v)MS_1^3 + 2\sqrt{2}VMS_3(S_2^2 - \tfrac{1}{3}S_3^2)\}. \quad (3)$$

Thus, for sufficiently large M, we shall have $\tilde{r}_2 < \tilde{r}_1$, and eventually [at $T_2(p)$] we reach a phase transition in which S_2 and S_3 order. In the range $\tilde{r}_2 < \tilde{r}_1$ we can iterate the renormalization-group transformation so that $\tilde{r}_1$ is kept constant, until the fluctuation term $(VS_1)^2$ becomes negligible.[14] At the same time, the terms involving S_1^3 and S_1^4 will also be small, and the S_1 coordinates will be easily integrated out from the partition function. The net result is then

$$\mathcal{H}_{\text{eff}} = \int d^dx \{\tfrac{1}{2}[\tilde{r}_2(S_2^2 + S_3^2) + (\nabla S_2)^2 + (\nabla S_3)^2] + \tilde{u}_2(S_2^2 + S_3^2)^2 + wS_3(S_2^2 - \tfrac{1}{3}S_3^2)\},$$

where $\tilde{u}_2$ is a combination of u, v, and $\tilde{r}_1$, while $w \simeq 2\sqrt{2}vM$. This is exactly the continuous version of the three-state Potts model,[6] studied previously using the renormalization group.[12,13]

For $w = 0$, the Hamiltonian (4) represents a second-order XY-like phase transition. However, w is a relevant variable, with exponent[13] $\lambda_w = 1 - \epsilon/10 - 3\epsilon^2/100 + O(\epsilon^3)$. Simple scaling arguments[13] now yield for $w \neq 0$ a first-order transition, with an order-parameter discontinuity $|\langle \Delta\vec{S} \rangle| \propto |w|^{\delta^*}$, where $\delta^* = (d - x)/\lambda_w = \frac{1}{2}(d - 2 + \eta)/\lambda_w$. Combining the linear dependence of w on M [following Eq. (4)] and the ϵ expansion of η and λ_w leads to the result quoted above.

Since v is quite small ($v/u \simeq -\frac{1}{6}$ for $SrTiO_3$, from Ref. 1; $|v/u|$ is estimated to be even smaller in Ref. 15), we have the advantage of having a relatively small w for a wide range of values of M or of p. However, the above scaling prediction should no longer hold for very large M, where mean-field theory should work, nor for very small values of M, near the Heisenberg-like bicritical point. A separate study of scaling near this point is necessary.[4,6]

The EPR experiments were described in detail in Ref. 1. There, the first-order phase boundary was determined at constant temperature T by applying successively higher stresses $p_{[111]}(T_2)$ (see Fig. 1 of Ref. 1) and observing the Fe^{3+}-V_O EPR line splittings ΔH_c for the magnetic field direction $\vec{H} \| [1\bar{1}0]$. Because of the unavoidable inhomogeneity in the stress, the determination of $p(T_2)$ [or $T_2(p)$] was relatively inaccurate: Over a range of values of p, the EPR lines of the trigonal monodomain and the pseudotetragonal phase were observed simultaneously. In that range, the line positions corresponding to the two phases were detected essentially at the same position, because of the first-order character. Only their relative amplitudes changed as a function of p.

This now allowed us to extract from the earlier data the discontinuity of ΔH_c, $\delta(\Delta H_c) \propto \langle \delta\varphi_{[100]} \rangle$, and $\Delta H_c[111] \propto \langle \varphi_{[111]} \rangle$ in the trigonal phase above the transition, with a higher degree of accuracy compared to that of the phase diagram itself.

These two quantities $\{\delta(\Delta H_c)$ and $\Delta H_c[111]\}$, together with new values measured now, are plotted against each other in Fig. 2. The origin marks the bicritical point of $p_{[111]} = 0$ and is fixed. Also shown in the figure is a curve computed with $\delta(\Delta H_c) = C(\Delta H_c)^{\delta^*}$, where $\delta^* = 0.62$, $C = 1.47$. These values were obtained from a least-squares fit of the above power law to all the points, with a correlation coefficient of $x = 0.98$. For a fit to the first six points from zero, we obtain $\delta^* = 0.63$ and $C = 1.4$, which yielded a correlation coefficient of $x = 0.87$. Clearly, a straight line through the origin, as predicted by mean-field theory, is ruled out. Taking into account possible systematic evaluation errors, we can safely conclude that $\delta^* = 0.62 \pm 0.10$ which embodies both renormalization-group predictions.

An interesting question arises from the apparent discrepancy between series work,[10,11] done on

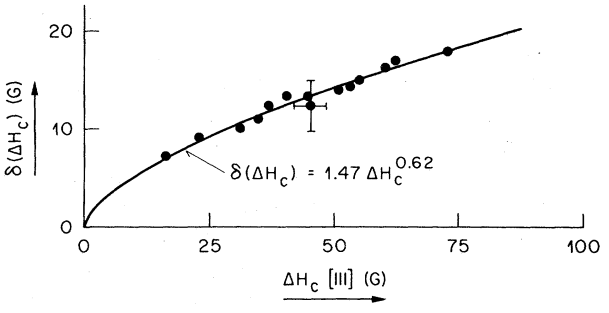

FIG. 2. The EPR splittings $\delta(\Delta H_c)$ vs $\Delta H_c[111]$ of Fe^{3+}-V_O at the first-order trigonal-tetragonal transition in $SrTiO_3$ for $\vec{H} \| [1\bar{1}0]$.

the discrete Potts model,[7] and the renormalization-group[12,13] and experimental work reported here. Could there be a difference between the continuous and discrete Potts models? Some series work on the continuous model would be very interesting.

One of us (A.A.) would like to acknowledge the hospitality of the IBM Zurich Research Laboratory, where he was visiting while most of this work was done.

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Electron–Surface-Plasmon Scattering Using a Parabolic Nontouching Trajectory

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Incident electrons follow a parabolic trajectory when an electric field is applied normal to the surface of a metal crystal with force vector directed outwards. Under appropriate conditions touching trajectories may be neglected, and electron–surface-plasmon scattering is dominated by trajectories with closest approach distance. Experimental results are presented for Mo indicating that only the 1.3-eV molybdenum surface plasmon is excited. Application of this new technique to measurements such as surface-plasmon dispersion is outlined.

In this paper we report on results interpreted as inelastic scattering of an electron, traveling just outside a clean metal surface, from surface-electron excitations. By applying an electric field normal to the surface, so as to give a force F on the electron directed outwards from the surface, the electron follows an approximately parabolic orbit (Fig. 1). It is thereby demonstrated explicitly that the electrostatic potential of the surface excitations (loosely referred to below as surface plasmons) does indeed penetrate into the vacuum: The theoretical result is that the surface-plasmon potential is proportional to $\exp(-Qz)$,[1] where Q is wave vector of the excitation parallel to the surface, and z is distance measured normally outward from the surface. We believe this to be the first recognized observation of this type, though an observation of an unresolved energy loss for electrons passing through holes in graphite[2] might bear a similar interpretation.

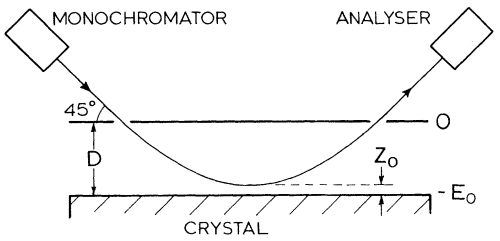

FIG. 1. One of the two experimental arrangements. Beam of energy $2E_0$ enters and leaves condenser via apertures at an incidence of approximately 45°. D is the plate separation, z_0 is the closest approach distance, and E_0 is the potential between plates.