Gennes's estimate: $W = 5 \times 10^{-14}$ erg. We have no explanation for this discrepancy.

The data for the A-H system suggest that there may be departures from $L^{-1/3}$ at large heights at room temperature (although there could be some doubt about equilibrium in the tallest samples). The data for the H-F system are inconsistent with $L^{-1/3}$ at $t = -0.002$ (no L dependence could be detected). Furthermore, the temperature dependence of h, as displayed in Fig. 4, is not fully consistent with Eq. (1). We could suppose that the intruding layer was stabilized not only by the free energy per unit area W/h^2 with $W > 0$ but also by an additional term of the form $\gamma \exp(-h/\xi)$ reflecting the effects of short-ranged forces.[2] Even with such a term we were not able to obtain a fully consistent account of the data at all L and ΔT, especially if the parameter γ were required to have the magnitude of a typical interfacial tension and ξ the magnitude and temperature dependence of a near-critical correlation length.

Near the critical point the picture of the wetting layer as a uniform film of l phase with sharp interfaces is undoubtedly oversimplified, and both the theory and the interpretation of the ellipsometric data might require a more realistic picture of the interfacial structure.

In summary, we find that near ambient temperature the L dependence of the thickness of the intruding layer is reasonably consistent with the theoretical picture of de Gennes.[2] Near the critical point there are inconsistencies that may require an altered picture.

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Separation of the D_{4h} and O_h Phases near the Surface of $SrTiO_3$

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Elastic compliance data are reported for thin plates of $SrTiO_3$. An analysis is presented in terms of two spatially separated phases, the one of low symmetry residing near the surface. From the thickness of the surface layers, a static correlation length $\xi = \xi_0(T/T_c - 1)^\nu$, with $\xi_0 = (0.35 \pm 0.02)$ μm and $\nu = -0.68 \pm 0.03$, is deduced.

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Recently, several reports have appeared on the separation of phases of different stoichiometric composition near the surface of alloys.[1-3] The conclusion was that a surface favored the presence of one component with respect to the other. This also held for the case of liquid ^{3}He-^{4}He mixtures investigated by third-sound propagation.[4] Coexistence of two phases of D_{4h} and O_h symmetry in crystalline $SrTiO_3$ has also been reported on the basis of x-ray depth profiling.[5] Neutron-scattering experiments[6] failed, however, to confirm these results. Stabilization of a low-symmetry phase by a surface is a fundamental lattice-dynamical problem for which as yet there is little experimental insight. In the present Letter, we analyze data on elasticity and deduce from them the coexistence of the two phases. From their equilibrium distribution, we deduce the autocorrelation length of the order parameter of the surface layer.

Our claim that two phases coexist above the bulk critical temperature, T_c, rests on measurements of elastic compliances in samples of different shapes and vibrating in different modes. Figure 1(a) shows the elastic compliance s_L for a length-extension mode[7] as a function of temperature in samples successively ground to smaller thickness. It is evident that $s_L(T)$ is substantially modified in thin samples, suggesting the presence of a surface layer. A direct evaluation of its elastic properties from the data of Fig. 1(a) would require that the sample thickness be known to within 10^{-3}, and presupposed that the polishing process leaves the elastic compliances invariant. Therefore, we have resorted to measuring both length-extensional modes and flexure, from which the elasticity and thickness of the surface layer can be deduced without precise knowledge of the sample geometry. For a sample of length l with two surface layers of the D_{4h} phase of thickness λ and an O_h phase of thickness $d-2\lambda$, having elastic compliances s_D and s_O, respectively, the resonance frequency of a length-extension mode is given by[7]

$$f_L=(2l)^{-1}(s_L\rho)^{-1/2}, \qquad (1)$$

where ρ is the mass density and the elastic compliance is

$$s_L^{-1}=s_O^{-1}+2(s_D-s_O)\lambda/d. \qquad (2)$$

The resonance frequency of a bar vibrating in flexure is given by[8]

$$f_F=(2l)^{-1}(3\sqrt{3}\pi d/8l)(s_F\rho)^{-1/2} \qquad (3)$$

with

$$\begin{aligned} s_F^{-1}&=s_D^{-1}+[1-(2\lambda/d)]^3(s_0^{-1}-s_D^{-1})\\ &=s_O^{-1}+6(s_D^{-1}-s_O^{-1})\lambda/d+O(\lambda/d)^2. \qquad (4)\end{aligned}$$

In the limit of $\lambda/d \ll 1$, the surface layer contributes to the effective rigidity of the bar 3 times as much for flexure modes as for length-extension modes. This difference of weight between the respective contributions (for which there is no electrical analog) allows determination of the layer thickness with the help of Eqs. (2) and (4):

$$\lambda=d(s_L^{-1}-s_F^{-1})/4(s_O^{-1}-s_D^{-1}). \qquad (5)$$

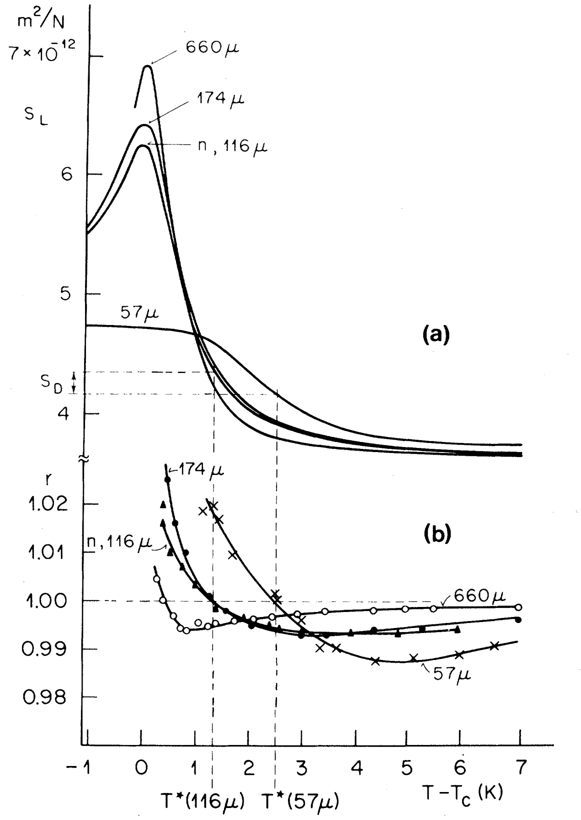

FIG. 1. (a) Elastic compliance as a function of temperature for different sample thicknesses (labeled in μm). The sample marked "n" has natural faces. (b) Ratio of flexure resonance to length-extensional resonance, normalized to 1 at $T=T_c+50$ K. Same samples as above. The elastic compliance of the surface layer gained from the condition of elastic homogeneity ($r=1$) is equal to s_D at $T \ll T_c$.

The small difference $s_L^{-1}-s_F^{-1}$ was determined as follows: Far away from T_c, it was found that $f_L/f_F=$ const and that $s_L=s_F$ to within the accuracy of the measured value of d/l. No surface layer is present in this temperature range, and setting $s_L(\infty)=s_F(\infty)$ allows d/l to be expressed in terms of resonance frequencies. It follows that

$$s_L^{-1}-s_F^{-1}=4l^2\rho f_L^{\,2}(1-r^2), \qquad (6)$$

where

$$r=[f_F(T)/f_L(T)][f_F(\infty)/f_L(\infty)]^{-1}. \qquad (7)$$

Here, $f_L(\infty)$ and $f_F(\infty)$ are resonance frequencies measured at $T>150$ K. In Fig. 1(b), r is plotted versus T: Near T_c, $r>1$, indicating that the surface is harder than the bulk. At some temperature T^* slightly above T_c, $r=1$, implying $s_O=s_D$ since $\lambda \neq 0$ [Eq. (5)]. The compliance of the surface layer $s_D=(4.2\pm0.1)\times10^{-12}$ m^2/N is therefore equal to that found by Rehwald,[9] $s(4\,\mathrm{K})=(4.3$

$\pm 0.1) \times 10^{-12}$ m^2/N, confirming the identification of the surface layer with the D_{4h} phase.

The thickness of the surface layer is now evaluated with the help of Eqs. (5), (6), and (7). The elastic compliance $s_O(T)$ is taken from the thickest sample and $s_D = s_O(T^*)$ is taken from the thicktic fit of $\lambda(t)$, $t = T/T_c - 1$, to a power law yields $\lambda = (0.39 \pm 0.06\ \mu\text{m}) \times t^{-0.88 \pm 0.03}$. From this critically growing surface layer, the intrinsic correlation length ξ of the order parameter may now be deduced. The order parameter, a rotation φ of the oxygen octahedra TiO$_6$, is given by[10] $\varphi = \varphi_S \exp(-|z|/\xi)$, where z is the distance from the surface and φ_S the order parameter induced by surface forces p_S. The associated stress[11] $p = A\varphi^2$ is large enough to stabilize the D_{4h} phase provided[12] $p > p_c = B(T - T_c)$. Here, $A = 10^{-4}$ if p is measured in units of s_O^{-1} and φ in degrees, and $B = 8 \times 10^{-5}$ K^{-1}. The associated spatial range of the elastic compliance s_D is thus

$$z_c = \lambda = \tfrac{1}{2}\xi \ln\{p_S/B(T - T_c)\} \tag{8}$$

giving for the correlation length

$$\xi = 2\lambda/\ln[p_S/B(T - T_c)]. \tag{9}$$

Assuming a surface relaxation strain of the order[13] of 3×10^{-2}, and converting this value into the surface stress p_S by dividing by the elastic compliance, one finds from Eq. (9) (Fig. 2), $\xi = \xi_0 t^{-\nu}$ with $\xi_0 = 0.35 \pm 0.02\ \mu$m, $\nu = 0.68 \pm 0.03$.

Further to the statistical errors quoted, some uncertainty in ξ_0 and ν is due to the estimate of the surface stress p_S. However, ξ_0 and especially ν are insensitive to the surface stress p_S: For $10^{-2} \leqslant p_S s_O \leqslant 10^{-1}$, $0.61 \leqslant \xi_0 \leqslant 0.23$ and $0.60 \leqslant \nu \leqslant 0.73$. All the samples were cut along $\langle 110 \rangle$; thus the surface stress stabilizes a monodomain in D_{4h} phase.[14] Accordingly, the experimental value of ν should be compared with the three-dimensional Ising value of $\nu = 0.638$.[15]

These results are independent of sample origin[16] except for Verneuil-grown crystals, and independent of sample thickness. Layer thicknesses obtained in a flux-grown natural-shape crystal are the same as those evaluated in a matched polished sample. This excludes the possible explanation in terms of a strained layer induced by the polishing treatment.[17] For this reason, Verneuil-grown crystals are not included in this search. Because of their large dislocation density,[18] they tend to deform plastically upon polishing; in addition, the acoustic anomaly is quenched even in large crystals, presumably because of D_{4h} condensation at dislocations in the bulk of the crystal.

So far, we have assumed that the elastic distribution was given by a (temperature-dependent) step function $s(z)$. In a more realistic picture, $s(z)$ is a continuous function with a maximum at z_c corresponding to a critical pressure p_c entailing critical fluctuations (Fig. 3). The corresponding relative contribution of $s(z) - s_{\text{step}}(z)$ has been estimated[19] to be $\Delta s_{\text{rel}} = \ln[p_S/B(T - T_c)]/(\ln 2)(T - T_c)$ which is less than 10% for $T - T_c > 1$ K. The justification for its neglect is also evidenced ex-

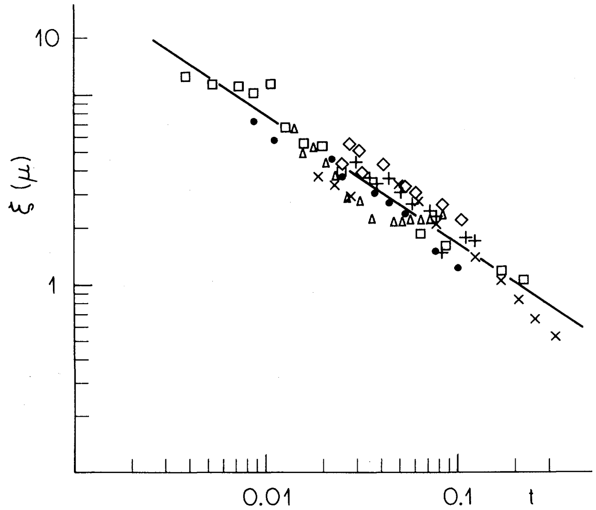

FIG. 2. Correlation length for six different samples determined from the surface-layer thickness by Eq. (9), assuming a surface stress $p_S = 3 \times 10^{-2}\, s_D$. Layer thickness in micrometers: diamonds, 44; plusses, 57; squares, 116; crosses, 174; dots, 660; triangles, 668.

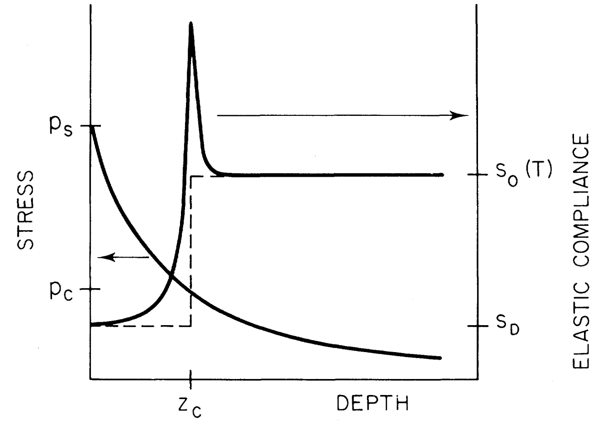

FIG. 3. Elastic compliances and internal stress as a function of depth at a fixed temperature $T > T_c$. Full line: true elastic profile (schematic). Broken lines: step function used for the approximate determination of the layer thickness.

perimentally by the coincidence of s_{layer} with s_D [Fig. 1(b)].

This evaluation of surface layers sheds light onto the controversy between x-ray[5] and neutron scattering[6] in the surface layer of $SrTiO_3$: An estimate of its thickness from x rays yielded 20 μm at $T_c + 4$ K. The used sample in Ref. 5 was Verneuil-grown and polished, a treatment known to induce biasing strains in the surface.[15] Neutron scattering failed to indicate the presence of a surface layer, presumably because the crystal had untreated rough surfaces which stabilize $\langle 100 \rangle$ and $\langle 111 \rangle$ rotations of TiO_6 octahedra with equal probability. A D_{4h} layer cannot form underneath such a rough surface. The present estimate for its thickness, 3.2 μm at $T_c + 4$ K for high-quality $SrTiO_3$, makes the detection of the layer by neutron scattering unlikely.

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