Crossover exponent and structural phase diagram of $SrTiO_3$

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The phase diagram of $SrTiO_3$ has been measured with uniaxial pressure along [100] in the neighborhood of its bicritical point. The phase boundary line follows a single power law, $T_c(p) - T_c(0) = Wp^{1/\phi}$, with the crossover exponent $\phi = 1.27 \pm 0.06$. The value of ϕ is in agreement with the theory for a Heisenberg $n = 3$, $d = 3$ system.

During the last few years an increased interest has been shown for phase diagrams of systems undergoing structural phase transitions.[1-6] With uniaxial pressure p along [100] a bicritical[1,4] point located at $p = 0$ has been observed in $SrTiO_3$. In other perovskites tricritical points have been observed, in $RbCaF_3$ (Ref. 5) for p along [100], and in $KMnF_3$ (Ref. 6) both for p along [100] and [110]. The renormalization-group theory and high-temperature series expansions have recently been used to find the shape of the phase boundary lines around bicritical points of systems like $SrTiO_3$ (Refs. 2 and 7) and in magnetic systems.[2,7-9] For the antiferromagnetic material $GdAlO_3$ the phase diagram has been carefully measured in the neighborhood of the bicritical[10,11] and the tetracritical[11] point. From the measured shape of the phase boundary lines the crossover exponents associated with a two component ($n = 2$) system and with cubic anisotropy were found. They were in good agreement with the theoretical predictions,[7,12] $\phi(n = 2) \approx 1.18$ and $\phi_v \approx 0$, respectively. $\phi(n = 3)$ has been measured in the antiferromagnetic material $RbMnF_3$, and was also found[13] to agree with the theoretical value[7] $\phi(n = 3) = 1.25 \pm 0.015$. On the other hand, no *direct* measurement of crossover exponents at any structural transition has been made. Previous measurements of the phase diagram of $SrTiO_3$ (Ref. 14) ($n = 3$) have not been accurate enough to allow ϕ to be determined. *Indirect* estimates of $\phi(n = 3)$ from sound velocity were made by Rehwald[15] in $SrTiO_3$, and from critical attenuation of ultrasound in $KMnF_3$ by Fossheim and Holt.[16] The sound-velocity measurements in $SrTiO_3$ (Ref. 15) indicate $\phi(n = 3) \approx 1.4$, while ultrasonic attenuation measurements in $KMnF_3$ are consistent with the theoretical value.

In the present report we present measurements of the phase diagram in $SrTiO_3$ for p along [100]. The curvature of the phase boundary line directly gives $\phi(n = 3)$. To our knowledge, this is the first direct observation of a crossover exponent in a structural system.

From renormalization-group theory the shape of the phase boundary lines are given by[2]

$$T_c^m(p) = T_c^0 + W_m p^{1/\phi} + A_m p + O(p^2) \quad . \tag{1}$$

Here T_c^m is the phase-transition temperature, $T_c^0 = T_c(p = 0)$, and W_m and A_m are the amplitudes of the nonanalytic and the analytic term, respectively. The index m refers to the number of components of the order parameter left when pressure is applied. For a perovskite-like $SrTiO_3$, displaying a cubic-to-tetragonal phase transition, $m = 2$ for $p > 0$ if p is perfectly aligned along [100], and $m = 1$ for $p < 0$.[1,2] The amplitudes W_m and A_m are not known, only the amplitude ratio W_1/W_2 has been calculated.[17]

We have determined the phase boundary line, $T_c(p)$ for $SrTiO_3$ with uniaxial pressure along [100] by measuring the specific-heat curve, $C_p(T)$, through T_c. The specific heat is measured by an ac technique using an automated system which has been described in detail elsewhere.[18,19] The sample was cut from a larger single crystal grown by National Lead Co. in 1979. It has the shape of a small rectangular plate with the dimensions $6.4 \times 3.1 \times 0.48$ mm^3. The largest surface is a (001) plane, and the pressure is applied to the smallest surface by putting weights on a piston resting on the sample. The absolute calibration of pressure has an uncertainty of ±5%, but the relative uncertainty is less than 1 bar. The largest surface, being painted black, is heated periodically by white light, and the temperature oscillation detected at the rear surface. Most of the $C_p(T)$ curves were measured with a chopper frequency $f = 0.5$ Hz, some with $f = 1.0$ Hz. The induced peak-to-peak temperature oscillation was always below 35 mK.

At each pressure applied $C_p(T)$ was measured through T_c both on cooling and heating. Starting at $p = 0$, $T_c(p)$ was measured with successively increasing pressure, always putting on the new pressure above T_c. The pressure was increased at $T \approx T_c(p) + 8.5$ K. Then $C_p(T)$ was measured down to $T \approx T_c(p) - 8.5$ K during 24 h of continuous mea-

surements. During the next 24 h the same curve was measured during heating. T was regulated in steps of about 60 mK each fifth min. Note that the sweep rate was as low as 0.7 K/h.

The resulting phase diagram is shown in Fig. 1. T_c is taken as the temperature where $d(\Delta C)/dT$ is a maximum, ΔC being the excess specific heat. The determination of T_c then has a typical uncertainty of ± 0.1 K. The maximum of ΔC was about 1% of the lattice specific heat, in agreement with previous measurements[20,21] on polydomain samples. The shape of the $C_p(T)$ curve does not change significantly with pressure. The shape of the phase boundary line would therefore have been the same if T_c was taken as the temperature where ΔC has the maximum. But polydomain $SrTiO_3$ crystals often show a maximum several degrees below T_c, as explained[21] from reconstruction of domain structure.

The phase boundary line of Fig. 1 is clearly bent upwards. In Fig. 2, $T_c(p)$ vs $p^{1/\phi}$ is plotted with $\phi = 1.25$. The data fall on a straight line. This indicates that the analytic terms in Eq. (1) are small. We made plots similar to that of Fig. 2 for several values of ϕ, and performed least-squares fits to straight lines. The root-mean-square temperature deviation is

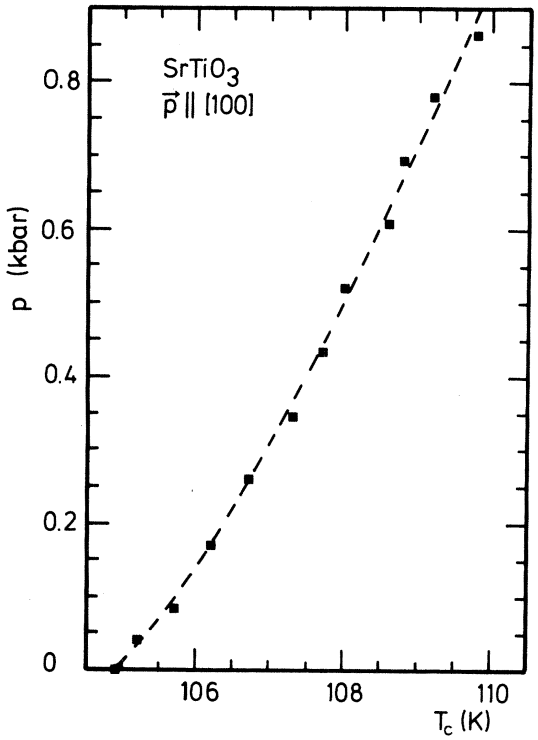

FIG. 1. Phase diagram of $SrTiO_3$ with uniaxial pressure p along [100] showing T_c vs p. The dashed line is $T_c(p) = T_c(0) + Wp^{1/\phi}$, with $T_c(0) = 104.89$ K, $W = 5.40$ K/(kbar)$^{0.8}$ and $\phi = 1.25$.

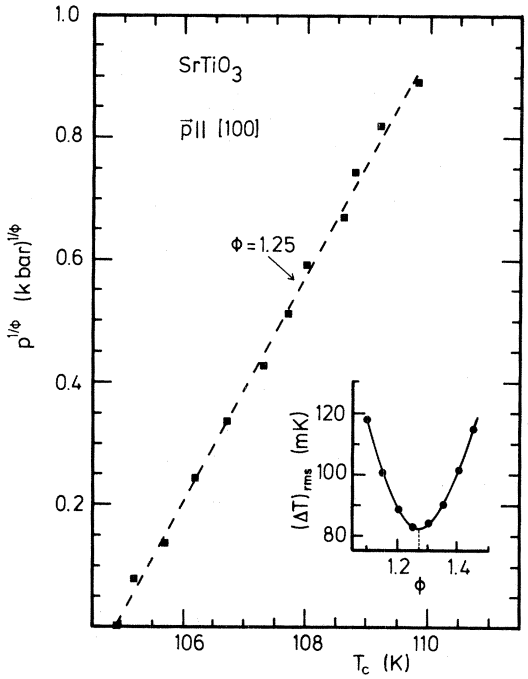

FIG. 2. The data given in Fig. 1 are shown here with T_c plotted as a function of $p^{1/\phi}$ with $\phi = 1.25$. The straight dashed line is the same as the line shown in Fig. 1. In the inset is shown the root-mean-square deviation as a function of ϕ when fitting the data to $T_c(p) = T_c(0) + Wp^{1/\phi}$.

shown as a function of ϕ in the inset of Fig. 2, showing that $\phi = 1.27$ gives the best fit. A least-squares computer analysis of the data, taking $T_c(p) = T_c^0 + W_p^{1/\phi}$, gave the results: $\phi = 1.27 \pm 0.06$ $W = (5.39 \pm 0.10)$ K/(kbar)$^{1/\phi}$, and $T_c^0 = (104.87 \pm 0.08)$ K. The value found for ϕ is in excellent agreement with the theoretical value[7] $\phi = 1.25 \pm 0.015$.

To test further whether the analytic term in (1) is small the data were fitted to $T_c(p) = T_c^0 + Wp^{1/\phi} + Ap$, with $\phi = 1.25$, the theoretical value. This gave $W = (5.8 \pm 1.1)$ K/(kbar)$^{0.8}$, $A = (-0.4 \pm 1.1)$ K/kbar, and $T_c^0 = (104.87 \pm 0.08)$ K. We see that at $p = 1$ kbar, using the highest value allowed for A within the uncertainty and the lowest value allowed for W, we have $Wp^{1/\phi} = 7Ap$, clearly showing that the nonanalytic term is dominating. Note that to have the two terms equal then, the pressure must be increased by a factor $(7)^5$ to about 10^4 kbar, and it must be increased by a factor $(7)^{10}$, to 10^8 kbar to have the analytic term dominating to the same extent as the $Wp^{1/\phi}$ term does at $p = 1$ kbar. It is therefore unlikely that the pressure can be increased until pure linear Landau dependence is observed without breaking the crystal.

In conclusion, we have shown that our data on the phase diagram of uniaxially stressed $SrTiO_3$ with p aligned along [100] confirm the predictions from renormalization-group theory. The phase boundary line fits well to a simple power law $T_c(p) - T_c^0 = Wp^{1/\phi}$ where we find the Heisenberg ($n=3$) crossover exponent to be $\phi = 1.27 \pm 0.06$, in good agreement with the theroretical value $\phi = 1.25 \pm 0.015$.

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