Critical behavior of ferroelectric $SrTi^{18}O_3$

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Accurate measurements of the temperature dependence of spontaneous polarization and dielectric constant in the vicinity of the phase transition from the paraelectric to the ferroelectric phase in $SrTi^{18}O_3$ were performed. Dielectric constant and soft mode frequency can be well described [Minaki *et al.*, J. Korean Phys. Soc. **42**, S1290 (2003); Takesada *et al.* (unpublished)] with the Salje expression [Salje *et al.*, Z. Phys. B: Conden. Matter **82**, 399 (1991)] which gives $\gamma=1$ close to T_c. The critical exponents β and γ have classical Landau values.

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$SrTi^{16}O_3$ (STO16) has many interesting properties,[1] and is considered to be a classical displacive soft mode system where the ferroelectric phase is suppressed by zero-point fluctuations leading to quantum paraelectricity.[2] The observed ferroelectricity[3] in $SrTi^{18}O_3$ (STO18) is a consequence of the larger mass of ^{18}O which reduces quantum fluctuations and allows the condensation of the polar soft mode.[4]

Recently Minaki *et al.*[4] showed by hyper-Raman scattering in the $SrTi(^{18}O_x{}^{16}O_{1-x})_3$ single crystal with $x=0.87$ that the Raman-inactive ferroelectric mode shows a softening behavior and seems to cause the ferroelectric transition at 26 K. Recently, the soft mode was studied in the system with $x=0.95$ by ultralow-frequency Raman scattering to clarify the ferroelectric phase transition mechanism.[5] It has been concluded that the phase transition is of an ideal displacive type accompanied by a perfect softening of the polar mode of E_u symmetry.

Dec *et al.*[6,7] showed that their values of critical exponents $\gamma=1.92$, $\beta=1.2$, and $\alpha=-2.1$ in $SrTi(^{18}O_{0.94}{}^{16}O_{0.06})_3$ significantly deviate from the classical Landau universality class. They determined the value of γ by fitting the data with the generalized quantum Curie-Weiss law.[8,9] The exponent β was determined from the scaling relation, and the authors stated that to the best of their knowledge the result $\beta>1$ has never been found in any theoretical system.

Because of unusual values of critical exponents determined recently[6–9] we decided to measure the spontaneous polarization and dielectric constant in the vicinity of the paraelectric to ferroelectric phase transition. Hysteresis loops in STO18 were studied before.[3]

The spontaneous polarization was measured with a Sawyer-Tower bridge at the frequency of 0.05 Hz. The temperature of the sample was stabilized to ±0.05 K with an Oxford Instruments continuous flow cryostat and ITC4 temperature controller. The dielectric constant was measured with an HP4284A precision LCR meter.

A STO18 single-crystal sample (94.7% ^{18}O) with dimensions $7\times2\times0.3$ mm^3 was covered first with evaporated Cu electrodes and then with sputtered gold electrodes. Electrodes covered the surfaces perpendicular to the crystallographic c axis.

Typical hysteresis loops are shown in Fig. 1. Spontaneous polarization was measured with increasing temperature. When approaching T_c the maximum electric field was decreasing in such a way that hysteresis loops were always saturated. Spontaneous polarization was determined by extrapolation of the saturated part of the loops to $E=0$ (Fig. 1), and is presented as a function of the temperature in Fig. 2.

The spontaneous polarization versus temperature is well described by

$$P_s = A(T_c - T)^{\beta}, \tag{1}$$

with $\beta=0.50\pm0.02$, $A=0.64\pm0.02$, and $T_c=28.40\pm0.02$ K.

The Salje expression[10] for the temperature behavior of the spontaneous polarization describes also the saturation of the spontaneous polarization at low temperatures, which is connected with quantum effects. While in the limit of high temperatures $T \gg T_1/2$ [see Eq. (2)] the Salje thermodynamic potential[10] becomes identical with the traditional Landau polynomial and the system behaves classically, at lower temperatures $T \leq T_1/2$ the potential describes quantum effects (the order parameter is independent of temperature). Thus, the temperature $T_1/2$ characterizes the crossover between classical and quantum mechanical behavior. As such a saturation of the spontaneous polarization at low temperatures was not observed, we applied Eq. (1) for $P_s(T)$, which means that quantum effects in STO18 are very small.

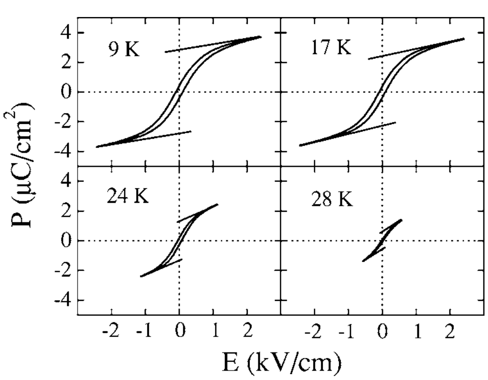

FIG. 1. Ferroelectric hysteresis loops at different temperatures in STO18.

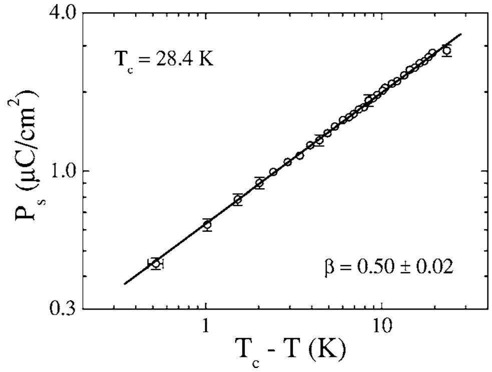

FIG. 2. Log-log plot of the spontaneous polarization versus temperature in STO18.

Figure 3 shows the measured inverse dielectric constant versus temperature. The measuring frequency was 1 kHz and the measuring electric field strength was 0.5 V/cm. The accuracy in capacitance measurements was better than 1%.

Following Minaki *et al.*[4] we used the Salje formula[10]

$$\frac{1}{\varepsilon} = BT_1\left[\coth\left(\frac{T_1}{2T}\right) - \coth\left(\frac{T_1}{2T_c}\right)\right] \tag{2}$$

to describe dielectric data, as the temperature dependence of $\varepsilon(T)^{-1}$ in STO18 is nonlinear in broad temperature range above T_c. Figure 3 shows that Eq. (2) describes the data well in the range $28 < T < 45$ K with the following values of the parameters: $B = (6.3 \pm 0.1) \times 10^{-6}$ K^{-1}, $T_1 = 96.5 \pm 1.5$ K, and $T_c = 25.2 \pm 0.2$ K.

When approaching T_c, the Salje formula transforms to the classical Curie-Weiss law, i.e., it gives $\varepsilon^{-1} = B_1(T - T_c)$, which means that $\gamma = 1$ (where $B_1 = B/\{2T_c^2[\sinh(B/2T_c)]^2\}$). From the inset to Fig. 3, where ε^{-1} is plotted versus $T - T_c$ in a log-log plot, we see that the value of γ is close to 1 in the range approximately $3 < T - T_c < 7$ K. The curve in the inset is also the fit with Eq. (2).

The Salje expression for the square of the soft mode frequency reads[4,10]

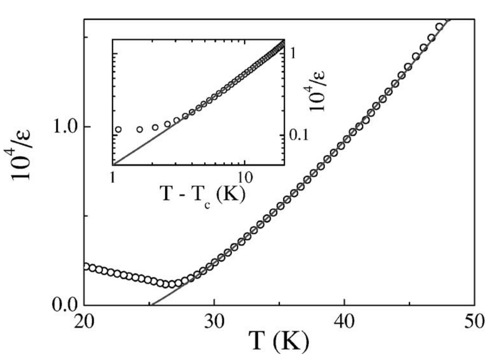

FIG. 3. Reciprocal dielectric constant as a function of the temperature. Inset shows log-log plot of the inverse dielectric constant versus $T - T_c$. Full line represents the fit with Eq. (2).

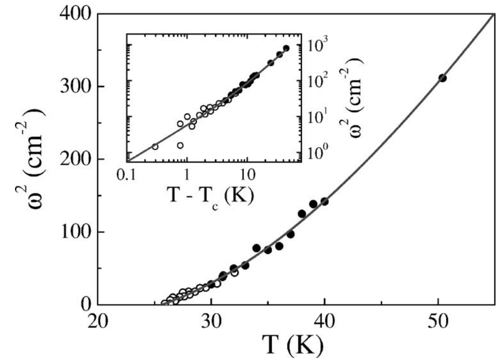

FIG. 4. Square of the soft mode frequency, ω^2, as a function of the temperature. Inset shows log-log plot of ω^2 vs $T - T_c$. Full line represents the fit with Eq. (4).

$$\omega^2 = DT_1\left[\coth\left(\frac{T_1}{2T}\right) - \coth\left(\frac{T_1}{2T_c}\right)\right], \tag{3}$$

and was used recently[4] only to determine T_c. In Fig. 4 the data from Ref. 4 and the data of the ferroelectric soft E_u mode[5] (the frequencies of the Raman shift were multiplied by a factor of 1.8) are plotted as a function of the temperature. The full line represents the fit of the data with Eq. (3) with parameters $D = 15 \pm 1$ cm^{-2} K^{-1}, $T_1 = 126 \pm 6$ K, and $T_c = 25.6 \pm 0.3$ K. In the inset of Fig. 4, the square of the soft mode frequency ω^2 versus $T - T_c$ is presented in a log-log plot. Close to T_c, γ is equal to 1. We see that the values of ω^2 lie on the line with $\gamma \approx 1$ till $T - T_c \leqslant 5$ K.

The dielectric constant and soft mode frequency in STO18 as a function of the temperature can be well described by the Salje expression in a broad temperature range. Experimental data show that $\gamma \approx 1$ close to T_c.

In summary, from measurements of the spontaneous polarization and dielectric constant close to T_c in STO18 the values of critical exponents β and γ were determined and they have classical mean field values. The dielectric constant and soft mode frequency[4,5] in STO18 as a function of the temperature can be well described by the Salje expression[10] in a broad temperature range, which gives $\gamma = 1$ close to T_c. We can conclude that the Lyddane-Sachs-Teller relationship[11,12] is obeyed in this system. It should be noted that in general[13] $\gamma - 2\beta \geqslant 0$, which is satisfied for our values of critical exponents, and is in contradiction with recent results[6,7] where $\gamma - 2\beta < 0$.

These values of critical exponents confirm that we are dealing with a classical paraelectric to ferroelectric transition of the soft mode type in agreement with recent optical studies.[4,5] The determined values of critical exponents[6–9] in STO18 are obviously a consequence of the use of the generalized quantum Curie-Weiss law, which is applicable for quantum paraelectrics. There exist indications that quantum effects are suppressed in STO18.[4,14]

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