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Anomalous zero-point motion in SrTiO₃: Results from γ -ray diffraction

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Bragg scattering of γ radiation at 316.5 keV was used to collect high-resolution structure-factor data sets on SrTiO₃ above and below the cubic-to-tetragonal transition temperature T_c . Moderate uniaxial pressure was applied to force a single domain sample in the low-temperature phase. Well below T_c an anomaly in the vibrational amplitudes is found which is a signature of the incipient ferroelectric transition. The magnitude of zero-point motion of the Ti atoms is substantially larger than the predicted static displacement. The oxygen atoms exhibit enhanced vibrations along all Ti-O bonds. [S0163-1829(99)07529-3]

The cubic-to-tetragonal phase transition in SrTiO₃ at $T_c \approx 106$ K is of antiferrodistortive nature, associated with a small static rotation of the oxygen octahedra around the c axis. Though the dielectric constant of SrTiO₃ increases according to a Curie-Weiss law, the crystal does not make a transition to a ferroelectric phase. It has been suggested by Müller and Burkhard¹ that quantum-mechanical atomic motion is strong enough already near 40 K to suppress the ferroelectric transition and to stabilize the so-called quantum paraelectric state. The present note reports results from γ -ray diffraction which substantiate the hypothesis of anomalous zero-point motion.

Up to now, no single crystal diffraction study has been reported below T_c from a monodomain sample. The reason for this has to be sought in the difficulty encountered with forcing a monodomain state and in the large extinction effects due to the high quality of the samples. These difficulties in structure analysis may be overcome by the use of γ -ray diffraction. With photon energies above 300 keV, full advantage can be taken of low absorption and extinction, no anomalous dispersion and reasonably large crystals.

The high-temperature phase of SrTiO₃ has the ideal cubic $Pm\bar{3}m$ perovskite structure, in which the oxygen octahedron contains a Ti atom at its center. In the low-temperature $I4/mcm$ phase,^{2,3} the oxygen octahedra remain rigid but rotate slightly around the tetragonal c axis. The sense of rotation is opposite for octahedra on adjacent (100) planes.

The single crystal used in the present investigation was a Verneuil-grown cube of dimensions $3.3 \times 3.3 \times 3.1$ mm³ with surfaces of (110) and (001), purchased from Lamprecht/Neuhausen (Germany). X-ray fluorescence analysis, performed by Garbe (HASYLAB), was used to check for the presence of Ba or Ca impurities in the sample. The content of these elements was found to be lower than 200 ppm.

Bragg intensities have been measured on the γ -ray diffractometer at the Hahn-Meitner-Institut. The most intense line of an ¹⁹²Ir source at 0.0392 Å (316.5 keV) was used. The diffracted γ rays were registered in ω -step scan mode with an intrinsic Ge planar detector. Data sets have been collected at 111 K ($=T_c + 5$ K) and 50 K with the sample mounted on a Displex closed cycle refrigerator. For the tetragonal phase, the particular value of 50 K was chosen as the octahedron rotation is almost complete but one is still sufficiently away from the proposed transition to a macroscopically coherent quantum state around 37 K.

In the tetragonal phase, the crystal will contain domains oriented with the c axis along each of the original $\langle 100 \rangle$ cubic axes. Domain formation can be prevented by uniaxial pressure along a cubic $\langle 110 \rangle$ direction. Since $c/a > 1$, the c axis can only expand perpendicular to $\langle 110 \rangle$. A pressure of 5.5 kp/mm² is reported to be sufficient to produce a monodomain sample.⁴ According to Ref. 5, the domains are seen to disappear already with 1.2 kp/mm². In the γ -ray study at $T = 50$ K, the sample was forced into a monodomain by 6 kp/mm². The force was controlled by means of a steel spring,

TABLE I. Mean square vibrational amplitudes in cubic SrTiO₃ at $T=111$ K. $U_{\parallel}(\text{O})$ is the amplitude along the Ti-O direction, and $U_{\perp}(\text{O})$ is in the Sr-O plane. Standard deviations (in parentheses) refer to the last digits given. Neutrons: Hutton and Nelmes (Ref. 6); Theory: Stirling (Ref. 7).

	γ rays	Neutrons	Theory
$\sin \theta/\lambda$ [\AA^{-1}]	<1.6	<2.1	
$U(\text{Sr})$ [\AA^2]	0.00259 (2)	0.00248 (7)	0.0026
$U(\text{Ti})$	0.00210 (2)	0.0021 (1)	0.0021
$U_{\parallel}(\text{O})$	0.00222 (8)	0.0022 (1)	0.0023
$U_{\perp}(\text{O})$	0.00571 (6)	0.00557 (6)	0.0053

thereby eliminating uncontrollable thermal stress during the cooling down process. One should note that the applied uniaxial pressure is negligible compared to the critical value at which the stress-induced ferroelectric transition occurs. A second method of obtaining monodomain crystals below T_c consists in the use of a specially shaped platelet.⁴ A number of reflections have been recorded in transmission geometry from a plate with edges 15 mm||[001], 5 mm||[110], and 0.3 mm||[110]. The intensities were calibrated to absolute scale by means of the 220 reflection from an ideally imperfect Si crystal.

Standard crystallographic least-squares refinements were carried out, minimizing $\chi^2 = \sum [F_o - F_c / \sigma(F_o)]^2$, where F_o and F_c are the observed and calculated structure factors, respectively. The effect of thermal motion about the equilibrium positions is accounted for by introducing Debye-Waller factors for each atom in F_c . The standard deviations $\sigma(F_o)$ were based on counting statistics. The extinction length for the strongest reflection amounts to 100 μm , so that the presence of primary extinction can be ruled out. Secondary extinction was treated using the Becker-Coppens formalism. The refined mosaicity parameter was within the experimentally determined range (1 min of arc). The five strongest structure factors have also been determined under extinction-free conditions from the thin platelet, so that the reduction in intensity below the kinematical value was at most 3%.

In Table I the mean square vibrational amplitudes for $T_c + 5$ K are presented and compared with results from a neutron diffraction study performed to unusually high resolution,⁶ as well as with a lattice-dynamical calculation.⁷ It is seen that there is remarkably good agreement. The higher sensitivity of γ -ray diffraction from the heavier atoms is reflected by the lower standard deviations. Because of the cubic site symmetry ($m\bar{3}m$), the motion of the Sr and Ti atoms is isotropic. The oxygen atoms, with site symmetry $4/mmm$, perform strongly anisotropic vibrations corresponding to the libration of the TiO₆ octahedra. The amplitudes along the bond direction are about the same for cation and anion. Thus the empirical rule enunciated in Ref. 8, that in cubic perovskite structures (ABX_3), $U(B) \approx U_{\parallel}(X)$, does hold in this case, too. Anharmonicity is expected as a precursor effect when the temperature approaches T_c . It has been the explicit aim of the neutron study by Hutton and Nelmes⁶ to obtain the magnitude and form of anharmonic thermal motion near T_c . Despite the extension up to very high diffraction vectors, no evidence of any anharmonic

TABLE II. Anisotropic mean square vibrational amplitudes U_{ij} and positional parameter x for tetragonal SrTiO₃ at $T=50$ K derived from γ -ray diffraction data. Indices indicate axial directions. The atomic positions are Sr at 4(b) $(0, \frac{1}{2}, \frac{1}{4})$, Ti at 4(c) $(0, 0, 0)$, O(1) at 4(a) $(0, 0, \frac{1}{4})$, and O(2) at 8(h) $(x, \frac{1}{2} + x, 0)$.

Sr	U_{11} [\AA^2]	0.00288(2)
	U_{33}	0.00278(3)
Ti	U_{11}	0.00286(3)
	U_{33}	0.00286(5)
O(1)	U_{11}	0.00567(14)
	U_{33}	0.00390(20)
O(2)	U_{11}	0.00429(23)
	U_{33}	0.00587(14)
	U_{12}	0.00063(26)
	x	0.2412(3)

component could be found. This issue is confirmed by our data which do not support a fourth-order anharmonic model of the thermal vibrations. (Cubic terms are all zero for the site symmetries considered here.)

The structural results for $T=50$ K are summarized in Table II. There are now nine independent thermal vibration parameters, two for each of Sr, Ti, and O(1), and three for O(2). [O(1) denote the set of oxygen atoms which are not displaced, whereas O(2) designate the displaced ones.] The amplitudes of thermal motion for all atoms are found to be substantially larger than at 111 K, and thus strongly deviate from the temperature dependence which is expected for an assembly of quantized harmonic oscillators. These deviations have to be attributed to the transition from the cubic to the tetragonal phase. The anomalous behavior applies in particular to Ti and the oxygen vibrations towards Ti, i.e., $U_{33}[\text{O}(1)]$ and $U_{11}[\text{O}(2)]$. The rms vibrational amplitude of Ti is 0.0458(2) \AA at 111 K, but 0.0535(4) \AA at 50 K. Note that a crystal with a Debye temperature of a few hundred K is at 50 K already very close to its vibrational ground state. From the refined value of the x position of the O(2) atom, the antiferrodistortive rotation angle is determined to $2.01(7)^\circ$, which is in good agreement with the value from electron paramagnetic resonance data, $1.90(7)^\circ$.⁹

Pure SrTiO₃ does not become ferroelectric under normal atmospheric pressure at any finite temperature, but yields an extrapolated Curie temperature of 36 K. The origin of the quantum-mechanical suppression has been accounted for by the following simple criterion: in order to stabilize the paraelectric state, the zero-point motion of the Ti ions should have a larger magnitude than Δz , the zero temperature ferroelectric displacement of Ti towards an off-center position. From a number of oxide ferroelectrics it was found that Δz is related to the Curie temperature by $k_B T_o = (1/2)\kappa(\Delta z)^2$ with the rather universal force constant $\kappa \approx 5.5 \times 10^4$ dyn/cm.^{10,1} With $T_o = 36$ K, this yields $\Delta z = 0.043$ \AA . From Table II it is seen that the Ti vibration is isotropic with $\sqrt{U} = 0.0535(4)$ \AA . Thus $\Delta z < \sqrt{U}$ is clearly fulfilled. The absolute magnitude of the vibrational amplitude exhibited by Ti, however, is not unusually large. It is rather the small would-so ferroelectric displacement that zero-point motion plays such a prominent role. Each phonon branch in the Brill-

louis zone contributes to the atomic mean square amplitudes of motion. It is therefore not surprising that all component atoms, not only Ti, have increased magnitudes. Additional support for the observed anomaly in thermal vibrations is provided by the elastic properties. There is copious experimental evidence that SrTiO₃ becomes elastically softer below T_c .¹¹⁻¹³

The analogy with ferroelectric perovskites, however, cannot be taken too strong. At 50 K, the Ti vibrations turn out to be isotropic, and the enhanced vibrations of the nonequiva-

lent oxygen atoms towards Ti barely differ from each other. No preference for a unique polar axis is thus exhibited. Vibrations along the six Ti-O bonds display octahedral symmetry, all of them associated with the characteristic features of suppressed dipoles. The observed absence of anisotropy is in qualitative agreement with the inference of Müller *et al.*¹⁴ that SrTiO₃ does become more cubic near 37 K. In conclusion, we have demonstrated from precision diffraction studies the enhancement in thermal amplitudes which prevents the formation of static Ti-O dipoles.

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