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Rietveld analysis of strontium titanate in the Müller state

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Abstract. We report a neutron and x-ray Rietveld analysis of strontium titanate down to 1.5 K. The results do not show evidence for any supplementary structural phase transition or local frozen polar ordering. These results are a supplementary indication that at very low temperature strontium titanate should display only weak local modifications of the static tetragonal structure with no strong signature in the diffraction pattern.

Strontium titanate is a well known quantum paraelectric (or latent ferroelectric) at very low temperatures, i.e. below 30 K. At room-temperature simple cubic $Pm3m$ perovskite structure transforms at 105 K to a non-ferroelectric tetragonal $I4/mcm$ (pseudo-cubic) phase: this transformation was considered for a long time as a textbook example of a phase transition driven by a soft-zone-boundary optical phonon [1–3]. The mechanism of this transition came again under discussion after the observation of the so-called central peak [4, 5] above the critical temperature, and once more after the observation of two length scales in the spatial correlation length (as revealed by x-ray diffuse scattering [6–8]). Moreover the observation of a very large anomaly in the dielectric constant associated with a high-frequency relaxation below 30 K [9, 10], the observation of a soft-zone-centre phonon near 40 K [11] and evidence of ferroelectricity induced by substitution of strontium atoms by calcium atoms [12] led to the conclusion that quantum fluctuations (i.e. zero-point motion) suppress the latent ferroelectricity of strontium titanate.

More recently Müller *et al* [13] proposed the existence of a coherent paraelectric quantum state on the basis of an EPR study. Neutron scattering and Brillouin scattering results [11] and elastic constant anomalies [14, 15] as well as the observation by EXAFS of an anomalous evolution of the (local) Debye–Waller factor [16] led to discussion about a possible supplementary phase transition (which could eventually be incommensurate) or at least the possibility of clusters with local polar order.

At first glance it may appear surprising that no structural evolution of $SrTiO_3$ has been reported up to now below 40 K. In fact, despite the great simplicity of the structure, several drastic experimental problems made the various attempts fail. These problems are mainly related to the existence of tetragonal domains, to a very large extinction effect due to the high quality of the single crystals, and, last but not least, to cryogenic problems which are inherent to very low-temperature four-circle diffractometry. On the other hand powder diffraction in perovskite-related structures has from long ago revealed its feasibility (see e.g. [17]), with minimization or quasi-absence of the experimental problems mentioned above. For instance in the study of the polar order in relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN),

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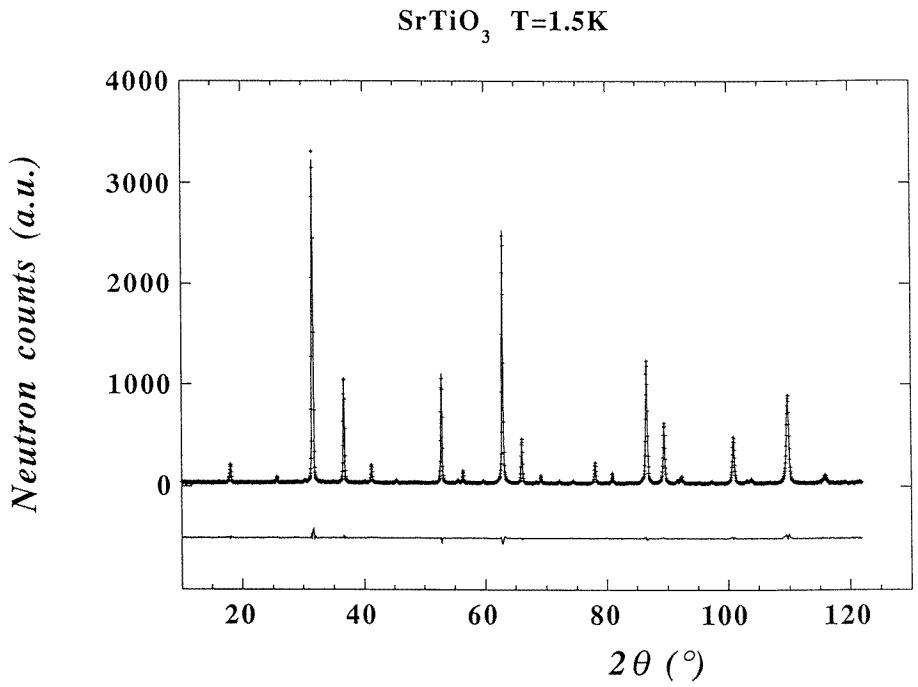

Figure 1. Observed (neutron) intensities, intensities calculated from the Rietveld refinement, and the difference at 1.5 K.

diffuse scattering induced by a local polarization inside the paraelectric cubic matrix was clearly detected in the neutron and x-ray powder patterns; it was then possible to refine the structure of the local ferroelectric phase [18]. Also some incommensurate phases have been evidenced and studied by the sole powder techniques (see e.g. [19]).

Full neutron diffraction patterns (with steps of 0.05° between 6 and 120° (2Θ))) were collected at 1.5, 32 and 50 K on the high-resolution two-axis powder diffractometer 3T2 ($\lambda = 1.226$ Å) at the Laboratoire Léon Brillouin using the Orphée reactor facilities. We have also recorded an x-ray diagram at 7.5 K (between 6 and 140° (2Θ) with steps from 0.004 to 0.01° and counting time between 12 and 48 s, depending on the angle range) using a high-resolution two-axis Bragg–Brentano goniometer with Cu Kβ monochromatic radiation issued from a 18 kW Rigaku rotating anode. The Rietveld refinements were performed using the XND program [20] and values of $b_{Sr} = 0.69$, $b_{Ti} = -0.33$, $b_o = 0.575$ in 10^{-12} cm units were used for the neutron scattering lengths.

An overall view of the neutron pattern at 1.5 K is shown in figure 1. The main difference between the three neutron patterns of the different temperatures is in the intensity of the superstructure lines associated with the rotation of the oxygen octahedra, which are clearly observed (figure 2). Careful comparison of the different patterns does not reveal any evidence for additional peaks than those associated with the tetragonal structure; nor is there any additional distortion observed in the (high-resolution) x-ray pattern. Examination of the background level in the neutron patterns shows no differences between the three experiments, except in the high-Q range where a weak increase is observed (with increasing temperature) due to the diffuse scattering associated with the thermal agitation.

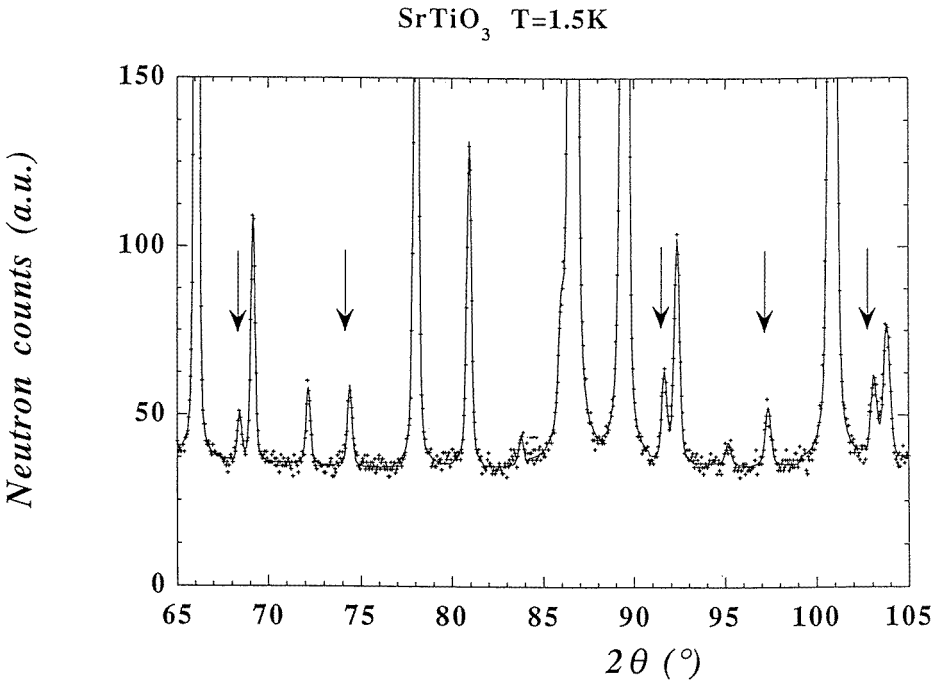

Figure 2. An enlarged part of figure 1. The black arrows indicate the weak superstructure lines due to the tilting of oxygen octahedra.

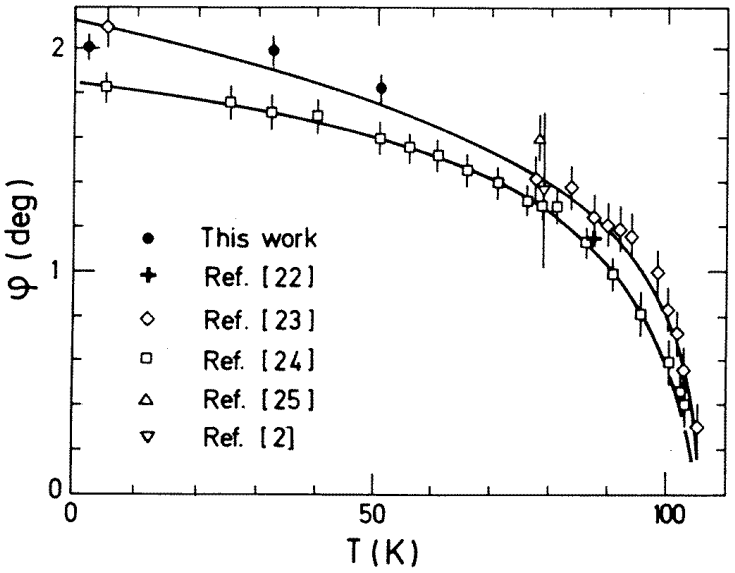

Figure 3. A comparison of the present results with other results, compiled by Tsuda and Tanaka [22].

Table 1. Structural and Debye–Waller parameters refined from the neutron diagrams. ε_s is the spontaneous strain and φ the rotation angle of the oxygen octahedra.

	1.5 K	32 K	50 K
a (Å)	5.5134(10)	5.5138(10)	5.5148(10)
c (Å)	7.8072(20)	7.8067(18)	7.8068(18)
ε_s (10^{-3})	1.29	1.15	0.99
φ (°)	2.01(5)	1.99(5)	1.81(5)
O_2 (8 h) x	0.2412(2)	0.2413(2)	0.2421(2)
B_{iso} (Å^2)	0.46(8)	0.46(8)	0.46(8)
β_{11}	0.0030(8)	0.0030(8)	0.0030(8)
β_{33}	0.0025(6)	0.0025(6)	0.0025(6)
β_{12}	0.0001(8)	0.0001(8)	0.0001(8)
Sr (4b) B_{iso} (Å^2)	0.34(2)	0.34(2)	0.34(2)
β_{11}	0.0024(6)	0.0024(6)	0.0024(6)
β_{33}	0.0018(4)	0.0018(4)	0.0018(4)
Ti (4a) B_{iso} (Å^2)	0.15(4)	0.15(4)	0.15(4)
β_{11}	0.0007(8)	0.0007(8)	0.0007(8)
β_{33}	0.0012(4)	0.0012(4)	0.0012(4)
O1 (8f) B_{iso} (Å^2)	0.47(14)	0.47(14)	0.47(14)
β_{11}	0.0050(9)	0.0050(9)	0.0050(9)
β_{33}	0.0012(2)	0.0012(2)	0.0012(2)
R_{wp} (%)	4.4	4.4	4.5
R_b (%)	2.4	2.2	2.6
R_{exp} (%)	3.2	3.2	3.2
GOF	1.4	1.4	1.4

The refinement of the diffraction patterns has been performed in the $I4/mcm$ tetragonal space group. The only structural parameters are the x positions of the four equivalent oxygen atoms of the octahedra, whose rotation is responsible for the cubic to tetragonal transition, and the Debye–Waller B factors of the Sr (0 1/2 1/4), O1 (0 0 1/4), O2 (x 1/2 + x 0) and Ti (0 0 0) atoms. The refinements converged in a few cycles to a very good value for the goodness of fit; in particular we obtain excellent fits for the superstructure peaks due to the tilting of the oxygen octahedra (figure 2). The structural results from the neutron experiments and the classical agreement factor are summarized in table 1. The values for the cell parameters and the spontaneous strain $\varepsilon_s = 1-2a/c$ are in good agreement with the measurements by Sato *et al* [21]. We have calculated from the refined value of the x position of the O2 atoms the tilting angles φ of the oxygen octahedra (see table 1); these values are also reported in figure 3. Our experiments provide the first non-local 'bulk' measurement of this tilting at these low temperatures: they are in good agreement with the convergent beam electron microscopy measurements of Tsuda and Tanaka [22] and the electron spin resonance experiments of Unoki and Sakudo [23] which indicated slightly higher values than those obtained from EPR by Müller *et al* [24]. For the B thermal parameters we found classical stable values which within the precision of the measurements are constant whatever the temperatures are. These isotropic parameters could be decomposed into anisotropic factors but with no significant gain in the agreement factors. We also refined the x-ray data at 7.5 K, which gave, to the precision of the measurements, the same results for strontium and titanium (the B and x values of oxygen atoms were not refined) as those obtained at 1.5 K from the neutron data.

In conclusion, we have found that the structure of strontium titanate in its very low-temperature phase shows no departure below 32 K from the classical tetragonal structure. Moreover we did not observe the anomalies in the (local) Debye–Waller *B* factor observed by EXAFS: in fact for these factors we obtained the standard values. We also believe that the presence of clusters of local (frozen) polarization with sizes as small as 50 Å should manifest itself by the presence of diffuse scattering intensity as in the relaxor PMN, which has not been observed in our measurements. The results presented in this paper are thus a supplementary indication that the so-called Müller state [26] is a weak local modification of the static tetragonal structure.

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