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A Synchrotron Radiation Study of Strontium Titanate

BY E. N. MASLEN AND N. SPADACCINI

Crystallography Centre, University of Western Australia, Nedlands 6009, *Western Australia*

T. ITO

Department of Chemical Technology, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-02, *Japan*

F. MARUMO

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta-machi 4259 *Midori-ku, Yokohama* 227, *Japan*

AND Y. SATOW

Faculty of Pharmaceutical Sciences, University of Tokyo, 7-3-1 *Hongo Bunkyo-ku, Tokyo* 113, *Japan*

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Abstract

Electron deformation densities $\Delta\rho$ for $SrTiO_3$ have been determined from diffraction data measured using focused synchrotron radiation with $\lambda = 0.7000(2)$ Å at the Photon Factory, KEK, Japan. Corrections for secondary extinction were estimated from the variation of diffraction intensity with path length, and checked from the λ-dependence of the strong intensities indicated by measurements using a weaker parallel beam with $\lambda = 0.5000(2)$ Å. The 0.7 Å study is more precise than earlier analyses with Mo $K\alpha$ radiation. The difference density near the Ti nucleus is mildly anisotropic, and the $\Delta\rho$ topography is similar to those for closed-shell atoms in related perovskite structures.

Introduction

At room temperature $SrTiO_3$ is isomorphous with the KMF_3 compounds with M = Mn, Co, Fe, Ni and Zn, which have the cubic $Pm\bar{3}m$ structure that characterizes the perovskite series. There is strong scientific interest in this series, partly because of the ferroelectricity, superconductivity and other technologically important properties of particular members. Some of these properties are related to deviations from the ideal structure. Full understanding of the effect of structural distortions is more likely to be achieved when the ideal case is thoroughly understood.

Diffraction studies of $SrTiO_3$ with Mo $K\alpha$ radiation by Buttner & Maslen (1992) yielded atomic charges

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consistent with atomic electronegativities. The vibration parameters indicate that Ti vibrates more strongly than the O atom along the Ti—O bond. In most cases light anions vibrate more than the heavier cations to which they are bonded. The M—O bond stretching for O atoms octahedrally coordinated to metal atoms with high formal charges in lattice structures is an exception to this generalization. This phenomenon appears to play an important role in physical properties such as ferroelectricity. Consequently, we have sought to study the relationship between structure, vibrational motion and electron density in $SrTiO_3$ as precisely as possible by diffraction methods.

The accuracy of studies of $SrTiO_3$ with X-ray tube sources is limited by extinction. In seven studies involving three separate crystals Buttner & Maslen (1992) obtained consistent results only when the extinction corrections were modest. Extinction can be reduced by the use of small crystals, but for measurements with tube sources there is a corresponding decrease in statistical precision for the weak reflections. Buttner & Maslen (1992) also inferred that the reliability of extinction corrections determined by minimizing the difference between observed and calculated structure factors was limited. In general, it appears unlikely that extinction parameters determined by minimizing $F_o - F_c$ differences satisfy the Gauss–Markov conditions for validity in least-squares processes.

Maslen & Spadaccini (1993) point out that unbiased secondary extinction corrections may be evaluated from the variation of reflection intensity with path length. The resulting corrections can be verified, and the significance of primary extinction assessed, from the variation of intensity with wavelength. Synchrotron radiation, being readily tuned to different wavelengths, is thus a valuable tool for studying extinction. Use of this radiation facilitates the study of crystals which are sufficiently small to ensure that diffracion is almost kinematic (Bachman, Kohler, Schulz & Weber, 1985). The high intensity improves the precision of measurements of the weaker structure factors. Reducing the effects of extinction improves the accuracy, especially of the strong low-order structure factors which are particularly important when measuring inter-atom movement of electrons, and hence polarity, for ionic structures.

Experimental

Vertically polarized radiation with $\lambda = 0.7000(2)$ Å diffracted from a Si(111) double crystal monochromator was focused with a curved mirror (Satow & Iitaka, 1989). By positioning the specimen slightly off-focus, changes to the synchrotron radiation intensity due to instabilities in the particle beam are reduced. The focusing mirror is not effective at shorter wavelength. An almost parallel beam with $\lambda = 0.5000(2)$ Å and similar polarization was diffracted from a Si(422) double crystal monochromator. The beam intensity at the sample was approximately one twentieth of that for the 0.7 Å focused beam.

Table 1. *Experimental and refinement data for* $SrTiO_3$

Formula weight, M_r	183.51	
Space group	$Pm\bar{3}m$	
Wavelength (Å)	0.7	0.5
Cell dimension (Å)	3.9131 (4)	3.9096 (3)
V (Å^3)	59.92 (1)	
D_x (Mg m^{-3})	5.086	
Maximum variation of standards based on I (%)	6.0	2.1
Instability factor c from standards $[\sigma^2(I) = \sigma^2_{counts} + cI^2]$	9.79×10^{-5}	4.88×10^{-5}
Reflections measured	2947	2459
Linear absorption coefficient (mm^{-1})	254.89	106.27
Absorption correction min/max	1.638; 2.882	1.229; 1.493
R_{int} (before; after absorption)	0.063; 0.033	0.061; 0.079
Independent reflections	95	93
R factor	0.015	0.015
wR factor	0.012	0.014
X	4.212	2.581
y_{min} (for 002)	0.86	0.96

$SrTiO_3$ crystals were prepared by high-temperature flux growth, as described by Buttner & Maslen (1992). The specimen selected for study was a rectangular prism, with dimensions $l(\pm 100)$, $l(0\pm 10)$ and $l(00\pm 1)$ of 10, 19 and 41 microns, respectively, where l is the distance from the face to a common origin. Reflection intensities were measured systematically for the complete sphere of reciprocal space with $\sin\theta/\lambda < 1.1$ Å^{-1}.

Six standard reflections were monitored every 100 reflections to check the stability of the incident beam. The measured intensities were modified for fluctuations in the standards and the variances were adjusted as suggested by Rees (1977). The stronger intensities were reduced by an absorber with an attenuation factor of 4.56. Lorentz, polarization and absorption correction (Alcock, 1974) were evaluated analytically. The procedure for the 0.5 Å data was similar, except that the attentuation factor for the stronger reflections was 1.841.

The greater accuracy of the 0.7 Å data is indicated by the lower R_{int} value in Table 1. This was partly due to the improved counting statistics for the weak reflections from the higher beam intensity, but at the longer wavelength there was closer agreement between equivalents for most of the stonger reflections, for which accuracy is limited more by beam stability than by counting statistics. This confirms that the 0.7 Å beam was more stable than the 0.5 Å beam, as expected from their focussed and parallel geometries.

Structure factors* were evaluated using the spherical atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), with dispersion corrections: $\Delta f'$, $\Delta f''$ of 0.089, 1.829 at 0.5 Å, −1.345,

*A list of structure factors has been deposited with the IUCr (Reference: AS0667). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3.159 at 0.7 Å for Sr; 0.174, 0.227 at 0.5 Å, 0.274, 0.435 at 0.7 Å for Ti; 0.004, 0.003 at 0.5 Å, 0.010, 0.006 at 0.7 Å for O, evaluated by Creagh (1990). Further details of the data measurement and analysis are included in Table 1. Computer programs *STARTX*, *DIFDAT*, *ABSORB*, *ADDATM*, *ADDREF*, *FC*, *CRYLSQ*, *BONDLA*, *FOURR*, *CHARGE*, *CONTRS*, *SLANT* and *PLOT* from the *Xtal*3.0 system (Hall & Stewart, 1990) installed on a Sun 280 computer were used in the analysis.

The intensities for the strong unique reflections were plotted as a function of path length which, because of the anisotropic shape of the crystal, changes for symmetry-related reflections. The intensities for the strongest reflections vary systematically with path length, *i.e.* the intensity *versus* path length line had a significant slope consistent with the effects of extinction. The r^* values (Zachariasen, 1967) were evaluated to be $0.22\,(4) \times 10^{-4}$ for both data following the formalism of Maslen & Spadaccini (1993). The reasonableness of that result is confirmed by the y_{min} values for the reflections measured with 0.7 and 0.5 Å radiation, which show the expected λ-dependence (Table 1).

Vibration parameters

The vibration parameters are compared with the best set from Buttner & Maslen (1992) in Table 2. The vibration parameters for the two synchrotron studies are consistent except for Sr, where the $\lambda = 0.5$ Å value is somewhat higher. The standard deviations in the mean-square vibration amplitudes for the 0.7 Å data are roughly half those from the Buttner & Maslen (1992) analysis, while the vibration parameters are systematically *ca* 5% smaller. A small part of the discrepancy could be attributed to the extinction corrections, which interact with the vibration amplitudes *via* the scale factor. By over-correcting the values measured for the strong low-order reflections the temperature factor is increased, but test calculations indicated that the effect is far too small to explain the whole discrepancy. There is some possibility that this problem is related to scan truncation. For example, an increased temperature factor would be expected if the Mo$K\alpha$ reflections were increasingly truncated at high angles due to α_1/α_2 splitting. Truncation of background with the two synchrotron radiations would not be identical because the profiles for focused and parallel beams differ.

Atomic charges

Atomic charges, calculated by projecting $\Delta\rho$ onto atomic density basis functions (Hirshfeld, 1977) for the 0.7 Å data are compared with values from the best set from Buttner & Maslen (1992) in Table 3. The $\lambda = 0.5$ Å results, being limited in accuracy by an unreliable (001) structure factor, are omitted. The atomic charges

Table 2. *Vibration parameters* ($\times 10^5$ Å^2)

	0.7 Å		0.5 Å		Buttner & Maslen (1992)	
	U_{11}	U_{22}	U_{11}	U_{22}	U_{11}	U_{22}
Sr	613 (6)		658 (8)		683 (13)	
Ti	478 (6)		476 (10)		535 (14)	
O	290 (28)	923 (21)	283 (52)	937 (38)	293 (63)	975 (42)

Table 3. *Atomic charges from the Hirshfeld partitioning of* $\Delta\rho$, *in electrons*

	0.7 Å	0.5 Å	Buttner & Maslen (1992)
Sr	1.16 (7)	−0.09 (5)	0.59 (6)
Ti	0.72 (7)	1.03 (5)	0.26 (6)
O	−0.62 (5)	−0.31 (4)	−0.30 (4)

estimated from the Buttner & Maslen (1992) data with extinction corrections determined from F_o *versus* F_c agreement were approximately half those from the 0.7 Å study. It is probable that extinction is over-estimated for all the structures reviewed by Maslen &

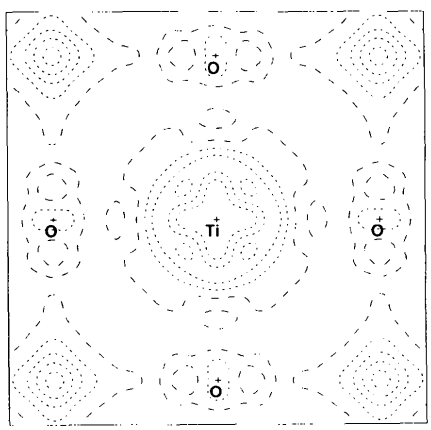

Fig. 1. $\Delta\rho$ for $SrTiO_3$ (100) plane, map borders 5.0 × 5.0 Å. Contour intervals 0.25 e Å^{-3}, zero contour dashed, negative contours broken.

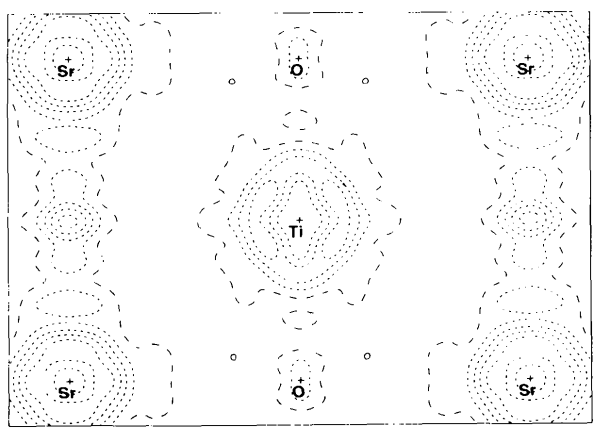

Fig. 2. $\Delta\rho$ for $SrTiO_3$ (110) plane, map borders 7.0 × 5.0 Å. Contour intervals 0.25 e Å^{-3}, zero contour dashed, negative contours broken.

Spadaccini (1989) because the relevant extinction corrections were determined from F_o *versus* F_c agreement. The positive charge on the transition metals would be correspondingly underestimated in that review, changing slightly the trends originally reported by these authors.

$\Delta\rho$ maps for the 0.7 Å data shown in Figs. 1 and 2 are (100) and (110) planes corresponding to Figs. 1(*a*) and 2 of Buttner & Maslen (1992). Although the maps for the different radiations are similar in general, there are differences in detail. At the atomic sites local maxima in the synchrotron radiation map replace minima in the Mo $K\alpha$ map.

The region of depleted density surrounding the Sr and Ti cations is clearly defined in Figs. 1 and 2. There is also a strong minimum in the density at the structural cavity (relative to the rock-salt structure) mid-way between adjacent Sr atoms. Electron density is transferred from the vicinity of the atoms and the structural cavity to the broad sea of positive density in the internuclear region.

To within a scale factor $\Delta\rho$ near the Ti position closely resembles that observed near Zn in the isostructural $KZnF_3$ compound, as reported using similar data measured at the Photon Factory (Maslen, Spadaccini, Ito, Marumo & Satow, 1995). In both maps there is a local maximum in $\Delta\rho$ at the transition-metal atom sites, flanked by minima directed towards the K or Sr cations. There are local maxima 0.8 and 1.0 Å along Sr—Ti and K—Zn, respectively. These features near Ti are less compact than those near Zn, as would be expected since the effective nuclear charge for Ti is lower than that for Zn. Ti^{4+} and Zn^{2+} are closed-shell cations with outer shell configurations $3d^0$ and $3d^{10}$, respectively. The higher degree of polarization around Ti is consistent with a formally empty $3d^0$ subshell being more polarizable than a $3d^{10}$ configuration. Presumably, that subshell is partly occupied because of overlap with the valence electrons from neighbouring O and Sr atoms.

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The Chemical Bond and Atomic Displacements in $SrTiO_3$ From X-ray Diffraction Analysis

BY YU. A. ABRAMOV AND V. G. TSIRELSON

Mendeleev University of Chemical Technology, Moscow 125047, *Russia*

V. E. ZAVODNIK AND S. A. IVANOV

Karpov Institute of Physical Chemistry, ul.Obucha 10, *Moscow* 103064, *Russia*

AND I. D. BROWN

Institute for Material Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

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Abstract

The deformation electron-density (dynamic Fourier) maps and the anharmonicity of atomic displacements in strontium titanate, $SrTiO_3$ (Gram–Charlier model), were studied by high-precision single-crystal X-ray diffraction analysis at 145(1) and 296(2) K. Space group $Pm\bar{3}m$, cubic, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $Z = 1$, $F(000) = 84$,