

The twofold superstructure of titanium(III) oxybromide at $T = 17.5$ K

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The low-temperature ($T = 17.5$ K) structure of titanium(III) oxybromide, TiOBr, is reported as a twofold superstructure of the crystal structure at room temperature. Weak superlattice reflections were measured with synchrotron radiation X-rays and were analyzed by structure refinements employing superspace techniques. Both the low-temperature and the room-temperature structures of TiOBr are isostructural with the corresponding structures of TiOCl. The results indicate that at low temperatures TiOBr is in a spin-Peierls state, similar to that of TiOCl, but with the modulations and relevant interactions smaller than in the latter compound.

Comment

TiOBr (von Schnering *et al.*, 1972) and TiOCl (Schäfer *et al.*, 1958) are isostructural compounds that crystallize in the FeOCl structure type (Fig. 1). On cooling, they undergo two phase transitions, as evidenced by anomalies in the temperature dependencies of the magnetic susceptibilities (Seidel *et al.*, 2003; Kato *et al.*, 2005; Lemmens *et al.*, 2005). Previously, we have shown that in the lowest-temperature phase ($T < 67$ K) the crystal structure of TiOCl is a twofold superstructure of the structure at room temperature (Shaz *et al.*, 2005). The superstructure involves the formation of Ti–Ti dimers on the chains of Ti atoms parallel to [010], thus suggesting a spin-Peierls state by direct exchange on the quasi-one-dimensional chains of Ti atoms (Shaz *et al.*, 2005). Recently, Sasaki *et al.* (2005) reported superlattice reflections for TiOBr at low temperatures, but they did not report a satisfactory structure model because of the limited number of measured reflections (two reflections).

We report here the low-temperature twofold superstructure of TiOBr at $T = 17.5$ K. It is found that the pattern of displacements in TiOBr is similar to that in TiOCl, but with amplitudes that are only about half of the displacement

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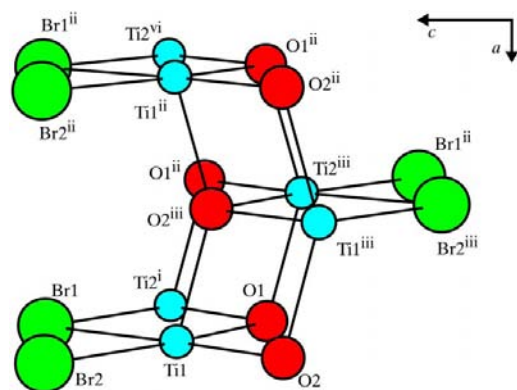


Figure 1

A perspective view of one layer of the crystal structure of TiOBr. Atomic labels and symmetry codes correspond to those given in Table 1, with the addition of (vi) $x - 1, y - 1, z$.

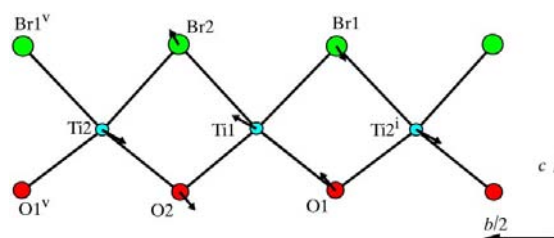


Figure 2

One ribbon, parallel to [010] at $x = 0$, containing the chain of Ti atoms. Deviations from the average structure are given by arrows (20 times their true values). Unit-cell axes are indicated. Atomic labels and symmetry codes correspond to those given in Table 1.

amplitudes in TiOCl (Fig. 2 and Table 1). These results indicate that TiOBr is in a spin-Peierls state at low temperatures, similar to that of TiOCl but with the relevant interactions smaller than in TiOCl, in accordance with the transition temperatures being lower in TiOBr ($T_{c1} = 27$ K and $T_{c2} = 47$ K) than in TiOCl ($T_{c1} = 67$ K and $T_{c2} = 90$ K; Seidel *et al.*, 2003; Shaz *et al.*, 2005).

Experimental

Crystals of TiOBr were grown by gas transport following published procedures (Schäfer *et al.*, 1958). Ti (Alpha, 99.99% purity), TiO₂ (Alpha, 99.99%) and TiBr₄ (Aldrich, 99.99%) were mixed with a 40% surplus of Ti and TiBr₄, and placed in a sealed and evacuated ($p = 1.5 \times 10^{-2}$ kPa) quartz glass tube, which was heated in a temperature gradient of 923–823 K for 72 h. The tube was cooled to room temperature at a rate of 15.6 K h⁻¹. The light-brown crystals had a needle-to-plate-like habit and developed a grey–white patina in air. They were thus handled under an inert atmosphere.

Crystal data

TiOBr
 $M_r = 143.8$
Monoclinic, $P2_1/m11$
 $a = 3.7852$ (12) Å
 $b = 6.9366$ (9) Å
 $c = 8.501$ (3) Å
 $\alpha = 90.00$ (2)°
 $V = 223.21$ (10) Å³
 $Z = 4$
 $D_x = 4.277$ Mg m⁻³

Synchrotron radiation
 $\lambda = 0.5$ Å
Cell parameters from 24 reflections
 $\theta = 10.0$ – 23.0 °
 $\mu = 8.35$ mm⁻¹
 $T = 17.5$ K
Platelet, translucent light brown
 $0.27 \times 0.13 \times 0.00$ mm

Data collection

Huber four-circle diffractometer $R_{\text{int}} = 0.054$
 Profile data with ω scans $\theta_{\text{max}} = 20.5^\circ$
 Absorption correction: Gaussian $h = -5 \rightarrow 5$
 (JANA2000; Petricek *et al.*, 2000) $k = -9 \rightarrow 3$
 $T_{\text{min}} = 0.475, T_{\text{max}} = 0.978$ $l = -10 \rightarrow 0$
 989 measured reflections 3 standard reflections
 416 independent reflections frequency: 90 min
 336 reflections with $I > 3\sigma(I)$ intensity decay: none

Refinement

Refinement on F $(\Delta/\sigma)_{\text{max}} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.018$ $\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{Å}^{-3}$
 $wR(F^2) = 0.029$ $\Delta\rho_{\text{min}} = -0.57 \text{ e } \text{Å}^{-3}$
 $S = 1.03$ Extinction correction: B–C type 1
 416 reflections Gaussian isotropic (Becker &
 21 parameters Coppens, 1974)
 $w = 1/[\sigma^2(F) + 0.0004F^2]$ Extinction coefficient: 0.09 (2)

Table 1
 Selected geometric parameters (Å, °).

| | | | |
|--------------------------|-------------|--|-------------|
| Ti1–Ti2 | 3.4110 (8) | Ti1–O2 ^{iv} | 1.9586 (6) |
| Ti1–Ti2 ⁱ | 3.5259 (8) | Ti2–O1 ^v | 2.228 (2) |
| Ti1–Ti1 ⁱⁱ | 3.7852 (13) | Ti2–O1 ⁱⁱⁱ | 1.9611 (6) |
| Ti2–Ti2 ⁱⁱ | 3.7852 (13) | Ti2–O1 ^{iv} | 1.9611 (6) |
| Ti1–Ti1 ⁱⁱⁱ | 3.1723 (7) | Ti2–O2 | 2.208 (2) |
| Ti1–Ti2 ⁱⁱⁱ | 3.1843 (7) | Ti1–Br1 | 2.5451 (7) |
| Ti2–Ti2 ⁱⁱⁱ | 3.1976 (7) | Ti1–Br2 | 2.5312 (7) |
| Ti1–O1 | 2.219 (2) | Ti2–Br1 ^v | 2.5535 (7) |
| Ti1–O2 | 2.201 (2) | Ti2–Br2 | 2.5406 (7) |
| Ti1–O2 ⁱⁱⁱ | 1.9586 (6) | | |
| Ti1–Br2–Ti2 | 84.53 (2) | Ti2 ⁱ –O1–Ti2 ^{iv} | 99.32 (6) |
| Ti1–Br1–Ti2 ⁱ | 87.51 (2) | Ti2 ⁱⁱⁱ –O1–Ti2 ^v | 149.63 (13) |
| Ti1–O2–Ti2 | 101.39 (9) | Ti1–O2–Ti1 ^{iv} | 99.25 (6) |
| Ti1–O1–Ti2 ⁱ | 104.91 (10) | Ti1 ⁱⁱⁱ –O2–Ti1 ^{iv} | 150.17 (13) |
| Ti1–O1–Ti2 ^{iv} | 99.05 (6) | Ti1 ^{iv} –O2–Ti2 | 99.52 (6) |

Symmetry codes: (i) $x, y - 1, z$; (ii) $x - 1, y, z$; (iii) $x - \frac{1}{2}, -y + \frac{3}{4}, -z$; (iv) $x + \frac{1}{2}, -y + \frac{3}{4}, -z$; (v) $x, y + 1, z$.

Diffraction at room-temperature confirmed the FeOCl structure type with space group $Pnmm$. Diffraction at 17.5 K indicated the presence of superlattice reflections at positions $q = (0, \frac{1}{2}, 0)$ from the main reflections. Accordingly, all Bragg reflections at low temperature were indexed with respect to the orthorhombic unit cell of the room-temperature structure and the modulation wavevector q , employing four integers ($hklm$). The main reflections are described by $m = 0$, while $m = 1$ indicates the superlattice reflections. Owing to the presence of the cryostat, only a limited range of setting angles of the crystal could be reached. This set-up allowed the measurement of most Bragg reflections in one octant that represents the unique reflections with respect to mmm symmetry. Furthermore, 16 observed main reflections and 24 observed satellite reflections could be measured within a second octant that would be required for a complete unique data set within monoclinic symmetry.

The structure was refined within the superspace formalism as a commensurately modulated structure having superspace group $Pnmm(0\beta 0)$, with $\beta = \frac{1}{2}$ and $t_0 = \frac{1}{8}$. Section $t_0 = \frac{1}{8}$ of superspace indicates monoclinic symmetry for the supercell. Therefore, one parameter was introduced for pseudo-merohedral twinning of the monoclinic structure on the pseudo-orthorhombic lattice. The refined volume fraction of the second twin domain was obtained as 0.492 (7). This result implies a 1:1 ratio of volumes of the two twin domains and an apparent mmm symmetry of the diffraction pattern. Therefore, the measured single octant represents a complete data set for the twinned crystal, as was confirmed by the good fit to the reflections measured for the second octant.

The superspace refinement allowed the structural parameters to be separated into parameters of the basic structure, as defined by the strong main reflections, and modulation parameters that give rise to the weak superstructure reflections (satellites). One modulation wave was refined, leading to two modulation parameters for each atom. Partial R values at convergence [$R(\text{main reflections}) = 1.59\%$ and $R(\text{satellites}) = 4.86\%$] show that a good fit to the superstructure reflections was obtained.

Subsequently, the structure was transformed to a twofold superstructure, leading to two independent atoms in the supercell instead of one in the basic structure unit cell. To allow for direct comparison of the superstructure and the room-temperature structure, a non-standard setting ‘monoclinic a unique’ with an inversion center at $(\frac{1}{4}, \frac{3}{8}, 0)$ was used. An ordinary structure refinement was performed in the supercell but with additional restrictions as they were derived from the superspace approach; the displacement parameters of the two independent atoms of the same species were made equal, the displacement parameter U_{23} of all atoms was set equal to 0, and $y(A2)$ was set equal to $\frac{1}{2} + y_{\text{ave}} - y(A1)$, where y_{ave} is the y coordinate of atom A in the room-temperature structure with values $y_{\text{ave}} = 0.5$ when A is Ti, and $y_{\text{ave}} = 0$ when A is O or Br. Omitting these restrictions leads to severe correlations between the parameters as a result of the pseudo-orthorhombic nature of the structure.

Data collection: *DIF4* (Eichhorn, 1996); cell refinement: *DIF4*; data reduction: *REDUCE* (Eichhorn, 1991) and *JANA2000* (Petricek *et al.*, 2000); program(s) used to solve structure: *JANA2000*; program(s) used to refine structure: *JANA2000*; molecular graphics: *DIAMOND* (Brandenburg, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1825). Services for accessing these data are described at the back of the journal.

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