Crystal symmetry and superlattice reflections in spin-Peierls system TiOBr

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Abstract

We have demonstrated the direct observation of the crystal symmetry by electron and synchrotron X-ray diffraction analyses. Although the crystal structure at room temperature can be explained by orthorhombic Pmmn symmetry in our powder X-ray diffraction analysis, we detected weak reflections which should be the forbidden reflections of the Pmmn symmetry by electron and synchrotron X-ray diffraction analyses using single-crystalline TiOBr samples. We concluded that the crystal symmetry of TiOBr is different from the orthorhombic Pmmn symmetry. In this report, we discuss the crystal symmetry on the basis of the subgroup of orthorhombic Pmmn at room temperature and low temperature below $T_c$ ($=27$ K).

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1. Introduction

Spin-Peierls transition is associated with an intrinsic lattice instability in a system of quantum mechanical antiferromagnetic chains, where $S = 1/2$ spins interact with each other via a Heisenberg exchange interaction and are coupled to the lattice. From the experimental point of view, all the spin-Peierls compounds discovered so far have been organic and difficult to substitute the other atoms. However, in 1993 Hase et al. discovered the first inorganic spin-Peierls material CuGeO$_3$ [1]. The discovery of CuGeO$_3$ has not only deepened our understanding of spin-Peierls system but also resulted in new phenomena, such as impurity effects [2]. Discovering a new inorganic spin-Peierls material is, therefore, considered to be highly valuable.

Recently, TiOX (X = Cl and Br) has been suggested to be a quasi-one-dimensional (1D) $S = 1/2$ spin system due to an one-dimensional overlapping of the wave function and a spin-Peierls compound [3]. The temperature dependence of the susceptibility of TiOX showed two successive phase transitions with a sudden drop to zero at $T_{c1}$ and started to gradually decrease at $T_{c2}$ ($T_{c1} = 67$ K and $T_{c2} = 95$ K for X = Cl [3], and $T_{c1} = 27$ K and $T_{c2} = 47$ K for X = Br [4]). Subsequently, heat capacity measurement confirmed these successive phase transitions, i.e. $T_{c1}$ is the first-order, and $T_{c2}$ is the second-order phase transition temperatures [5]. According to the nuclear spin resonance (NMR) analysis [6], TiOCl exhibited a pre-existing pseudo-spin gap above $T_{c2}$ and the unconventional intermediate state accompanying the decrease of $1/T_1$ between $T_{c2}$ and $T_{c1}$, and a first-order phase transition into a singlet ground state with an unusual large energy gap.

TiOX has a FeOCl-type crystal structure [4,7], where the TiO$_4$X$_2$ bilayers separate from each other along the c-axis, as schematically shown in Fig. 1. Direct exchange interactions are produced in the chains along the $b$-axis. Seidel et al. have suggested three types of chains; the strong one-dimensionality along the $b$-axis have been confirmed by electron spin resonance (ESR) analysis [8], which was supported by the temperature dependence of optical reflectivity [9] and angle-resolved photoelectron spectroscopy (ARPES) [10].

Recently, two successive lattice distortions related to the spin-Peierls transition were observed below $T_{c1}$ [4,11,12] and the incommensurate modulation within $T_{c1} < T < T_{c2}$ (intermediate temperature) [13,14]. Superlattice reflections were...
observed at (h, k + 1/2, 0) below \( T_{c1} \) and at (h ± \( \delta_h \), k ± \( \delta_k \), l) between \( T_{c1} \) and \( T_{c2} \). Strong diffuse scattering was observed along the h- and l-directions above \( T_{c2} \), indicating that the structural correlation along the chains develops far above \( T_{c2} \). This structural short-range correlation above \( T_{c2} \) can explain the well-fitted Bonner–Fisher curve to the temperature dependence of susceptibility of TiOBr [3,4,15]. \( T_{c1} \) is a first-order incommensurate to commensurate phase transition temperature with the spin-Peierls lattice distortion, and \( T_{c2} \), a second-order phase transition temperature which is related to the spin-Peierls lattice distortion with an incommensurate structure [16]. The study of both superstructures, the commensurate (below \( T_{c1} \)) and incommensurate (intermediate) phases, is the best way of solving this problem.

Two-fold superlattice reflections indicate the dimer formation of Ti–Ti on the chains along the b-axis below \( T_{c1} \), where a dimerized superstructure was reported in TiOX [4,11,12]. Palatinus et al. and Shaz et al. considered that superstructure exhibits a monoclinic symmetry and the space group \( P2_1/m \) (a-axis unique) with a doubled lattice constant \( b \) observed below \( T_{c1} \) [11,12]. However, they also pointed out the possibility that this superstructure can be explained by an orthorhombic symmetry. In conclusion, they could not experimentally determine the final crystal symmetry of the lowest temperature phase, because they did not have direct information necessary for resolving the symmetry due to the limited range of setting angles of the crystal.

In our present paper, we report on electron diffraction patterns at the \( hk0 \) reciprocal lattice plane under various temperatures in TiOBr [13,16]. We conclude that the crystal symmetry of TiOBr at room temperature is different from the orthorhombic \( Pmmm \) symmetry.

2. Experimental details

Polycrystalline and single-crystalline samples of TiOBr were prepared by a chemical vapor transport technique [4,15]. Rammed mixtures of Ti, TiO\(_2\) and TiBr\(_4\) were vacuum-encapsulated in a quartz ampoule. The mixtures were set on one side (hot side) of the ampoule, which was heated up to 680 °C with a gradient of 100 °C within 20 cm. It took 2 days for the samples to cool down to room temperature. Although single crystals were obtained on both sides, polycrystals and high-quality single crystals were obtained on the hot side. The crystals are dark brown and have rectangular shape with a typical surface area of 2×8 mm\(^2\) at the \( ab \)-plane.

Thin specimens for electron diffraction were prepared by crushing or thinning the samples by Ar\(^+\) ion sputtering. Some samples were ground using CCl\(_4\) and dispersed on Cu grids coated with carbon support films. These specimens were analyzed using a Hitachi HF-3000 high-voltage transmission electron microscopy (TEM) operating at 300 kV. For precise crystal structure determination, a synchrotron radiation (SR) powder X-ray diffraction experiment was carried out using a large Debye–Scherrer camera installed at BL02B2, SPring-8. The obtained powder data were analyzed by the Rietveld method. For precise crystal symmetry determination, SR X-ray diffraction experiments were carried out using the four-circle diffractometer at BL46XU, SPring-8. A single crystal with dimensions of 1.5×6×0.03 mm\(^3\) was glued on a BN plate, which was mounted on a refrigerator with the \( hk0 \) reciprocal plane parallel to the \( \chi \)-axis.

3. Experimental results

Fig. 2 shows the SR powder X-ray diffraction pattern of TiOBr with a wavelength of 0.0922 nm at room temperature. The crystal structure of TiOBr was determined by the Rietveld analysis of the SR powder X-ray diffraction pattern. The main reflections can be explained with orthorhombic \( Pmmm \) symmetry. A small amount of Ti\(_2\)O\(_3\) impurities was found, which might be formed by the reaction of TiOBr with moisture. In our powder X-ray diffraction experiments at room temperature, these data could roughly explain the orthorhombic structure model with the space group \( Pmmm \). Table 1 shows the atomic parameters of TiOBr at room temperature, assuming the \( Pmmm \) space group.
We observed the electron diffraction patterns of various reciprocal lattice sections for TiOBr single crystal under various temperatures; below $T_{c1}$, intermediate and room temperature. Fig. 3 shows typical electron diffraction patterns at the $(hk0)$-plane. Here, we indexed the main diffraction spots in Fig. 3 as the orthorhombic unit cell notation, according to the usually believed crystal structure of TiOBr. However, we observed weak spots, which should be the forbidden positions of the $Pmmm$ symmetry, such as $h=2n+1$ for $(h00)$, $k=2n+1$ for $(0k0)$ and $h+k=2n+1$ for $(hk0)$. Although we could not confirm that the weak spots at $(h00)$ are not due to the multiple scattering, we checked that the other weak spots do not correspond to the multiple scattering by carefully examining the possibility of the multiple scattering conditions. We also confirmed the existence of the weak reflections at $(0k0)$ and $(hk0)$ by using single crystal SR X-ray diffraction. These results suggest that TiOBr does not exhibit an orthorhombic $Pmmm$ symmetry at room temperature. The results of our electron and SR X-ray diffraction experiments using single crystal are not consistent with those of our SR powder X-ray diffraction experiments. Actually, it is difficult to detect the weak reflections in our X-ray powder diffraction experiment, because the ratio of the integrated intensity of the main reflection at $(020)$ to that of weak reflection at $(030)$ was almost $10^{-6}$. The forbidden reflections of $Pmmm$ are always observed, being independent of temperature. It is noted here that there is no forbidden reflection in the $(hk0)$-plane.

The superlattice reflection spots shown in Fig. 3(b) and (c) agree well with the results of previous SR X-ray diffraction experiments using a single-crystalline samples of TiOBr [14,16]. At the intermediate temperature, superlattice reflections are clearly visible near $(h, k+1/2, 0)$ with incommensurate structure. Below $T_{c1}$, superlattice reflection patterns show the two-fold superstructures along the $k$-direction at $(h, k+1/2, 0)$, accompanying the first-order phase transition. This superlattice reflections indicate the spin-Peierls lattice distortion in the chains parallel to the $k$-direction ($b$-axis). Fig. 4 shows various electron diffraction patterns within the $[111]$-, $[211]$- and $[121]$-zones at room temperature and low temperature below $T_{c1}$. Here, we indexed the main diffraction spots in Fig. 4 as the orthorhombic symmetry. We confirmed that the crystal symmetry remains unchanged against temperature. Fig. 4(e) shows the superlattice reflections indexed by $(1, 1/2, 1)$. The reflections below $T_{c1}$ can be explained using the two-fold unit cell along $b$-axis assuming the same crystal symmetry at room temperature [12,11,16].

We determined the diffraction patterns at various planes by electron and SR X-ray diffractions. At room temperature, the crystal symmetry of TiOBr is different from the orthorhombic $Pmmm$ symmetry. On the basis of infrared optical properties, Caimi et al. proposed that the effective space group corresponds to symmetry lower than that assumed so far [17]. The crystal symmetry below $T_{c1}$ is the same as that at room temperature. Therefore, we should determine the crystal structure at room temperature.

Table 2 shows the maximal non-isomorphic subgroups of the structure derived from an orthorhombic $Pmmm$ symmetry. Such subgroups are feasible, because the results of powder diffraction analysis can approximately explain $Pmmm$. We should assume the subgroups of $Pmmm$ to explain the weak forbidden reflection clearly observed in the electron diffraction patterns. Considering the results obtained by Shaz et al. [12] and Palatinus et al. [11] and no forbidden reflection in the $(hk0)$-plane obtained by the present authors, the $Pmmn2$ symmetry is most likely for the crystal structure at room temperature. However, $Pmmn2$ involves four independent atoms in this unit cell. This cannot explain the NMR results, which indicate that Ti and Cl atoms occupy the only one site at room temperature [6,18]. The crystal symmetry at room temperature may be the other symmetry which borders on $Pmmn$, or NMR measurement cannot detect the different two or more sites since its broken symmetry is so small in this system.

![Fig. 3. Electron diffraction patterns of single crystal of TiOBr at (hk0)-plane at (a) room temperature, (b) 27.7 K (incommensurate phase), (c) 4.2 K (commensurate phase). Arrows indicate the superlattice reflections. However, the superlattice reflections in (b) appear as streaky double peaks along the $h$-direction.](image-url)
Below $T_c$, Shaz et al. suggests the two crystal symmetry; monoclinic $P2_1/m$ and orthorhombic $Pmmn$ [12]. Finally, they concluded that monoclinic $P2_1/m$ are most likely, however, this is not consistent with our results, since crystal symmetry of TiOBr does not have forbidden reflections. Kato et al. suggested that the anisotropy and the temperature dependence of the electron spin resonance (ESR) profile widths of TiOX can be understood by considering the Dzyaloshinsky–Moriya interaction [15]. This is favorable for the lower symmetry.

4. Conclusion

In summary, we have demonstrated the direct observation of the crystal symmetry by electron and SR X-ray diffraction analyses. The crystal symmetry of TiOBr at room temperature is different from the orthorhombic $Pmmn$ symmetry. Actually, many forbidden reflections for the $Pmmn$ symmetry appear in our electron diffraction experiments. Although we discuss the crystal symmetry on the basis of the subgroup of orthorhombic $Pmmn$, it is difficult to uniquely determine the crystal symmetry at this stage. We believe that to determine the crystal structure accurately play a key role in this system, for which we should discuss the crystal symmetry at room temperature.

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| Crystal class | Space group | Unique choice | Extinction rule |
|---------------|-------------|---------------|-----------------|
| Orthorhombic  | $P2_12_12_1$ | $c_2$         | No              |
| Monoclinic    | $P112/m(P2/c)$ | f, 2          | $h00$; $h+k=2n+1$, $h00$; $h=2n+1$, $0k0$; $k=2n+1$ |
| Monoclinic    | $P12_1/m(P2_1/m)$ | b, 2          | $0k0$; $k=2n+1$ |
| Orthorhombic  | $Pmm2$      | $h00$; $h=2n+1$    |
| Orthorhombic  | $Pn2_1,Pn(Pmm2)$ | No            | $h00$; $h+k=2n+1$, $0k0$; $k=2n+1$ |
| Orthorhombic  | $P2_1mn(Pmm2)$ | $h00$; $h=2n+1$    |
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