

Preparation, Crystal Structure, and Electrical Resistivity of SbRe_2O_6 with a Re–Re Bond

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The rhenium compound SbRe_2O_6 has been prepared by reaction of $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ with rhenium metal in a sealed silica tube. Its structure was determined by single-crystal X-ray diffraction. Crystal data: monoclinic $C2/c$, $a = 16.048(2) \text{ \AA}$, $b = 4.920(1) \text{ \AA}$, $c = 5.480(2) \text{ \AA}$, $\beta = 91.90(2)^\circ$, $V = 432.4(2) \text{ \AA}^3$, $Z = 4$, $R (R_w) = 0.028(0.028)$ for 560 reflections. The structure comprises Re_2O_6 layers, which are slices of the rutile structure along the $10\bar{1}$ plane, and antimony atoms connecting the layers. The Re_2O_6 layers contain pairs of ReO_6 octahedra sharing an edge and the Re–Re distance is $2.517(1) \text{ \AA}$. SbRe_2O_6 has ordered stacking of Re_2O_6 layers in the sequence ABAB The electrical resistivity of SbRe_2O_6 along the bc plane shows metallic behavior ($2 \mu\Omega\text{-cm}$ at 5 K and $61 \mu\Omega\text{-cm}$ at 280 K). © 1998 Academic Press

INTRODUCTION

Some of the ternary oxides of rhenium, ruthenium, and osmium are known to have metal–metal bonds. The reported examples of rhenium compounds are $\text{La}_4\text{Re}_6\text{O}_{19}$ (1, 2), $\text{Nd}_4\text{Re}_2\text{O}_{11}$ (3), $\text{La}_4\text{Re}_2\text{O}_{10}$ (4), $\text{La}_6\text{Re}_4\text{O}_{18}$ (5), BiRe_2O_6 (6), $\text{Dy}_5\text{Re}_2\text{O}_{10}$ (7), and $\text{La}_3\text{Re}_2\text{O}_{10}$ (8). Most of these compounds contain bioctahedral $M_2\text{O}_{10}$ units in which two MO_6 octahedra share an edge. However, they take a large variety of crystal structures as indicated by their different stoichiometries. A common feature of these compounds is that they contain large trivalent cations. The choice of the trivalent cation seems crucial for the formation of metal–metal bonds in these oxides. For example, while $\text{Bi}_3\text{Ru}_3\text{O}_{11}$ (9) has Ru–Ru bonds, the isostructural compound $\text{La}_3\text{Ru}_3\text{O}_{11}$ does not (10, 11). In this paper we report another rhenium oxide, SbRe_2O_6 , having Re–Re bonds with smaller trivalent cations [Sb(III)]. Its structure is close to that of the bismuth analogue BiRe_2O_6 , but the space groups of the two compounds are different.

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The very high electrical conductivity of ReO_3 is well known, and dioxides of rhenium, ruthenium, and osmium are all metallic (12). From the simple consideration that the formation of metal–metal bonds will lead to the localization of valence electrons, we expect a lower conductivity for the ternary oxides with M – M bonds. However, conductivity measurements of $\text{La}_4\text{Re}_6\text{O}_{19}$ at two temperatures showed that it was a very good metallic conductor (1). In this article, we also report the conductivity of the new compound.

EXPERIMENTAL

Preparation of SbRe_2O_6 . The hydrate $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ was used as the antimony source. Originally the compound $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ was obtained by a hydrothermal reaction (13), but we found that the powder form of the compound could be obtained by the simple reaction of an aqueous solution of Re_2O_7 and Sb_2O_3 powder (14). The reaction of $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ with an equivalent amount of rhenium metal (Aldrich) in an evacuated sealed silica tube at 500°C for 3 days yielded black powder of SbRe_2O_6 . Single crystals of SbRe_2O_6 were obtained by a chemical transport reaction. A pressed pellet of a mixture of $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ (424 mg, 1.00 mmol) and rhenium metal (187 mg, 1.00 mmol) was sealed with iodine (11.6 mg) in an evacuated silica tube (outer diameter 10 mm; length, 350 mm), and the tube was heated in a thermal gradient for 7 days. Though most of the crystals were polycrystalline plates, a few prismatic crystals were obtained and used for single-crystal X-ray studies. The molar ratio Sb/Re determined by X-ray fluorescence analysis was 0.47.

Structure determination. All X-ray measurements were made with a Rigaku AFC5R diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation. The search and indexing procedures with the diffractometer showed that most of the crystals were twinned. The two components of the twinned crystals were related by a rotation of 180° around the c axis, and they had a common $hk0$ reciprocal plane. Among 10 crystals examined, only one crystal was found to be single

TABLE 1
Summary of the Crystallographic Data for SbRe_2O_6

Crystal system	Monoclinic	Chemical formula	$\text{O}_6\text{Re}_2\text{Sb}$
Space group	$C2/c$ (No. 15)	Formula weight	590.2
a	16.048(2) Å	Crystal size	$0.03 \times 0.05 \times 0.20$ mm
b	4.920(1) Å	ρ_{calc}	9.08 g/cm ³
c	5.480(2) Å	T	295 K
β	91.90(2)°	λ	0.7107 Å
V	432.4(2) Å ³	μ	620 cm ⁻¹
Z	4	R, R_w^a	0.028, 0.028 ^a

^aThe function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$.

and it was used for all X-ray measurements. The intensity data of all 2514 reflections within the 2θ range 5–60° were measured with the 2θ - ω scan mode and empirically corrected for absorption by the ψ -scan method (relative transmission factor, 0.568–0.977) (15). The space group was unequivocally determined from the observed systematic absences. Averaging the equivalent reflections yielded 627 independent reflections ($R_{\text{int}} = 0.088$), among which 580 reflections were observed ($|F_o| > 3\sigma(|F_o|)$). Positions of metal atoms were determined by the direct method (SHELXS-86) (16), and oxygen atoms were located by the Fourier method (SHELXS-76) (17). The structure was refined by the full-matrix least-squares method, with isotropic temperature factors for oxygen atoms and anisotropic factors for other atoms (ANYBLK) (18), where scattering factors were taken from the standard sources (19). Empirical extinction correction was included in the refinements and the refined extinction parameter (rT) was $7.4(3) \times 10^{-9}$ cm² (20). Table 1 summarizes the crystal data.

Electrical resistivity measurements. The ac resistivity measurements were carried out with the standard four-probe technique at the Institute for Solid State Physics. The crystal used for the measurements was a thin plate ($0.4 \times 0.3 \times 0.1$ mm) growing along the bc plane, and gold wires were bonded on it with conductive gold paste.

RESULTS AND DISCUSSION

Preparation

Only two compounds are known in the ternary Re–Sb–O system. One of them is the layered compound $\text{Sb}_4\text{O}_5(\text{ReO}_4)_2$ composed of cationic $(\text{Sb}_4\text{O}_5)^{2+}$ layers and tetrahedral perrhenate ions between the layers, where the oxidation state of rhenium is VII (14). The other compound is that reported here. Both of them have been prepared from the hydrate $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ (13). Heating the hydrate with or without Sb_2O_3 in a sealed tube yields $\text{Sb}_4\text{O}_5(\text{ReO}_4)_2$. If the hydrate is reduced by rhenium metal, the product is

SbRe_2O_6 , which contains rhenium with the oxidation number +4.5. Other products identified by powder X-ray diffraction were ReO_3 and $\alpha\text{-ReO}_2$.

Structure

The new compound SbRe_2O_6 is made of layers of composition $[\text{Re}_2\text{O}_6]^{3-}$ and antimony ions connecting the layers (Fig. 1). The Re_2O_6 layer can be regarded as a slice of the rutile structure. The slice is parallel to the $(10\bar{1})$ plane of the rutile structure and its thickness is twice the c edge of the rutile structure, which is equal to the length of two octahedra sharing an edge. The arrangements of rhenium atoms in the adjacent layers are identical in SbRe_2O_6 . However, oxygen atoms can be placed in two ways for a given arrangement of rhenium atoms as shown in Fig. 2. The two arrangements are different in the direction of each ReO_6 octahedron. One of them can be converted into the other by rotating every ReO_6 octahedron by 90° around its Re–Re axis. This operation is equivalent to a shift in the layer of $1/2, 1/2, 1/2$ in the rutile structure. These two types of Re_2O_6 layers are alternately stacked approximately along the c axis of the original rutile structure. The stacking accompanies a small shift along the a axis of the rutile structure. If we define the direction of the “original c axis” of a Re_2O_6 layer as the projection of the Re–Reⁱⁱ vector on the ac plane of a SbRe_2O_6 cell, the angle between the “original c axis” and the vector connecting the corresponding rhenium atoms in the adjacent layers is 10.2° (Fig. 3). The bismuth analogue BiRe_2O_6 reported by Rae Smith and Cheetham also consists of similar Re_2O_6 layers and connecting bismuth(III) ions (6). While Re_2O_6 layers in SbRe_2O_6 are stacked in the sequence of ABAB ..., each

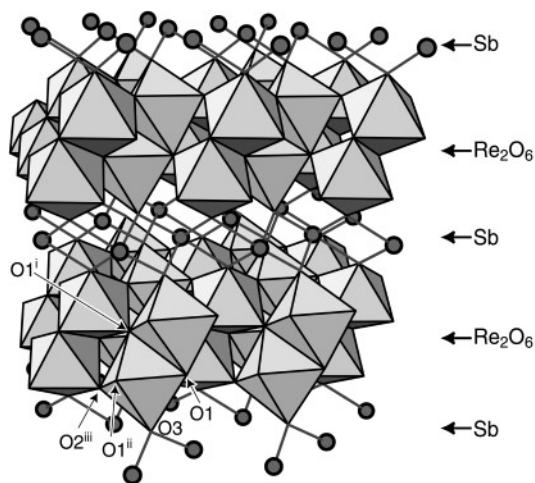


FIG. 1. Structure of SbRe_2O_6 . The octahedra show the ReO_6 units and the circles indicate the sites of antimony atoms. Symmetry codes are given in Table 3.

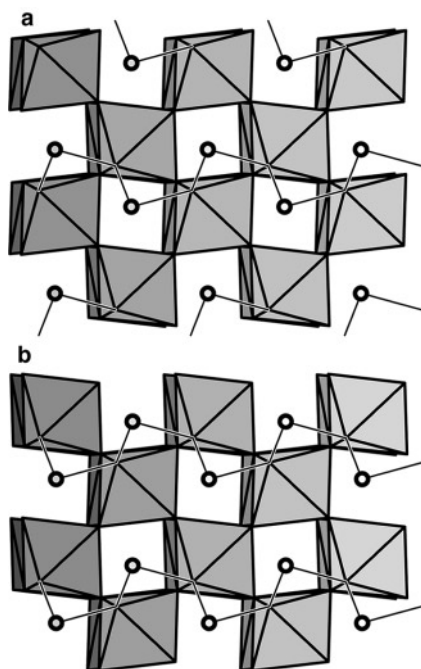


FIG. 2. The Re₂O₆ layers projected along the [101] direction. The octahedra show the ReO₆ units and the circles indicate the sites of antimony atoms. Darkness of an object in the figure indicates the depth: deeper objects are darker gray. (a) Layer between $x = 0$ and $x = 0.5$. (b) Layer between $x = 0.5$ and $x = 1.0$.

layer is disordered in two possible arrangements in BiRe₂O₆. Because only the sites of the oxygen atoms are different in the two patterns of layers, the arrangements of the rhenium atoms are similar in the two compounds.

In SbRe₂O₆, the coordination geometry of the four oxygen atoms around an antimony atom is a butterfly type, and the antimony atoms are close to the midpoint of two wing-tip oxygen atoms. In BiRe₂O₆, bismuth atoms have two possible coordination polyhedra. One is similar to that of the antimony atom in SbRe₂O₆, which is observed between the layers with different arrangements of oxygen atoms.

TABLE 2A
Atomic Coordinates and (Equivalent) Isotropic Thermal Parameters for SbRe₂O₆

Atom	x/a	y/b	z/c	U_{eq}^a or U_{iso}
Re	0.18044(3)	0.23356(13)	−0.11194(10)	0.0031(3)
Sb	0.0	0.3006(3)	0.25	0.0062(6)
O1	0.2160(6)	0.474(2)	0.169(2)	0.007(2)
O2	0.1399(6)	−0.034(2)	0.109(2)	0.008(2)
O3	0.0688(6)	0.418(2)	−0.078(2)	0.008(2)

^aThe isotropic equivalent thermal parameters are defined as $U_{\text{eq}} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

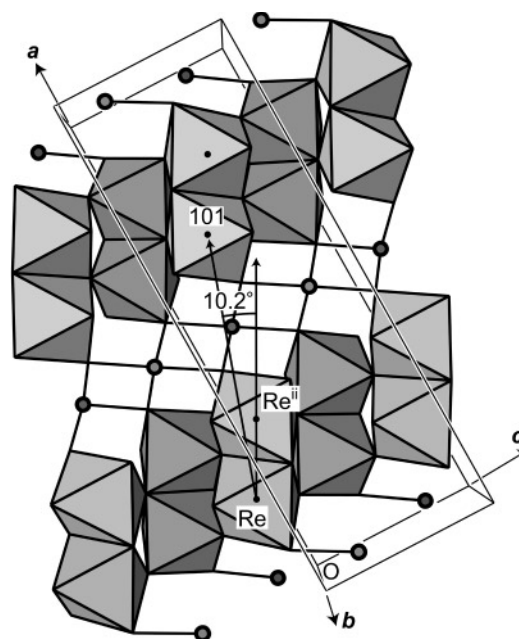


FIG. 3. Structure of SbRe₂O₆ projected on a 010 plane illustrating the stacking of Re₂O₆ layers. The vertical arrow indicates the “original c axis,” which is the projection of the Re–Reⁱⁱ vector on the ac plane. The octahedra show the ReO₆ units and the circles indicate the sites of antimony atoms. Darkness of an object in the figure indicates the depth: deeper objects are darker gray. Symmetry codes are given in Table 3.

Another coordination geometry is found for a bismuth atom between the layers with the same arrangement, and is a deformed octahedron. The latter coordination is not suitable for an antimony atom requiring larger space for its lone pair electrons, and this is presumably the reason why SbRe₂O₆ has stacking only of the ABAB ... type.

Because of the difference in the stacking sequence of the Re₂O₆ layers, SbRe₂O₆ and BiRe₂O₆ belong to different space groups (SbRe₂O₆, $C2/c$; BiRe₂O₆, $C2/m$). The unit-cell vectors of the antimony compound (\mathbf{a}_{Sb} , \mathbf{b}_{Sb} , \mathbf{c}_{Sb}) can be related to those of the bismuth compound (\mathbf{a}_{Bi} , \mathbf{b}_{Bi} , \mathbf{c}_{Bi}) in the following way. The direction of the unique axis is common in both structures ($\mathbf{b}_{\text{Sb}} \approx \mathbf{b}_{\text{Bi}}$), which corresponds to the [010] direction of the rutile structure. Another direction in which the Re₂O₆ layer extends, the [101] direction in the rutile structure, is along the \mathbf{c}_{Sb} vector in SbRe₂O₆ and along the $-\mathbf{a}_{\text{Bi}}$ vector in BiRe₂O₆ ($\mathbf{c}_{\text{Sb}} \approx -\mathbf{a}_{\text{Bi}}$). The layers

TABLE 2B
Anisotropic Thermal Parameters for SbRe₂O₆ (1000/Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	18(2)	17(3)	58(3)	0(2)	16(2)	−2(2)
Sb	42(6)	37(7)	108(6)	0	12(5)	0

TABLE 3
Selected Interatomic Distances (Å) and Angles (Degrees)

Re–Re ⁱ	2.517(1)	O1–Re–O3	84.0(4)
Re–O1	2.011(10)	O1 ⁱⁱ –Re–O1 ⁱ	91.1(2)
Re–O1 ⁱⁱ	1.968(10)	O1 ⁱⁱ –Re–O2	176.0(4)
Re–O1 ⁱ	1.986(10)	O1 ⁱⁱ –Re–O2 ⁱⁱⁱ	89.1(4)
Re–O2	1.919(10)	O1 ⁱⁱ –Re–O3	90.2(4)
Re–O2 ⁱⁱⁱ	1.911(11)	O1 ⁱ –Re–O2	92.8(4)
Re–O3	2.022(10)	O1 ⁱ –Re–O2 ⁱⁱⁱ	82.8(4)
Sb–O3	2.219(10)	O1 ⁱ –Re–O3	174.0(4)
Sb–O3 ^{iv}	1.987(10)	O2–Re–O2 ⁱⁱⁱ	92.2(2)
Sb–O3 ^v	1.987(10)	O2–Re–O3	86.0(4)
Sb–O3 ^{vi}	2.219(10)	O2 ⁱⁱⁱ –Re–O3	91.3(4)
O1–Re–O1 ⁱⁱ	87.5(2)	O3–Sb–O3 ^{iv}	85.4(3)
O1–Re–O1 ⁱ	101.9(4)	O3–Sb–O3 ^v	73.6(4)
O1–Re–O2	90.9(4)	O3–Sb–O3 ^{vi}	149.8(5)
O1–Re–O2 ⁱⁱⁱ	174.2(4)	O3 ^{iv} –Sb–O3 ^v	91.7(6)

Symmetry code. (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $x, 1 - y, z - \frac{1}{2}$; (iii) $x, -y, z - \frac{1}{2}$; (iv) $x, 1 - y, z + \frac{1}{2}$; (v) $-x, 1 - y, -z$; (vi) $-x, y, -z + \frac{1}{2}$.

stack along the c_{Bi} vector in BiRe_2O_6 and along the vector of $\mathbf{a}_{\text{Sb}} + \mathbf{c}_{\text{Sb}}$ in SbRe_2O_6 [$\mathbf{c}_{\text{Bi}} \approx (\mathbf{a}_{\text{Sb}} + \mathbf{c}_{\text{Sb}})/2$ or $\mathbf{a}_{\text{Bi}} \approx \mathbf{a}_{\text{Sb}} + 2\mathbf{c}_{\text{Bi}}$].

The bioctahedral Re_2O_{10} units constituting the Re_2O_6 layers are on the inversion centers. Each ReO_6 octahedron is distorted as shown in Fig. 4, and the shift of a rhenium atom toward the neighboring rhenium atom is small ($\text{O1}^{\text{ii}}\text{--Re--O2}$, 176°). The shape of the ReO_6 octahedron in SbRe_2O_6 is slightly different from that in BiRe_2O_6 , mainly because of the shift of the O3 atom, which bridges a rhenium atom and two antimony atoms. Among the corresponding O–O distances of ReO_6 octahedra in the antimony and bismuth compounds, the O2–O3 distance shows the largest difference (0.07 Å). However, Re–Re distances in the two compounds are almost identical [2.517(1) Å in SbRe_2O_6 and 2.508(1) Å in BiRe_2O_6].

Electrical Conductivity

The formation of metal–metal bonds generally causes the localization of valence electrons and lower electrical

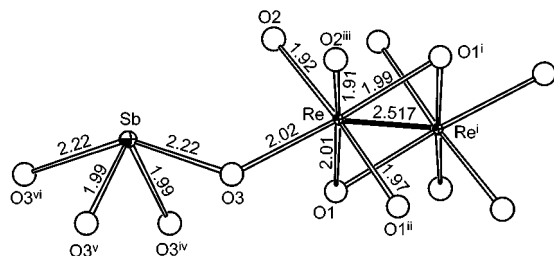


FIG. 4. ORTEP drawing of the coordination of metal atoms. Thermal ellipsoids are drawn at the 80% probability level. Symmetry codes are given in Table 3.

conductivity as illustrated by the metal–semiconductor transitions of VO_2 and V_2O_3 accompanied by the formation of V–V bonds (21). So far we have found only two reports on the conductivities of ternary oxides with Re–Re bonds. $\text{La}_3\text{Re}_2\text{O}_{10}$ is reported to be semiconducting (1) while $\text{La}_4\text{Re}_6\text{O}_{19}$ is metallic (8). These data indicate a wide diversity in the electrical properties of these ternary oxides.

The measurements have shown that SbRe_2O_6 is a very good conductor (Fig. 5). The conductivity of SbRe_2O_6 is lower than that of ReO_3 (22) but higher than that of ReO_2 (12). The resistivity of SbRe_2O_6 is approximately proportional to $T^{1.65}$ between 80 and 240 K, and the temperature dependence of the conductivity is also smaller than that of ReO_3 and larger than that of ReO_2 . The electrical conductivity of ReO_3 was analyzed with the function

$$\rho_{\text{cal}} = A + B \left(\frac{T}{\theta_R} \right)^5 \int_0^{\theta_R/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} + C \frac{\theta_E/T}{\sinh^2(\theta_E/(2T))} \quad [1]$$

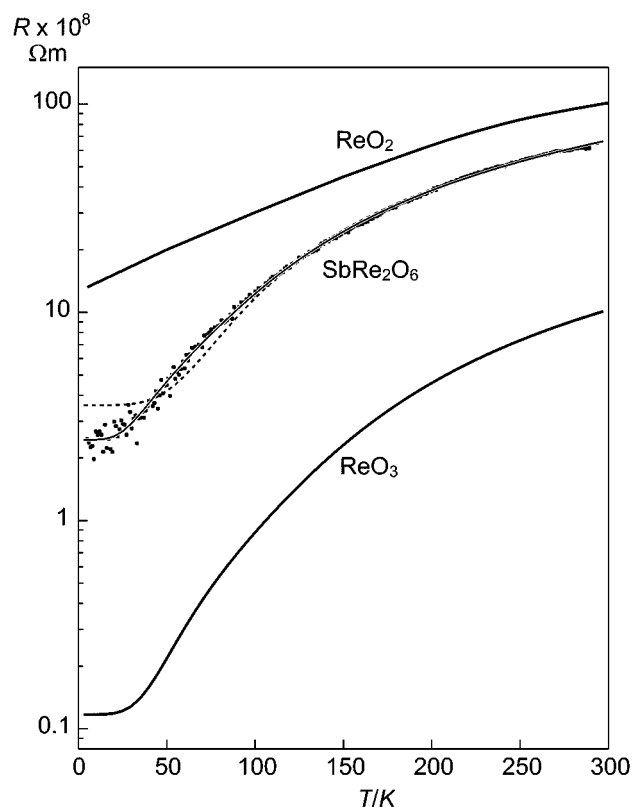


FIG. 5. Temperature-dependent resistivity of SbRe_2O_6 along the bc plane. The observed data are represented by dots. The thin curve is calculated with function [1] (see text), and the broken curve, with a function that contains the first two terms of function [1]. The parameter sets of the functions were independently determined by least-squares methods (Table 4) and are not the same in the two curves. The resistivities of ReO_2 and ReO_3 are taken from Refs. (12) and (22), respectively.

TABLE 4
Parameters for Electronic Conductivity

	SbRe ₂ O ₆	ReO ₃ ^a
Θ _R (K)	199	330
Θ _E (K)	535	880
A (Ω-m)	2.44 × 10 ⁻⁸	0.117 × 10 ⁻⁸
B (Ω-m)	75.1 × 10 ⁻⁸	15.4 × 10 ⁻⁸
C (Ω-m)	21.4 × 10 ⁻⁸	8.05 × 10 ⁻⁸

^aThe values are taken from Ref. (22).

where θ_R and θ_E are the Debye temperature and Einstein temperature, respectively (22). The first term is the residual resistivity and the second is the resistivity due to the electron scattering by acoustic phonons (Bloch–Grüneisen term). The third term is the contribution of the scattering of electrons by optical phonons, which is characteristic of compounds with ionic nature. We have found that the measured resistivity of SbRe₂O₆ can be fit with the same function (Fig. 5). The parameters θ_R , θ_E , A , B , and C have been determined so that the sum of $(\rho_{\text{cal}} - \rho_{\text{obs}})^2$ has the minimum value. The parameters obtained are listed in Table 4 with the corresponding values for ReO₃. The lower Debye and Einstein temperatures of SbRe₂O₆ with those of ReO₃ are reasonable because the formal oxidation state of rhenium in SbRe₂O₆ is lower than that in ReO₃. The lower oxidation state makes the Re–O bonds weaker, which leads to a softer lattice. Without the third term of function [1], satisfactory fitting of the calculated curve is not possible, as shown in Fig 5. Therefore, the scattering by optical phonons is not negligible in the resistivity of SbRe₂O₆ as discussed for ReO₃.

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