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BRIEF COMMUNICATION

Structure of Two-Dimensional Conductor of Sr_2RhO_4

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The structure of the two-dimensional conductor Sr_2RhO_4 was refined by powder X-ray diffraction analysis at room temperature. Sr_2RhO_4 crystallizes with the symmetry of space group $I4_1/acd$ (No. 142-2), isostructural with Sr_2IrO_4, and the room temperature lattice parameter $a = 0.54516(1)$ nm and $c = 2.57539(4)$ nm. The rotating angle of RhO_6 octahedra about the c axis is 10°. The structural data was found to be almost same as that for semiconducting and antiferromagnetic Sr_2IrO_4.

Recently, many studies on 3*d* transition metal oxides have been carried out for the purpose of finding new superconductors. According to the ligand field theory, 3*d* transition metals in the sixfold coordination site can occur in both high-spin and low-spin states, while 4*d* and 5*d* transition metals tend to take the low-spin state. It is of interest whether we can obtain a new metallic conductor containing 4*d* and 5*d* transition metals. Some of our previous studies (1–4) are focused on the development of new metallic conductors containing platinum-group metals. Semiconducting $LaRhO_3$ with low-spin Rh^{3+} (t_{2g}^6: ground term $^1A_{1g}$) can be doped with holes in the t_{2g} band by the substitution of Ca^{2+}, Sr^{2+}, and Ba^{2+} for La^{3+} (2). By this substitution conductivity increased about three orders of magnitude at room temperature. On the contrary, semiconducting two-dimensional $SrLaRhO_4$ with low-spin Rh^{3+} was doped with holes by a change in the Sr/La ratio (4). The positive temperature coefficient of resistivity was confirmed in the range $0.0 < x \leq 0.15$ in $Sr_{2-x}La_xRhO_4$; however, the absolute value of the resistivity was fairly large, larger than 10^2 mΩcm. This is the second example of the appearance of metallic conductivity in the 4*d* and 5*d* transition-metal oxides with K_2NiF_4 structure, the first compound having been Sr_2RuO_4 (5) with a $4d^4$ configuration. Quite recently, Crawford *et al.* (6) reported that Sr_2IrO_4 with low-spin Ir^{4+} (t_{2g}^5: ground term $^2T_2$) crystallizes with the symmetry $I4_1/acd$ (No.142-2) instead of $I4/mmm$, as determined by the powder neutron diffraction technique. In this structure, IrO_6 octahedra are rotated about the crystallographic c axis by about 10.5°. In our previous report on the structure of Sr_2RhO_4 (4), the orthorhombic space group *Cmca* or *Fmmm* was assigned to explain the additional superreflection lines, due to superstructures other than the $I4/mmm$ space group. In this case, almost all the peaks were explained by considering the orthorhombic symmetry, but some of very small supereflection lines could not be explained using these space groups.

In this paper, we have reexamined the structure of Sr_2RhO_4 by the powder X-ray diffraction technique.

Sr_2RhO_4 was prepared by the conventional solid state reaction technique. Stoichiometric amounts of $SrCO_3$(99.9%) and La_2O_3(99.9%) were mixed in an agate mortar with ethanol. The dried mixture was pressed into a pellet 1 mm thick and 12 mm in diameter, under a static pressure of about 80 MPa. The pellet was cooled to room temperature and reground in an agate mortar, followed by mixing and pelletization. This pellet was sintered at 1523 K for 36 h in an O_2 gas flow. Phase characterization and determination of the lattice parameter were carrier out using a Mac Science MXP^{18} powder X-ray diffractometer equipped with a graphite monochromator. The experimental conditions were: accelerating voltage, 50 kV; current, 300 mA; and Cu target. The data were collected by accumulating counts for 1 *s* in the range $2\theta = 20°$ to 120°. The crystal structure of the sample was analyzed using the Rietveld analysis program, RIETAN (7).

Figure 1 shows the results of the powder X-ray diffraction measurement, together with the Rietveld refinement and difference plot at 293 K. The inset shows the enlarged part between 35° and 39°. Reflection lines (211) and (213) originate from the superstructure with dimensions of 2 c and $\sqrt{2}\,a$, compared with the primitive cell of the K_2NiF_4 structure. Other additional feasible peaks due to the superstructure were not observable by the X-ray diffraction technique. Crawford *et al.* (6) used the complete ordered

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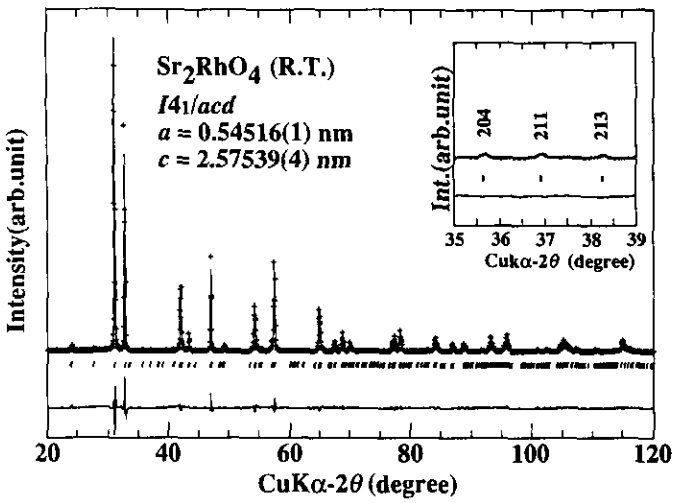

FIG. 1. Powder X-ray diffraction pattern and Rietveld refinement for Sr_2RhO_4 at 293 K. The crosses are the data, the solid line is the fitted pattern, the vertical markers indicate expected peak positions, and the residuals appear at the bottom of the figure. The inset shows the enlarged portion between 35° and 39°.

model of the rotation of IrO_6 octahedra about the c axis for Sr_2IrO_4 with the space group $I4_1/acd$, which is the same for Ca_2MnO_4 (8). The refinement using the space group $I4_1/acd$ yielded the R values, R_{wp} = 13.19%, R_p = 9.39%, R_R = 11.39%, R_E = 3.46%, R_I = 3.19%, and R_F = 3.43%. Huang *et al.* (9) applied the partial disordered model in the rotation of IrO_6 octahedra. In the ordered structure, the arrangement of the oxygen atoms obeys the symmetry requirements of the screw axis 4_1 parallel to c axis. On the contrary, in the disordered model an uncorrelated rotation of the IrO_6 octahedra with respect to the

TABLE 1
Crystallographic Information for Sr_2RhO_4 at Room Temperature

Lattice parameters (nm)

a	0.54516(1)
c	2.57538(4)

Atomic positions and isotropic thermal parameters (nm^2)

Sr(16d)	z	0.5511(1)
	B	0.0060(9)
Rh(8a)	B	0.0029(9)
O1(16d)	z	0.455(1)
	B	0.007(5)
O2(a)(16f)	x	0.294(7)
	B	0.002(7)
	g	0.12(9)
O2(b)(16f)	x	0.206(7)
	B	0.002(7)
	g	0.88(9)

Bond distance (nm) and angles (degree)

Rh–O1	(X2)	0.205(2)
Rh–O2	(X4)	0.1957(6)
Sr–O1	(X1)	0.248(3)
Sr–O1	(X4)	0.2730(1)
Sr–O2	(X2)	0.248(2)
Sr–O2	(X2)	0.296(2)
Rh–O2–Rh		160(2)
Rh–O1–Sr		86.8(5)

R_{wp} = 13.17%	R_p = 9.34%
R_R = 11.35%	R_E = 3.46%
R_I = 2.85%	R_F = 2.75%

Note. The structure was refined in the tetragonal space groupe $I4_1/acd$. The five unique atoms have the following positions: Sr, (0, 0.25, z); Rh, (0, 0.25, 0.375); O1, (0, 0.25, z); O2(a), (x, x + 0.25, 0.125); O2(b); (x, x + 0.25, 0.125).

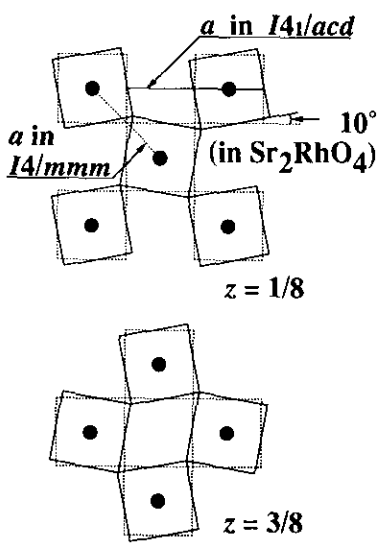

FIG. 2. Structure diagram of Sr_2RhO_4 with $I4_1/acd$ space group, showing the RhO_6 octahedra rotation at z = 1/8 and z = 3/8. The broken lines show the primitive K_2NiF_4 structure.

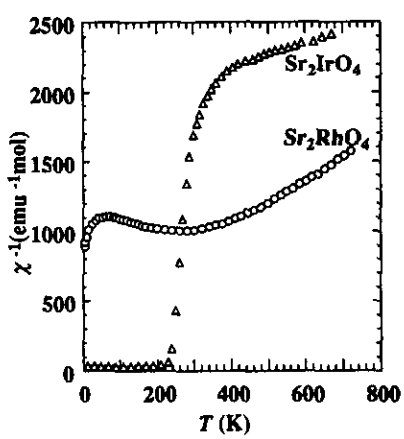

FIG. 3. Temperature dependence of the reciprocal magnetic susceptibilities for Sr_2RhO_4 and Sr_2IrO_4.

TABLE 2
Comparison of the Crystallographic Parameters for Sr_2RhO_4, Sr_2RuO_4[12], and Sr_2IrO_4[13]

Compound	a/nm	c/nm	Space group	d_{M-O}/nm (a axis)	d_{M-O}/nm (c axis)	$d_{M-O(c)}/d_{M-O(a)}$	Rotating angle of MO_6
Sr_2RhO_4	0.54516(1)	2.57539(4)	$I4_1/acd$	0.1953(5)	0.205(2)	1.049	10°
Sr_2IrO_4	0.549556(7)	2.57933(5)	$I4_1/acd$	0.1977(3)	0.2058(1)	1.041	10.5°
Sr_2RuO_4	0.3871(1)	1.2702(4)	$I4/mmm$	0.19355(4)	0.2071(19)	1.070	0°
	0.5474(2)[a]	2.5404(8)[b]					

[a] Multiplied by $\sqrt{2}$.
[b] Multiplied by 2.

other octahedra may be permitted, independent of symmetry. Applying such a disordered model to the structural refinement of Sr_2RhO_4, we obtained smaller R values, R_{wp} = 13.17%, R_p = 9.34%, R_R = 11.35%, R_E = 3.46%, R_I = 2.85%, and R_F = 2.75%. The results of structural refinement is given in Table 1. The occupation factors for O2(a) and O2(b) imply that the crystal statistically exhibits a partial disordering with respect to the rotation of RhO_6 octahedra. When the occupation factor g is equal to 0.5 for O2(a) and O2(b) sites, disordering of the rotation of the RhO_6 octahedra in the clockwise and counterclockwise directions occurs; thereby the crystallographic space group for Sr_2RhO_4 changes to $I4/mmm$, as observed for $Sr_3Ir_2O_7$ (11). In $Sr_3Ir_2O_7$, the angle of Ir–O–Ir in the IrO_2 plane is smaller than 180°. Further discussion on the structural refinement was impossible since X-rays are insensitive to the position of oxygen ions. The above results indicate that Sr_2RhO_4 has the same structure as Sr_2IrO_4, with space group $I4_1/acd$, i.e., the c axis length must be doubled and the a axis length must be multiplied by $\sqrt{2}$. In Sr_2RhO_4, the RhO_6 octahedra rotates by 10° about the crystallographic c axis, while the rotating angle of IrO_6 in Sr_2IrO_4 is 10.5°. Figure 2 shows the RhO_2 layers along the c axis for z = 1/8 and 3/8.

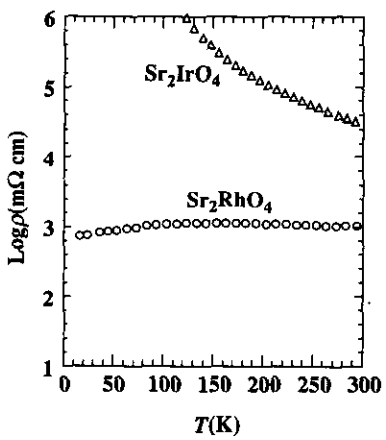

FIG. 4. Temperature dependence of the electrical resistivities for Sr_2RhO_4 and Sr_2IrO_4.

Figure 3 shows the magnetic susceptibility for Sr_2RhO_4 (4) and Sr_2IrO_4 (11). Antiferromagnetic behavior can be observed for Sr_2IrO_4 (12), but we did not observe any magnetic hysteresis for Sr_2RhO_4 even at 5 K (4). Since the low-spin Rh^{4+} ion has the spin 1/2, as does Ir^{4+}, the magnetic structure for single crystalline Sr_2RhO_4 should be determined by neutron diffraction or by the muon spin rotation technique. Figure 4 shows the electrical resistivities for Sr_2RhO_4 (4), Sr_2IrO_4 (11).

Table 2 compares the crystallographic parameters for Sr_2RhO_4, Sr_2RuO_4 (12), and Sr_2IrO_4 (13). The structural analysis data for Sr_2IrO_4 was obtained by the powder neutron diffraction technique. Elongation of the Ru–O distance along the c axis is clearly observed in these compounds. The elongation is largest in Sr_2RuO_4, dRu–O(c)/dRu–O(a) = 1.070, this value being considered to have originated from the cooperative Jahn–Teller distortion of high-spin Ru^{4+} ions (12). The values for Sr_2RhO_4 and Sr_2IrO_4 are almost the same; the t_{2g}^5 electronic configuration in Rh^{4+} and Ir^{4+} leads to the same distortion of the MO_6 octahedra, although the Rh and Ir belong to the second and third transition metals, respectively.

In conclusion, Sr_2RhO_4 and Sr_2IrO_4 have the same structure. It is to be noted that Rh^{4+} and Ir^{4+} have almost same ionic radii, 0.620 and 0.625 nm (15), respectively, and it can be recognized in the lattice parameters and interionic distances, as shown in Table 2. The explanation for the difference in the properties is not simple because the structures for Sr_2RhO_4 and Sr_2IrO_4 are almost same, including the rotating angles of RhO_6 and IrO_6. The following two factors are considered to affect the properties of these two compounds: (a) a difference in size of the 4d and 5d electron orbitals of Rh^{4+} and Ir^{4+} ions and (b) differences in the energy levels for O2p, Rh4d, and Ir5d. These factors definitely determine the properties of these two compounds and the itinerant or localized states of the electron.

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