Similarities and Differences in the Structural and Electronic Properties of Ruthenium and Iridium Pyrochlores $A_2M_2O_{7-y}$ (M = Ru, Ir)

H.-J. Koo and M.-H. Whangbo

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

and

B. J. Kennedy

School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia

Electronic band structures of the ruthenium and iridium pyrochlores $A_2M_2O_6O'_{1-y}$ (M = Ru, Ir) were examined using the extended Hückel tight-binding method. The metal versus semiconductor behaviors of these pyrochlores are explained in terms of the Mott–Hubbard localization concept. The M–O, A–O, and A–O′ distances and M–O–M angles of $A_2M_2O_6O'_{1-y}$ (M = Ru, Ir) were analyzed in terms of the A cation ionic radius. The M–O distance and the M–O–M angle are strongly influenced by the overlap repulsion between the filled shells of the A cation and O^{2-} anions. The O′ vacancies of the pyrochlores $A_2M_2O_6O'_{1-y}$ with polarizable A cations such as Tl^+, Pb^{2+}, or Bi^{3+} occur most likely to reduce the overlap repulsion associated with the 6s orbitals of the A cations. © 1998 Academic Press

INTRODUCTION

The structure of a pyrochlore, $A_2B_2O_6O'$, consists of two interpenetrating B_2O_6 and A_2O' sublattices (1). In the B_2O_6 sublattice each of the oxygen atoms of BO_6 octahedra are corner-shared and can be viewed as forming regular B_4 tetrahedra. In the A_2O' sublattice each oxygen O′ is coordinated with four A cations to form a second tetrahedral network. Each A cation of $A_2B_2O_6O'$ is surrounded by six O and two O′ atoms, and each O is surrounded with two B and two A cations in a distorted tetrahedron with local C_{2v} symmetry (Fig. 1). The pyrochlores with polarizable A cations (e.g., Tl^+, Pb^{2+}, or Bi^{3+}) tolerate a high degree of vacancy on the O′ atom sites so that their compositions are written as $A_2B_2O_6(O')_{1-y}$, i.e., $A_2B_2O_{7-y}$ if the distinction between the two different oxygen atoms O and O′ is not made.

Ruthenium pyrochlores $A_2Ru_2O_{7-y}$ have been widely studied due to their technological importance (2–12). They are magnetic semiconductors with rare earth A cations but are metals with polarizable A cations such as Tl^+, Pb^{2+}, or

Bi^{3+}. The analogous iridium pyrochlores $A_2Ir_2O_{7-y}$ (13–16) have considerably higher electrical conductivities, have very small band gaps even with rare earth A cations, and are best described as semimetals. A recent electronic structure study of ruthenium pyrochlores indicated (17) that their metal versus semiconductor behavior can be explained in terms of the concept of Mott–Hubbard electron localization (18). Specifically, the t_{2g}-block bandwidths of $A_2Ru_2O_{7-y}$ increase with increasing the A cation ionic radius, so that beyond a certain ionic radius the bandwidth becomes greater than a critical value, thereby making $A_2Ru_2O_{7-y}$ metallic. It is interesting to see if this concept is also applicable to the iridium pyrochlores $A_2Ir_2O_{7-y}$.

Powder neutron diffraction studies of the $A_2Ru_2O_{7-y}$ pyrochlores reveal (11, 12, 15, 16) that the metallic pyrochlores possess the following structural features: (1) The O′ site is invariably not fully occupied. (2) The Ru–O bond is shorter than that observed for semiconducting pyrochlores. (3) The Ru–O–Ru bond angle is larger than expected by extrapolation from the trend observed for the semiconducting pyrochlores. In terms of ionic bonding, the Ru–O bond shortening implies an enhanced oxidation of the Ru cation, but this view is inconsistent with the occurrence of oxygen vacancies in the structure. This conceptual problem can be resolved by considering a partial charge transfer from the Ru to the A cation (15), because it will increase the ionic radius of the A cation while reducing that of the Ru cation. This suggestion explains the observation that the metallic pyrochlores have shorter Ru–O bonds and longer A–O and A–O′ bonds than do most semiconducting pyrochlores. Although the electronegativities of the p-block cations (Tl^+, Pb^{2+}, Bi^{3+}) are considerably larger than those of the lanthanides, they are still slightly less than that of Ru or Ir. Thus while some mixing of the $M\,d$ and $A\,6p$ orbitals (via the bridging oxygen O) might be expected, the
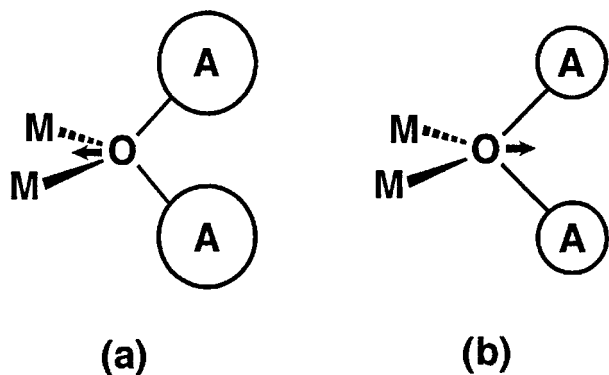
FIG. 1. Coordinate environment of the O atom in ruthenium pyrochlore $A_2M_2O_6O'$ (M = Ru, Ir) showing the effect of the A cation size on the local structure: (a) large A cation; (b) small A cation.

electronegativities suggest that reduction of the M cation should be favored. In addition, why extensive O' vacancies occur in the pyrochlores $A_2Ru_2O_6O'_{1-y}$ with polarizable A cations has not been properly discussed. Thus it is important to examine the electronic and structural effects of polarizable A cations in the pyrochlores $A_2M_2O_{7-y}$ (M = Ru, Ir).

To probe the aforementioned questions, we analyze the crystal and electronic structures of the ruthenium and iridium pyrochlores by making use of the powder neutron diffraction structural data reported in the literature (12, 15, 16). The electronic band structures of these compounds were calculated using the extended-Hückel tight-binding (EHTB) method (19) and the atomic parameters listed in Table 1.

TABLE 1
Exponents ζ_i and Valence Shell Ionization Potentials H_{ii} of Slater-Type Orbitals χ_i Used for Extended-Hückel Tight-Binding Calculation[a]

Atom	χ_i	H_{ii} (eV)	ζ_i	$c_1{}^b$	ζ_i'	$c_2{}^b$
Ru	$5s$	-6.43	2.091	1.0000		
Ru	$5p$	-3.49	1.420	1.0000		
Ru	$4d$	-15.3	4.357	0.5394	2.265	0.6062
Ir	$6s$	-6.59	2.457	1.0000		
Ir	$6p$	-3.33	2.457	1.0000		
ir	$5d$	-15.2	4.680	0.6195	2.490	0.5384
O	$2s$	-33.7	2.246	1.0000		
O	$2p$	-17.1	2.227	1.0000		

[a] H_{ii}'s are the diagonal matrix elements $\langle\chi_i|H^{eff}|\chi_i\rangle$, where H^{eff} is the effective Hamiltonian. In our calculations of the off-diagonal matrix elements $H^{eff} = \langle\chi_i|H^{eff}|\chi_j\rangle$, the weighted formula was used (J. Ammeter, H.-B. Bürgi, J. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.* **100,** 3686 (1978)).

[b] Contraction coefficients used in the double-ζ Slater-type orbital.

NON-NEAREST-NEIGHBOR EFFECTS ON BOND LENGTHS

To a first approximation, bond distances of solid-state inorganic compounds are often discussed in terms of ionic bonding (e.g., the use of ionic radii). At the next level of description, one may employ the bond valence sum approach (20), in which the ionic and covalent bonding concepts are combined such that the oxidation state of an atom is equated to the number of electrons the atom loses to form the covalent bonds with its nearest-neighbor ligands. In
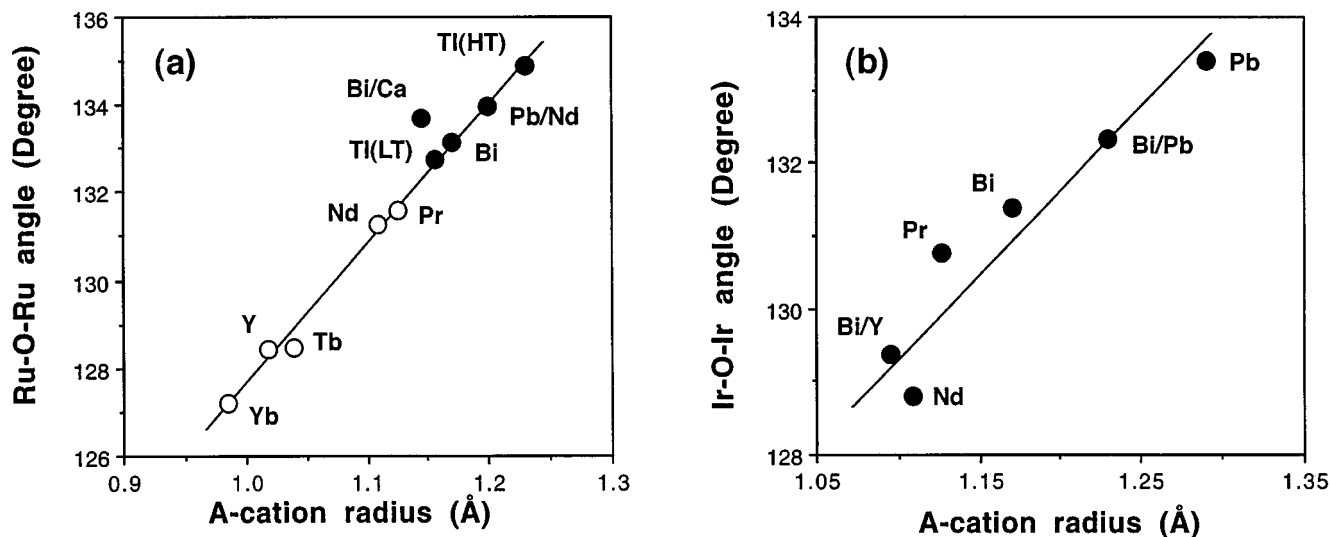

FIG. 2. M–O–M angles of $A_2M_2O_{7-y}$ as a function of the A cation ionic radius: (a) M = Ru; (b) M = Ir. The metallic and semiconducting pyrochlores are indicated by filled and empty circles, respectively. In (a), Tl(HT) and Tl(LT) refer to the high- and low-temperature forms of $Tl_2Ru_2O_{7-y}$, respectively. As discussed in ref 17, the y value of 0.15 was used for Tl(LT).
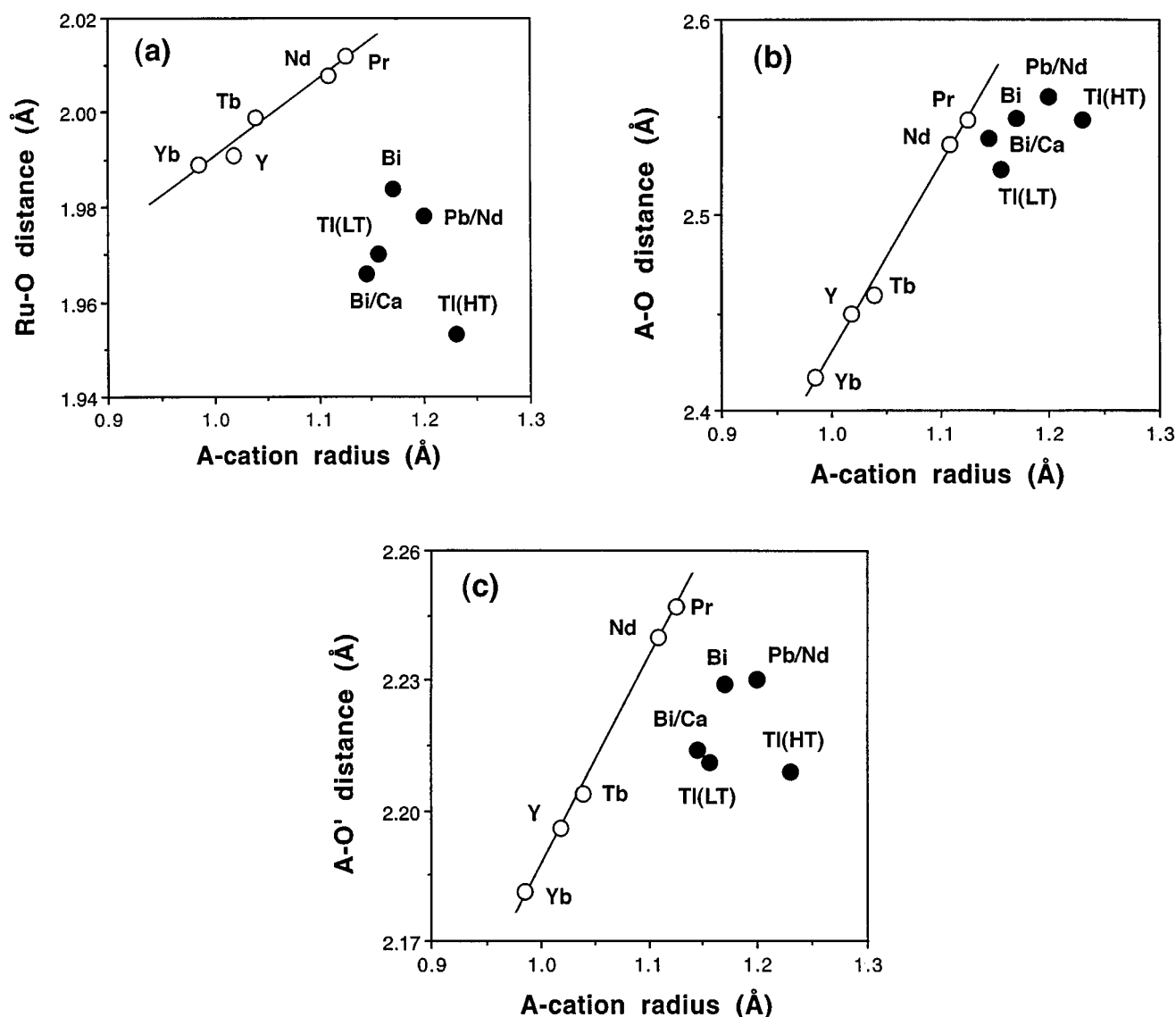
FIG. 3. Bond distances of $A_2Ru_2O_{7-y}$ as a function of the A cation ionic radius: (a) Ru–O distance; (b) A–O distance; (c) A–O′ distance. The metallic and semiconducting pyrochlores are indicated by filled and empty circles, respectively.

these two approaches, a bond distance between two atoms is regarded as being determined solely by the properties of the two atoms. The bond distances of a given solid reflect the minimum-energy arrangement of its atoms. A bond distance is determined mainly by the atoms constituting the bond but can be strongly affected by the non-nearest-neighbor atoms surrounding the bond (21, 22).

Such a situation also occurs in the pyrochlores $A_2M_2O_{7-y}$ (M = Ru, Ir). As depicted in Fig. 1, each O atom of $A_2M_2O_{7-y}$ (M = Ru, Ir) is surrounded with two M and two A cations to form a distorted tetrahedron. A recent electronic structure study of ruthenium pyrochlores (17) suggested that large A cations in an OA_2M_2 tetrahedral arrangement push the oxygen atom O farther away from

them (along the bisector of the M–O–M angle) and hence increase the M–O–M angle and shorten the M–O bond length. As shown in Fig. 2a for $A_2Ru_2O_{7-y}$, the M–O–M bond angle increases quite linearly with increasing the A cation ionic radius. A similar relationship is also found for $A_2Ir_2O_{7-y}$ (Fig. 2b).

Figs. 3a–c respectively plot the Ru–O, A–O, and A–O′ bond distances of $A_2Ru_2O_6O'_{1-y}$ as a function of the A cation ionic radius. For the semiconducting pyrochlores, these bonds increase quite linearly with increasing ionic radius. Compared with the value expected from these linear relationships, the Ru–O bonds of the metallic pyrochlores are significantly shorter, and so are the corresponding A–O and A–O′ bonds. In the presence of a Ru to A cation charge
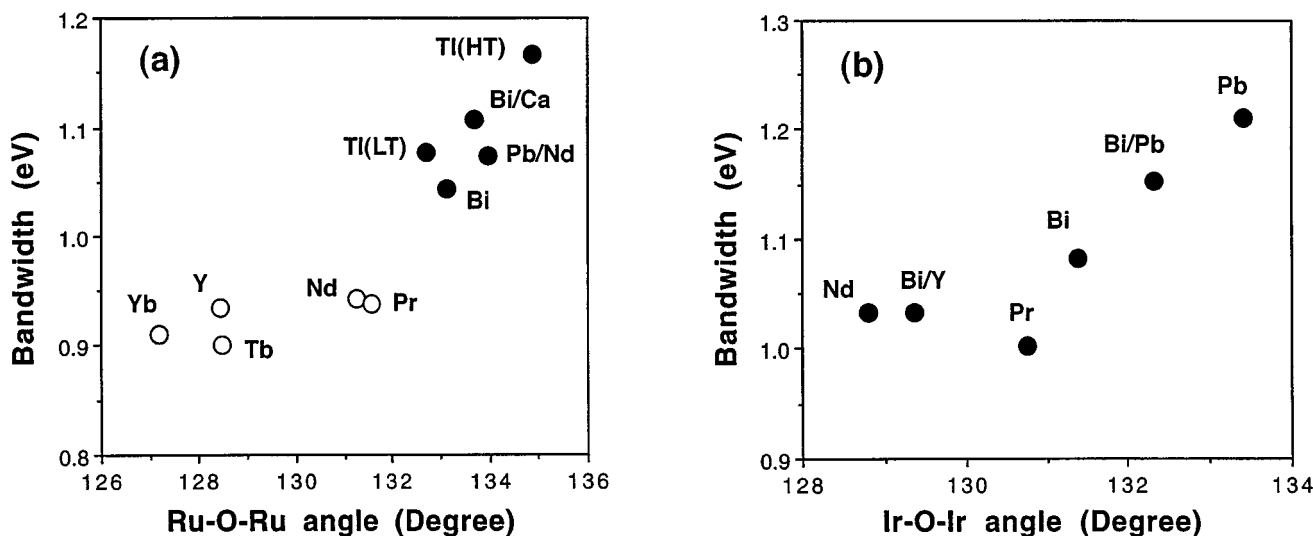
FIG. 4. t_{2g}-block bandwidths of $A_2M_2O_{7-y}$ as a function of the M–O–M angle: (a) M = Ru; (b) M = Ir. The metallic and semiconducting pyrochlores are indicated by filled and empty circles, respectively.

transfer, and A–O and A–O′ bonds would be longer, not shorter, than expected from the linear relationship of the semiconducting pyrochlores.

CAUSE FOR THE OXYGEN VACANCIES

In each OA_2M_2 tetrahedral arrangement (Fig. 1), larger A cations more strongly repel the O atom than smaller A cations, because the overlap repulsion between the filled shells of the O^{2-} anion and A cations (i.e., two-orbital, four-electron destabilizing interaction (23)) is larger. This repulsion is particularly strong with polarizable A cations such as Tl^+, Pb^{2+}, and Bi^{3+} because their $6s$ orbitals enhance the overlap with the $2p$ orbitals of O^{2-}. The polarizable A cations lead to O′ vacancies in the $A_2O′$ sublattice of $A_2M_2O_{7-y}$ (M = Ru, Ir). The occurrence of these vacancies is energetically favorable in several ways: (1) the overlap repulsion between the A cations and $O′^{2-}$ anions is removed by O′ vacancies, (2) the $6s$ orbital of the A cation adjacent to an O′ vacancy can hybridize with its $6p$ orbitals to form a lone pair, and (3) the lone pair orbital is directed toward the O′ vacancy site, i.e., away from the six surrounding O atoms, which reduces the overlap repulsion between the O^{2-} anions and A cations. This will in turn shorten the average A–O distance, as is observed. The directionality of the lone pair electrons is evident in the structures of $Pb_2Ru_2O_{6.5}$ (24) $Pb_2Ru_2O_{6.5}$ (16).

METALLIC CHARACTER OF IRIDIUM PYROCHLORES

To examine why the electrical conductivity of the iridium pyrochlores, which have (semi) metallic conductivity, is in-

variably greater than that of the ruthenium pyrochlores, which can be metallic or magnetic semiconducting, we carried out EHTB electronic band structure calculations (19) for the M_2O_6 sublattice of $A_2Ir_2O_{7-y}$ (M = Ru, Ir). The previous EHTB study (17) of $A_2Ru_2O_{7-y}$ showed that the t_{2g}-block bandwidths of the metallic pyrochlores are wider than those of the semiconducting pyrochlores, thereby suggesting the applicability of the Mott–Hubbard localization concept. The higher observed conductivity of the iridium pyrochlores $A_2Ir_2O_{7-y}$ suggests that the t_{2g}-block bandwidths of the iridium pyrochlores should be wider than those of the semiconducting ruthenium pyrochlores. Therefore, it is necessary to compare the t_{2g}-block bandwidths of the iridium pyrochlores with those of the ruthenium pyrochlores. Such a comparison based on semiempirical EHTB calculations requires the use of balanced atomic orbital parameters. The atomic parameters used in our calculations (Table 1) were taken from the work of Clementi and Roetti for O and Ru (25) and from the work of McClean and McClean for Ir (26). The parameters of Ru and O differ slightly from those used in ref 17. but the essential conclusions remain the same (see Concluding Remarks).

The t_{2g}-block bandwidths calculated for the ruthenium pyrochlores are plotted as a function of the M–O–M angles in Fig. 4a, and those for the iridium pyrochlores in Fig. 4b. The t_{2g}-block bandwidths of the semiconducting ruthenium pyrochlores are narrower than 0.95 eV, and those of the metallic ruthenium pyrochlores are wider than 1.04 eV (27). The t_{2g}-block bandwidths of all iridium pyrochlores are larger than 1.0 eV, i.e., larger than those of the semiconducting ruthenium pyrochlores. It is also clear that the iridium pyrochlores with a lanthanide or yttrium as an A cation have a narrower t_{2g} band than those containing only a

p-block *A* cation. This is in agreement with the observed conductivity of the iridium pyrochlores.

CONCLUDING REMARKS

Our work shows that the metal versus semiconductor behaviors of the ruthenium and iridium pyrochlores are explained in terms of the Mott–Hubbard localization concept. The ruthenium pyrochlores with rare earth *A* cations have *M*–O–*M* angles smaller than $132°$, and so do the iridium pyrochlores with rare earth *A* cations. Nevertheless, the latter possess a wider t_{2g}-block bandwidth than do the former. This reflects the fact that the Ir 5*d* orbital is more extended than the Ru 4*d* orbital, so the overlap between the metal *nd* and oxygen 2*p* orbitals is better for the iridium pyrochlores. Our analysis of the *M*–O, *A*–O, and *A*–O′ distances and *M*–O–*M* angles indicates that the *M*–O distance and *M*–O–*M* angles are strongly affected by the overlap repulsion between the filled shells of the *A* cation and O^{2-} anions. The O′ vacancies in the pyrochlores with polarizable *A* cations (e.g., Tl^+, Pb^{2+}, or Bi^{3+}) occur most likely to reduce the enhanced overlap repulsion associated with the 6*s* orbitals of the *A* cations. The presence of the O′ vacancies in the metallic, but not in the semiconducting, Ru or Ir pyrochlores is a necessary requirement for a further reduction of the overlap repulsion of the oxygen 2*p* orbitals and the 6*s* orbitals of the polarizable *A* cations (Tl^+, Pb^{2+}, or Bi^{3+}) and the formation of the lone pair electrons.

ACKNOWLEDGMENTS

REFERENCES

1. M. A. Subramanian, G. Aravamudan, and G. V. Subba Rao, *Prog. Solid State Chem.* **15,** 55 (1983), and references cited therein.
2. R. G. Edgell, J. B. Goodenough, A. Hamnett, and C. C. Naish, *J. Chem. Soc., Faraday Trans. I* **79,** 893 (1983).
3. H. S. Horowitz, J. M. Longo, H. H. Horowitz, and J. T. Lewandowski, *ACS Symp. Ser.* **127,** 143 (1985).
4. T. R. Felthouse, P. B. Fraundorf, R. M. Friedman, and C. L. Schosser, *J. Catal.* **127,** 421 (1991).
5. P. F. Garcia, A. Ferreti, and A. Suna, *J. Appl. Phys.* **53,** 5282 (1982).
6. H. S. Jarrett, A. W. Sleight, J. F. Weiher, J. L. Gillson, C. G. Frederick, G. A. Jones, R. S. Swingle, D. Swatzfager, J. E. Gulley, and P. C. Hoell, *in* "Valence Instabilities and Related Narrow Band Phenomena" (R. D. Parks, Ed.), p. 545. Plenum Press, New York, 1977.
7. P. A. Cox, J. B. Goodenough, P. J. Tavener, D. Telles, and R. G. Edgell, *J. Solid State Chem.* **62,** 360 (1986).
8. G. Facer, M. M. Elcombe, and B. J. Kennedy, *Aust. J. Chem.* **46,** 1897 (1993).
9. R. Kanno, Y. Takeda, T. Yamamoto, Y. Kawamoto, and O. Yamamoto, *J. Solid State Chem.* **102,** 106 (1993).
10. R. Kanno, J. Huang, and A. W. Sleight, *in* "Proceedings of the Fifth International Symposium on Advanced Nuclear Energy Research," p. 127, 1994.
11. H. Kobayashi, R. Kanno, Y. Kawamoto, T. Kamiyama, F. Izumi, and A. W. Sleight, *J. Solid State Chem.* **114,** 15 (1995).
12. B. J. Kennedy and T. Vogt, *J. Solid State Chem.* **126,** 261 (1996), and references therein.
13. R. J. Bouchard and J. L. Gillison, *Mater. Res. Bull.* **6,** 669 (1971).
14. V. L. Nazarev and I. S. Shaplygin, *Russ. J. Inorg. Chem.* **23,** 163 (1978).
15. B. J. Kennedy, *Physica B*, in press.
16. B. J. Kennedy, *J. Solid State Chem.* **123,** 14 (1996).
17. K.-S. Lee, D.-K. Seo, and M.-H. Whangbo, *J. Solid State Chem.* **131,** 405 (1997).
18. (a) N. F. Mott, "Metal–Insulator Transitions." Barnes and Noble, New York, 1977. (b) B. H. Brandow, *Adv. Phys.* **26,** 651 (1977). (c) M.-H. Whangbo, *J. Chem. Phys.* **70,** 4963 (1979).
19. M.-H. Whangbo and R. Hoffman, *J. Am. Chem. Soc.* **100,** 6093 (1978).
20. (a) I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41,** 244 (1985). (b) N. E. Brese and M. O'Keefe, *Acta Crystallogr. Sect. B* **47,** 192 (1991).
21. M.-H. Whangbo and C. C. Torardi, *Science* **249,** 1143 (1991).
22. S. Wang, S.-J. Hwu, J. A. Paradis, and M.-H. Whangbo, *J. Am. Chem. Soc.* **117,** 5515 (1995).
23. T. A. Albright, J. K. Burdett, and M.-H. Whangbo, "Orbital Interactions in Chemistry." Wiley, New York, 1985.
24. R. A. Beyerlein, H. S. Horowitz, J. M. Longo, M. E. Leonowicz, J. D. Jorgensen, and F. J. Rotella, *J. Solid State Chem.* **51,** 253 (1984).
25. E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14,** 177 (1974).
26. A. D. McClean and R. S. McClean, *At. Data Nucl. Data Tables* **26,** 197 (1981).
27. As discussed in ref 17, we regard the low-temperature phase of $Tl_2Ru_2O_{7-y}$ as metallic.