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Electrical Conductivities of Niobium Iodides

H. KAWAMURA

National Research Institute for Metals, 2-3-12, Nakameguro, Meguro-ku, Tokyo 153, Japan

I. SHIROTANI

The Institute for Solid State Physics, The University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo, Japan

AND K. TACHIKAWA

National Research Institute for Metals, 2-3-12, Nakameguro, Meguro-ku, Tokyo 153, Japan

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The temperature and pressure dependences of the electrical resistivities in the single crystals of the niobium iodides, NbI_5, NbI_4 and Nb_3I_8, were measured. The resistivity in *ab* plane of Nb_3I_8 was 50 Ω cm and along the *c* axis was about 100 Ω cm. The activation energy was 0.26 eV at atmospheric pressure. The electrical resistivity along niobium chain in NbI_4 was about 300 Ω cm. The resistivity ratio of the single crystal ($\rho_\perp/\rho_\parallel$) is nearly 5. At around 150 kbar, only NbI_4 showed the transition from insulator to metal. The relation between electrical properties and the crystal structure is discussed.

Introduction

Niobium iodides which have definite crystal structures and components in the equilibrium state are NbI_5, NbI_4 and Nb_3I_8. Crystal structures of these iodides are based on a hexagonal close-packing of the iodine atoms, depending on the manner how the octahedral holes are occupied by niobium atoms. Nb_3I_8 is crystallized in a two-dimensional layer structure similar to CdI_2 structure (*1*). As expected from the compositional ratio, one-fourth of niobium atoms are left out from the niobium layers. An infinite array of triangular clusters of niobium atoms is formed as shown in Fig. 1. The distance between two iodine octahedron centers is 3.8 Å. Positions of niobium atoms are shifted from the centers of iodine octahedra. Nb–Nb distances within a cluster are 3.0 Å and the shortest Nb–Nb distance between clusters is 4.6 Å. In NbI_4, all niobium atoms in *b*-rows of Fig. 1 are left out, and the two-dimensional array of niobium atoms completely disappears. NbI_4 crystal consists of one-dimensional niobium chains surrounded by iodine atoms (*2*). However, the niobium atoms are displaced from iodine octahedron

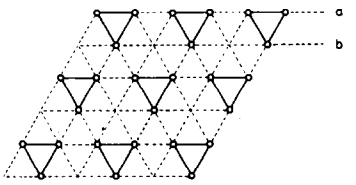

FIG. 1. The structure of the niobium layer in Nb_3I_8.

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centers so that the niobium–niobium distance becomes alternately short and long (3.31 Å and 4.36 Å) due to the direct bonding between pairs of niobium atoms. In this compound the pressure induced insulator to metal transition has been found at a pressure around 150 kbar (*3*). The structure of solid NbI_5 is also based on a hexagonal close-packing of the iodine atoms, the iodine-iodine distance being 4.0 Å (*4*). One-fifth of the available octahedral holes are occupied by niobium atoms. This compound has the characteristics of a typical molecular crystal. In this paper we report the electrical conductivities of these niobium iodides, and discuss the relation between electrical properties and crystal structures.

Experimental

Niobium pentaiodide was prepared from niobium metal and 10% excess iodine heated at 510° and 180°C respectively (*5*). The obtained NbI_5 was in the form of plates with a brass colour. The single crystals of NbI_4 were prepared by the thermal decomposition of the niobium pentaiodide in a hot-cold tube (*5*). The crystals ($2\times0.30\times0.3$ mm) were grown at a temperature around 270°C. The crystals showed a metallic appearance with lustrous dark gray faces. The Nb_3I_8 was prepared by heating NbI_5 with 20% excess niobium metal at 610°C for 1 day in a sealed quartz tube and then crystalizing in the hot–cold tube (750°–680°C) for four days (*6*). The crystals grew in the form of plates with a metallic dark gray appearance. The X-ray diffraction data of NbI_4 and Nb_3I_8 were identical with the respective reported results (*1, 2*). According to the chemical analysis of Nb_3I_8, the I/Nb ratio was 2.82. Since niobium iodides, especially NbI_5 and NbI_4, are unstable in air and water, all manipulations were carried out in a dry box.

The electrical conductivity at atmospheric pressure was measured by a dc method using a four-probe technique. The electrical leads were mounted with silver paste. The temperatures of the samples were regulated by the cooled dry helium gas. The temperature was determined by a thermocouple suspended near the sample. The pressure dependence of the electrical resistivity was measured by the Drickamer type resistance cell. The sample dimensions of each iodide were measured under a microscope. Using these dimensions, the observed resistance under high pressures were transformed into resistivities. The pressure was determined by Drickamer's revised fixed points for the Bi-transition at 74 kbar and Pb-transition at 130 kbar (*7*). The applied maximum pressure for the measurement was about 160 kbar. The temperature of the sample was changed using a nichrome heater wound outside the pressure cell.

Results and Discussions

The anisotropy of the electrical resistivity in Nb_3I_8 was measured at room temperature. The resistivity in the *ab* plane was 50 Ω cm and that along the *c* axis was about 100 Ω cm. The resistivity ratio, $\rho_\perp/\rho_\parallel$, is nearly 2. Figure 2 shows the electrical resistivity in the *ab* plane as a function of

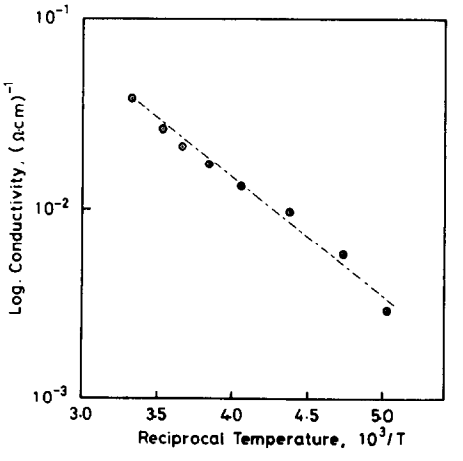

FIG. 2. The temperature dependence of the electrical resistivity parallel to the layer of Nb_3I_8.

temperature. This value is slightly larger than that of Nb_3Cl_8 reported by Kepert and Marshall (*8*). The electrical resistivity and the activation energy of NbI_4 agrees approximately with their results. The resistivity of this single crystal is anisotropic, the resistivity ratio, $\rho_\perp/\rho_\parallel$, being nearly 5. The thermoelectric power of NbI_4 was also measured to be +0.8 mV/deg at room temperature. From this sign, it is thought that electrons contribute to the electrical conduction.

The structure of NbI_4 is composed of octahedrally coordinated niobium atoms, each NbI_6 octahedron sharing opposite edges with two similar octahedra to form infinite strings parallel to the *a* axis of orthorhombic unit cell. The metal atoms are displaced from their octahedron centers so that the Nb–Nb distances are alternately short and long (3.31 Å, 4.36 Å). Similar structures are observed for $NbCl_4$ (*9*). There is an unpaired *d* electron in each niobium atom of NbX_4. Overlap of the *d* orbitals can produce the unfilled band. Because of the direct bonding between pairs of niobium atoms, the *d* band is splitting; thus the lower band is completely filled. As shown in Table I, NbX_4 shows the semiconducting behavior at atmospheric pressure. The decrease in the activation energy along the series $NbCl_4 > NbBr_4 > NbI_4$ has been already reported (*8*).

TABLE I

THE ACTIVATION ENERGIES AND THE RATIOS OF TWO DIFFERENT Nb–Nb DISTANCES

	Activation energy (eV)		Ratio of Nb–Nb distances
	Single	Powder	r_{short}/r_{long}
$NbCl_4$	0.44[a]	0.45[a]	0.81
$NbBr_4$	0.37[a]	0.35[a]	—
NbI_4	0.12[a,b]	0.16[a]	0.76
Nb_3Cl_8	—	0.21[a]	0.71
Nb_3Br_8	—	—	0.68
Nb_3I_8	0.26[b]	–	0.65

[a] Ref. (*8*). [b] Present work.

The ratio of two different Nb-Nb distances in a niobium chain, r_{short}/r_{long}, for NbX_4 depends on the halide anions, decreasing towards the bottom of the Periodic Table. These results suggest that the energy gap for NbX_4 is not sensitive for the Nb-Nb distances, but depends mainly on the halide anions.

Nb_3I_8 is crystallized in a two-dimensional layer structure similar to CdI_2 structure. An infinite array of triangular clusters of niobium atoms is formed. Nb-Nb distances within a cluster are 3.0 Å and the shortest distance between clusters is 4.6 Å. The ratio of these Nb–Nb distances, r_{short}/r_{long}, for Nb_3X_8 decreases along the series $Nb_3Cl_8 > Nb_3Br_8 > Nb_3I_8$. For the activation energies, however, the observed tendency in the series of NbX_4 is not found in those of Nb_3X_8.

Figure 3 shows the electrical resistance of NbI_5 at high pressure. The resistance

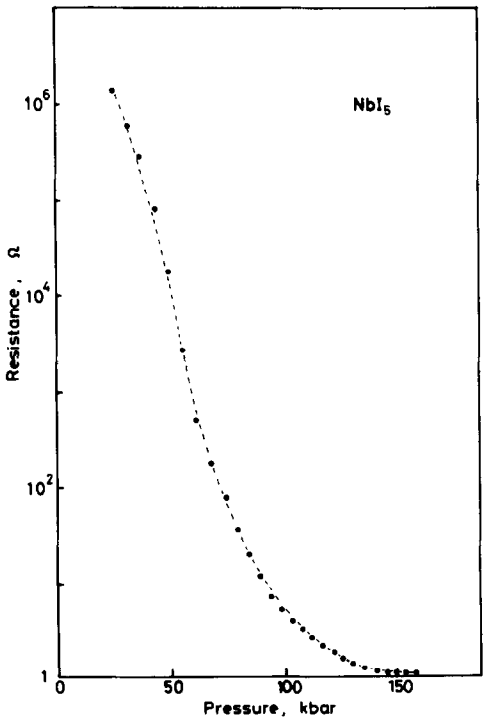

FIG. 3. The pressure dependence of electrical resistance in NbI_5.

decreased rapidly with increasing pressure up to 100 kbar. Above this pressure, the decrease in the resistance is saturated. The resistivity was about $10^3\ \Omega$ cm at around 160 kbar. The temperature coefficient of resistivity was negative at this pressure. The pressure dependence of resistance for this compound indicates the characteristics of molecular crystals such as I_2, SnI_4 (*10*) and C_6I_6 (*11*). The large change of the resistance with pressure in NbI_5 arises mainly from the increase of intermolecular I---I interaction at high pressure. Since NbI_5 is extremely sensitive to moisture and oxygen, the measurement of resistivity is very difficult at atmospheric pressure. The resistivity estimated from the extrapolation of high-pressure data was nearly $10^{12}\ \Omega$ cm at atmospheric pressure.

Electrical resistivities and activation energies of NbI_4 and Nb_3I_8 are summarized in Table II. The activation energy of Nb_3I_8 is larger than that of NbI_4. On the contrary, it should be noted that the resistivity in *ab* plane of Nb_3I_8 is smaller than that along the needle axis (*a* axis) of NbI_4. 4*d*-electron numbers per a niobium atom in the outer shell are 7/3 for Nb_3I_8 and 1 for NbI_4 (among the 15 electrons within the triangle eight are accommodated in bonds with iodine atoms). Owing to this difference in electron number, Nb_3I_8 becomes more conductive in spite of its larger activation energy. The electrical properties of these iodides are anisotropic, the resistivity ratio, $\rho_\perp/\rho_\parallel$, being small as shown in Table II. The iodine atoms in the iodides array the hexagonal close-pack in the crystal. The most intermolecular I---I distances are considerably shorter than the normal van der Waals distance of 4.3 Å. The intermolecular I---I bond is much stronger. These facts show that the iodine atoms in these iodides contribute to their electrical properties..

Figure 4a exhibits the pressure dependence of the electrical resistance in the *ab* plane of the Nb_3I_8 single crystal. The resistance decreased monotonously by a factor of approximately 10^{-3}. The change of the resistance with pressure is the smallest in three niobium iodides. The activation energies vs pressure curve is shown in Fig. 4b. This compound shows the semiconducting behavior at about 160 kbar. Judging from this curve the pressure where the activation energy goes down to zero seems to exceed 200 kbar. The pressure dependence of the electrical resistance along the niobium chain of NbI_4 is shown in Fig. 5a. The resistivity decreased rapidly with increasing pressure, reaching the order of $10^{-3}\ \Omega$ cm at about 150 kbar. Figure 5b indicates the effect of pressure on the activation energy of this compound. It goes down to zero at pressure of about 150 kbar and above this pressure NbI_4 shows metallic behavior. The insulator

TABLE II

ELECTRICAL RESISTIVITIES AND ACTIVATION ENERGIES OF NbI_5, NbI_4 AND Nb_3I_8.

		Resistivity (Ω cm)	Activation energy (eV)	Resistivity (at 160 kbar, Ω cm)	Nb–Nb distances (Å)	
					r_{short}	r_{long}
NbI_5		10^{12} [a]	—	10^3	—	—
NbI_4	*a*-axis	300	0.12	10^{-3}	3.31	4.36
	bc plane	1600	—			
Nb_3I_8	*ab* plane	50	0.26	10^{-1}	3.00	4.60
	c plane	100	—			

[a] Extrapolated value from high pressure data.

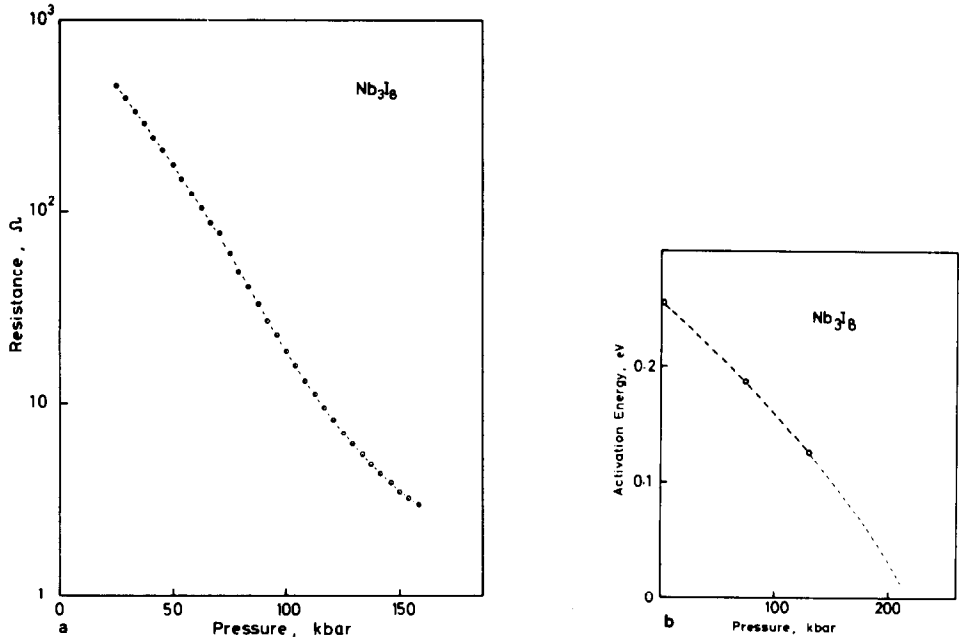

FIG. 4a. The pressure dependence of the electrical resistance parallel to the layer of Nb_3I_8.

FIG. 4b. The pressure dependence of activation energy parallel to the layer of Nb_3I_8.

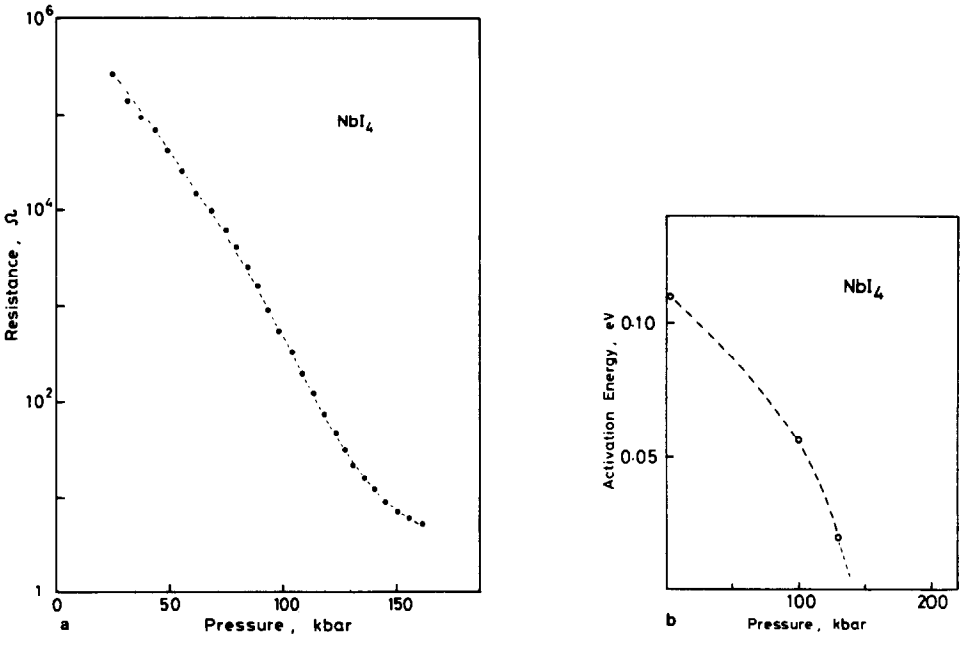

FIG. 5a. The pressure dependence of the electrical resistance along the niobium chain of NbI_4.

FIG. 5b. The pressure dependence of activation energy along the niobium chain of NbI_4.

to metal transition in NbI_4 gradually proceeds with increasing pressure.

Since three niobium iodides consist of the hexagonal close-packing of iodine atoms, these compounds may be very compressible such as I_2 and SnI_4. The compressibilities of these iodides are not yet measured. Judging from their crystal structures, the compressibility of Nb_3I_8 seems to be the smallest. The change of the resistance with pressure in Nb_3I_8 is smaller than that of other iodides. This seems to be due to the smaller compressibility.

As shown in Table II, the Nb-Nb distance in Nb_3I_8, 3.0 Å, is shorter than that, 3.31 Å, in NbI_4. This means the metal–metal bonds within a cluster of Nb_3I_8 are strong compared with that of pairs in a niobium chain of NbI_4. Therefore, the *d* electron of Nb_3I_8 is easy to be localized in a cluster. Nb_3I_8 did not show the metallic behavior, but NbI_4 became metallic at pressure around 160 kbar. The niobium chain in NbI_4 plays an important role to the metallic conduction.

Acknowledgments

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