Reflectivity of Two-dimensional Cluster Compound, Nb_3I_8

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Synopsis. The reflectivity spectrum of two-dimensional cluster compounds, Nb_3I_8, is measured from 5×10^3 to 35×10^3 cm^{-1} and compared to that of Ag_2F. The spectrum has four peaks, at 7.5, 11.8, 20.0, and 28.6×10^3 cm^{-1}.

The physical properties of quasi-low-dimensional compounds have been a subject of considerable interest in recent years. Triniobium octaiodide, Nb_3I_8, is a two-dimensional semiconductor at atmospheric pressure. The resistivity on the ab plane of Nb_3I_8 is 50 Ω-cm, while that along the c axis is about 100 Ω-cm.[1] In a previous paper we have reported the reflectivity of two-dimensional metal Ag_2F and discussed the plasma frequency in the two-dimensional metal.[2] In this report we wish to present the reflectivity spectrum of the single crystal of Nb_3I_8 and compare it to that of Ag_2F.

The crystal structure of Nb_3I_8 is based on a hexagonal closed-packing of the iodine atoms, and three-eighths of the octahedral holes of the iodine octahedra are occupied by niobium atoms. Nb_3I_8 is crystallized in a layer structure similar to the CdI_2 structure. As is to be expected from the compositional ratio, one-fourth of the niobium atoms are left out from the niobium layers. Therefore, the metal atoms are arranged in triangular clusters. The distance between two iodine octahedron centers is 3.8 Å. The positions of the niobium atoms are shifted from the centers of the iodine octahedra. The Nb–Nb distance within a cluster are 3.0 Å, while the shortest Nb–Nb distance between clusters is 4.6 Å.[3] The magnetic property of Nb_3I_8 has also been reported in Ref. 3 to be a weak paramagnetism.

The single crystals of Nb_3I_8 were prepared by the known technique.[4] The crystals grew in the form of plates with a metallic dark gray appearance. The surface of a plate is found by X-ray diffraction analysis to be parallel to the layers of the triangular clusters. A detailed description of reflectivity measurement has already been presented in an earlier paper.[5]

Figure 1 shows the reflectivity spectrum of the Nb_3I_8 single crystal. The reflectivity reaches about 35% at its maximum point. This value is considerably lower than that of the two dimensional metal Ag_2F. The reflectivity spectrum of Ag_2F shows the typical metallic features which are to be expected from Drude's classical free electron theory. On the contrary, the reflectivity spectrum of Nb_3I_8 has four peaks at 7.5, 11.8, 20.0, and 28.6×10^3 cm^{-1}. The Drude-type spectrum is not observed in this two-dimensional semiconductor. Figure 2 shows the real, ε_1, and imaginary, ε_2, parts of the complex dielectric constant. These values are obtained by applying the Kramers-Kronig

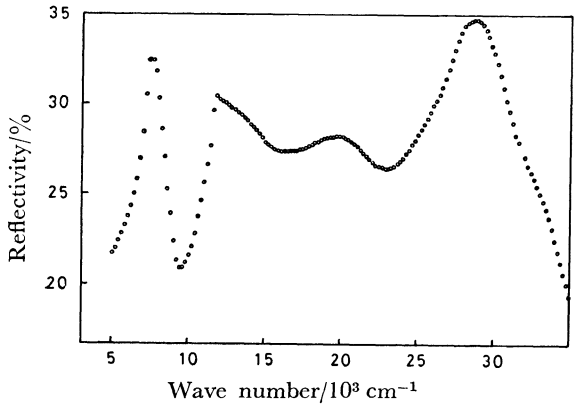

Fig. 1. Reflectivity spectrum of Nb_3I_8 against wave number.

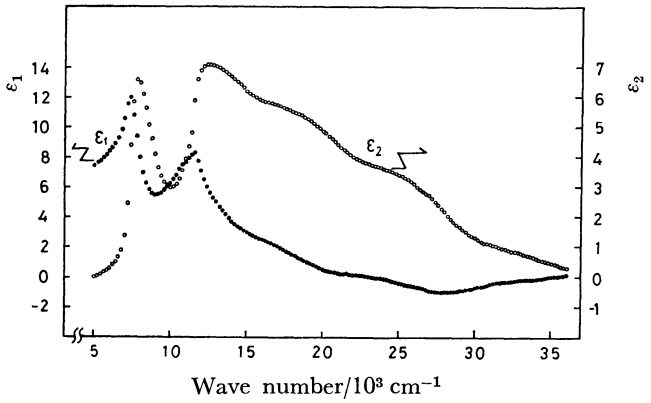

Fig. 2. Plot of the real part (ε_1, ●) and imaginary part (ε_2, ○) of the complex dielectric constant (ε).

analysis to the reflectivity data shown in Fig. 1. The absorption coefficient in Ag_2F increases with a decrease in the wave number in the near-infrared region. On the other hand, in Nb_3I_8, ε_2, which is proportional to the absorption coefficient, decreases with a decrease in the wave number. This suggests that Nb_3I_8 is a typical semiconductor. The resistivity on the ab plane of Nb_3I_8 is 50 Ω-cm, and the thermal-energy gap is about 0.52 eV. The metallic behaviour is not observed even at very high pressures.[1] The 4d electrons in niobium atoms hop among triangle clusters constructed from niobium atoms. The optical-energy gap estimated from the edge of the reflectivity spectrum is comparable to the thermal-energy gap obtained from the temperature dependence of the reflectivity. Therefore, we suggest that the near-infrared band at 7.5×10^3 cm^{-1} may arise from the charge transfer between niobium clusters.

Since NbI_4 is extremely sensitive to water and oxygen, the reflectivity spectrum of NbI_4 has been measured in dry nitrogen stream at room temperature.[7] A broad band was observed at around $21\times10^3\,cm^{-1}$. Judging from the study of the absorption spectra of NbI_4 in pyridine,[8] the broad band in the NbI_4 single crystal may be assigned to the charge-transfer band between niobium and iodine atoms. Therefore, the band near $20\times10^3\,cm^{-1}$ in Nb_3I_8 must be attributable to the charge-transfer band between niobium and iodine atoms. Though it is very difficult to identify the two bands at 11.8 and $28.6\times10^3\,cm^{-1}$, these bands may tentatively be assigned. The bond lengths between a central niobium atom and surrounding iodine atoms are listed in Table 1.[3] These bond lengths are divided into two groups. One group of lengths range in distance from 2.75 to 2.76 Å, with a mean distance of 2.75 Å, while the others range in distance from 2.92 to 3.02 Å, with a mean distance of 2.95 Å. On the other hand, the Nb–I lengths of NbI_4 are in the range of 2.65 to 2.90 Å,[6] and the mean length is 2.75 Å. The band $28.6\times10^3\,cm^{-1}$ may be assigned to the charge-transfer absorption of the longer-bond-length group. The niobium atoms in a Nb_3I_8 crystal are octahedrally surrounded by iodine atoms, and, according to the chemical analysis of Nb_3I_8, the I/Nb ratio was 2.82. Therefore, the valence state of a niobium atom is considered to be $Nb^{3+}(d^2)$. The bands at $11.8\times10^3\,cm^{-1}$ may be assigned to the d-d transition among energy levels split by the octahedral ligand field of iodine atoms.

Table 1. Interatomic distances/Å of Nb_3I_8

Nb-Nb	3.00, 4.60
Nb-I	2.75, 2.76
	2.92, 3.02

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