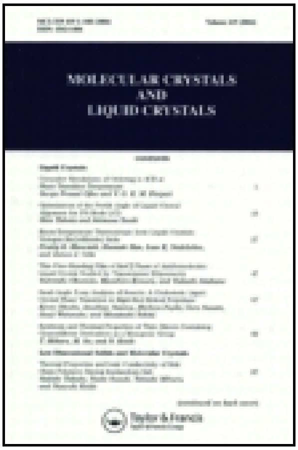

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STRUCTURAL PHASE TRANSITION IN $(NbSe_4)_3I$

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Abstract We have studied the second-order structural phase transition of $(NbSe_4)_3I$ on the basis of dc-electrical-resistivity and x-ray-diffraction measurements. No evidence of the charge-density-wave formation has been observed. Typical dc resistivity and Hall coefficient at 295 K are 1.4 ohm-cm and -6×10^{-6} m^3C^{-1}, respectively. $(NbSe_4)_3I$ has the aspects which differ from those observed in other related compounds, $(NbSe_4)_{10/3}I$, $(NbSe_4)_2I$ and $(TaSe_4)_2I$.

INTRODUCTION

The linear-chain compounds $(MX_4)_nY$ (M=Nb,Ta; X=S,Se; Y=Cl,Br,I; n=2,3,10/3,4) promise a new developement of the study of transition-metal chalcogenides.[1] Among them $(NbSe_4)_3I$ has been known since 1977.[2] It has been assigned as a narrow-gap semiconductor and there has been no report of a phase transition until 1983.[1-5] We have found out the evidence of a phase transition in $(NbSe_4)_3I$ by dc electrical resistivity, far-infrared reflectance and x-ray diffraction.[6,7] Electron-diffraction study by Roucau et al. has also confirmed the existence of the phase transition.[8] The motivation of our work is to clarify the characteristics of the newly observed phase transition in this compound.

DC ELECTRICAL RESISTIVITY AND HALL COEFFICIENT

Both the dc electrical resistivity and the Hall coefficient were measured at 295 K. The magnetic field up to 1.45 T was used. The dc resistivity along the c chain axis at zero magnetic field was typically 1.4 ohm-cm. Hall voltage was measured on three samples and it was proportional to the magnetic field within our experimental accuracy. The Hall coefficient was -6×10^{-6} m^3C^{-1}. If we assume simply the existence of only one type of carrier, the observed Hall coefficient corresponds to the electron density of 1×10^{18} cm^{-3}. The number of the electron per Nb atom is $\sim 10^{-4}$. The result strongly supports the conclusion of the electronic band calculation[9], i.e., $(NbSe_4)_3I$ is primarily a semiconductor. Dc resistivity is shown as a function of temperature in Fig. 1. Resistivity anomaly was observed around 274 K. The shape of the resistivity anomaly with respect to the inverse temperature strongly depends on the sample. In Fig. 1 the sample exhibits only the increase of the resistivity instead of the feature of the metal-insulator transition as shown in Fig. 1 of ref. 6. Meerschaut[5] and Gressier et al.[1] have reported that there are only two kinds of activation-type conduction at low temperatures. However, in our case, the conduction property at low temperature strongly depends on the sample and is characterized by the various values of the activation energy.

X-RAY DIFFRACTION AND THE PHASE TRANSITION

To investigate the correlation between the resistivity anomaly and the x-ray diffraction we performed both of the measurements on the same sample. Figure 2 shows the integrated intensity of the (0,5,12) reflection as a function of temperature. The reflection at $(0,k,l)$ point, where $k+l=2n+1$, is most sensitive to the phase transition. Transition temperature (T_c) was 274.2 K. More detailed study of this sample has been reported in another paper.[7] After the x-ray measurement we measured dc electrical resistance of the identical sample (see Fig. 1). A continuous resistance anomaly was observed around 274 K. Good correlation was achieved between the resistive anomaly and the structural variation. Between 296 K and 7

K no other phase transition has been observed, which has also been confirmed by far-infrared-reflectance and Raman-scattering measurements.[6,10] The observed phase transition is not associated with the CDW formation. We have proposed that the possible space group below T_c is P4, $P\bar{4}$ or P4/m.[7] This means that Nb and I atoms displace along the c chain axis in the low-temperature phase. In the case of P4 we may observe the ferroelectric phase transition. On the other hand, the antiferroelectric phase transition may occur in the case of $P\bar{4}$.

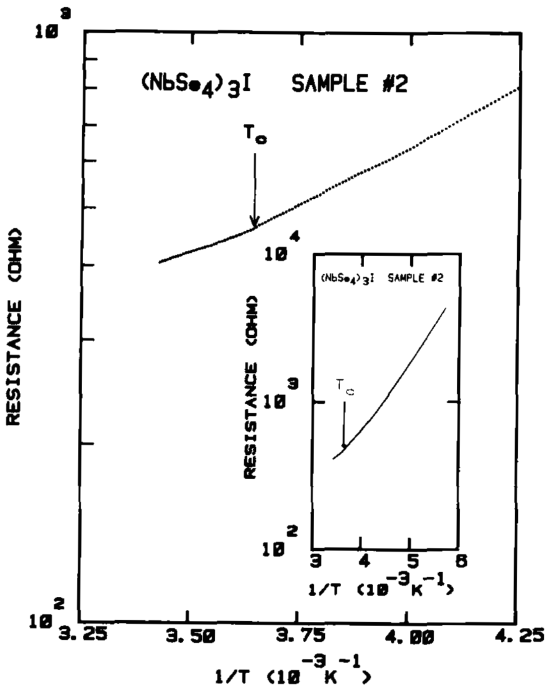

FIGURE 1 The dc electrical resistance of $(NbSe_4)_3I$ as a function of temperature. The inset shows the dc electrical resistance of the identical sample down to 175 K. The sample was the same that had been used in the x-ray study (see Fig. 2).

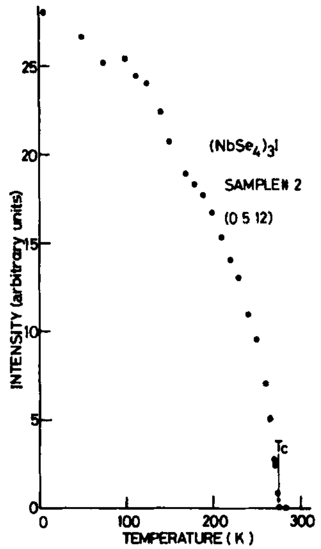

FIGURE 2 Temperature dependence of the integrated intensity of (0,5,12) reflection in $(NbSe_4)_3I$.

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