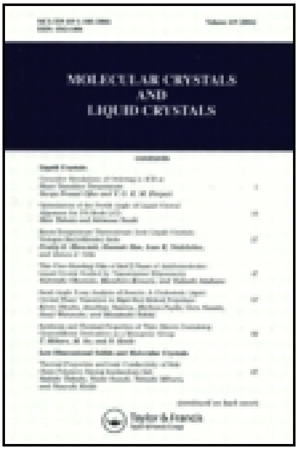

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Electrical Properties of Ta(S_x Se_{1-x})$_3$

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ELECTRICAL PROPERTIES OF $Ta(S_xSe_{1-x})_3$

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In $Ta(S_xSe_{1-x})_3$ the temperature dependence of the electrical resistivity changed systematically from a metallic to a semiconducting behavior as increasing of the sulfur concentration. The superconducting transition was observed in $TaSe_3$ but not in all sulfur-doped samples above 1.2 K. In $Ta(S_{.15}Se_{.85})_3$ one-dimensional diffuse scattering was observed above 150 K. The position of the diffuse scattering along the b* axis is (0.283 ± 0.007)b*, which is the incommensurate value. The one-dimensional diffuse scattering, the semiconducting behavior and the lack of superconducting transition found in $Ta(S_{.15}Se_{.85})_3$ are interpreted in terms of the formation of charge-density wave.

1) INTRODUCTION

In the group of the transition-metal trichalcogenides MX_3, TaS_3[1-3] and $NbSe_3$[4,5] have been found to exhibit the charge-density wave (CDW) transition. On the other hand, $TaSe_3$ is a superconductor with a T_c of (2 ± 0.5) K and shows no anomalies associated with low dimensional phase transition. It is therefore interesting to investigate systematically the electrical properties in the $TaSe_3$ - TaS_3 system. It is known[6] that $Ta(S_{.04}Se_{.96})_3$ is a metallic but the residual resistivity ratio is very low (~2) compared with that of $TaSe_3$ (60-70), and $Ta(S_{.06}Se_{.94})_3$ is a non-metallic with a minimum at 40 K and a maximum at 150 K in the temperature dependence of the electrical resistivity. Both samples also are found to be no evidence for superconductivity down to 1.2 K. These experimental results suggest that $Ta(S_xSe_{1-x})_3$ with higher concentration of sulfur shows the semiconducting behavior and undergoes the CDW transition at low temperatures.

In this paper we report the first existence of CDW in $Ta(S_{.15}Se_{.85})_3$, by electron diffraction above 150 K and the temperature variation of the electrical resistivity.

2) EXPERIMENTS

$Ta(S_xSe_{1-x})_3$ was synthesized by direct reaction of Ta, S, and Se in stoichiometric proportions. The mixture was sealed in quartz under vacuum of 1 x 10^{-5} Torr and heated to 650°C for 3 weeks before cooling. The heating temperature was kept to be lower than that of $TaSe_3$ (700°C). The crystals are oriented along the b-axis and the dimensions of sample were approximately 0.1 x 0.03 mm^2 in the cross sections and 2 cm in the length which were smaller than those of $TaSe_3$. X-ray diffraction by the powder method confirmed the reported structure[7)].

DC electrical resistivity was measured by a four-probe method along the b-axis with a current of 5.0 μA. Electrical contact was made by evapolating Te and Au successively and painting silver paste onto the evapolated area. Ohmic conductivity was confirmed for current between 1.0 μA and 50 μA at the temperatures of 295 K, 77 K and 4.2 K, respectively. Temperatures of sample were determined by the Ge- and Pt-resistance thermometer. Superconductivity was detected by a resistance measurement with a current of 1.0 μA.

Electron diffraction of $Ta(S_xSe_{1-x})_3$ was performed with the acceleration voltage of 200 kV. The sample holder was kept at 150 K. But the temperature of the individual crystal may be slightly higher as a result of irradiation by the electron beam, though a heat link to the sample holder would release some of the heat.

3) RESULT AND DISCUSSION

In Fig. 1 is shown the temperature dependence of the electrical resistivity in $Ta(S_{.15}Se_{.85})_3$ where the concentration of sulfur is nominal value. The value of the resistivity in MX_3 is typically (5 ± 2) x 10^{-4} Ohm-cm at room temperature and includes a large uncertainty because of the very small cross section. The value of the resistivity in

$Ta(S_{.15}Se_{.85})_3$ therefore is normalized to 5.0×10^{-4} Ohm-cm at room temperature. As shown in Fig. 1, the temperature dependence of the resistivity varies from crystal to crystal even in samples obtained from the same batch. This suggests that as the real concentration of sulfur is different from crystal to crystal it must be determined for the individual crystal. The analysis of the chemical composition for the individual crystal is now progress.

Two groups for resistivity behavior are found in Fig.1. One of them is the group with #4a- and 4b-crystal, in which the resistivity behavior is very similar to that of #2-sample (sulfur concentration of 6%) shown in Fig. 2. In the other group of #4c- and 4d-crystal the semiconducting behavior is observed, though the temperature dependence of the resistivity can not be simply described in the exponential form.

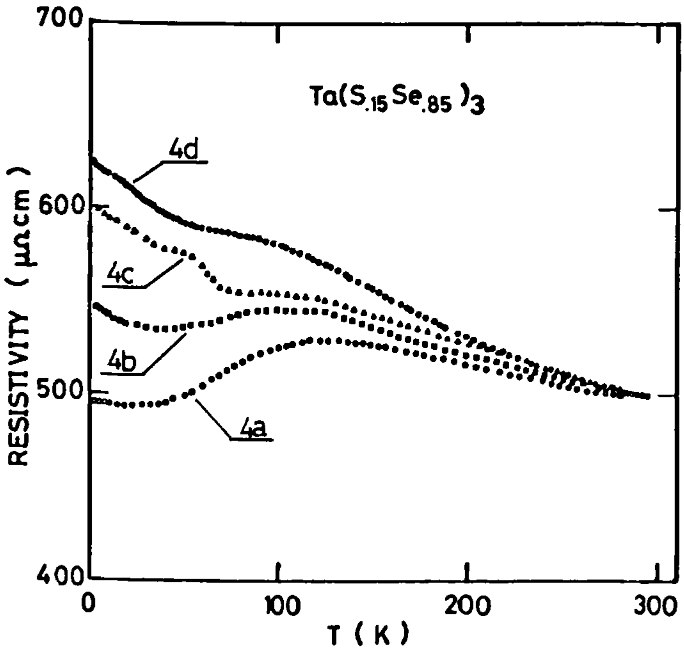

FIGURE 1 The electrical resistivity as a function of temperature in $Ta(S_{.15}Se_{.85})_3$ (the sample number is #4).

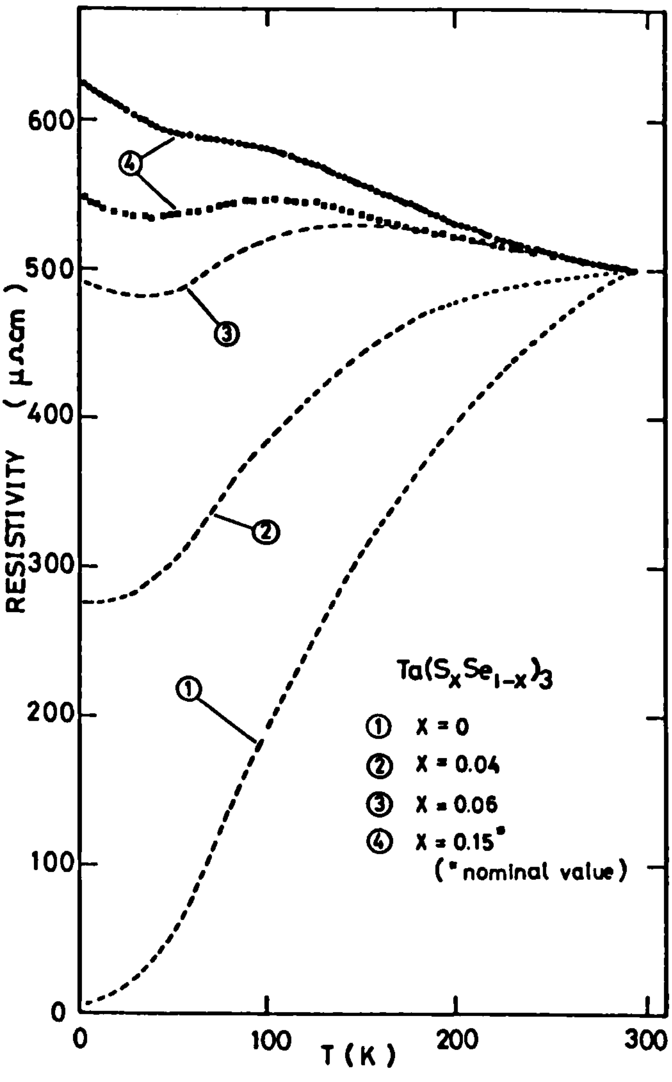

FIGURE 2 The electrical resistivity as a function of temperature for four samples in $Ta(S_xSe_{1-x})_3$.

Fig. 2 shows the temperature variation of the electrical resistivity in samples with different concentration of sulfur. It is found that the temperature dependence of the resistivity changes systematically from a metallic to a semiconducting behavior as increasing of sulfur concentration. In #1-, 2-, and 3-sample the temperature dependence of the resistivity is almost same among all crystals measured and their chemical compositions have been determined by XMA[6]. Although the chemical compositions in crystals of #4-sample have not yet been determined, the values of the compositions may be estimated from the experimental result shown in Fig. 2. Since the electrical resistivity in #4a- and 4b-crystal shown Fig. 1 is very similar to that of #3-sample (x=0.06), their sulfur concentrations are expected to be about 6%, and those in #4c- and 4d-crystal may be above 6%, because the semiconducting behavior has been observed in the temperature dependence of the resistivity. It seems that the sulfur concentration in the crystals increases successively from #4a- to #4d-crystal.

No evidence associated with periodic lattice distortion has been observed in the electron diffraction patterns of #1-, 2-, and 3-sample above 150 K. Fig. 3 shows the reciprocal lattice above 150 K in $Ta(S_{.15}Se_{.85})_3$. The anomaly in diffuse scattering can be clearly seen to be one-dimensional. The position of this one-dimensional anomaly along the b*-axis is $(0.283 \pm 0.007)b^*$, which is constant over the crystals within experimental errors and larger than the commensurate value of 0.25b*. This incommensurate streaks correspond to the Kohn anomaly couped with CDW.

In $Ta(S_{.15}Se_{.85})_3$ the satellite spots caused by the existence of CDW could not be observed above 150 K (the limitation of our cooling apparatus). Even if the temperature of crystals could be sufficiently cooled down, it would be difficult to observe the satellite spots, because as the crystals are alloies the long range order of CDW is hardly established in the disorder system. We therefore try to estimate the approximate value of the CDW transition temperature from the temperature dependence of the resistivity shown in Fig. 1. Since the resistivity in #4a- and 4b-crystal is very similar to that of $Ta(S_{.06}Se_{.94})_3$ with no anomaly in diffuse scattering, the CDW transition may be not discovered in #4a- and 4b-crystal. In #4c- and 4d-crystal an anomaly in the resistivity which may be associated with the CDW transition is found around 70 K, where the large change in the temperature coefficient of the resistivity is observed. The samples which show the semiconducting behavior are expected to undergo the CDW

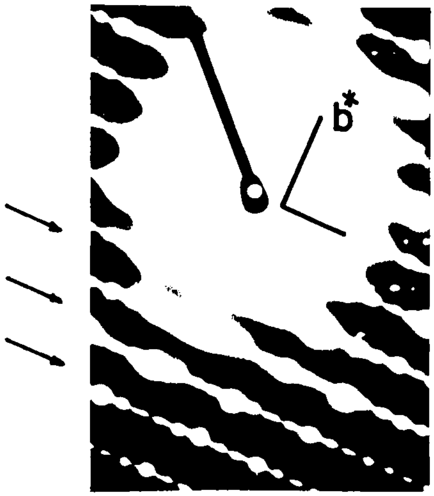

FIGURE 3 Electron diffraction pattern of $Ta(S_{.15}Se_{.85})_3$ above 150 K, showing one-dimensional anomaly in diffuse scattering (marked by arrows).

transition around 70 K. Thus our electron diffraction experiments and measurements of the temperature dependence of the electrical resistivity suggest that the existence of CDW in $Ta(S_{.15}Se_{.85})_3$.

Comparing the other MX_3 materials which undergo the CDW transition, the following points are worth noting:

(i) The low-temperature phase of TaS_3, $NbSe_3$ and $Ta(S_{.15}Se_{.85})_3$ which are the monoclinic crystal structure have the incommensurate superperiod, while it is commensurate in only orthorhombic TaS_3.

(ii) The period of the one-dimensional modulation of $Ta(S_{.15}Se_{.85})_3$ is larger than those of orthorhombic TaS_3[1,2], monoclinic TaS_3[3)] and $NbSe_3$[4,5)]. This suggests that the Fermi surface of $Ta(S_{.15}Se_{.85})_3$ is the high relative position in the Brillouin zone compared with those of TaS_3 and $NbSe_3$. This is consistent with the prediction by Willson[8)] that the carrier concentration of $TaSe_3$ is larger than that of $NbSe_3$.

(iii) $TaSe_3$ is a metallic and the Fermi surface is known to be nonplanar with both electrons and holes[9], while $Ta(S_{.15}Se_{.85})_3$ is a semiconducting at low temperatures. The Fermi surface of $Ta(S_{.15}Se_{.85})_3$ may be plane-like surface.

(iv) In $NbSe_3$ and orthorhombic TaS_3 the satellite spots also have components perpendicular to the chain axis, while in monoclinic TaS_3 only the component along the chain axis was observed. It is be very interesting for $Ta(S_{.15}Se_{.85})_3$ to determine whether the periodic lattice distortion has components perpendicular to the chain axis.

In order to investigate the change in the period of the lattice distortion in $Ta(S_xSe_{1-x})_3$, the study for samples with higher concentrations of sulfur is now in progress.

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REFERENCES

1. T. Sambongi, T. Tsutsumi, Y. Shiozaki, M. Yamamoto, K. Yamaya and Y. Abe, Solid State Commun, 22, 729 (1977).
2. K. Tsutsumi, T. Sambongi, S. Kagoshima and T. Ishigro, J. Phys. Soc. Japan, 44, 1735 (1978).
3. C. Roucaus, R. Ayrolles, P. Monceau, L. Guemas, A. Meerschaut and J. Rouxel, Phys. Status Solidi, (a) 62, 483 (1980).
4. K. Tsutsumi, T. Takagaki, M. Yamamoto, Y. Shiozaki, M. Ido, T. Sambongi, K. Yamaya and Y. Abe, Phys. Rev. Lett. 39, 1675 (1977).
5. R. M. Fleming, D. E. Moncton and D. B. McWhan, Phys. Rev. B18, 5265 (1978).
6. J. F. Kwak, R. L. Greene and K. Yamaya, Bulletin Amer. Phys. Soc., 24, 503 (1979).
7. E. Bjerkelund, J. H. Fermor and A. Kjekshus, Acta Chem. Scand. 20, 1836 (1966).

8. J. A. Willson, Phys. Rev. B19, 6459 (1979).
9. R. M. Fleming, J. A. Polo, Jr. and R. V. Coleman, Phys. Rev. B17, 1634 (1978).