Observation of the X-ray Diffuse Scattering and the Nonlinear Conduction in $(MSe_4)_2I$ (M=Ta and Nb)

H.Fujishita, M.Sato and S.Hoshino

Institute for Solid State Physics, University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106

X-ray diffraction and conductivity measurements have been made on $(MSe_4)_2I$, (M=Ta and Nb). A phase transition of $(NbSe_4)_2I$ was found and the transition temperature T_c was determined to be about 210K by the conductivity measurement. For $(TaSe_4)_2I$, T_c was about 260K as reported previously. Superlattice reflections due to the formation of charge density wave (CDW) in $(TaSe_4)_2I$ were observed at points $\bar{q}=(\pm 0.05, \pm 0.05, \pm 0.085)$. The type of CDW of $(NbSe_4)_2I$ is known to be identical to that of $(TaSe_4)_2I$. Temperature dependence of the threshold electric field of nonlinear conductivity is consistent with the result in previous reports.

§1 Introduction

Quasi one dimensional conductors are known to have phonon softning at $2k_F$ through an electron-phonon coupling, where k_F is a Fermi momentum. These phonons induce structural phase transitions, or Peierls transitions, and lattice modulations associated with electron charge density wave (CDW) occur. Nonlinear conductivity found in the low temperature phase is considered to be caused by the sliding motion of the CDW. When an applied electric field becomes larger than a certain threshold value E_t, the sliding motion sets in against the pinning force due to impurities or some other mechanisms.

In this paper we report the results of X-ray diffraction and conductivity measurements on $(TaSe_4)_2I$ and $(NbSe_4)_2I$. Gressier et al.[1] have analyzed a room-temperature structure of $(TaSe_4)_2I$. It has the tetragonal symmetry and the lattice parameters are a= 9.531 Å and c=12.824 Å. The structure has a marked one dimensional character as shown in Fig.1. Each chain of Ta atoms along the c axis is surrounded by Se atoms. I atoms

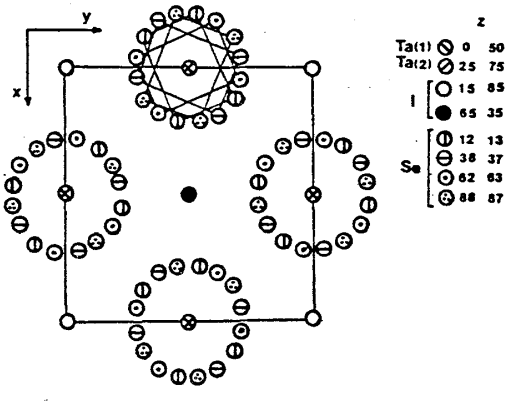


Fig.1 Structure projection on the ab plane reported by Gressier et al.[1]

are between the chains. Wang et al.[2] and Maki et al.[3] found a phase transition of $(TaSe_4)_2I$ by conductivity measurements. They also found nonlinear conductivity below $T_c \simeq 260K$. In the series of compounds, the presence of $(NbSe_4)_3I$ has been known for a long time.[4] Its structure is quite similar to that of $(TaSe_4)_2I$, but the periodicity along the c direction is 1.5 times as large as that of $(TaSe_4)_2I$. On the other hand in the present experiment, we prepared a compound with Nb atoms which has almost the same lattice parameters as those of $(TaSe_4)_2I$. Then we believe the compound has a formula of $(NbSe_4)_2I$ for the reasons stated later. $(NbSe_4)_2I$ is known to have a phase transition at about 210K by conductivity measurement. As an evidence of the CDW formation either for $(TaSe_4)_2I$ and $(NbSe_4)_2I$, we observed the superlattice reflections near the fundamental Bragg points in the low temperature phase. Above T_c, the diffuse scattering in a plane perpendicular to the c* axis has been observed. Threshold fields of nonlinear conductivity for both compounds have similar temperature dependence and consistent with the previous results obtained by Wang et al.[2] and Maki et al.[3]

§2 Experimental

Single crystals of $(TaSe_4)_2I$ and $(NbSe_4)_2I$ were prepared by reactions of stoichiometric mixtures of constituents in evacuated quartz tubes at about 500°C. For both compounds, needle like single crystals were obtained. This is the same method as previously reported by Maki et al.[2]

Measurements of DC resistivity R(T) were performed by the four terminal technique. Contacts of lead wires were made with silver paint. Nonlinear conductivity was studied by both I-V curve and differencial resistance dV/dI measurements as a function of DC current. In order to avoid an increase of sample temperature, we used very thin needle crystals.

X-ray Laue photographs and oscillation photographs around c* were taken for both compounds at room temperature and at low temperature, respectively. Rigaku rotating anode X-ray generator operated at 50kV 80mA was used. CuKα radiation with Ni filter was utilized. Diffraction intensity measurements of $(TaSe_4)_2I$ were carried out using a step sacn method on Rigaku computer-controlled automatic four-circle X-ray diffractometer. CuKα radiation monochromatized by a graphite crystal was obtained

from 1kW X-ray generator in this case. The sample crystals were cooled by a regulated nitrogen vapor stream.

§3 Results

3.1 Nonlinear conductivity

Low field DC resistivity R(T) and nonlinear conductivity of $(TaSe_4)_2I$ have been already reported as a function of temperature.[2,3] We also made these measurements for both compounds in order to know the transport properties of the present samples.

Results of measurements of R(T) are shown in Fig.2. Measurements of $(TaSe_4)_2I$ have reproduced the results reported previously.[2,3] Though $(NbSe_4)_2I$ has a phase transition at about 210K, gradients dlogR(T)/d(1/T) are almost the same for both samples in the low temperature phases. This fact supports that the compound is not $(NbSe_4)_3I$ but $(NbSe_4)_2I$. Both compounds show "nonmetallic" behavior near room temperature.

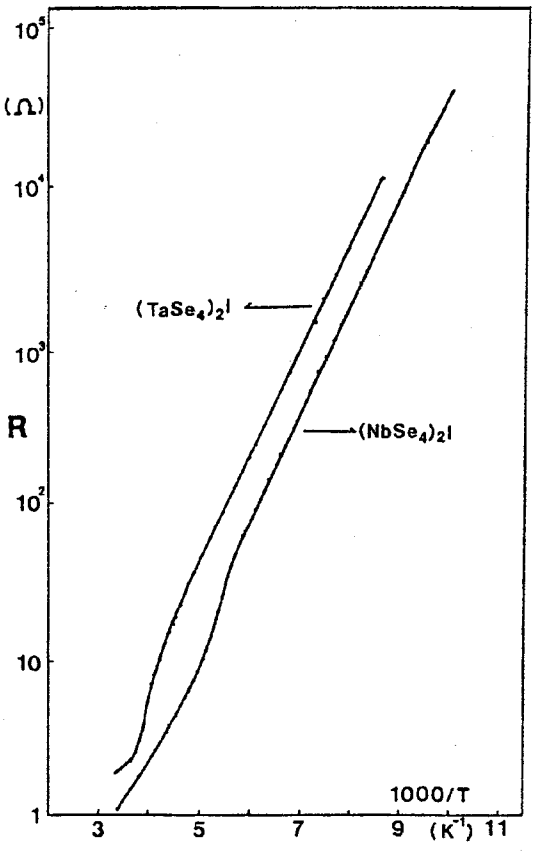


Fig.2 Temperature dependence of resistivity in $(MSe_4)_2I$, (M= Ta and Nb).

Below T_c threshold electric fields $E_t(T)$ of nonlinear conductivity in $(TaSe_4)_2I$ and $(NbSe_4)_2I$ decrease with increasing temperature as reported by the previous authors.[2,3] We observed nonlinear conduction even above T_c. However, more careful measurement is necessary to confirm the nonlinear conduction above T_c by removing possible suprious effects.

3.2 X-ray diffraction

X-ray diffraction measurement gives a direct evidence for the existence of CDW state. In the present experiment, X-ray oscillation photographs of both compounds have been taken in the low temperature phase. They are shown in Fig.3. Superlattice reflections can be seen near the fundamental Bragg spots. Though resolutions

of two photographs are different,detailed examination indicates the existence of the same type modulation in these compounds.

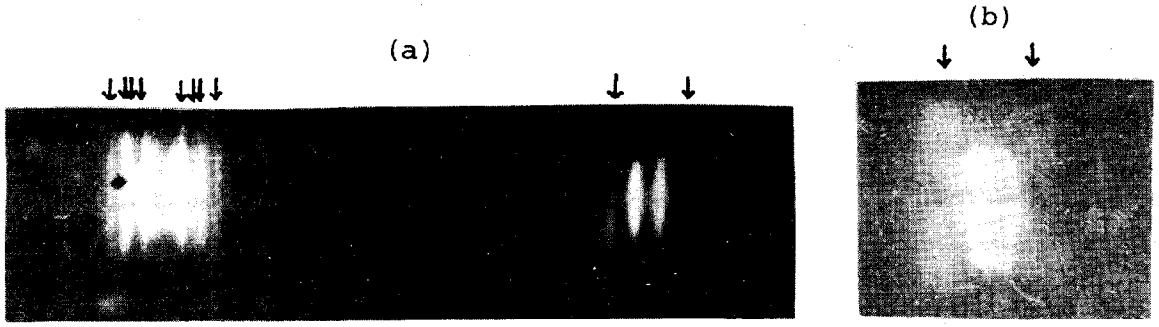


Fig.3 X-ray oscillation patterns with CuKα radiation from $(TaSe_4)_2I$ at 200K(a) and $(NbSe_4)_2I$ at 130K(b). On both patterns the c* direction is vertical. Arrows indicate superlattice reflections.

Diffraction intensity map around (554) Bragg reflection on the plane with ℓ=3.915 in the reciprocal space of $(TaSe_4)_2I$ measured by the four-circle diffractometer is shown in Fig.4. Four peaks are observed around the Bragg reflection on this plane. On the photograph of Fig.3(a), eight superlattice spots are seen around the left hand fundamental one. Four of them are due to the $CuK\alpha_2$ radiation. Because the vertical resolution is not sharp enough to resolve two superlattice peaks on a line along c*, these reflections appear as an elongated peak. Thus the four superlattice spots with the same ℓ on the photograph correspond to four peaks in Fig.4. In Fig.3(b) the split along c* can clearly be seen because of the better resolution. Profiles of the superlattice reflections along c* for $(TaSe_4)_2I$ are presented in Fig.5. These superlattice reflections appear at the points $\bar{q}=(\pm 0.05, \pm 0.05, \pm 0.085)$ apart from the fundamental Bragg spots. Remarkable asymmetry of the intensities of superlattice reflections was observed not only on the a*b* plane but along the c* direction as well.

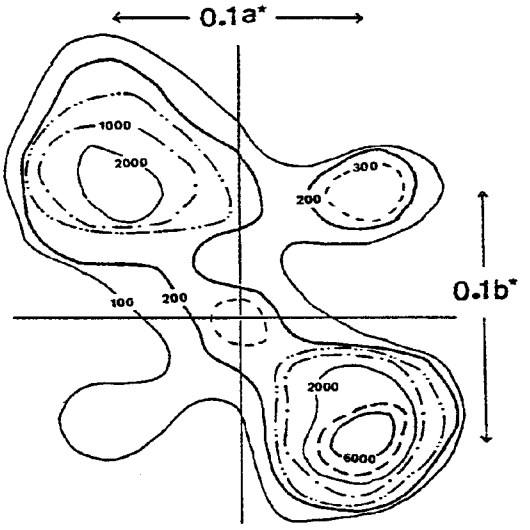


Fig.4 X-ray diffraction intensity map around (554) Bragg reflection on the plane with ℓ=3.915 in the reciprocal space of $(TaSe_4)_2I$. Contour lines are drown at unequal intervals.

Fig.6. shows the temperature dependence of peak intensity of superlattice reflection (5.05, 4.95, 3.915). The transition seems to be second order. Temperature dependence of the wave vector of superlattice reflections was not observed. Fig.7 exhibits a comparison of profiles along a* of the superlattice reflection and the diffuse scattering at 280K. The full widths at half maximum(FWHM) of the superlattice reflection and the diffuse scattering are 0.038a* and 0.10a* respectively. The profile of the diffuse scattering along c* is shown in Fig.8. It is difficult to deduce the FWHM of the diffuse scattering along c*, because another diffuse scattering was observed at ℓ=4.0. Therefore we cannot discuss the difference between the correlation lengths along a* and c*. The diffuse scattering at ℓ=4.0 was observed in the Laue photograph at room temperature as shown in Fig.9, which was taken using Ni filter. The diffuse scattering was also observed in the Laue photograph of $(NbSe_4)_2I$. At present it is not clear whether the diffuse scattering condenses to superlattice reflections or not.

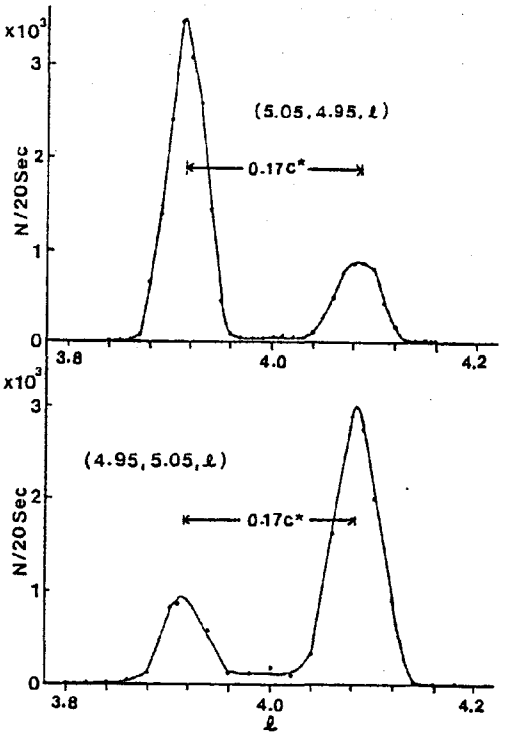


Fig.5 X-ray diffraction profiles of superlattice reflections along c* at (5.05 4.95, ℓ) and at (4.95, 5.05, ℓ).

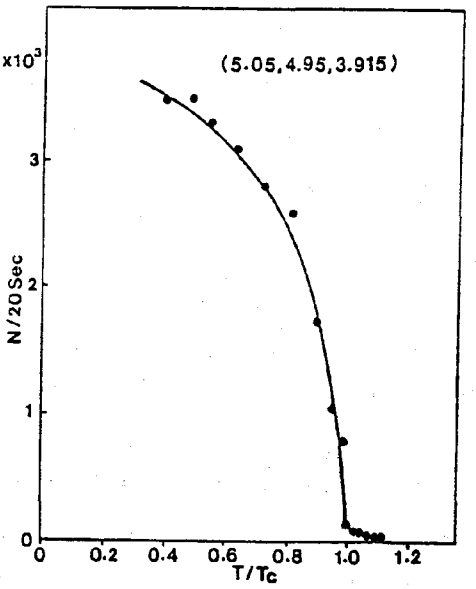


Fig 6 Temperature dependence of peak intensity of superlattice reflection at (5.05 4.95 3.915) $T_C \simeq 260K$.

§4 Discussions

The superlattice reflections of the compounds $(MSe_4)_2I$, (M=Ta and Nb) observed near the fundamental Bragg spots give the direct evidence for the formation of CDW. These superlattice reflections were expected by

Fig.7 Comparison of profiles of the superlattice reflection along a* at 137K and the diffuse scattering at 280K.

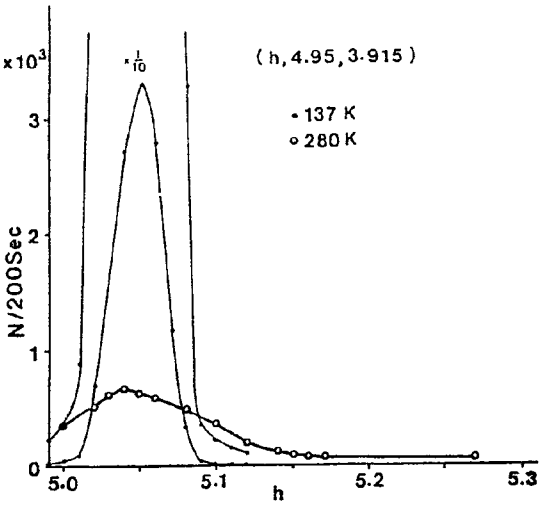
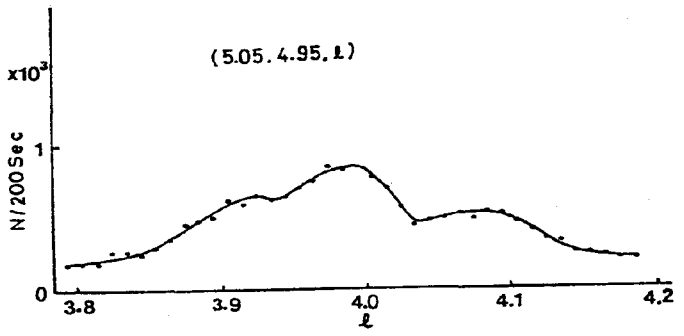


Fig.8 Profile of the diffuse scattering along c* at 280K.



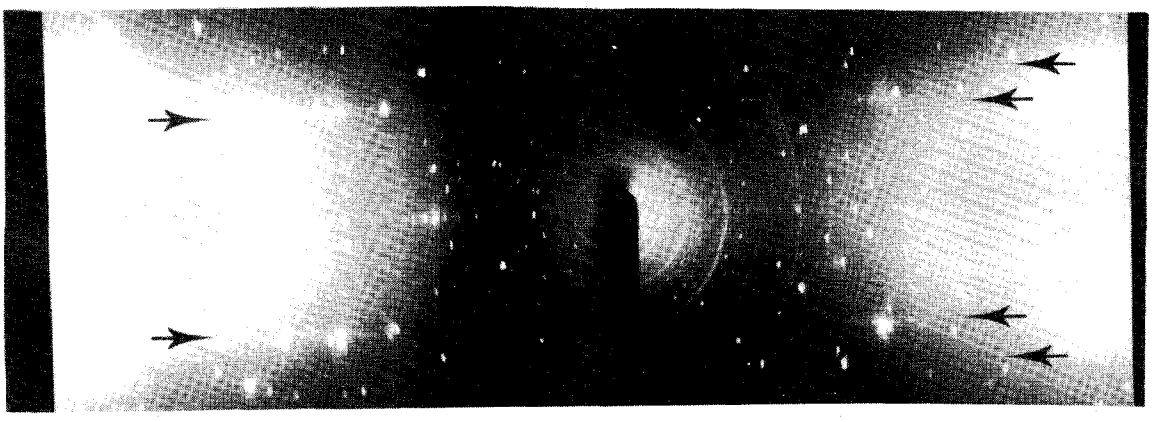


Fig.9 X-ray Laue photograph of $(TaSe_4)_2I$ at room temperature with CuKα radiation using Ni filter. The c* direction is vertical. Arrows indicate the diffuse scattering on the plane with ℓ=integer.

Wang et al.[2] to appear near the fundamental spots. Based on an assumption of a purely ionic crystal of a formula $M^{4+}M^{5+}4(Se_2^{2-})I^-$, they deduced $2k_F$ to be $2\pi/c$, which is exactly equal to the reciprocal vector c*. The superlattice reflections were observed at points 0.085c* apart from the fundamental spots along c* for $(TaSe_4)_2I$. Then $2k_F$ instability can be considered to occur at 1.085c* due to an incomplete ionicity.

The value of the wave vector of CDW perpendicular to the quasi one dimensional axis seems not to be easily understood. Asymmetry of the intensities of superlattice reflections along c* and in the a*b* plane is quite remarkable. If we assume that the transition is due to a condensation of the acoustic phonon with the wave vector $\bar{q}$=(0.05, 0.05, 0.085), the asymmetry can not be explained. This may support the idea that the CDW has a wave vector component 1.085c*. The detailed assignment of the CDW remains as a future problem.

$(NbSe_4)_2I$ shows the same physical properties as those of $(TaSe_4)_2I$; their lattice parameters are almost the same and the temperature dependences of the resistivities of both compounds show similar behavior. In addition, the types of the CDW are identical. These facts assure that the Nb compound has the formula $(NbSe_4)_2I$.

Diffuse scattering on the plane with ℓ=integer remains unclarified. It seems necessary to examine it in detail for the further understanding of the transition.

Acknowledgement

The authors are grateful to Dr.S.Sato of ISSP for kind help in the measurement with the four-circle diffractometer.

References

1) P.Gressier, L.Guemas and A.Meerschaut, Acta Cryst.B38(1982)2877.
2) Z.Z.Wang M.C.Saint-Lager, P.Monceau, M.Renard, P.Gressier, A.Meerschaut, L.Guemas and J.Rouxel, Solid State Commun.46 (1983)325.
3) M.Maki, M.Kaiser, A.Zettle and G.Grüner, Solid State Commun.46. (1983)497.
4) A.Meerschaut, P.Palvadeau and J.Rouxel, J.Solid State Chem.20 (1977)21.