

Elastic and Inelastic Neutron Scattering Study on  
the Metal-Insulator Transition in  $K_{0.3}MoO_3$

M. Sato, H. Fujishita and S. Hoshino

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

-ABSTRACT- Results of the neutron scattering experiments on the structural transition of the quasi one dimensional conductor  $K_{0.3}MoO_3$  are reported. The incommensurate wave vector of the charge density wave has a smooth temperature dependence and does not undergo a lock-in transition down to about 6 K, although it approaches the commensurate value 0.75. The temperature dependence of the order parameter is approximately described by a simple relation, which turned out to describe that of another quasi one dimensional conductor  $(TaSe_4)_2I$ , too. The phonon dispersion curves are also shown and the character of the soft phonon which induces the lattice instability is roughly viewed.

## §1 Introduction

Compounds with a formula  $M_xT O_n$  are usually called bronze, where M is an alkali metal and T is a transition metal atom. Because rigid molecular units of  $TO_m$  form a cage-like structure<sup>1)</sup> these compounds exhibit various characteristic features; large volume of vacancies can exist in tungsten bronze  $M_xWO_3$ <sup>1)</sup> and a marked anisotropy of electric conductivity in  $M_{0.3}MoO_3$ <sup>2)</sup>, has been known. The possible effect of the vacancies in  $M_xWO_3$  on the superconducting transition temperature has been discussed by Sato et al.<sup>3)</sup> based on the results of neutron scattering experiment. Possibility of a bipolaron formation may be another characteristic feature of these molecular crystals.<sup>4)</sup>  $K_{0.3}MoO_3$  and  $Rb_{0.3}MoO_3$  have a metal-insulator transition at  $T=180$  K as a consequence of the quasi one dimensionality of electronic transport.<sup>2), 5)</sup> The incommensurate charge density wave (CDW) state was confirmed by the x-ray work by Pouget et al.<sup>6)</sup> and by the observation of nonlinear conductivity by Dumas et al.<sup>7)</sup> and Dumas and Schlenker.<sup>8)</sup> Because, as stated above, the quasi one dimensional nature of the conductivity does not mean the quasi one dimensionality of the crystal structure in such molecular crystals, large crystals can be prepared. Therefore

measurements which can hardly be done for needle-like crystals as  $\text{NbSe}_3$ , become possible for such molecular crystals.

Here we mainly report the present stage of our neutron scattering study on  $\text{K}_{0.3}\text{MoO}_3$ . The order parameter and the incommensurate wave vector of the CDW are shown as a function of temperature. The phonon dispersion curves including a soft phonon branch are also shown. A part of the present data has been already published in our previous letter.<sup>9)</sup>

## §2 Experiment

Single crystals were grown by electrolysis described by Wold et al.<sup>10)</sup> The resistivity measurements were carried out by the four terminal technique. The contacts of the lead wires were made with silver paint. At low temperature an electrometer was used because resistivity of the sample became very large. Neutron scattering measurements were carried out using ISSP ND-1 spectrometer at JRR-2 in JAERI. The triple axis condition was always used with the collimation of 40'-40'-40'-40' and the incident neutron energy was 13.7 meV in most cases. The sample temperature was measured by AuFe-Chromel thermocouple.

## §3 Results and Discussions

Neutron diffraction measurements using a powder as well as the single crystal of  $\text{K}_{0.3}\text{MoO}_3$  at room temperature showed the consistent result with the monoclinic structure reported by Graham and Wadsley.<sup>11)</sup> Figure 1 shows the temperature dependence of the resistivities of the crystal. They are measured along the directions parallel to the one dimensional axis ( $b^*$  axis), perpendicular to the  $b^*$  axis and within a plane of the  $\text{MoO}_3$  clusters, and perpendicular to the plane. The ratios of the specific resistivities are roughly 1:20:2000,<sup>12)</sup> which are almost similar to those obtained by Perlstein et al.<sup>2)</sup> and Pouget et al.<sup>6)</sup> No more than 10% decrease of the resistivity from 300 K to 180 K has been observed. In the temperature region  $20 \text{ K} < T < 50 \text{ K}$ , the slopes of  $\log R$ - $T$  curves are almost equal in all directions. At very low temperature  $T < 20 \text{ K}$ , the saturation of the resistivity is seen, which may be attributed to certain spurious effects like surface conductivity.

The superlattice peak,  $(1, \pm q_b, \overline{0.5})$  away from the fundamental one was first reported by Pouget et al.<sup>6)</sup> In figure 2, the temperature

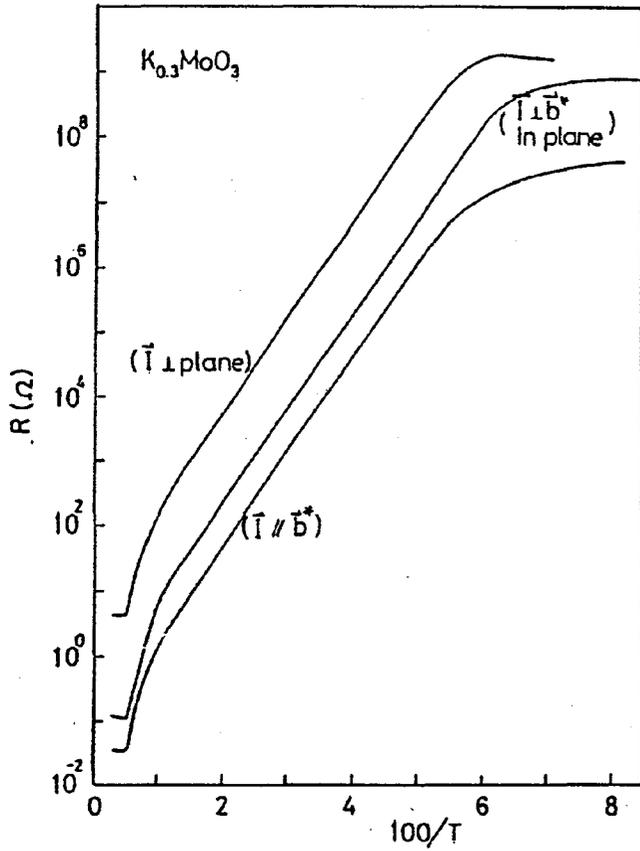


Fig.1 Temperature dependence of the resistivities of  $K_{0.3}MoO_3$  for three orthogonal directions. The directions of current vector  $I$  are attached to the curves. The planes consist of the clusters of  $MoO_6$  octahedra and are perpendicular to the  $[2, 0, \bar{1}]$  reciprocal direction.

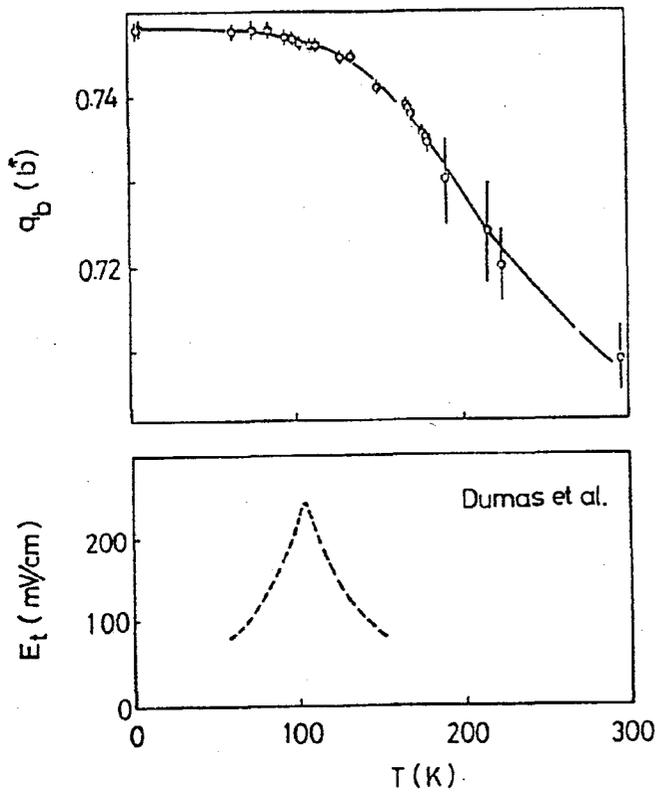


Fig.2 Temperature dependence of the incommensurate wave vector  $q_b$  is shown (top) with that of the threshold electric field  $E_t$  of the nonlinear conductivity observed by Dumas et al.<sup>6)</sup> (bottom).

dependence of the incommensurate wave vector  $q_b$  is shown. Although  $q_b$  seems to approach the commensurate value 0.75, as the temperature decreases, it does not undergo a lock-in transition. The smooth temperature variation of  $q_b$  indicates the fact that the anomalous temperature dependence of threshold electric field  $E_t$  of the nonlinear conductivity observed by Dumas et al.<sup>6)</sup> seems not to be relevant to the behavior of  $q_b(T)$ . Following comment may be valuable to be made. Although our simple measurement of V-I curves of the present crystals reproduced the qualitative character of  $E_t(T)$ , more careful measurement of the differential resistivity of the present crystals showed no anomaly in the  $E_t - T$  curve.<sup>13)</sup>

In figure 3, the square of the normalized peak intensity,  $i^2 \equiv \{I(t)/I(0)\}^2$  at  $(1, 4-q_b, 0.5)$  is shown as a function of the square of the normalized temperature,  $t^2 \equiv (T/T_c)^2$ . We have already reported

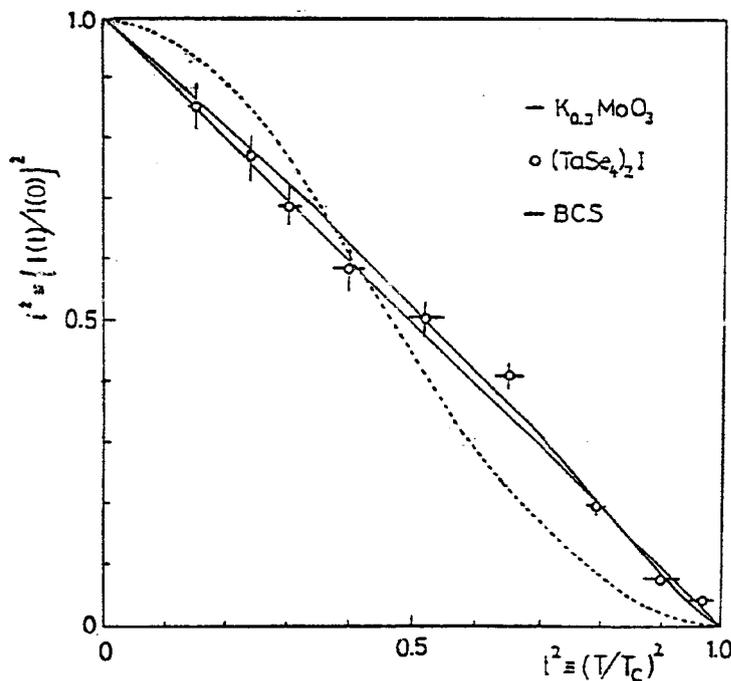


Fig.3 Square of the normalized intensity of the superlattice reflection,  $i^2 \equiv \{I(t)/I(0)\}^2$ , is shown as a function of  $t^2 \equiv (T/T_c)^2$ . Solid line shows the result for  $K_{0.3}MoO_3$  and open circles are for  $(TaSe_4)_2I$ . Thin solid line shows the relation  $i^2 + t^2 = 1$ . Broken line indicates the curve predicted by the BCS theory.

the relation,  $i^2 + t^2 = 1$  is approximately valid for  $K_{0.3}MoO_3$ <sup>9)</sup>. Here, the same plot of the intensity of a superlattice peak for  $(TaSe_4)_2I$ , which also shows the metal-insulator transition of quasi one dimensional conductor,<sup>14), 15)</sup> is also shown. These data were taken by x ray.<sup>16)</sup> We can see that the relation  $i^2 + t^2 = 1$  is approximately valid for  $(TaSe_4)_2I$ , too. The direction of the deviation from the BCS

result may be understood by the consideration of the fluctuation for both of the temperature regions,  $T=0$  and near  $T_c$ . However, the validity of the simple relation for both of those compounds may imply the presence of more fundamental explanation.

Figure 4 shows the dispersion curves of certain phonon branches. The open symbols indicate the results taken at room

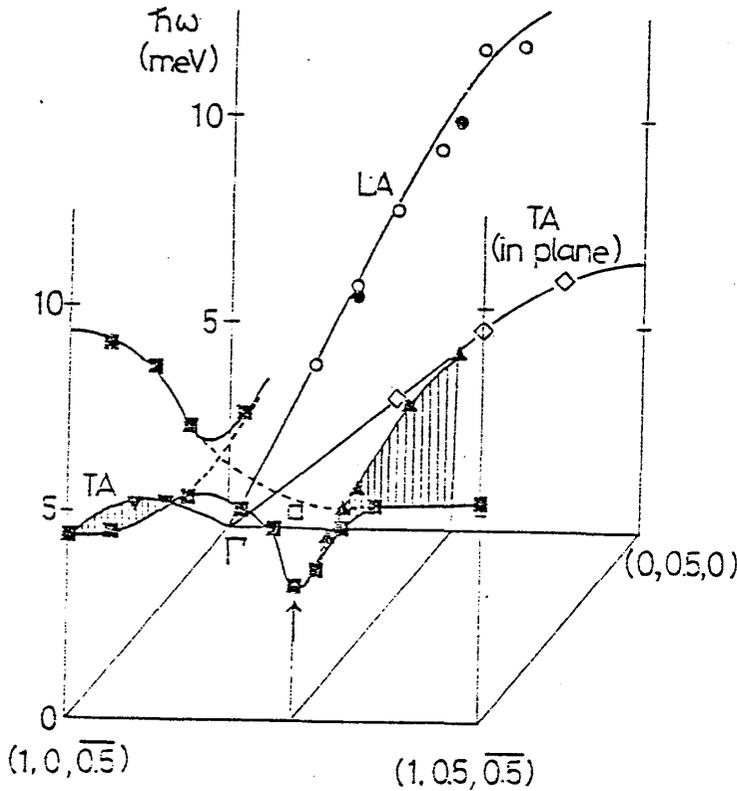


Fig.4 Dispersion curves of the phonons measured in the present experiment. The open symbols are the data at room temperature and closed ones are taken at about 219 K. All data except the in-plane TA branch are taken with the spectrometer setting to measure phonons polarized mainly along the  $b^*$  direction. The broken lines show the possible behavior of the curves without anticrossing.

temperature and the closed ones indicate those taken at about 219 K. All branches except the in plane TA mode were measured with the spectrometer setting to measure the phonons polarized along the  $b^*$  direction. The in-plane TA mode polarizes almost within a plane of the cluster of  $\text{MoO}_6$  octahedra and perpendicular to the  $b^*$  axis. Phonon softening occurs at the point which corresponds to the superlattice point below  $T_c$ . The phonon energy at room temperature shown by the open square decreases to the closed square point at 219 K as indicated by the arrow. At the zone boundary point  $(1,0,0.5)$ , the branch which includes the soft phonon, coincides with the transverse acoustic mode along the  $[1,0,0.5]$  reciprocal direction. However, the anticrossing of two branches indicated by the broken curves in the figure seems to take place and therefore without anti-

crossing, the soft phonon branch should be connected with the upper branch shown near  $(1,0,\overline{0.5})$  reciprocal point. Then, the rough feature of the low lying phonon which induces the lattice instability through the coupling with the electrons can be seen.

Increasing interest exists in the detailed mechanism of the lattice instability of molecular crystals with quasi one dimensional conductivity. Feinberg and Ranninger<sup>17)</sup> discussed the lattice instability with the bipolaron formation. In order to examine if this mechanism is relevant to the present metal-insulator transition, it might be useful to assign the soft phonon mode. However, the present data are not enough for the purpose and it remains as a future problem.

Even the largest intensity of the superlattice reflection measured within  $(2h,k,\bar{h})$  reciprocal plane is no more than 0.3% of that of  $(0,4,0)$  Bragg reflection in the low temperature limit. With an assumption of the equal amplitude and in-phase modulations along the  $b^*$  direction for all atoms within a plane of the clusters of the  $\text{MoO}_6$  octahedra, the modulation amplitude is deduced as less than 0.02 Å. Pouget et al.<sup>6)</sup> suggested the existence of two antiphase CDW within a cluster of eight  $\text{MoO}_6$  octahedra. It might explain the observed weak intensity of the superlattice reflections. However, a preliminary analysis of the structure factor seems not to support their suggestion.

#### Concluding remarks

Results of the neutron scattering experiment are reported. Although the present study has not been finished, certain features of the transition of  $\text{K}_{0.3}\text{MoO}_3$  are clarified. From the view point of the neutron scattering experiment, the interests are mainly in two points. One is the problem of the mechanism of the transition of such a molecular crystal with quasi one dimensional conductivity. The other is the dynamical aspect of the lattice instability which is closely connected with the electron correlation. The appearance of the central (or nearly elastic) peak in the dynamical structure factor  $S(q,\omega)$  observed by the present authors<sup>9)</sup> in  $\text{K}_{0.3}\text{MoO}_3$  is the problem to be understood. Large single crystals of the quasi one dimensional conductor as  $\text{K}_{0.3}\text{MoO}_3$  seems to be useful to study such problems as mentioned above and these will be done in the near future.

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