

## Thermal study of the phase transitions of blue bronze $K_{0.3}MoO_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 7129

(<http://iopscience.iop.org/0953-8984/3/37/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 11/05/2010 at 12:33

Please note that [terms and conditions apply](#).

## Thermal study of the phase transitions of blue bronze $K_{0.3}MoO_3$

Yin Jiang†, Zhi-guo Liu†, Xue-Xuan Qu†, X J Zhang‡ and X Y Zhou§

† Laboratory of Solid State Microstructure of Nanjing University, Nanjing 210008, People's Republic of China

‡ Department of Physics, Zhejiang University, People's Republic of China

§ Department of Modern Physics, University of Science and Technology of China, Hefei, People's Republic of China

Received 31 December 1990, in final form 7 May 1991

**Abstract.** DSC measurements have been performed on blue bronze  $K_{0.3}MoO_3$  between 110 and 295 K. Two anomalies at 240 and 180 K were observed in heating runs. A hysteresis of nearly 40 K at the 240 K anomaly was observed in a cooling run, which indicates a first-order transition.

The potassium molybdenum oxide  $K_{0.3}MoO_3$ , the so-called blue bronze undergoes a metal-to-semiconductor transition at around 180 K [1]. Although this transition was found more than 10 years ago, it was established only recently that blue bronze has a quasi-one-dimensional electronic structure [2]. Various properties of blue bronze  $K_{0.3}MoO_3$  which were due to charge-density-wave (CDW) formation have been studied widely, such as non-linear conductivity [3], x-ray diffraction [4], thermoelectric power [5] and magnetic susceptibility [6]. In this paper we report calorimetric studies on CDW formation. The measurements were made using a Perkin-Elmer model DSC-2 differential scanning calorimeter; all experimental processes were carried out with a computer system.

The crystal  $K_{0.3}MoO_3$  was prepared by electrolytic reduction of a  $K_2CO_3$ - $MoO_3$  melt with a  $K_2CO_3$ -to- $MoO_3$  ratio of 1 to 4.32. The method of preparation has been described in detail elsewhere [7]. In a recent study on  $K_{0.3}MoO_3$  which had been prepared by a new method we found a peak in the temperature dependence of resistivity, which is in accordance with the behaviour of thermoelectric power [5] and the magnetic susceptibility [6]. Figure 1 shows the temperature variation of the normalized resistivity. The peak was attributed to formation of another CDW which is responsible for the weak semiconductor behaviour in the temperature variation of resistivity between 180 and 240 K. In the experiment we used 56.9 mg of the sample, and the scan rate was  $20\text{ K min}^{-1}$  in both heating and cooling runs. We can roughly consider the results of DSC study as the temperature dependence of the heat capacity.

We have found two specific heat anomalies at 240 and 180 K, which were consistent with CDW transitions where anomalies in the electric resistivity, magnetic susceptibility

**Table 1.** Parameters obtained for  $K_{0.3}MoO_3$  near the two phase transitions.  $\nu$  is the total electronic specific heat coefficient corresponding to a density of states of  $0.592 \text{ states erg}^{-1} \text{ molecule}^{-1}$  calculated from the magnetic susceptibility data.  $X_c$  is the fraction of condensed electrons deduced from the observed transition entropy.  $R_0$  is the gas constant and is equal to  $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ .

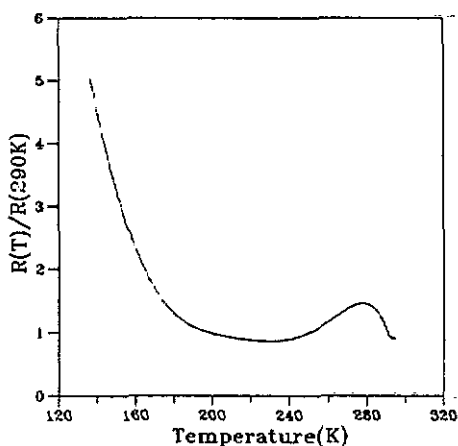
$T_c$ (K)	$C_p/R_0$ (units of $R_0$ )	$\Delta C_p/C_p$ (%)	$\Delta T$ (K)	$\Delta S = \int_{T-T_c}(C_p dT)/T$ (units of $R_0$ )	$\nu T_c$ (units of $R_0$ )	$X_c$ (%)
240	8.38	8.87	$\approx 13.8$	0.022	0.097	20
180	5.47	3.36	$\approx 9.4$	—	—	—

and thermoelectric power were observed. The thermodynamic characteristics of the phase transitions are summarized in table 1. The 240 and 180 K transition region shown in figure 2 were measured in both heating and cooling runs where no pre-transitional effects at two anomalies were observed. The upper anomaly in the heat capacity has a width of 13 K, the 180 K anomaly is small and narrow with a width of 9 K.

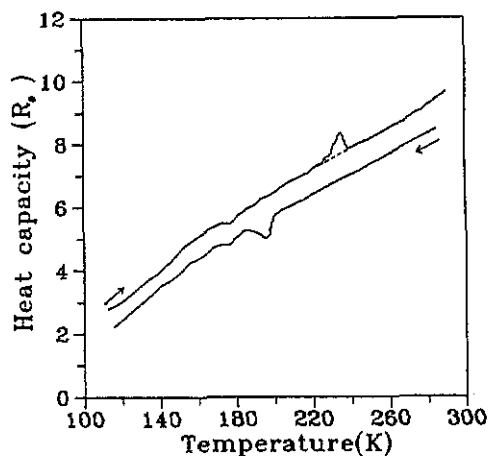
We have estimated the total change in entropy of the transition from the areas under the upper peak, using the background lines shown in the figure as a broken line. We obtained values of  $0.022 R_0$  for the 240 K anomaly. As to the 180 K transition where the anomaly is step shaped and also shows a weak peak we have to abandon the calculation of the change in entropy. In table 1 these numbers are compared with total conduction electron entropy  $\nu T_c$  at  $T_c$ , where the electronic specific heat coefficient

$$\nu = \frac{1}{2} \pi^2 k_B^2 n_F$$

with  $n_F = 0.592 \text{ states erg}^{-1} \text{ molecule}^{-1}$  calculated from the magnetic susceptibility data [6], neglecting any possible change in the density of states of the uncondensed electrons



**Figure 1.** The temperature dependence of the normalized resistivity  $R(T)/R(290 \text{ K})$  along the  $b$  axis for a  $K_{0.3}MoO_3$  single crystal.



**Figure 2.** Specific heat in units of  $R_0$  versus  $T$  for the 240 and 180 K transition regions as measured in both heating and cooling runs at a scan rate of  $20 \text{ K min}^{-1}$ . The gas constant is  $R_0 = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ .

as a result of CDW formation. Another mechanism which changes the magnetic susceptibility of  $K_{0.3}MoO_3$  from paramagnetism to diamagnetism after the 180 K transition leaves us with the great difficulty of estimating the density of states of the Fermi level before the gap on the Fermi surface opens. We can only estimate that about 20% of the conduction electrons are condensed at  $T_1$  (240 K), which is comparable with a 15% decrease in paramagnetism [6]. In the above estimates we neglected the phonon entropy in accordance with the thermodynamic behaviour of a Peierls insulator in the mean-field approximation [8]. That is, electrons near the gap edge cannot respond to lattice vibrations with wavevectors further than  $\xi_0^{-1}$  from the nesting vector (where  $\xi_0$  is the coherence length of the lattice distortion); thus the number of phonon modes which participate in the CDW phase transitions is limited. So, if the coherence length is long compared with the lattice spacing, the phonon entropy is unimportant; the only important part is from single-particle excitation across the gap. From the x-ray investigations of Pouget and Kagoshima [4] and Graham [9],  $\xi$  is greater than four lattice spacings, but the shapes of the observed anomalies are not at all BCS like.

In order to determine the order of these transitions, measurements of heat capacity were also performed in cooling runs. The shift of the peak on heating and cooling runs for the upper CDW transition (240 K) is about 40 K, and the shift of the peak for the lower transition (180 K) is about 1 K, which may be due to the higher scan rate; however, the upper transition is a real shift. From the shape of the heat capacity curve and its hysteresis with temperature we believe that the upper transition is of first order, and the lower of second order, or weak first order. Friend *et al* [10] believed that generally incommensurate CDW modulations are connected with second-order phase transitions, whereas commensurate CDWs often lead to first-order transitions. We all know that a CDW formed below 180 K is of an incommensurate nature. The CDW formed below 240 K may be of commensurate type which cannot be detected by x-ray diffraction. Generally, commensurate CDWs are pinned by the lattice and impurities [11], just like those formed in  $Nb_3Te_4$  [12] crystals below two transition temperatures, where no effect due to the motion of the CDW was observed. So it is not peculiar that no non-linearity of the DC conductivity has been found above 180 K over many years, but we are puzzled by the fact that anomalies in the resistivity and thermoelectric power are very consistent in the temperature at which they occur (about 290 K) and that the anomalies in the magnetic susceptibility and heat capacity are also very consistent in the temperature at which they occur (about 240 K). Why these two groups of physical anomalies in temperature are separated by a gap of about 40 K (which is exactly the width of the peak of resistive anomaly in temperature) is not understood clearly. Further study of this must be continued.

In summary, we have conducted high-resolution calorimetric work on  $K_{0.3}MoO_3$  and observed two specific heat anomalies at 240 and 180 K. The variation in entropy associated with upper transition is  $0.022 R_0$ . Using a density of states at the Fermi level of  $0.592 \text{ states erg}^{-1} \text{ molecule}^{-1}$  calculated from the magnetic susceptibility data and neglecting the phonon entropy we find that about 20% of the conduction electrons are condensed below 240 K, which is comparable with the variation in magnetic susceptibility. In the heat capacity curve we cannot observe a pre-transition at 180 K; so we think that the weak-semiconductor behaviour of the resistivity of  $K_{0.3}MoO_3$  between 180 and 240 K can be ascribed to the CDW transition at 240 K. Hysteresis at the upper CDW transition suggests that it may be commensurate and is of first order, and other information shows that the lower transition is second order or weak first order.

### Acknowledgment

The authors acknowledge helpful assistance with the experiments by Mr Qinping Dai from the Center of Materials and Analysis of Nanjing University, People's Republic of China.

### References

- [1] Fogle W and Perlstein J H 1972 *Phys. Rev. B* **6** 1402
- [2] Travaglimi G, Wachter P, Marcus J and Schlenker C 1981 *Solid State Commun.* **37** 599
- [3] Maeda A, Furuyama T and Tanaka S 1985 *Solid State Commun.* **55** 951
- [4] Pouget J P and Kagoshima S 1983 *J. Physique Lett.* **44** L114
- [5] Bouchard G H Jr, Perlstein J and Sienko M J 1976 *Inorg. Chem.* **6** 1682
- [6] Morris B L and Wold A 1968 *Rev. Sci. Instrum.* **39** 937
- [7] Jiang Yin, Liu Zhi-guo and Qu Xue-Xuan 1991 to be published
- [8] Berlinsky A J 1976 *Contemp. Phys.* **17** 331
- [9] Graham J 1966 *Acta Crystallogr.* **20** 93
- [10] Friend R H, Miljak M and Jerome D 1978 *Phys. Rev. Lett.* **40** 1048
- [11] Leung M C 1974 *Solid State Commun.* **15** 879; 1975 *Phys. Rev. B* **11** 4372
- [12] Sekine T, Kinchi Y and Matsuura E 1978 *Phys. Rev. B* **36** 3153