THERMAL CONDUCTIVITY OF LOW DIMENSIONAL MOLYBDENUM BRONZES AND OXIDES

E.B. LOPES, M. ALMEIDA
Dept. Quimica, ICEN-LNETI, P-2686 SACAVEM Codex, PORTUGAL
J. DUMAS, C. ESCRIBE-FILIPPINI and J. MARCUS
LEPES-CNRS, BP166, F-38042 GRENOBLE Cedex, FRANCE

ABSTRACT

Measurements of thermal conductivity, k, of $Rb_{0.3}MoO_3$, η-Mo_4O_{11}, and $K_{0.9}Mo_6O_{17}$ in the range 40-300 K are reported, with special attention to the charge density wave (CDW) transition. In all cases the CDW transition is seen as an anomalous decrease of k as T decreases at the transition. While in the first two compounds the anomaly is ascribed to the electronic contribution and to the condensation of the normal carriers at Tc, in the later case the anomaly is very large and it is essentially due to the lattice, that undergoes a commensurate distortion.

INTRODUCTION

$Rb_{0.3}MoO_3$, η-Mo_4O_{11} and $K_{0.9}Mo_6O_{17}$ are all molybdenum oxides which display reduced electronic dimensionality and charge density wave transitions [1]. $Rb_{0.3}MoO_3$ is a quasi one dimensional conductor with a Peierls transition at 182 K associated with an incommensurate CDW [2]. η-Mo_4O_{11} is a quasi-two-dimensional metal that undergoes also a commensurate CDW transition at 107 K [3]. $K_{0.9}Mo_6O_{17}$ is also a quasi-two-dimensional metal that undergoes a commensurate CDW transition at 120 K [4]. In order to further understand the CDW transitions and their relation with the structure we have initiated a systematic study of the thermal conductivity in different molybdenum bronzes and oxides, and in this paper we give a preliminary account of the measurements performed in the title compounds.

EXPERIMENTAL

In all cases thermal conductivity was measured along the high electrical conductivity direction in elongated samples of typical dimensions 4x1x0.2 mm^3, using a 4 probe slow a.c. ($\approx 5x10^{-3}$ Hz) method, relatively to a constantan wire as previously described [5]. Thermal gradients were monitored using chromel-constantan thermocouples and the gradient across the sample was 1 K, except near CDW transition where the it was kept <0.5 K. Measurements were performed on warming at a rate of 10 K/hr, and 5 K/hr near the transitions, after a pre-cooling of the sample to 20 K at 40 K/hr.

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smaller fraction of the condensed electrons (the bidimensional Fermi surfaces suffers only a partial decrease) and of a larger lattice contribution. The larger lattice conductivity when compared with the blue bronzes is a consequence of a more perfect structure without the cation deficiency of the blue bronzes. The magnitude of the observed anomaly and the overall results are consistent with a smooth lattice contribution and an electronic part given by the Wiedmann-Franz law.

Thermal conductivity of the purple bronze $K_{0.9}Mo_6O_{17}$ along the a.b plane is shown in Fig. 3. Here again we find room temperature values higher than in the blue bronzes, 12 ± 2 $WK^{-1}m^{-1}$, k increasing as T decreases.A very large anomaly is present at 102K, seen as a maximum of dk/dT. This temperature corresponds to the CDW transition in agreement to the temperature where the electrical resistivity has also a maximum in dk/dT. However the magnitude of the anomaly is too large to be accounted for by the decrease of the electronic contribution, as shown by the dashed line of Fig. 3, that represents an estimate of the thermal conductivity of the electrons K_e given by Wiedmann-Franz law and the experimental conductivity σ ($K_e = L_o \sigma T$) multiplied by 10. The observed anomaly is at least 15 times larger than the estimated electronic contribution. Therefore, the observed decrease of k at Tc is due to a decrease of the lattice contribution as a consequence of the commensurate distortion (doubling of the cell along a and b). In this respect it is worth mention that specific heat measurements in this compound showed an excess entropy

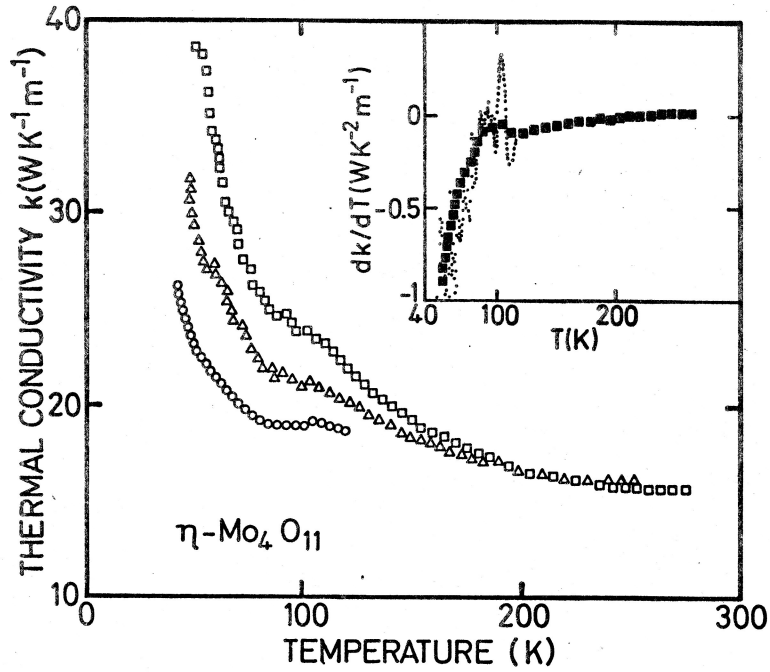

Fig. 2 - Thermal conductivity k of three samples of η -Mo_4O_{11} as function of temperature. dk/dT for two samples is shown in the inset.

RESULTS AND DISCUSSION

The thermal conductivity along the high electrical conductivity b axis of the blue bronze $Rb_{0.3}MoO_3$ in the range 40-300 K is shown in Fig. 1 for two samples. The results were found essentialy equal to those previously reported by us [5,6] for the K analogue with a room temperature value of 5 ± 0.5 $WK^{-1}m^{-1}$. A large anomaly, better seen as a sharp peak in the slope dk/dT (inset Fig. 1) is present at 181K. The large decrease of thermal conductivity bellow Tc is ascribed to the decrease of the electronic contribution of the condensed electrons at the CDW transition. As in the K analogue the results can be explained in good approximation by the Wiedmann-Franz law [5-6]. As illustrated in Fig. 1, different samples can have slightly different temperature dependence of thermal conductivity above 200K. In spite of the small gradients (0.5K) and of the small thermal rate (5 K/hr) used, in no case we have found any evidence for a peak of k near Tc as recently reported by Kwok and Brown [7] in $K_{0.3}MoO_3$.

Thermal conductivity, measured also along the b axis of high electrical conductivity in three different samples of η-Mo_4O_{11} is shown in Fig. 2. At room temperature k in this compound was found to be 15 ± 3 $WK^{-1}m^{-1}$ significantly larger than in the blue bronzes. A much smaller anomaly is seen at 102 K, as a change of the slope dk/dT associated with the CDW transition. The smaller magnitude of this anomaly is a consequence of both a

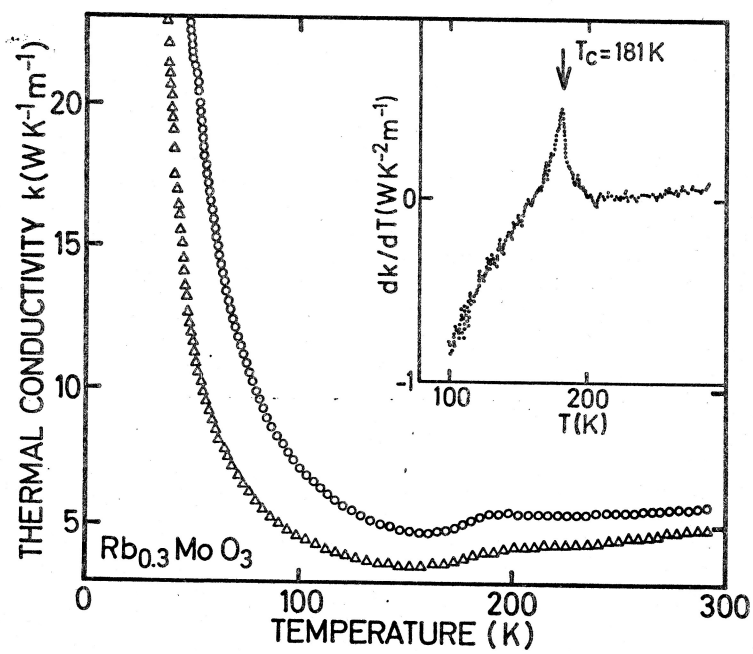

Fig. 1 - Thermal conductivity k of two samples of $Rb_{0.3}MoO_3$ as a function of temperature. dk/dT is shown in the inset.

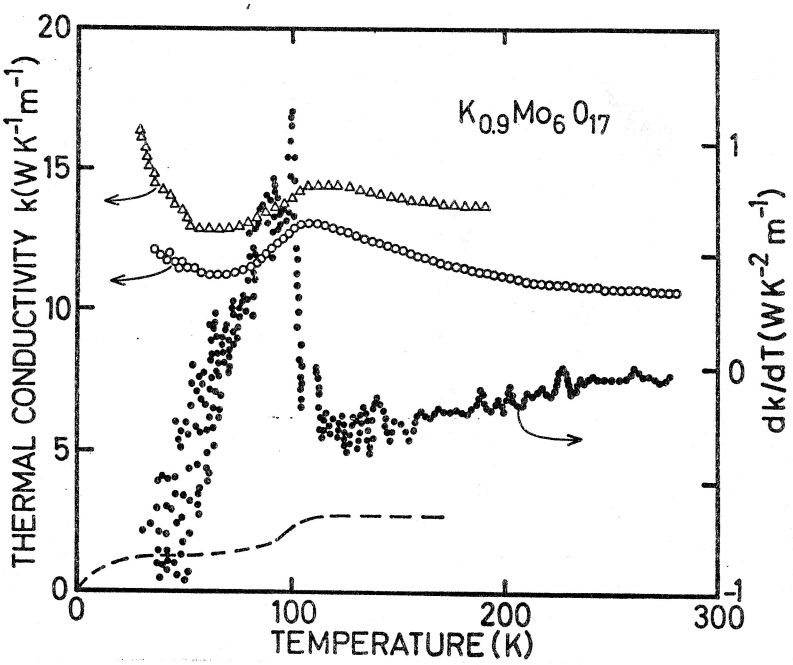

Fig. 3 - Thermal conductivity k and dk/dT as a function of temperature for $K_{0.9}Mo_6O_{17}$. The dashed line is 10 times the electronic contribution.

change that could not be explained only by the electronic contribution, suggesting also a significant lattice contribution.

ACKNOWLEDGMENTS

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