Thermal conductivity of the charge density wave molybdenum oxides gamma -Mo_4O_{11}, eta -Mo_4O_{11} and KMo_6O_{17}

LETTER TO THE EDITOR

Thermal conductivity of the charge density wave molybdenum oxides γ-Mo$_4$O$_{11}$, η-Mo$_4$O$_{11}$ and KMo$_6$O$_{17}$

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Abstract. The thermal conductivity (k_T) of the charge density wave (CDW) compounds γ-Mo$_4$O$_{11}$, η-Mo$_4$O$_{11}$ and KMo$_6$O$_{17}$ was measured in the range 20–300 K. At the CDW transition there is an anomalous decrease of k_T in all compounds as T decreases. In γ-Mo$_4$O$_{11}$ the anomaly can be ascribed to the decrease of the electronic contribution due to the decrease of the carrier concentration at the transition, the lattice remaining smooth, but in η-Mo$_4$O$_{11}$ there is evidence for an additional anomalous increase of the lattice contribution below the CDW transition. In KMo$_6$O$_{17}$ there is a very large anomaly which is ascribed almost entirely to the lattice.

γ-Mo$_4$O$_{11}$, η-Mo$_4$O$_{11}$ and KMo$_6$O$_{17}$ belong to a class of molybdenum oxides with quasi-two-dimensional electronic properties, presenting metallic properties at room temperature and charge density wave (CDW) transitions at lower temperatures (Schlenker *et al* 1989). In these compounds, as a consequence of their quasi-two-dimensional nature and the imperfect nesting of the Fermi surface, at the CDW transition the Fermi surface is only partially reduced and the electrical resistivity shows a significant increase but remains in general metallic below the transition.

η-Mo$_4$O$_{11}$ is a quasi-two-dimensional metal at room temperature with moderate anisotropy in the bc plane of highest electrical conductivity ($\rho_c : \rho_b \simeq 2$). At 109 K it undergoes an incommensurate CDW transition with wave vector $q_b = (0.23 \pm 0.005)b^*$, and the electrical resistivity along the high conductivity axis b increases from approximately 1.0×10^{-5} Ω cm at 110 K to 2.5×10^{-5} Ω cm at 90 K (Guyot *et al* 1985). At ~30 K a second transition, the nature of which is not yet completely clear, is seen as a further small increase of resistivity. γ-Mo$_4$O$_{11}$ has properties very similar to those of the η polymorph but without a clear metallic regime of resistivity below the transition as occurs at 100 K, and without the low temperature transition. The purple bronze, KMo$_6$O$_{17}$, is a quasi-two-dimensional metal without anisotropy in the ab plane and it undergoes a commensurate CDW at 110 K associated with the doubling of the unit cell along a and b ($q = \frac{1}{2}(a^* + b^*)$) (Escribe-Filippini *et al* 1984). As a consequence, the electrical resistivity increases by a factor of $\simeq 1.3$ when cooled from 110 K (1.3×10^{-3} Ω cm) to 80 K (1.7×10^{-3} Ω cm). Recent crystallographic refinements lead to the chemical formula KMo$_6$O$_{17}$ (de Boer and Meetsmaa 1992) and not K$_{0.9}$Mo$_6$O$_{17}$ as previously found. In the present work we present results of

thermal conductivity measurements in these compounds in the range 20–300 K, with special attention to the behaviour at the CDW transition.

As samples we used single crystals with elongated geometry, typically $4 \times 1 \times 0.2$ mm^3. Since these crystals were often obtained as platelets, when it proved necessary they were cut in order to obtain an elongated geometry with more favourable dimensions for the measurements. The measurement technique used was a four-probe comparison technique, using as a reference a constantan wire of $\phi = 125$ μm or 250 μm, as previously described (Lopes *et al* 1988). The thermal gradients were measured with thin ($\phi = 12$ μm) chromel–constantan thermocouples and two Keithley 181 nanovoltmeters using a slow AC technique (on–off–on–off, at $\simeq 5 \times 10^{-3}$ Hz) to avoid stray voltages. Due to the poor sensitivity of the chromel–constantan thermocouples, which limited the measurements to below 40 K, in the case of γ-Mo$_4$O$_{11}$ and η-Mo$_4$O$_{11}$ the measurements were repeated using as thermocouples gold–0.07 at.% Fe versus chromel wires ($\phi = 25$ μm). The results obtained with these thermocouples were essentially equal to those obtained with the chromel–constantan thermocouples above 40 K and allowed extension of the results down to the limit of the closed cycle cryostat used (~20 K). The thermal gradient across the sample was always of 1 K except near the CDW where it was kept <0.5 K. The measurements were taken on heating at a stable rate between 5 and 10 K h^{-1}. In order to avoid error due to sample electrical resistivity (ρ) dependence, as illustrated by the different values reported by different authors in the literature, electrical resistivity was measured as a function of temperature, as far as possible in the same sample after thermal conductivity measurements, using four evaporated indium electrodes.
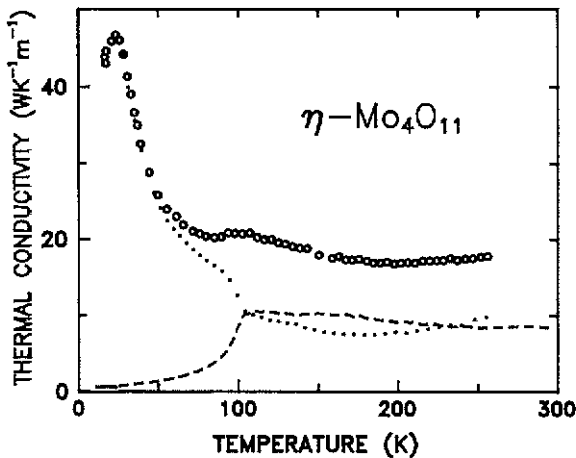

Figure 1. The thermal conductivity k_T of η-Mo$_4$O$_{11}$ along the b axis as a function of temperature. The dashed line represents the electronic contribution based on the Wiedmann–Franz law and the dotted line the estimated lattice contribution.

The measurement of the thermal conductivity of η-Mo$_4$O$_{11}$ is displayed in figure 1. At room temperature we have found $k_T \simeq 18 \pm 4$ W K^{-1} m^{-1}. k_T increases upon cooling until a maximum is reached at ~25 K and there is an anomaly at $\simeq 102$ K. The low temperature transition ($\simeq 30$ K is not clearly noticeable. As for γ-Mo$_4$O$_{11}$, we have obtained a value 21 ± 4 W K^{-1} m^{-1} for the thermal conductivity at room temperature, which increases upon cooling and presents an anomaly at the CDW

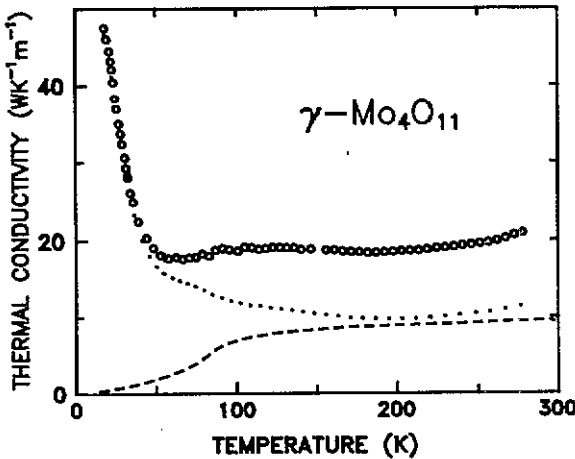**Figure 2.** The thermal conductivity k_T of γ-Mo_4O_{11} along the b axis as a function of temperature. The dashed line represents the electronic contribution based on the Wiedmann–Franz law and the dotted line the estimated lattice contribution.

transition, as in the η polymorph, and as displayed in figure 2. In KMo_6O_{17} we have obtained a value of $\simeq 12 \pm 2$ W K^{-1} m^{-1} at room temperature, that also increases upon cooling as displayed in figure 3. However, in this case a much stronger anomaly is observed at $\simeq 100$ K where a large decrease of k_T occurs, also clearly seen as a sharp increase of dk_T/dT at 100 K. It is worth noting that the temperatures of the k_T anomalies are slightly below the reported temperature for the CDW transition in these solids, but in good agreement, to within 1 K, with the temperature at which a maximum is observed of the electrical resistivity derivatives in these materials.

Due to the metallic nature of these solids, the thermal conductivity k_T can be given as the sum of the electronic, k_e, and lattice k_p, contributions: $k_T = k_e + k_p$. The lattice contribution is expected to approach a $1/T$ proportionality in the temperature range near the Debye temperature θ_D (Berman 1979). In our case, with $\theta_D = 335 \pm 10$ K, 41 ± 10 K and 320 ± 10 K for η-Mo_4O_{11}, γ-Mo_4O_{11} and KMo_6O_{17} respectively (Konaté 1984, Bervas 1984, Schlenker *et al* 1989), this behaviour is expected in the range around the CDW transition. The electronic contribution can be estimated assuming the Wiedmann–Franz law, according to which $k_e = L_0 T/\rho$ where L_0 is the free electron Lorentz number ($L_0 = 2.45 \times 10^{-8}$ W K^{-2} Ω).

The relatively small anomaly of k_T in η-Mo_4O_{11} cannot be accounted for by the decrease of the electronic contribution estimated from the experimental electrical resistivity ρ using the Wiedmann–Franz law (dashed line of figure 1); since the electrical resistivity has a sharper anomaly and k_e has a smaller decrease, this implies that the lattice has an increase at the transition in addition to the $1/T$ contribution. In other bidimensional CDW systems like 1T-TaS_2 and 2H-$TaSe_2$ a large lattice anomalous increase was also found below the CDW transition, which was interpreted as the result of discommensurations of the CDW (Núñez-Regueiro *et al* 1985) according to a pseudospin model. In this case of an incommensurate CDW with fixed wave vector, a different explanation, not clear at present, should be considered. The absence of a noticeable k_T anomaly at the low temperature ($\simeq 30$ K) transition in η-Mo_4O_{11} can be explained by the large value of the lattice contribution compared with the negligible electronic term in this range.

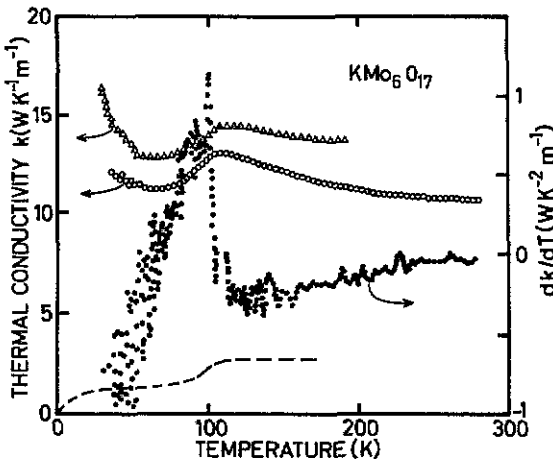**Figure 3.** The thermal conductivity k_T, and dk_T/dT in two samples of KMo_6O_{17} as a function of temperature. The dashed line represents ten times the electronic contribution based on the Wiedmann–Franz law.

In the case of γ-Mo_4O_{11}, if we make the same decomposition as in the case of η-Mo_4O_{11}, the small anomaly of k_T is well accounted for by the decrease of the electronic contribution estimated by the Wiedmann-Franz law, plus a smooth lattice term that varies approximately as $1/T$. Any change of k_p at the transition is negligible. A similar approach was previously used with success to explain a relatively much larger anomaly of k_T in the one-dimensional blue bronzes $K_{0.3}MoO_3$ (Lopes *et al* 1988 and Lopes *et al* 1989) and $Rb_{0.3}MoO_3$ (Lopes *et al* 1990). In the blue bronzes, the anomaly is similar but it is relatively larger due both to a smaller lattice contribution and to a slightly larger electronic contribution (in the blue bronzes $k_e/k_p \simeq 2$ at room temperature while $k_e/k_p \simeq 0.9$ in γ-Mo_4O_{11}). The smaller k_p in the blue bronzes is regarded as a consequence of the intrinsic disorder associated with alkaline vacancies, which decrease the phonon mean free path. Also in the quasi-one-dimensional blue bronze all the conduction electrons with energies below the Fermi level are condensed at the CDW transition where k_e decreases towards zero, while in the quasi-two-dimensional oxides only a partial decrease of the k_e is expected, as a consequence of a partial condensation of the carriers and of a partial Fermi surface reduction.

However when the same approach is used in KMo_6O_{17} a different situation becomes evident. In this case using the Wiedmann–Franz law and from $\rho = 7 \times 10^{-4}$ Ω cm at room temperature we estimate $k_e/k_p \simeq 0.06$, and therefore the observed anomaly is too large to be accounted for by the decrease of the electronic contribution given by the Wiedmann–Franz law and $\rho(T)$ taken from previous measurements (Escribe-Filippini *et al* 1984), as shown in the dashed line in figure 3, that represents ten times k_e. The anomaly in the electronic contribution is at least 15 times smaller than the observed anomaly in k_T, and therefore the k_T anomaly is ascribed essentially to the lattice. This behaviour appears to be associated with the commensurate distortion of the lattice. In this respect it is interesting to note that specific heat measurements performed in KMo_6O_{17} when compared with those in η-Mo_4O_{11} revealed an excess of entropy change at the CDW transition that could not be explained by the electronic contribution alone (Konaté 1984, Schlenker *et al*

1989), also suggesting a strong lattice change.

In conclusion we have shown that the CDW transition in the quasi-two-dimensional conductors η-Mo_4O_{11}, γ-Mo_4O_{11} and KMo_6O_{17} manifests itself as anomalies in the thermal conductivity. In the incommensurate system γ-Mo_4O_{11} the anomaly is ascribed to the electronic contribution, in good agreement with the Wiedmann–Franz law without major lattice changes; in η-Mo_4O_{11} there also seems to be an anomaly in the lattice contribution, which increases at the transition; however, in the commensurate system KMo_6O_{17}, the anomaly is mainly ascribed to the lattice contribution that decreases after the commensurate distortion.

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