Thermal conductivity of the molybdenum blue bronze $Rb_{0.3}MoO_3$

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Thermal conductivity, k_T, of $Rb_{0.3}MoO_3$ was measured in the temperature range 40–300 K. At the charge-density-wave transition there is a large anomaly of k_T that decreases upon cooling. The anomaly is consistent with a decrease of the electronic contribution to the thermal conduction, in agreement with the prediction based on the Wiedemann-Franz law and with a smooth lattice contribution.

The molybdenum blue bronzes with general formula $A_{0.3}MoO_3$, with A being an alkali metal like K or Rb, or a pseudo-alkali-metal like Tl, belong to a family of low-dimensional metals that undergoes a Peierls transition at $T_P \simeq 182$ K associated with the formation of an incommensurate charge-density wave (CDW).[1,2] These compounds have been intensively studied recently due to the observation below T_P of a large variety of novel charge-transport properties associated with the CDW state, such as nonlinear electrical conductivity.[3,4] In spite of all these detailed studies the thermal conductivity k_T has been studied in these materials only recently. In a previous paper, using a comparative method, we have shown that $K_{0.3}MoO_3$ presents a large anomaly of k_T at the Peierls transition,[5] and that thermal-conductivity behavior could be explained in good agreement with the Wiedemann-Franz law. These results were later confirmed[6] by more accurate measurements and through a comparison with measurements in the insulating red bronze $K_{0.33}MoO_3$.

In a recent paper Kwok and Brown,[7] using an absolute method, reported that in addition to the same general behavior previously described, they found a peak of k_T at the phase transition, associated with a peak in specific heat C_p (related to the phonon scattering at the CDW transition). This peak was also found by Smontara *et al.*[8] using the same method as ours. Although with poorer resolution, recent independent measurements both using absolute[9] and comparative methods[10] have not revealed such a peak in agreement with our previous work.

In this paper we present the results of measurements of k_T in $Rb_{0.3}MoO_3$ in the temperature range 40–300 K. Due to the similarities between $K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$ that are isostructural compounds[11] and have identical T_P,[1] the measurements reported here in $Rb_{0.3}MoO_3$ provide an extra check for the above referred controversy on the k_T results of $K_{0.3}MoO_3$. While the present results are, in general, identical to those previously reported by us in $K_{0.3}MoO_3$ and with no peak of k_T near T_P, independently of the thermal heating or cooling rate used, the high-temperature results (200–300 K) show some sample dependence correlated with the electrical resistivity.

Crystals of $Rb_{0.3}MoO_3$ were obtained by standard electrolytic reduction with Pt electrodes of MoO_3/Rb_2MoO_4 melts having a 3.35/1 mole ratio at 565 °C. Three single crystals of $Rb_{0.3}MoO_3$ with approximate dimensions ($5\times1\times0.2$ mm^3) were used in measurements of thermal conductivity along the b axis of maximum electrical conductivity. The measurement technique was a standard four contact, slow ac ($\simeq 5\times10^{-3}$ Hz) comparison method relative to a 120-μm-cross-sectional-diameter Constantan wire as described in Ref. 5. The thermal gradients were monitored with 12-μm-cross-sectional-diameter Chromel-Constantan thermocouples and measured with two Keithley 181 nanovoltmeters. The thermal gradient across the sample was $\simeq 1$ K except near the CDW transition, in the range 160–200 K, where it was kept < 0.5 K.

Under the experimental conditions used, the errors due to radiation losses or to heat lost through the thermocouple wires are estimated to be less than 1% of the heat flowing through the sample. The reproducibility of the measurements was $\simeq 0.5\%$, but the absolute accuracy was $\simeq 10$–20% essentially determined by the inaccuracy of the sample and reference dimension measurements. These measurements were performed under a binocular scale, but the cross section of the sample was more accurately determined by weighting the sample and using the known density of this bronze $\rho = 4.52$ g/cm^3.[11]

Measurements were performed mainly on warming at a rate kept uniform and smaller than 10 K/h and at 5 K/h in the range 160–200 K near T_P, after a previous cooling of the sample down to 20 K at $\simeq 40$ K/h. Thermal cycling of the sample near T_P showed no evidence of any significant hysteresis. In order to investigate the possible influence of the thermal rates used on the results, in a different run the measurements were taken both in cool-

ing and in warming, using the same slow and uniform rates mentioned before. In all cases the results were identical without any significant hysteresis or changes.

Typical thermal-conductivity behavior observed in the $Rb_{0.3}MoO_3$ sample is shown in Fig. 1, where results obtained in two samples are displayed. These results are very similar to those previously reported in $K_{0.3}MoO_3$. At room temperature k_T was found to be 5 ± 0.8 $W\,K^{-1}\,m^{-1}$, a value identical to that previously found in $K_{0.3}MoO_3$ (Refs. 5 and 6) as shown in Fig. 1. Upon cooling and depending on the samples we observe either an almost temperature-independent behavior, as in sample A, or a slight decrease of k_T, as in sample B, until $T_P \simeq 181$ K, where a sharp decrease of k_T occurs followed by an increase at lower temperature. The thermal-conductivity anomaly is better seen in the derivative dk_T/dT also shown in Fig. 1, that has a sharp λ-type peak at 181 K, almost at the same temperature where a similar anomaly is observed in electrical resistivity.

Following the previous analysis applied for $K_{0.3}MoO_3$,[5,6] the measured total thermal conductivity can be considered as the sum of the lattice, k_P, and the electronic, k_e, contributions: $k_T = k_p + k_e$. The last contribution can be estimated from the electrical resistivity ρ and using the Wiedemann-Franz law: $k_e = L_0 T/\rho$, where L_0 is the free-electron Lorentz number ($L_0 = 2.45\times10^{-8}$ $W\,\Omega\,cm^{-2}\,K$). After thermal-conductivity measurements the samples were carefully removed and dc electrical conductivity was measured in the same samples using four indium evaporated electrodes contacted with silver paint to 25-μm-cross-sectional-diameter gold wires. The electrical resistivity measured in the two samples A and B showed significant differences. In sample B, having a more irregular shape and poorer quality, as judged from the external appearance, it was measured as $\sigma_{RT} = 400$ $\Omega^{-1}\,cm^{-1}$ with a slightly less sharp transition than in sample A where it was measured as $\sigma_{RT} = 1400$ $\Omega^{-1}\,cm^{-1}$ with a sharper transition. These variations are not surprising since the electrical resistivity measured by different authors in different samples shows a range of values and with minor variations in the temperature dependence. This variability is only partially due to the sample quality and it reflects mainly the difficulty in obtaining homogeneous current injection in highly anisotropic materials like this blue bronze.

Subtracting the electronic contribution, estimated from the previous resistivity measurements and $k_e = L_0 T/\rho$, from the total thermal conductivity measured, it is possible to obtain the phonon contribution, as shown in Fig. 2. For sample A this subtraction gave a smooth lattice contribution. In sample B, in order to obtain a similar smooth lattice term, it was necessary to multiply the experimentally measured electrical conductivity by a factor of 4, possibly reflecting an error in ρ measured in this sample, due to its irregular shape. Indeed, typical values of room-temperature electrical conductivity in this compound are of the order of 1000 $\Omega^{-1}\,cm^{-1}$ or larger.[1] Apart from this uncertainty in the absolute value of k_e, as seen in Fig. 2, the anomaly in k_T at T_P is well accounted for by the anomaly in k_e. Both the sharpness of the transition and the different temperature-dependent behavior above T_P in the two samples correlate well with the electrical resistivity behavior.

The phonon contribution is expected to approach a temperature dependence proportional to $1/T$ near the Debye temperature Θ_D ($\Theta_D \simeq 310$ K in this case[12]). Using the simple Debye theory it is possible to estimate the phonon mean free path l from the relation $l = k_p/3C_p v$, where C_p is the specific heat ($\simeq 70$ J mol^{-1} K^{-1} at 300 K)

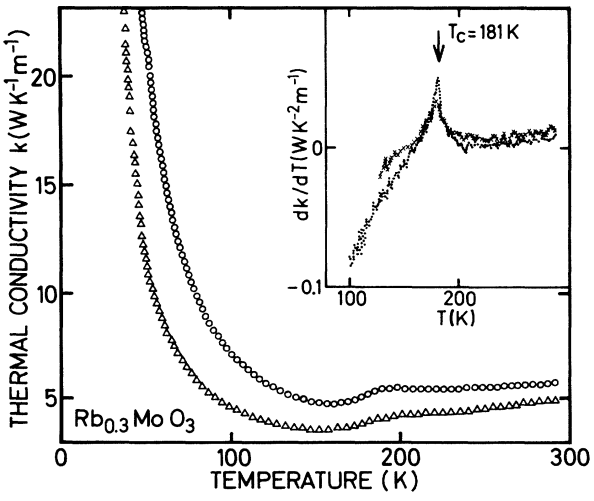

FIG. 1. Temperature dependence of the thermal conductivity k_T along the b axis of two samples of $Rb_{0.3}MoO_3$ (△, sample A; ○, sample B). The inset shows dk_T/dT near the phase transition at 181 K (×, sample A; ●, sample B).

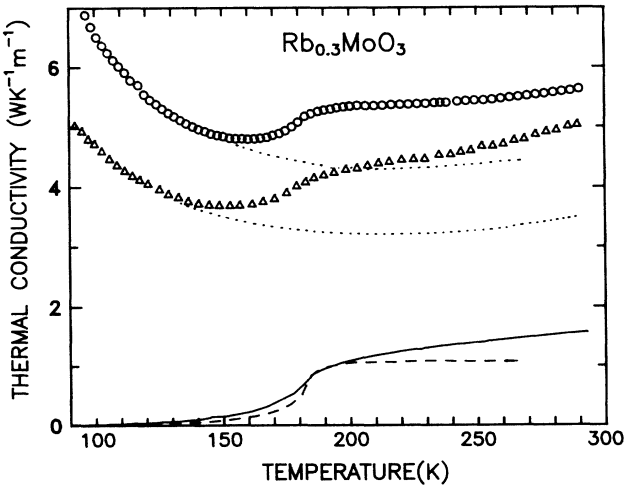

FIG. 2. Thermal conductivity k_T of two samples of $Rb_{0.3}MoO_3$ as a function of temperature (△, sample A; ○, sample B). The dashed and solid lines represent the electronic contribution k_e for samples A and B, respectively, based on the Wiedemann-Franz law and the measured electrical resistivity ρ, multiplied by 4 in the case of sample B (solid line). The dotted lines represent the lattice contributions k_P obtained by the subtraction $k_P = k_T - k_e$.

(Refs. 2 and 7) and v is the average sound velocity. The sound velocity for the longitudinal mode along b was measured by ultrasound techniques in $K_{0.3}MoO_3$ and found to be 4.5×10^3 m s^{-1}.[13] From the phonon dispersion relations measured by inelastic neutron scattering, it is possible to calculate the following sound velocities along b: $v_{LA}=7.3\times10^3$ m s^{-1}, $v_{TA1}=3.5\times10^3$ m s^{-1}, and $v_{TA2}=2.4\times10^3$ m s^{-1}.[14] Taking an average sound velocity of 4.4×10^3 m s^{-1} and $k_p=3$ W m^{-1} K^{-1} it is possible to estimate the phonon mean free path as 9 Å at room temperature, a value that is of the same order of the lattice parameter $b=7.5$ Å,[11] and therefore the temperature dependence of the phonon contribution is expected to deviate from the $1/T$ law in these conditions, to saturate or even to have a slight increase at higher temperatures. The phonon contribution, derived as explained above, has a temperature dependence comparable to the thermal conductivity of the red bronze $K_{0.33}MoO_3$ that was previously measured by us using the same technique.[6] The red bronze is insulating and has a similar structure based on the same MoO_6^{6-} octahedra as building blocks and virtually the same Debye temperature. The slightly smaller value of k_p in this blue bronze ($\simeq3$ W K^{-1} m^{-1} at 300 K compared to 4 W K^{-1} m^{-1} in the red bronze $K_{0.33}MoO_3$) may reflect the more disordered structure, with alkali-metal vacancies and spatial fluctuations of the alkali-metal atoms as observed by Auger spectroscopy.[15] Clearly the deviations of k_p from the $1/T$ law at high temperatures is dependent on the lattice disorder, which can vary from sample to sample and could also explain, at least in part, the observed sample variation of the temperature dependence of k_T above 200 K.

Finally, we would like to comment on the possible origin of the peak of k_T observed by some authors near T_P, but never observed by us in many (>15) samples of both $K_{0.3}MoO_3$ and $Rb_{0.3}Mo_3$. The fact that the peak has been observed by different authors using different techniques seems to rule out the possibility of a measurement error and suggest instead the possible existence of different types of samples, possibly of different purity and with different pinning mechanisms. However, the presence of such a peak is not only unexpected in view of all the other experimental results, but also it is difficult to ascribe it to extra heat carried by phase or amplitude fluctuations near T_P as suggested by Kwok and Brown.[7]

In fact, the analysis of the x-ray diffusion scattering in the reciprocal space[14] revealed, on cooling from room temperature, a progressive evolution from a one-dimensional (1D) fluctuating regime dominated by intrachain correlations with a crossover at $\simeq220$ K to a 2D regime with short-range interchain coherence lengths, then to a 3D regime without any anomaly at T_P. In agreement with the mean-field picture of the second-order phase transitions, the amplitude mode does not go to zero at T_P. Thus, so far, the thermal conductivity and the specific heat, according to Ref. 7, remain the only properties displaying such an anomaly, while all other properties,[1] such as magnetic susceptibility, and even channeling experiments,[16] that probe more directly the order parameter, all show a smooth evolution.

In conclusion, $Rb_{0.3}MoO_3$ has a thermal-conductivity behavior similar to $K_{0.3}MoO_3$, with a strong anomaly at the CDW transition, seen as a peak of dk_T/dT at 180 K, but without any peak of k_T at T_P independently of the heating or cooling rates used. The decrease of k_T at T_P is due to the decrease of the electronic contribution, in good agreement with the Wiedemann-Franz law, the lattice contribution remaining smooth. The behavior of k_T above 200 K is dependent on sample quality, in some cases being almost temperature independent while in others it can have a slight increase.

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