Thermal Conductivity of the Charge-Density-Wave Systems $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ near the Peierls Transition

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We report on measurements of the thermal conductivity κ_T close to the Peierls transition temperature T_P in $K_{0.3}MoO_3$ and $(TaSe_4)_2I$. In both cases there is an enhancement of κ_T that peaks at the transition. Simultaneous measurements of the specific heat suggest that the anomalous behavior is a result of mode occupation rather than changes in electron- or phonon-scattering processes.

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The charge-density-wave (CDW) systems $K_{0.3}MoO_3$ (blue bronze) and $(TaSe_4)_2I$ have been thoroughly studied with respect to their electrical transport properties[1] because of the small threshold fields required to observe nonlinear conduction[2] and the strong frequency-dependent conductivity $\sigma(\omega)$ observed down to very low frequencies.[3] To a great extent, measurements of other macroscopic properties have not been studied as intensely. The thermal conductivity fits into that class of measurements. However, the formation and novel charge transport properties of the CDW state indicate that thermal conductivity measurements and investigations that are, in general, related to the Onsager transport coefficients[4,5] will assist in a more complete understanding of transport in these systems. There are at least two points to consider for the thermal conductivity: (1) the role of CDW fluctuations in scattering electrons and propagating phonons, and (2) whether the development of the soft phonon mode is important for heat transport.

The materials known to form an incommensurate charge-density-wave state are quasi-one-dimensional with respect to charge transport properties. A result of the one-dimensional nature is that the situation is ideal for the study of fluctuation effects in various thermodynamic[6] and transport properties. Because of the wide variation of anisotropy between materials, it is not surprising that the strength and range of temperatures where fluctuations are observed will differ also.[1] Furthermore, previous experimental work may not have addressed all aspects of the effect of CDW formation on the thermal conductivity.[7] In particular, it would be surprising if one could separate a fluctuating thermal conductivity from the total and properly describe the experimental results using the electrical conductivity and the Wiedemann-Franz law.

The mean-field description of the CDW state is associated with the opening of a gap at the Fermi surface accompanied by a soft phonon mode at the $2k_F$ position in reciprocal space. The lattice degrees of freedom will not directly contribute to charge transport, but that may be untrue for thermal transport. The low phonon energies $\omega(q)$[8] about $q=2k_F$ are accompanied by a high mode occupation level, and the finite values for $d\omega/dq$ provide a mechanism for heat transport.

In this Letter, we present our results on the thermal conductivity of the blue bronze $K_{0.3}MoO_3$ and $(TaSe_4)_2I$ in zero electric field with special emphasis on the behavior near T_P [$T_P=180$ K for the blue bronze and 263 K for $(TaSe_4)_2I$]. In each case, the component of the thermal conductivity tensor along the chain direction was measured. For both materials, there is a peak in the total thermal conductivity κ_T at the phase transition which is not predicted by the simplest interpretation where the lattice contribution is smooth near T_P and the electronic part can be discussed in terms of the Wiedemann-Franz law.[9,10] The results are surprising in view of the fact that fluctuation effects around a phase transition could be expected to introduce a minimum in κ_T at T_P, instead of the observed peak. We propose that the phase-transition region is more complicated because of the phonon softening associated with the new CDW formation, and this is reflected in both the thermal conductivity and specific-heat data.[11]

In total, we measured four samples of the $(TaSe_4)_2I$ and two samples of the blue bronze. $(TaSe_4)_2I$ single crystals came from three different sample preparation batches. The two blue bronze samples were from different batches. The measurement technique was a direct, steady-state linear heat-flow method with one end of the sample anchored to a large block of copper that served as the thermal reservoir, and a resistive wire heater wound around the other end. The temperature difference along the sample ΔT_s was measured using a differential AuFe-Chromel thermocouple with the joints anchored at two well-separated positions along the sample. Radiation heat losses were minimized using a stainless-steel heat shield with a diameter approximately 2 to 3 times the sample diameter. The shield tempera-

ture was controlled at one end and anchored to the thermal reservoir at the other so that the temperature profile would be the same as that of the sample. Boundary thermal resistance problems were monitored by measuring the temperature difference between the shield and the sample at both ends of the crystal. Systematic errors introduced by boundary resistances were considered to be negligible when both shield-sample temperature differences were very small compared to ΔT_s, a condition that was easily satisfied in practice.

The results for the total measured thermal conductivity κ_T are shown in Fig. 1. First, we will discuss the blue bronze [Fig. 1(a)]. Overall, the shape is similar to the previously reported results.[9,10] At high temperatures, the thermal conductivity is weakly temperature dependent, reminiscent of a metal with a lower carrier concentration. Below the phase transition, κ_T decreases more quickly before going through a conductivity maximum centered near 20 K. The behavior at the phase transition itself is distinctive: There is a sharp peak approximately 4 K wide [Fig. 1(a) inset], and the increase is slightly greater than 5%. The features of the peak reproduced in two experimental runs on the same sample. A second blue bronze sample also showed a peak, but somewhat smeared out as compared to that shown here. The sample dependence at the phase transition seems to be correlated with the low-temperature behavior. The sample

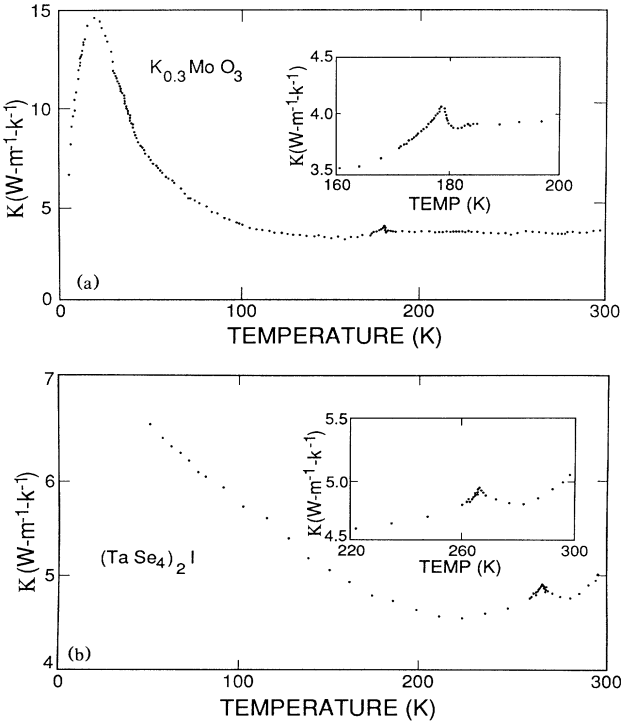

FIG. 1. Thermal conductivity as a function of temperature for (a) $K_{0.3}MoO_3$ and (b) $(TaSe_4)_2I$. Inset: Data near the Peierls phase transition for each of the two materials.

with the larger low-temperature conductivity maximum also has the narrow anomaly at T_P. Because both samples were very similar geometrically, it is likely that lattice defects affect both aspects of κ_T.

The $(TaSe_4)_2I$ samples that were measured exhibit similar behavior, as shown in Fig. 1(b). κ_T is decreasing as the temperature is lowered from above T_P, with a change in curvature closer to the transition. At T_P (verified by resistance measurements), there is a peak before a decrease again at lower temperatures. It is likely that the overall temperature dependence above T_P is related to the strong fluctuations in this material.[1] At low temperatures, κ_T begins to slowly increase as expected. The qualitative temperature dependence between samples, however, does not reproduce over the entire range of temperature measured. A large variation between samples has been observed below 220 K, with two of the samples having a nearly temperature-independent κ_T between approximately 30 and 220 K before decreasing at lower temperatures.

For the purposes of brevity, the results for the blue bronze will be analyzed in detail, although the same procedure has been applied to the $(TaSe_4)_2I$ with similar results. We begin by assuming that the total conductivity κ_T can be described by a sum of two terms:

$$\kappa_T = \kappa_p + \kappa_e , \tag{1}$$

where κ_p is the contribution from phonons and κ_e is the heat carried by the electrons. In general, the contribution to κ_T from each source is proportional to $C_v v l$, where C_v is the appropriate specific heat at constant volume, v is the velocity, and l is the mean free path.

At low temperatures, κ_T for the blue bronze is characteristic of insulators where l constant, increasing as T^3 below 1 K.[12] It continues to about 20 K before dropping approximately as $1/T$ over the range 40 to 110 K. As T_P is approached from below, the increase is presumably from quasiparticles excited across the Peierls gap. This behavior is very similar to that observed in conventional superconductors. At temperatures above T_P, CDW fluctuations persist,[8,13] so the continuing increase in κ_T is expected from an increasing electronic component. A more detailed analysis is necessary, however, to qualitatively understand the origin of the peak at the CDW transition. We will show that changes in the scattering rates of phonons or electrons are an unlikely explanation. Because the specific heat shows similar behavior, we suggest that the reason for the bump is mode occupation associated with the soft phonons.

The "lattice" contribution will remain if it is possible to subtract κ_e from the total. In ordinary metals, it would suffice to estimate κ_e at high temperatures from the Wiedemann-Franz law

$$\kappa_e/\sigma T = L_0 , \tag{2}$$

where the Lorenz number is $L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2}, and σ is the dc electric conductivity. The main assump-

tion for the validity of Eq. (2) is that the same scattering processes dominate for electrical and thermal transport. Therefore, it will hold at higher temperatures (on the order of the Debye temperature Θ_D), where the dominant phonon wave vectors can bring about transitions to the opposite side of the Fermi surface. The full line in Fig. 2 is the electronic contribution κ_e as calculated using the Wiedemann-Franz law and resistivity measurements. The decrease in κ_e as the temperature is lowered is the direct result of the decrease of free charge carriers. The "lattice" conductivity $\kappa_p = \kappa_T - \kappa_e$ is also shown, with the shape of the anomaly at T_P essentially unchanged.

However, the situation in these materials is more complicated than in a simple metal because of the opening of the gap at the Fermi surface. As for semiconductors, there is an additional "electronic" contribution to κ_T from recombination of electrons and holes.[14] If an electron and hole traverse the length of the sample before recombining, then the full gap energy is transported over that distance. The enhancement is a maximum when the electron and hole mobilities are equal. Even in that extreme case, the peak at T_P cannot be explained by purely electronic mechanisms.

Phonon thermal resistivity $1/\kappa_p$ results from scattering processes with phonons (W_p^p, as in insulators), or with electrons (W_e^p) so that $\kappa_p = (W_p^p + W_e^p)^{-1}$. An estimation of W_p^p can be made by extrapolating the $1/T$ behavior of the insulating state to T_p, and W_e^p is given by[15]

$$W_e^p = \frac{\rho_p^e}{L_0 T}\frac{\pi^2 n_a^2}{3}, \tag{3}$$

where n_a is the number of electrons per atom, and ρ_p^e is the electrical resistivity from scattering by phonons. From the measured resistivity and band filling,[16] $W_e^p(180\ \mathrm{K}) = 4\times10^{-2}\ W_p^p$, leading to a relative change in κ_T of about 0.025. Therefore, the thermal resistivity of the phonons is provided almost completely by the phonon gas itself.

As in the new high-temperature superconductors, it is expected that W_e^p will decrease at the phase transition.[17] There are two reasons why this does not account for the feature at T_P. The first is that the shape is not described by Eq. (3) and the second is that the ratio W_e^p/W_p^p is more than 2 times too small even if we assume that $W_e^p \to 0$ within 2 K below T_P. Therefore, it is necessary to consider other possibilities.

The specific heat for the blue bronze sample of Fig. 1(a) is shown in Fig. 3 over the temperature range 4–300 K. A detailed description of the measurement and analysis of fluctuations about T_P will be presented elsewhere.[11] If the specific-heat anomaly at T_P is described by a jump, then $\Delta C_p/C_p \sim 0.06$, similar to the thermal conductivity. Because scattering processes do not explain the behavior, it is compelling to associate the two results with the same phenomenon. Therefore, the effect in κ_T is probably related to mode occupation and not scattering processes.

Accompanying the opening of the gap in the CDW transition is a softening of the phonon mode near $2k_F$. When the coherence length is long, there is only one phonon mode involved. In that case, there is no contribution to the heat capacity from the lattice and the mean-field prediction (which is the same as the BCS value) is

$$\Delta c_p^{\mathrm{MF}} = 1.43\gamma T_{\mathrm{MF}} \tag{4}$$

where $\gamma = (\pi^2/3)k_B^2(1+\lambda)N(0)$, $N(0)$ is the free electron density of levels at the Fermi surface, λ is the electron-phonon coupling constant, and T_{MF} is the mean-field transition temperature. Using $N(0) = 1$ state eV^{-1} (formula unit)$^{-1}$ (Ref. 13) and $\lambda \sim 0.3$ (Ref. 16), $\Delta C_p^{\mathrm{MF}} \sim 0.4$ J/mol K. That value is more than 1 order of magnitude smaller than the value deduced from Fig. 3. In addition, the substantial width of the heat-capacity anomaly is consistent with the inappropriateness of mean-field theory.

In this case, it is more useful to examine the entropy associated with the formation of the low-temperature phase. The full line in Fig. 3 is a polynomial fit to the

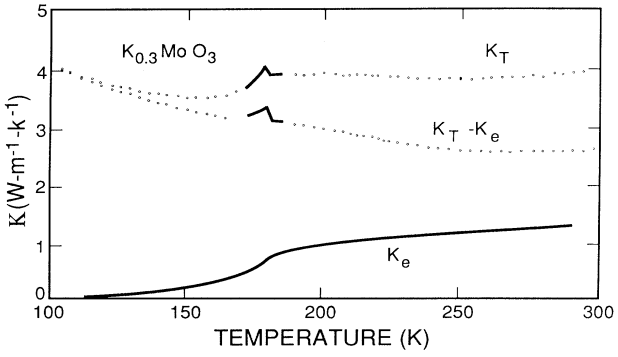

FIG. 2. Thermal conductivity κ_T of $K_{0.3}MoO_3$. The solid line is the estimated electronic contribution to the thermal conductivity. The difference is also shown.

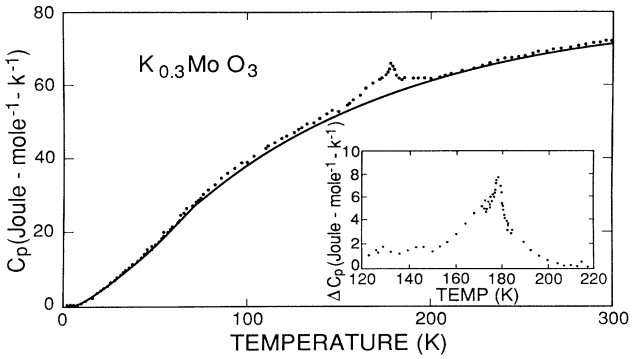

FIG. 3. Temperature dependence of the specific heat of $K_{0.3}MoO_3$. The full line is a polynomial fit through the background. Inset: Difference between the data and the fit.

data at temperatures far above and far below T_P, from which an excess specific heat and entropy can be found. Admittedly, this results in a crude estimate, but we claim the result is likely to be a lower bound because it only includes contributions from a limited temperature range where effects of the transition appear to dominate the temperature dependence. Proceeding in this way, we find a value ($\sim$1.5 J/mol K) that is about 5 times larger than the calculated electronic contribution $\gamma T_p = 0.3$ J/mol K.

McMillan[18] pointed out that this implies a significant contribution from the lattice, which is possible only if the coherence length is short, (i.e., the transition involves a significant number of phonon modes). From the specific heat, we estimate a coherent volume $\sim(35\ \text{Å})^3$ (Ref. 19). Diffraction studies[8,20,21] confirm that the coherence lengths are short. For instance, the x-ray studies of Girault, Moudden, and Pouget[20] indicate that $\xi \sim 100$ Å less than 2 K above T_P. The calculated zero-temperature value $\xi(0) = \hbar v_F/2\Delta(0)$ (Ref. 16) is somewhat less, $\sim$30 Å. Given the behavior of the specific heat near T_P and the fact that the softening implies a nonzero group velocity $d\omega/dk$ near $2k_F$, we tentatively suggest that the increase of κ_T is a result of heat carried by the soft phonons. The heat would be transported because the modes near $2k_F$ are propagating, and there is a substantial heat capacity resulting from their occupation.

In summary, we find a peak in the thermal conductivity of the Peierls systems $K_{0.3}MoO_3$ and $(TaSe_4)_2I$. A subtraction of the charge-carrier contribution to κ_T leaves a remaining lattice contribution that is not smooth through the transition, in contrast to previous discussions. The increase in the lattice term cannot be completely accounted for by scattering processes alone. The overall shape is not unlike the specific-heat anomaly, indicating that the two results are linked to the same phenomenon. The short coherence lengths deduced from the specific heat imply that a large number of modes are involved in the softening, suggesting that it is possible that the soft mode is also responsible for the peak in κ_T. Because the results cannot be explained in mean-field theory, we believe they are important to understanding fluctuation effects in Peierls systems.

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