On the transport and thermodynamic properties of quasi-two-dimensional purple bronzes $A_{0.9}Mo_6O_{17}$ ($A$=Na, K)

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We report a comparative study of the specific heat, electrical resistivity and thermal conductivity of the quasi-two-dimensional purple bronzes $Na_{0.9}Mo_6O_{17}$ and $K_{0.9}Mo_6O_{17}$, with special emphasis on the behavior near their respective charge-density-wave transition temperatures $T_P$. The contrasting behavior of both the transport and the thermodynamic properties near $T_P$ is argued to arise predominantly from the different levels of intrinsic disorder in the two systems. A significant proportion of the enhancement of the thermal conductivity above $T_P$ in $Na_{0.9}Mo_6O_{17}$, and to a lesser extent in $K_{0.9}Mo_6O_{17}$, is attributed to the emergence of phason excitations.

I. INTRODUCTION

It is well known that in many low-dimensional compounds, Fermi surfaces are unstable against a Peierls instability below a critical temperature, $T_P$. The mean-field description of this so-called charge-density-wave (CDW) state is characterized by the opening of the electronic gap at the Fermi level, accompanied by a softening in the phonon spectrum at $Q = 2k_F$, with $k_F$ the Fermi wave vector. As first pointed out by Lee, Rice and Anderson, this soft-phonon spectrum splits into two new modes of collective oscillations: one corresponds to optic-like amplitude mode and the other one to an acoustic-like phase mode. This phase mode or phason existing at zero frequency in the ideal CDW corresponds to the sliding motion of the CDW as proposed by Fröhlich. In real materials, however, the phason excitations are gapped out primarily due to impurity pinning. While these gapped phason excitations may not contribute to the charge transport directly, they may still play a role in the thermal transport owing to the finite value of $d\omega/dq$ in their spectrum.

The quasi-two-dimensional (Q2D) purple bronzes $Na_{0.9}Mo_6O_{17}$ and $K_{0.9}Mo_6O_{17}$ undergo CDW transitions at $T_P \approx 80K$, 120K respectively, which has been confirmed by various probes such as electrical resistivity and magnetic susceptibility. In $K_{0.9}Mo_6O_{17}$, diffuse X-ray scattering and electron diffraction experiments have also revealed the three nesting wave vectors of $(a^*, 0, 0)$ and its symmetrical equivalents below $T_P$ while STM studies further observed the $(2 \times 2)$ superstructure imposed on the crystal lattice at low temperatures. With regard to their crystal structures, these two compounds share a great deal of commonality albeit with slight differences in symmetry, i.e., trigonal $P3$ symmetry in $K_{0.9}Mo_6O_{17}$ versus monoclinic $C2$ symmetry in $Na_{0.9}Mo_6O_{17}$. The main building block in both systems is the slabs of Mo-O corner-sharing polyhedra, consisting of four MoO$_6$ octahedral layers terminated on either side by a layer of MoO$_4$ tetrahedra. These slabs lie perpendicular to the $c$-axis and are separated from each other by a layer of alkali metals. The MoO$_4$ tetrahedra in adjacent layers do not share corners, disrupting the Mo-O-Mo bonding along the $c$-axis. This layered structure is expected to lead to a Q2D electronic structure, as confirmed by dc transport measurements.

The precise topology of the $Na_{0.9}Mo_6O_{17}$ Fermi surface (FS), as revealed by angle-resolved photoemission spectroscopy (ARPES), remains controversial, with different ARPES groups claiming a FS topology that is either similar to or distinct from that of $K_{0.9}Mo_6O_{17}$. According to Breuer et al., there is only one electron pocket centered around the $\Gamma$-point in $Na_{0.9}Mo_6O_{17}$, rather than the two pockets found in $K_{0.9}Mo_6O_{17}$. Moreover, while the FS of $K_{0.9}Mo_6O_{17}$ can be viewed as a combination of pairs of quasi-one-dimensional (Q1D) Fermi sheets which can be nested to one another by the so-called ‘hidden’ nesting vectors. Breuer et al. find no evidence for the 1D FS parallel to the $\Gamma X$ direction in sodium purple bronze. These subtle yet important differences in the proposed electronic structure are supported, on a qualitative level at least, by the observation that the thermoelectric power $S(T)$ below $T_P$ is dramatically different in the two systems, while $S(T)$ in both systems decreases linearly with decreasing temperature towards zero at $T = T_P$, below $T_P$, $S(T)$ shows a large negative (positive) peak for $A$ = Na (K) respectively, suggesting that the dominant carrier has an opposite sign in the two cases.

To gain further insight into the nature of the CDW formation in these two compounds, in particular the changes in the nature of their electronic and phononic sub-systems at $T = T_P$, we present in this paper a comparative study of the specific heat, electrical resistivity and thermal conductivity of $Na_{0.9}Mo_6O_{17}$ and $K_{0.9}Mo_6O_{17}$ over a broad temperature range above and below their respective CDW transitions. A number of
key features are uncovered. Firstly, the anisotropy of the electrical resistivity is found to be an order of magnitude higher than has been reported in the existing literature. Secondly, in Na$_{0.9}$Mo$_6$O$_{17}$, the in-plane thermal conductivity $\kappa_{ab}(T)$ is found to decrease across the CDW transition, in marked contrast to the significant enhancement of $\kappa_{ab}(T)$ observed at $T_P$ in K$_{0.9}$Mo$_6$O$_{17}$. Finally, in the heat capacity data, a large $\lambda$-shape anomaly is observed in K$_{0.9}$Mo$_6$O$_{17}$, while in Na$_{0.9}$Mo$_6$O$_{17}$, the heat capacity exhibits a broad hump with no discernible feature at $T_P$. We argue here that the principal origin of these distinct physical responses in the two systems is the difference in their alkali-metal stoichiometry. We also reveal the first possible manifestation of phason excitations in the thermal conductivity of these archetypal CDW bronzes above $T_P$.

II. EXPERIMENTAL

The single crystals used in this study were grown by electrolytic reduction of a melt of A$_2$CO$_3$-MoO$_3$ ($A = \text{Na, K}$) with an appropriate molar ratio. The details of the sample growth procedure are described elsewhere. Good single crystallinity of the as-grown samples was confirmed by a single-crystal X-ray diffractometer. The platelet-like samples were then cut into bar shapes of appropriate geometry for in-plane and out-of-plane transport measurements. The resistivity of each sample was measured with a standard four-probe $ac$ lock-in detection technique.

For the thermal conductivity measurements, we developed a zero-field apparatus housed in a $^4$He flow cryostat that covers the temperature range 10K $< T < 300$K. We employed a modified steady-state method, shown schematically in Figure S2 of Ref., in which a temperature gradient, measured using a differential thermocouple, is set up across the sample through a pair of calibrated heat-links attached to each end. The sample is suspended by the free ends of the heat-links between two platforms that are weakly coupled to the heat-bath. Each platform houses a heater that enables a temperature gradient to be set up across the sample in both directions at a fixed heat-bath temperature. The heat-links are also differential thermocouples that allow the heat flowing into and out of the sample to be measured simultaneously in order to determine the heat loss across the sample in steady state.

The heat capacity measurements were performed in a commercial Quantum Design PPMS system. The measurements were done on a large single-crystal piece of Na$_{0.9}$Mo$_6$O$_{17}$ (of 2.495mg in weight), and two pieces of single-crystalline K$_{0.9}$Mo$_6$O$_{17}$ (total weight 1.190mg). The heat capacity of the addenda was determined in a separate run and subtracted from the total heat capacity. In the $C_p(H)$ measurements, a static magnetic field of 14 Tesla was applied along the crystallographic $c$-axis.

III. RESULTS

Fig. 1 summarizes both the in-plane ($\rho_{ab}$) and inter-plane ($\rho_c$) resistivities of our Na$_{0.9}$Mo$_6$O$_{17}$ and K$_{0.9}$Mo$_6$O$_{17}$ single crystals. Overall, the temperature dependence in each case is in good agreement with what has been reported previously. Specifically, both $\rho_{ab}(T)$ and $\rho_c(T)$ are approximately $T$-linear at high temperatures then pass through a well-defined minimum around $T = T_P$. At the lowest temperature studied, both systems develop a second upturn that is larger in the $A = \text{Na}$ bronze. In both cases, the zero-temperature resistivity tends towards a finite value, confirming that these CDW transitions are metal-metal transitions. As the resistivity minima at $T_P$ in both systems are rather broad, we use their derivatives $d(ln \rho)/dT$, plotted in Fig. 2, to define the onset of the CDW transition, as is the normal. From both $d(ln \rho_{ab})/dT$ and $d(ln \rho_c)/dT$, deep minima are identified at $\sim 80$K and $\sim 100$K for Na$_{0.9}$Mo$_6$O$_{17}$ and K$_{0.9}$Mo$_6$O$_{17}$ respectively, in good agreement with previous studies. Evidently, the width of the derivative minimum at $T = T_P$ is much sharper in K$_{0.9}$Mo$_6$O$_{17}$ than in Na$_{0.9}$Mo$_6$O$_{17}$, suggestive of a lower intrinsic disorder level in the former. We shall return to this point in the Discussion section.

In addition to the similarities highlighted above, there
are also some notable differences between our measurements and those reported in the literature. While the $\rho_c$ values of both systems are comparable with earlier reports, the absolute values of $\rho_{ab}$ are roughly one order of magnitude lower, making the corresponding resistivity anisotropy ($\sim 3000 - 4000$) significantly higher than previously reported. We attribute these lower in-plane resistivity values to an improved shorting out of the highly resistive inter-plane current paths. This was achieved by ensuring that the voltage and current contact pads cover the entire thickness of the crystal. If this is not done carefully, any current flow perpendicular to the conducting planes will lead to a much larger apparent resistivity being measured. We have used this method previously to successfully isolate the low resistivity direction in a variety of low dimensional materials and refer the interested reader to our recent work on the Q1D superconductor from the same family (Li$_{0.9}$Mo$_6$O$_{17}$), in which we again found a significantly lower resistivity than had been previously reported.\[16\] Significantly, in that case, the resulting in-plane resistive anisotropy (i.e. for currents parallel and perpendicular to the conducting chains) was found to be consistent with that obtained independently from both optical spectroscopy measurements and the measured upper critical field anisotropy. Such good agreement highlights the efficacy of our technique in isolating the individual components of the conductivity tensor of highly anisotropic systems.

The origin of the second resistive upturn in both bronzes at low temperatures is still unresolved, with spin density wave (SDW) formation, a second CDW transition and localization all put forward as possibilities. Significantly, in Li$_{0.9}$Mo$_6$O$_{17}$, a similar upturn is also seen, though in this case, the excellent scaling observed in the longitudinal intrachain magnetoresistance is considered to point more towards some form of DW gapping than in-plane resistivity fluctuations.\[20\]
The total in-plane thermal conductivity \( \kappa_{ab} \) as a function of temperature is plotted as red two-tone squares in the panels (a) of Fig. 3 and Fig. 4 for Na\(_{0.9}\)Mo\(_6\)O\(_{17}\) and K\(_{0.9}\)Mo\(_6\)O\(_{17}\) respectively. Compared to the zero-field resistivities, which have similar magnitudes and overall display similar behavior (bar the size of the resistive upturn), the in-plane thermal conductivities of the two systems show some notable differences. In Na\(_{0.9}\)Mo\(_6\)O\(_{17}\), \( \kappa_{ab}(T) \) is nearly \( T \)-independent above \( T_p \), then as \( T \) cools below \( T_p \), \( \kappa_{ab}(T) \) first develops a well-defined downturn, goes through a minimum around 50K then finally peaks at around 15 K. The thermal conductivity of K\(_{0.9}\)Mo\(_6\)O\(_{17}\), on the other hand, while showing a slight kink at \( T \sim 120 \) K, increases significantly below \( T_p \), reaching a peak value at \( T = 20 \)K that is approximately four times higher than that of Na\(_{0.9}\)Mo\(_6\)O\(_{17}\). The low temperature peak is typical of the thermal response of phonons and results from the competition between increasing numbers of propagating phonons (with increasing \( T \)) and the concomitant reduction of their mean free path. The larger magnitude of the peak amplitude of \( \kappa_{ab} \) below \( T_p \) in K\(_{0.9}\)Mo\(_6\)O\(_{17}\) compared with Na\(_{0.9}\)Mo\(_6\)O\(_{17}\) again reflects a lower level of static disorder in the former.

The total thermal conductivity of a metal consists of the contributions from free carriers, lattice vibrations and other possible excitations. The electronic component \( \kappa_e \) in an ordinary metal can be estimated from the Wiedemann-Franz law:

\[
\frac{\kappa_e}{\sigma T} = L_0
\]  

where \( \sigma \) is the dc electrical conductivity and \( L_0 = 2.45 \times 10^{-8} \) WΩK\(^{-2}\) is the so-called Lorenz number. Although deviations in this relation are observed in most metals at intermediate temperatures, due to the differing effects of small- and large-angle scattering on the electrical and thermal conductivities, these are typically only of order 20-30\% and as a first approximation, they can be ignored.

The blue open circles in panel (a) of Fig. 3 and Fig. 4 represent the electronic contribution \( \kappa_e \), calculated from Eqn. (1) and the electrical resistivity data plotted in Fig. 1. The kinks in \( \kappa_e \) of both systems at \( T = T_p \) result primarily from the substantial decrease of the carrier density at the CDW transition. The residual part, \( \kappa_T - \kappa_e \), as replotted in (b) of Fig. 3 and Fig. 4 accordingly, thus represents the contributions to the thermal conductivity arising from phonons and any other excitations. Note that the slight kink in \( \kappa_{ab}(T) \) of K\(_{0.9}\)Mo\(_6\)O\(_{17}\) is effectively removed once \( \kappa_e \) is subtracted from the raw data. By contrast, for Na\(_{0.9}\)Mo\(_6\)O\(_{17}\), the kink is still very much evident even after subtraction of \( \kappa_e \). It is important to note that this difference is not simply due to our overestimate of \( \kappa_{ab} \), since we obtained \( \kappa_{ab} \) values of a similar magnitude on a second crystal, nor to any possible underestimate of \( \sigma_{ab} \). Indeed, in order to remove the kink in \( \kappa_T - \kappa_e \) completely, we would have had to underestimate \( \sigma_{ab} \) by a factor of 5, i.e. by an amount more than one order of magnitude greater than our experimental uncertainty (of order 30\%). Moreover, the magnitude of \( \sigma_{ab} \) that we measure is already one order of magnitude higher than in previous reports. We are confident therefore that this kink is an intrinsic feature of \( \kappa_{ab}(T) \) in Na\(_{0.9}\)Mo\(_6\)O\(_{17}\).

The main component of \( \kappa_T - \kappa_e \) is the contribution from the phonons. In our subsequent analysis, we employ the Debye model for the phonon Boltzmann transport theory:

\[
\kappa_{ph} = \frac{1}{2\pi^2v} \int_0^{\omega_{max}} \hbar \omega^3 \tau \frac{(\hbar\omega/k_BT^2)\exp(\hbar\omega/k_BT)}{[\exp(\hbar\omega/k_BT) - 1]^2} d\omega \quad (2)
\]
where $\omega$ is the phonon frequency, $\omega_{\text{max}}$ is the maximum phonon frequency related to the Debye temperature $\Theta_D$ via $\hbar \omega_{\text{max}} = k_B \Theta_D$, $\nu = \Theta_D (k_B / \hbar) (6\pi^2 n)^{-1/3}$ is the mean sound velocity with $n$ the number density of atoms, while $\tau$ is the phonon relaxation time which takes account of all the phonon scattering mechanisms. We assume here that these individual scattering processes act independently so that $\tau_\Sigma^{-1} = \Sigma_i \tau_i^{-1}$, where $\tau_i$ corresponds to each individual relaxation time. The main phonon scattering mechanisms come from scattering off two-dimensional defects and phonon-phonon scattering, that is:

$$\tau_\Sigma^{-1} = A \omega^2 + B a^2 T \exp(-\Theta_D / b T).$$

In the same way that the quasiparticle mean-free-path $\ell$ cannot become shorter than the interatomic spacing $a$ (the so-called Mott-Ioffe-Regel limit)\textsuperscript{23,24} we follow the procedure of Kordonis et al.\textsuperscript{25,26} and assume here that the phonon mean-free-path must also have a lower limit $\ell_{\text{min}}$ with $\tau = \max(\tau_\Sigma, \ell_{\text{min}} / \nu)$.\textsuperscript{23} We thus set the parameters $A$, $B$ and $b$ and $\ell_{\text{min}}$ as freely adjustable parameters and use the Debye temperature extracted from low-$T$ heat capacity data, as shown below, to obtain the resultant fitting curves displayed as solid red lines in Fig. 3(b) and Fig. 4(b) for Na$_{0.9}$Mo$_6$O$_{17}$ and K$_{0.9}$Mo$_6$O$_{17}$ respectively. The corresponding fitting parameters are listed in Table I. The values for $A$, $B$ and $b$ are typical for $\kappa_{\text{ph}}$ in oxide systems. The values for $\ell_{\text{min}}$, on the other hand, are rather large, though as mentioned by Kordonis et al.\textsuperscript{26} the inclusion of $\ell_{\text{min}}$ has little bearing on the fitting of the low-temperature $\kappa_{\text{ph}}(T)$. Above the fitting range, we assume the typical 1/$T$ decay in the phonon thermal conductivity due to phonon-phonon scattering. These tails are depicted in Fig. 3(b) and Fig. 4(b) as dashed blue lines.

As mentioned above, the most striking feature of the $\kappa_T - \kappa_e$ data for Na$_{0.9}$Mo$_6$O$_{17}$ shown in Fig. 3(b) is the enhancement of the thermal conductivity beginning at $T = 50$ K. This enhanced conductivity, plotted in the inset of panel (b), is reminiscent of that seen in other CDW systems such as (NbSe$_4$)$_{10}$I$_3$, K$_{0.3}$MoO$_3$, and (TaSe$_4$)$_2$I$_3$\textsuperscript{25,26} for which it was attributed to the emergence of phason excitations associated with the CDW transition. Note that in these other CDW systems, this contribution exists both above and below $T_P$ where it typically peaks. The contribution above $T_P$ is considered to arise from fluctuations associated with the phason excitations. Moreover, as noted by Smontara \textit{et al.}\textsuperscript{27} the phason fluctuations may extend to very high temperature due to slow decay of the damping rate $\Gamma$. Hence, while we do not expect that phason excitations account for the full excess of thermal conductivity in Na$_{0.9}$Mo$_6$O$_{17}$, they may well account for a significant proportion of it. A similar enhancement can also be inferred, though less convincingly, in the thermal conductivity data of K$_{0.9}$Mo$_6$O$_{17}$ plotted in the inset of Fig. 4(b) from extrapolation of the 1/$T$ decay to higher temperature (dotted curve in Fig. 4(b)). Note that it is not possible to fit the full $\kappa(T)$ data of K$_{0.9}$Mo$_6$O$_{17}$ using Eqn. (2) and that a fit to the high-$T$ $\kappa(T)$ data incorporating $\ell_{\text{min}}$ gives unphysical values for $A$, $B$, and $b$ and strongly underestimates the enhancement in $\kappa(T)$ below $T_P$.

The specific heat $C_p(T)$ data, shown in Fig. 5\textsuperscript{28,29} and Fig. 6\textsuperscript{28,29} uncover another marked difference between the two systems. For K$_{0.9}$Mo$_6$O$_{17}$, a large, well-defined heat capacity anomaly, clearly associated with the CDW transition, is observed. The anomaly shown in Fig. 5(a) is in fact much sharper than has been reported previously.\textsuperscript{28} By contrast, the corresponding feature in Na$_{0.9}$Mo$_6$O$_{17}$ is extremely broad and as such, is difficult to pinpoint. In contrast with the resistivity data, no additional anomalies could be found at lower temperatures in either system due to any putative sub-dominant CDW/SDW transitions. A magnetic field of 14 Tesla is found to have no effect on the shape or position of the specific heat anomaly in both systems.

Plots of $C_p/T$ versus $T^2$ at the lowest temperature allow us to separate out the electronic ($= \gamma T$) and phononic ($= \beta T^3$) contributions, as shown in panels (b) of Fig. 5\textsuperscript{28,29} and Fig. 6\textsuperscript{28,29}. From the extracted $\gamma$ values, given in the Figure caption, we determine the density of states of normal carriers at the Fermi level to be 1.515 eV$^{-1}$ per molecule and 0.275 eV$^{-1}$ per molecule for Na$_{0.9}$Mo$_6$O$_{17}$ and K$_{0.9}$Mo$_6$O$_{17}$ respectively. Debye temperatures of 333 K and 228 K for Na$_{0.9}$Mo$_6$O$_{17}$ and K$_{0.9}$Mo$_6$O$_{17}$ respectively can also be estimated from the formula $\Theta_D = \frac{\pi^4 r}{2} R \beta^{-1}$ with $R$ the gas constant and $r$ the total number of atoms in one formula unit ($r=24$ for both cases). We note that the $\Theta_D$ value extracted here for K$_{0.9}$Mo$_6$O$_{17}$ is somewhat lower than those reported in the literature\textsuperscript{28,29}.

### IV. DISCUSSIONS AND CONCLUSION

In many CDW compounds, the thermal conductivity is enhanced substantially below the Peierls transition, as a result of changes in the electron- or phonon-scattering processes. However, in other CDW compounds, such as (NbSe$_4$)$_{10}$I$_3$, K$_{0.3}$MoO$_3$, and (TaSe$_4$)$_2$I$_3$\textsuperscript{25,26} the thermal conductivity is observed to pass through a well-defined minimum below the Peierls transition before increasing again at lower temperatures. It has been proposed that...
FIG. 5: (Color online) Panel (a): The temperature dependence of the specific heat in both zero field (black square) and 14 Tesla magnetic field (red triangle) of Na$_{0.9}$Mo$_6$O$_{17}$. Evidently, an applied magnetic field has little effect on its overall heat capacity. Panel (b): The low-temperature zero-field $C_p/T$ data plotted as a linear function of $T^2$ to allow the normal electronic and acoustic phonon contributions to the specific heat to be delineated. The fitting gives $\gamma=3.57$ mJ/K$^2$mol, $\beta=1.05$ mJ/K$^4$mol.

FIG. 6: (Color online) Similar to Fig. 5 panel (a) shows the temperature dependence of the specific heat in both zero field (black square) and 14 Tesla magnetic field (red triangle) of K$_{0.9}$Mo$_6$O$_{17}$. As noted, an applied magnetic field has little effect on the total heat capacity. Panel (b) separates the normal electronic and acoustic phonon contributions by fitting $C_p/T$ of $H=0T$ data as a linear function of $T^2$ at very low temperatures. The resultant fitting parameters are $\gamma=0.65$ mJ/K$^2$mol, $\beta=3.30$ mJ/K$^4$mol.

this additional contribution results from phason modes with large velocity. Given the strong similarity in the behavior of $\kappa_{ab}(T)$ in Na$_{0.9}$Mo$_6$O$_{17}$ with those systems listed above, it would seem appropriate to ascribe at least part of the excess thermal conductivity shown in the inset of Fig. 3(b) to the same origin.

While there is no well-defined minimum in $\kappa_{ab}(T)$ in K$_{0.9}$Mo$_6$O$_{17}$ in the region of the Peierls transition, inspection of Fig. 4(b) reveals a small excess thermal conductivity above the high-$T1/T$ decay of $\kappa_{ph}$ that could correspond to the same phason contribution seen much more clearly in Na$_{0.9}$Mo$_6$O$_{17}$. Evidence for phason excitations from measurements of the low-temperature specific heat of K$_{0.9}$Mo$_6$O$_{17}$ was claimed in Ref. 28 through the observation of a broad hump in $C/T^3$ around $T = 16$ K. Given that this temperature coincides with the onset of the low-temperature upturn in the resistivity of K$_{0.9}$Mo$_6$O$_{17}$, it is not yet clear whether this feature can be ascribed unambiguously to phasons or to a second density-wave transition.

The origin of the striking difference in the thermoelectric power of the Q2D purple bronzes below $T = T_P$, as described briefly in the Introduction, remains to be resolved, though it is likely to arise from subtle differences in the electronic structure, as hinted at by ARPES as well as in the relative mobilities of the carriers on the remnant Fermi surface(s). According to Breuer et al., the Fermi surface in Na$_{0.9}$Mo$_6$O$_{17}$ comprises an elliptical electron pocket, i.e. around the $\Gamma$ point, that is less prone to nesting, and a diamond-shaped hole pocket with flat
is substantially higher below $T_P$ in Na$_{0.9}$Mo$_6$O$_{17}$ is therefore consistent with the notion that the remnant Fermi surface below $T_P$ will be predominantly located about the more-rounded sections of the single electron pocket.

The second electron pocket found in K$_{0.9}$Mo$_6$O$_{17}$ uncovered by Gweon et al. is star-like. Intriguingly, between the apices of the stars, lie rounded regions of Fermi surface with negative curvature, i.e. that are centered around the edges of the Brillouin zone rather than around its center. Hence, while the second pocket in K$_{0.9}$Mo$_6$O$_{17}$ is electron-like, those regions unaffected by the CDW transition will have predominantly hole-like character. In the heavily overdoped cuprate La$_{2-x}$Sr$_x$CuO$_4$ ($x = 0.30$), which also has an electron pocket with regions of negative curvature, a similar inversion of the sign of the thermopower and of the Hall coefficient is observed. In this regard, it would be very interesting to explore the evolution of the in-plane Hall coefficient in both purple bronzes above and below $T_P$.

One of the most notable findings of this study is the observation that the Q2D purple bronzes Na$_{0.9}$Mo$_6$O$_{17}$ and K$_{0.9}$Mo$_6$O$_{17}$ display distinct transport and thermodynamic properties associated with their CDW transitions. Given the possible differences in the Fermiologies of the two systems, as inferred by ARPES and their very different thermoelastic responses below $T = T_P$ as described above, these differences might, on first inspection, suggest that the nature and mechanisms of CDW formation in these two Q2D bronzes are in fact distinct. However, we argue here that a more consistent explanation of these contrasting behaviors can be provided by considering the different crystal chemistries of the two systems and the resulting variation in disorder content.

Regarding the latter, we note from the high-temperature $T$-linear resistivities plotted in Fig. 4 that the extrapolated residual resistivity in Na$_{0.9}$Mo$_6$O$_{17}$ is significantly higher than in K$_{0.9}$Mo$_6$O$_{17}$. Moreover, the low-$T$ resistivity in the Na-bronze is approximately twice that at the resistive minimum, while in K$_{0.9}$Mo$_6$O$_{17}$, it remains comparable, even though the low-$T$ heat capacity data reveal that the density of states in Na$_{0.9}$Mo$_6$O$_{17}$ is substantially higher below $T_P$. This comparison implies that the A = Na bronze is significantly more susceptible to localization effects, an indicator of higher levels of disorder scattering. This conclusion is further corroborated by the observation that the peak in the phonon thermal conductivity at low temperatures, a quantitative measure of the phonon mean-free-path, is approximately four times lower in Na$_{0.9}$Mo$_6$O$_{17}$ than in K$_{0.9}$Mo$_6$O$_{17}$. This argument is also consistent with what was seen in Fig. 2 where the width of negative peak of $d(\ln \rho)/dT$ at $T_P$, a strong indicator of disorder level, is much narrower in K$_{0.9}$Mo$_6$O$_{17}$. Finally, the anomaly in the heat capacity, while sharp in our K$_{0.9}$Mo$_6$O$_{17}$ crystal, is smeared out in the Na-doped counterpart. A similarly broad heat capacity anomaly was also reported for Na$_{0.9}$Mo$_6$O$_{17}$ almost three decades ago in crystals grown by a different group, though unfortunately, there is no accompanying transport data in that study to allow us to compare their residual resistivities directly. Nevertheless, such variation in the heat capacity anomaly in what are nominally the same compound does suggest that there is indeed a strong sample dependence in the thermodynamic properties of the two systems.

The Na$_{0.9}$Mo$_6$O$_{17}$ system is known to possess a variable Na content. Variation in stoichiometry in the sodium purple bronzes is usually considered to be a characteristic that exists between crystals, rather than within an individual crystal. However, given the higher mobility of sodium atoms within the melt relative to that of the potassium, we speculate here that there may be more of a tendency for the Na ions to form clusters within each crystal, which in turn will lead to enhanced elastic scattering of the quasiparticles on the conducting molybdate chains. It is also noted that clustering of Na ions may lead to a distribution of transition temperatures and therefore increase the breadth of the transition, as indeed seen in Fig. 2. However, a distribution of concentration could yield a distribution of the Fermi vectors in different parts of the crystal, favoring the incommensurate character of the CDW, a necessary condition to have phasons which does not seem to be fulfilled in K$_{0.9}$Mo$_6$O$_{17}$.

In summary, we have studied the transport and thermodynamic properties of two Q2D purple bronzes Na$_{0.9}$Mo$_6$O$_{17}$ and K$_{0.9}$Mo$_6$O$_{17}$ and have revealed significant differences in their physical properties above and below their CDW transitions. These differences appear to arise from differences in their stoichiometry, possibly caused by the volatility of sodium during crystal growth. An unusual enhancement of the thermal conductivity has been attributed, in comparison with other CDW systems, to the possible emergence of phason excitations in these two systems. Finally, measurements of the electrical resistivity reveal an electrical anisotropy that is one order of magnitude larger than previously thought.

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