# Thermal Conductivity of $1T$-TaS$_2$ and $2H$-TaSe$_2$

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We present measurements and analysis of the basal thermal conductivity for two dichalcogenides: $1T$-TaS$_2$ and $2H$-TaSe$_2$. The data which are obtained for the first time cover the range 80–400 K. The lattice contribution is important for each compound and possesses specific features related to charge-density-wave–type transitions; in particular, that of TaS$_2$ exhibits a quite unusual upward jump. For TaSe$_2$ we use an order-disorder picture to explain both the lattice conductivity and the entropy variation in unison with the electrical resistivity.

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Layered transition-metal dichalcogenides show strong two dimensionality. This character favors the development of the so-called charge-density-wave (CDW) transition[1] which results from a natural instability of a one-dimensional or two-dimensional electron sea. Indeed, the electronic susceptibility has a strong anomaly at the $2\mathbf{k}_F$ wave vector that perfectly screens any perturbation with the same wave vector. In this way the $2\mathbf{k}_F$ phonon can be frozen out, thus becoming the soft mode of a displacive transition. Above the transition temperature the metallic character is expected, whereas electrons and phonons generally form a complicated condensed system in the distorted state. The first description of the transition between these two phases[2] treated the electron-phonon interaction in the weak-coupling limit: The metallic state is maintained down to the transition temperature, below which a gap develops at the Fermi level with a temperature variation similar to that of superconductors. However, analysis of experimental data soon proved that the best-studied materials (e.g., $2H$-TaSe$_2$) show strong deviations from this simple behavior. For example, the ratio $2\Delta/k_BT_c$ (where $\Delta$ is the measured gap, $k_B$ is the Boltzmann's constant, and $T_c$ the measured transition temperature) appeared to be one order of magnitude larger than 3.5, the expected value. Mc Millan[3] was the first to point out that the short coherence length $\xi_0$ of the CDW (of the order of the superstructure unit cell) implied that phonon entropy rather than the electronic one is controlling the transition. In this way he could explain the low value for $T_c$, which now relates to the establishment of long-range order (LRO) in contrast to the short-range order (SRO) that appears at much higher temperatures. More recently, Varma and Simons[4] developed a strong-coupling theory for this transition and found that electronically induced anharmonicity and mode-mode coupling are indeed responsible for the large depression of the transition temperature. Now, Varma[5] shows that this implies a violation of Migdal's theorem, as in strongly coupled $A15$ superconductors.[6]

One can expect the thermal conductivity of the dichalcogenides to be strongly modified at the CDW transition. Firstly, as in superconductors, the relative contributions of electrons and phonons in the energy transport must be changed. In second place, long-wavelength phonons which play the predominant role in the lattice conductivity should be sensitive to the specific transitional anharmonicities. However, little experimental work exists[7] to check the above predictions in any detail. In this Letter, we present the first measurements of the basal thermal conductivity of two typical layered CDW compounds: $1T$-TaS$_2$ and $2H$-TaSe$_2$. In the latter case, our results show that an abnormally large phonon scattering develops in the SRO region which disappears below $T_c$. We show that an interpretation based on an anharmonicity caused by two almost degenerate phasings for the CDW can explain our experimental results along with the value of the transitional entropy and the temperature dependence of the electrical resistivity.

We have carried out experiments in the range 80–400 K using a specially designed sweeping method. For each compound, two samples were studied having typical dimensions $5\times2\times0.1$ mm$^3$. Electrically insulating epoxy resin was used to attach the samples in series with a stainless-steel reference sample between two copper blocks at different sweeping temperatures. The gradients on both samples are measured with use of AuFe-chromel thermocouples; the unknown thermal conductivity is then determined by the ratio of the gradients, a geometrical factor, and the thermal conductivity of the reference. Thermal shields and carefully controlled heat fluxes minimize radiation heat leaks. A typical cycling speed is 0.5 K/min and the temperature drops are of about 1 or 2 K. The precision of the measured points is about 2 K in the presented results. More details on the particular difficulties of measuring transition-metal dichalcogenides, on sample mounting, and on the use of the method will be given elsewhere.[8]

The thermal conductivity of $1T$-TaS$_2$ was obtained during cooling; it is shown in Fig. 1. The incommensurate CDW (ICDW) → nearly commensurate CDW (NCCDW) and the NCCDW → commensurate CDW (CCDW) transitions are clearly seen at 350 and 180 K,

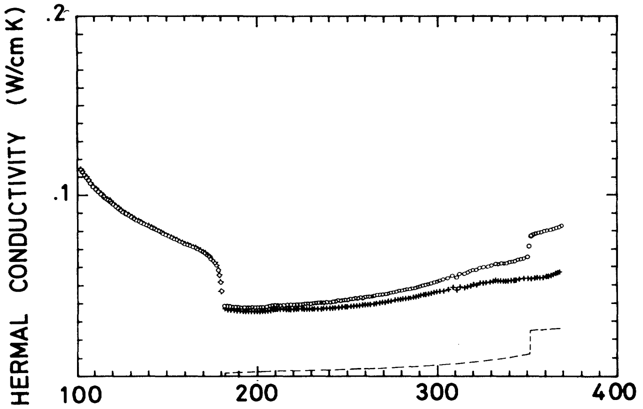

FIG. 1. Thermal conductivity of $1T$-TaS$_2$. Open circles, experimental results. Dashed line, electronic contribution from Wiedeman-Franz law. Crosses, estimated lattice contribution.

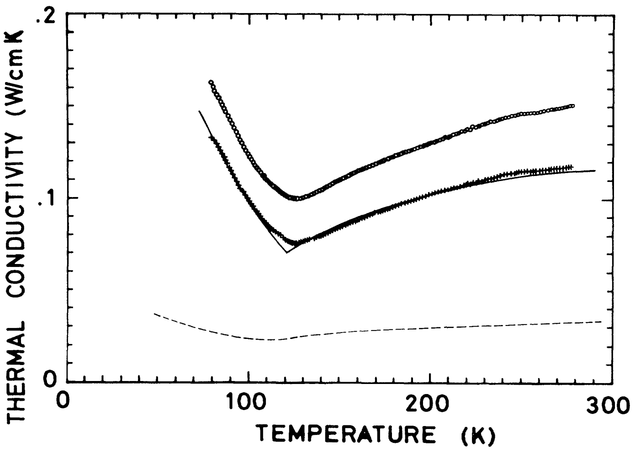

FIG. 2. Thermal conductivity of $2H$-TaSe$_2$. Symbols have the meaning of Fig. 1. Full line is the phenomenological fit.

respectively: the first one as a sharp decrease and the second as an abrupt recovery of the thermal conductivity. We have also plotted in Fig. 1 the electronic thermal conductivity ($K_e$) as estimated from the electrical resistivity measured on the same sample and assuming the validity of the Wiedeman-Franz law. At any temperature, $K_e$ is more than 3 times smaller than the measured conductivity. It is thus reasonable to retain for the lattice thermal conductivity ($K_{\text{ph}}$) the difference between the measured value and $K_e$. Clearly the anomaly at 350 K just reflects the loss of electrical carriers, while no change in $K_{\text{ph}}$ is perceptible. It is clear that the second anomaly cannot be explained in the same way: Indeed, the thermal conductivity is increased by nearly a factor of 2 when $K_e$ is expected to be further reduced by one order of magnitude. The jump thus comes from $K_{\text{ph}}$ and such an astonishing behavior is quite unusual for lattice conduction. It looks as if the causes of strong phonon scattering disappear below the transition and that the sample is subsequently recovering its "normal" (Umklapp, boundaries, etc.) lattice thermal conductivity in the insulating CCDW phase. More specifically, we can imagine that specific defects (such as discommensurations) are present in the incommensurate phases which disappear or at least are significantly reduced in the commensurate phase. Also, the very strong change in the electronic concentration can be responsible for the jump. Indeed, when one passes from the NCCDW to the CCDW phase, the electrical resistivity is strongly increased. Considering that this increase essentially reflects the change in the density of states, we can correlate it to the expected upward jump of the ideal, electron-limited, lattice conductivity using Bloch-Grüneisen–type formulas (Berman,[9] p. 133). Our estimation gives a change by more than three orders of magnitude and this is consequently compatible with the much lower intensity of the observed jump. This approach, however, does not explain the slight increase in $K_{\text{ph}}$ with temperature above the transition. This fact requires a better understanding of the NCCDW; all the more so, since as we shall now see, a somewhat similar effect is obtained for $2H$-TaSe$_2$.

The thermal conductivity of $2H$-TaSe$_2$ is drawn in Fig. 2. A minimum is clearly present at the transition temperature ($T_{NI} \sim 120$ K) between the normal and the ICDW phases but without any sharp features. The qualitative temperature dependence is not unlike that of $1T$-TaS$_2$: a low thermal conductivity slightly decreasing with temperature and recovering quickly. Note, however, that the effect is not now associated with the lock-in transition (about 90 K). As with the $1T$-TaS$_2$, we have estimated the electronic contribution using the Wiedeman-Franz law from the electrical resistivity measured on the same sample. This approach is justified since we expect to be in a nearly elastic regime. $K_e$ does not exceed 25% of the total conductivity in the whole explored temperature range, and, consequently, $K_{\text{ph}}$ can be nicely evaluated by difference. In particular, we note that the calculated $K_e$ is unable to reproduce the steepness of the dip around $T_{NI}$. The importance of this result is evident upon considering the impossibility for such a minimum to emerge from the lattice conductivity should the relaxation time ($\tau$) depend only on the frequency (whatever the form of that dependence). Clearly, a temperature variation of $\tau$ is needed. In order to obtain some insight into this variation, it is worth going back to the electrical resistivity curve.[10] Its shape, identical to that of a magnetic metal developing an antiferromagnetic order below $T_{\mathrm{AF}}$, may be decomposed into two separate resistivities.[10] The first one describes the scattering of electrons against impurities and phonons and approximately follows the Bloch-Grüneisen law. The second one is due to the disordering of the spins and when $T > T_{\mathrm{AF}}$ it is constant. But, when $T < T_{\mathrm{AF}}$, the scattering decreases with increasing order, roughly following a $1-\Delta^2$ law ($\Delta$ is the order parameter) in the vicinity of $T_{\mathrm{AF}}$. At lower temperatures a more complicated inelastic behavior takes place. Following these ideas we are thus tempted to introduce a "pseudospin" concept for analyzing the thermal conductivity of our CDW compound. Such entities can be naturally associated with a SRO that fluctuates in regions of the size of the superlattice unit cell following McMillan's idea. For $T > T_{NI}$, the different conditions of the pseudospins will be degenerate in energy, the scattering of the phonons by them will be elastic, and their mean free path will not depend on their energy. The same will roughly be true just below $T_{NI}$ as the LRO remains weak. On the other hand, the small size of our pseudospins implies that all long-wavelength phonons are scattered in the same way. As a consequence, a good guess for the phonon relaxation time is the following: $\tau_{ps}$ is taken as constant for $T > T_{NI}$ and increasing like $1-\Delta^2$ when $T$ decreases below $T_{NI}$. The latter phenomenological law is chosen because it appears to be valid for several order-disorder transitions and the order parameter follows the temperature dependence of the CDW gap. Now, we can describe the $2H$-TaSe$_2$ data by the usual expression for the thermal conductivity (Ref. 9, p. 23):

$$K = \frac{k_{\mathrm{B}}}{2\pi^2 v}\left(\frac{k_{\mathrm{B}}}{\hbar}\right)^3 T^3 \int_0^{\theta_{\mathrm{D}}/T} \tau_r(x)\,\frac{x^4 e^x}{(e^x-1)^2}\,dx,$$

where $x = \hbar\omega/k_{\mathrm{B}}T$, $\tau_r^{-1} = \tau_c^{-1} + \tau_{\mathrm{ps}}^{-1}$ is the total inverse relaxation time with $\tau_c^{-1}$ a frequency-independent, geometric, scattering rate and $\tau_{\mathrm{ps}}^{-1}$ the pseudospin term. The sound velocity is chosen $v = 25\times10^4\ \mathrm{cm\cdot s^{-1}}$ averaged from neutron-scattering data.[11] The fit obtained for the phonon thermal conductivity is shown in Fig. 2. The agreement is excellent for such a crude approach to the phase transition. The value of the Debye temperature $\theta_{\mathrm{D}}$ needed for such a fit is 500 K, which must be compared with 200 K obtained from specific-heat data.[12] The pseudospin scattering rate gives a mean free path of $\sim 50$ Å, i.e., of the order of magnitude of the supposed size of the pseudospin, namely, the superlattice unit cell. The geometric relaxation rate is twenty times bigger than $\tau_{\mathrm{ps}}^{-1}$. It is difficult to attribute to it a clear physical meaning as it certainly incorporates different scattering rates.

To extract more information about our entities, we must reanalyze the specific heat. The entropy ($\Delta S$) of an order-disorder transition is related to the number ($N$) of degenerate states in the disordered phase by the usual formula: $\Delta S = R\ln N$. The corresponding value can be extracted from the data of Harper, Geballe, and DiSalvo[12] using the baseline they give. If we consider that we have one pseudospin per superlattice unit cell, i.e., per nine molecules, we obtain a value of $\Delta S = 5.2\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$, reasonably close to the $5.8\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ that corresponds to two degenerate states. So phonon and electron transport together with the entropy of the transition give strong support to the pseudospin description of the CDW transition in $2H$-TaSe$_2$. In fact, the thermal properties of the latter render it quite similar to the ferroelectric $\mathrm{KH_2PO_4}$, the classical example of pseudospin order-disorder transitions: The behaviors of the specific heats[13] are alike though the transition is slightly first order in $\mathrm{KH_2PO_4}$ which, besides, has a minimum in the thermal conductivity at the transition temperature.[14] $2H$-NbSe$_2$ could also behave in the same way. Indeed, the similitude holds for the level of the transitional entropy and the temperature dependence of the electrical resistivity. This is natural as the distortion in this compound is very similar to that of $2H$-TaSe$_2$. Thermal conductivity measurements are under way to probe the generality of our analysis. However, we can already notice that its extension to some other CDW compounds proves more difficult as their transition entropy is much smaller (see, e.g., NbSe$_3$ [15]).

To conclude, let us try to obtain an incipient representation of the pseudospins. These not only involve ionic motions between two degenerate configurations like those of the hydrogen ions and phosphate radical in $\mathrm{KH_2PO_4}$; they also imply a correlated breathing in the density of the conduction electrons. Assuming that the commensurate state is a simple condensation of one of the two wanted configurations, we have first to consider the precise distortions in this state. This problem has recently reached a firmer understanding through the convergent-beam electron diffraction experiment of Bird, McKernan, and Steeds.[16] Figure 3(a) partially represents their result while Fig. 3(b) represents a conjecture for the second configuration. The present choice results from a re-

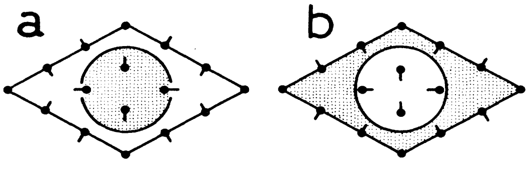

FIG. 3. One possibility for the two pseudospin configurations. (a) The commensurate unit cell: points represent tantalum ions and arrows their displacements. Selenium ions are omitted for clarity. Shaded area indicates a deficit of conduction electrons. (b) The alternative configuration.

cent analysis by Wilson,[17] who shows that the two configurations are related to the strong influence the $d_z^2$ band saddle points have on the nesting characteristic of the Fermi surface. Finally, we must notice that the real motion in the "normal" phase may involve the proposed configurations only in part.

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