Thermoelectric Aspects of Charge-Density-Wave Transport in TaS_3

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The field-dependent thermoelectric power of TaS_3 is measured, and a general analysis of thermoelectricity in non-Ohmic conductors is applied. The Peltier heat coefficient of the nonlinear electric current is zero at high temperatures and independent of applied voltage at all temperatures. The present results are consistent with a moving condensate accompanied by low-temperature phonon drag, but not with certain alternative nonlinear conduction mechanisms.

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A growing number of inorganic linear-chain compounds have been found to display remarkable nonlinear field- and frequency-dependent electrical properties[1] qualitatively consistent with the collective sliding transport of charge-density waves originally proposed by Fröhlich.[2] This behavior, first observed in $NbSe_3$, has attracted widespread theoretical attention.[1]

Experimentally, the implications of the Fröhlich mechanism have not been explored in full. For example, in its rigid ground state the sliding condensate can carry no entropy; and thermally excited internal deformations carry entropy but no net excess charge. Hence the thermoelectric power, or entropy per charge carrier, directly associated with the condensate should vanish. In contrast, an early study by Dee, Chaikin, and Ong[3] of $NbSe_3$ in its lower-temperature charge-density-wave state found the opposite effect: The thermoelectric power *increases* in magnitude as the electric field is raised into the non-Ohmic regime. This result has posed a persistent challenge to interpretations of the high-field behavior based upon the Fröhlich mechanism.

Here we resolve the paradox by analyzing the field-dependent Peltier heat of a different Fröhlich conductor, orthorhombic TaS_3. Below its 220-K Peierls transition, this material is simpler than $NbSe_3$ in that a single charge-density wave spans the entire Fermi surface to form a semiconductor at low electric fields.[1] We improve the experimental method and correct the analysis used in Ref. 3, and thereby develop a general approach to the thermoelectric properties of non-Ohmic conductors. By two different experimental techniques we show that to instrumental accuracy, the Peltier coefficient associated with the non-Ohmic conductivity of TaS_3 is indeed zero at higher temperatures, but grows with cooling to a field-independent negative value. We conclude that nonlinear conduction occurs without creation of any field-induced excitations; that is perhaps the most direct evidence yet obtained for transport by a current-bearing condensate. Finally we summarize preliminary data which support the same conclusion for other materials in the class, and reconcile our findings with Ref. 3.

Conventional discussions of thermoelectricity consider the effects of small thermal and electric gradients upon systems initially in thermodynamic equilibrium.[4] To generalize to the non-Ohmic regime, we consider instead the effects of such gradients upon systems initially in a non-equilibrium steady state driven by an electric field E_0 applied along the principal conducting axis of a sample at uniform temperature T. In response there will flow a steady electric current $J(E_0)$ and Peltier heat current $U(E_0)$. A small change δE in the electric field and a small thermal gradient ∇T will generate incremental changes in the electric current

$$\delta J(E) = J'(E_0)\delta E + L_{12}(E_0)\nabla T/T^2, \quad (1a)$$

and in the heat current

$$\delta U(E) = U'(E_0)\delta E + L_{22}(E_0)\nabla T/T^2. \quad (1b)$$

Here the partial derivatives $J'(E_0)$ and $U'(E_0)$ are the differential electrical and Peltier conductivities, and $L_{12}(E_0)$ and $L_{22}(E_0)$ are Onsager coefficients.

In Ohmic systems near equilibrium, thermal

conductivity and thermoelectric power are defined, respectively, as the heat current and electric field generated by a unit temperature gradient across an open electric circuit. In non-Ohmic systems near steady state, the analog of the open-circuit condition $J=0$ is the constant-current condition $\delta J=0$. From Eqs. (1) we obtain the thermal conductivity

$$\kappa(E_0)\equiv \delta U/\nabla T = (J'L_{22}-U'L_{12})/T^2J', \tag{2}$$

and the thermoelectric power

$$S(E_0)\equiv \delta E/\nabla T = -L_{12}/T^2J'. \tag{3}$$

Because the response to the temperature gradient is linear, Eqs. (2) and (3) have the form of the usual expressions[4] with the Ohmic electrical and Peltier conductivities replaced by their differential counterparts. This reasoning applies in some detail. For example, in the special case where each of N distinct types of carriers independently contributes a component J_i of the current and carries a thermoelectric power S_i, the total thermopower is

$$S=\textstyle\sum_i J_i'S_i/\sum_i J_i' \tag{4}$$

which reduces to the familiar conductivity-weighted average in the Ohmic limit.

On the other hand, the thermodynamic interpretation of the thermoelectric power defined by Eq. (3) requires special care. Although Eqs. (1) and (2) are of the same form as the conventional linear transport equations,[4] no simple Onsager equality obtains between the off-diagonal coefficients $L_{12}(E_0)$ and $U'(E_0)$.[5] Rather, the thermopower is connected with the *entire* Peltier heat through the full nonlinear transport equations,

$$J(E) = L_{11}(E)E/T + L_{12}(E)\nabla T/T^2, \tag{5a}$$

$$U(E) = L_{21}(E)E/T + L_{22}(E)\nabla T/T^2. \tag{5b}$$

We observe that just as in the Ohmic case, the driving forces E/T and $\nabla T/T^2$ are proper Onsager forces, or first partial derivatives of the rate of entropy production with respect to the currents, and that Eqs. (5) have the same time-reversal symmetry as their Ohmic counterparts. It follows[6] that the Onsager relation

$$L_{12}(E) = L_{21}(E) \tag{6}$$

is valid. We now fix the driving forces and rewrite the Peltier current in Eq. (5b) as

$$L_{21}(E_0)E_0/T = \Pi(E_0)J(E_0), \tag{7}$$

where the field-dependent Peltier coeffient $\Pi(E_0)$ is a direct measure of the heat reversibly transported by electrical carriers in response to the electric field. According to Eq. (6) it is related to the thermoelectric power of Eq. (3) by

$$\Pi(E_0) = TS(E_0)[J'(E_0)E_0/J(E_0)]. \tag{8}$$

The measured thermoelectric power differs from the conventional entropy transported per carrier by the ratio of the chordal conductivity $J(E_0)/E_0$ to the differential conductivity $J'(E_0)$. Equation (8) can also be inferred from thermodynamic reasoning parallel to the original arguments of Thomson[4]; the Thomson heat is $d[\Pi(E_0)/T]/d(\ln T)$.

This analysis suggests that $\Pi(E_0)$, rather than $S(E_0)$, is the quantity of direct thermodynamic interest, although the latter is easier to measure. We note that in the N-fluid situation described by Eq. (4), the Peltier coefficient is given by

$$\Pi = \textstyle\sum_i \Pi_i J_i/\sum_i J_i. \tag{9}$$

The field-dependent thermoelectric power of TaS_3 was measured separately at Exxon and at the University of California at Los Angeles by different four-probe techniques, both designed to forestall experimental difficulties not encountered under ordinary open-circuit conditions. The two sets of results were similar. In both methods the driving current was injected along the chain axis through silver-paint current contacts at the ends of the sample, and the temperature gradient was applied across an inner pair of voltage contacts in order to eliminate the effects of contact resistance and heat leakage through the thick current leads. Comparison of pulsed and dc resistivities indicated that Joule heating becomes appreciable at roughly thrice the threshold field, and our experiments were confined to applied fields below that limit.

Unless the applied thermal gradient is perfectly symmetric, it engenders a change δT in the average temperature of the sample, and adds to Eq. (1a) a term $(dJ/dT)\delta T$ which can dominate the terms of interest. This effect can be minimized by carefully balancing the thermal gradient, but in practice it is difficult to eliminate entirely. However, whereas Eq. (1a) is even with respect to the applied electric field E_0, the extraneous term is odd. It can therefore be cancelled by retaining only the even part of δE.

At the University of California at Los Angeles this was accomplished by fixing ∇T, applying E_0 as an ac square wave balanced about zero field,

and measuring δE as a dc voltage. The thermal gradient was then reversed and the results averaged. Square-wave frequencies of 50 and 500 Hz gave identical results. Especially at low temperatures and high currents, the silver-paint current contacts were found to be rectifying. They had to be anchored carefully to the same constant temperature in order to avoid large spurious dc signals.

At Exxon the experiment[7] was fully automated. The problem of the current contacts was eliminated by fixing J_0 with a dc constant-current generator, oscillating ∇T by passing a 2- or 5-Hz ac current through a thermoelectric heating element, and detecting the ac thermoelectric voltage δE of the sample with a lock-in amplifier. To obtain the even part, the lock-in output was stored digitally and averaged over opposite polarities of the applied current. No frequency-dependent or out-of-phase components were observed.

The zero-field thermopower of TaS_3 measured by both groups[8] as a function of temperature agrees with earlier results.[9] It is positive throughout the temperature range of interest, rising with cooling from small metallic values above the Peierls transition to a peak of 850 μV/K near 100 K. Its overall behavior is consistent with simple single-particle contributions, taking account of the temperature-dependent Peierls gap.[8]

As the applied field is increased, the measured thermopower $S(E_0)$ remains constant at first, then drops sharply at threshold, and continues to decrease monotonically. The behavior at 150 K measured at Exxon and shown in Fig. 1 is typical of the temperature range. Also plotted in the figure is the variation of the differential resistivity $[J'(E_0)]^{-1}$. The close similarity between the two functions suggests that the variation in $S(E_0)$ is dominated by the denominator of Eq. (3), with the Onsager coefficient $L_{12}(E_0)$ nearly independent of field. This would be the case if Eq. (4) applied and the Ohmic single-particle contribution to the numerator of $S(E_0)$ remained constant while the non-Ohmic charge-density-wave contribution remained small.

To make these remarks quantitative we smooth the two sets of data in Fig. 1 and combine them to obtain $L_{12}(E_0)/T^2$ according to Eq. (3), and subtract the zero-field Ohmic value. The result, multiplied by TE_0, is according to Eq. (7) the excess Peltier heat current associated with non-Ohmic conduction.

It is plotted against the non-Ohmic part of the electrical current for several temperatures in Fig. 2.

Beyond threshold, the excess Peltier heat current is closely proportional to the excess electrical current. This result divides the Peltier current into two effectively independent parts, one proportional to the Ohmic current J_1 and the other to the non-Ohmic current J_2, as in Eq. (9). The slope of the linear plots of Fig. 2 is then Π_2, the Peltier coefficient of J_2.

Above 150 K, Π_2 remains zero within our experimental error despite an increase of better than an order of magnitude in the differential

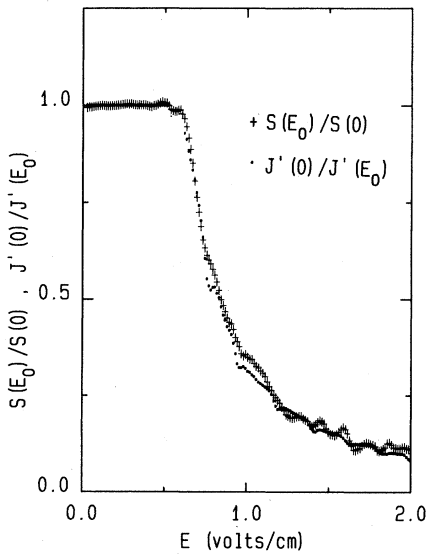

FIG. 1. Field-dependent thermoelectric power $S(E_0)$ and differential resistivity $[J'(E_0)]^{-1}$ of TaS_3 at 150 K.

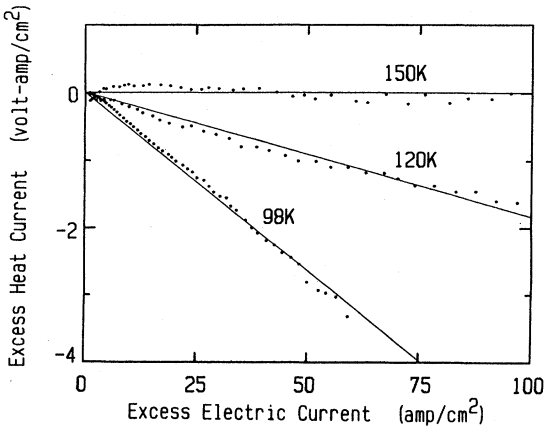

FIG. 2. Nonlinear Peltier heat current vs nonlinear electric current in TaS_3 at various temperatures.

conductivity as the field is raised. We estimate that the experiment is capable of detecting differences in Π_2 as small as 0.5 mV, or about 1% the Ohmic coefficient Π_1. At lower temperatures, Π_2 assumes negative values which rise with cooling to as much as −50 mV at 98 K. Surveys of several samples show some variation in the low-temperature values, but not in the qualitative temperature dependence or the linearity of the data.

The smallness of Π_2 demonstrates that at high temperatures, the non-Ohmic electrical current carries little or no heat. Its independence of E_0 demonstrates that at all temperatures, the energy distribution of the non-Ohmic current carriers is unchanged by the applied field.

These findings are inconsistent with non-Ohmic conduction by any mechanism which depends upon uncompensated field-induced charge excitations such as hot electrons, or upon field-dependent mobilities in a fluid of electrons or discommensurations. On the other hand, they appear fully consistent with conduction by a sliding ordered structure, such as a charge-density wave or a lattice of discommensurations, which carries no intrinsic Peltier heat but acquires appreciable phonon drag at low temperatures. The heat current dragged is inherently proportional to the dragging electric current, and its variability among samples can arise from variability in the phonon mean free path. We are not aware of a more direct demonstration that the non-Ohmic current is borne by a condensate.

Preliminary experiments performed at Exxon indicate that both $NbSe_3$ and $(TaSe_4)_2I$ behave much like TaS_3. In particular, for $NbSe_3$ at low temperatures our raw data agree with Ref. 3, but analysis suggests that Π_2 is negative, independent of applied field, and similar to that of TaS_3 in the phonon-drag regime. In the higher-temperature charge-density-wave state of $NbSe_3$, not studied in Ref. 3, Π_2 is zero. These experiments will be reported elsewhere in more detail.

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