Thermopower behavior in $La_2Mo_2O_7$: A possible charge-density-wave system with partial Fermi-surface nesting

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Thermoelectric power and resistivity measurements were carried out on the bronzelike compound $La_2Mo_2O_7$ in the temperature range 95–210 K. The observed temperature dependence was analyzed using an expression of the type $-\alpha T+\beta/T$ to separate the metallic and semiconducting contributions to the thermopower. Such an analysis should be valid for other similar systems where there is only a partial Fermi-surface nesting below the Peierls transition.

A new bronzelike compound, $La_2Mo_2O_7$, has recently been synthesised by the method of fused-salt electrolysis.[1] Crystal structure studies[2] on this compound show that its basic building blocks are Mo_2O_{10} units which in turn are made up of two edge-sharing MoO_6 octahedra. These basic units then share corners to build up a two-dimensional (2D) MoO network in the ac plane, as shown in Fig. 1. The Mo-Mo distance in the Mo_2O_{10} units is 2.478 Å, which is compatible with a double bond between Mo atoms. These units are linked by La ions in the *b* direction and the oxidation states are assigned as $(La^{3+})_2(Mo_2O_7^{6-})$ with oxidation state +4 for the Mo ions.

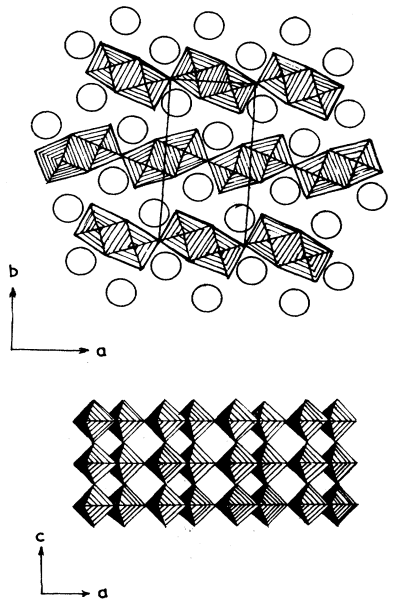

FIG. 1. Structure of La_2MoO_7 projected in the *ab* and *ac* planes. Open circles are La ions and shaded units are MoO_{10} clusters formed by two edge-sharing MoO_6 octahedra (Ref. 2).

Transport properties of this compound[2,3] show sample dependent resistivities at room temperature of about 10^{-3} Ω cm along the *c* direction and an order of magnitude higher along *a* and *b* directions. Below 125 K the resistivity shows an increase and $(1/\rho)d\rho/dT$ plot shows a large negative peak at this temperature indicative of a Peierls-like transition. The temperature variation of the magnetic susceptibility shows a large decrease in the susceptibility at 125 K consistent with the transition seen in resistivity data. In the present work we report thermoelectric power measurements on this compound to further understand the nature of this Peierls transition.

Thermoelectric power measurements were made in the temperature range 95–210 K using an experimental setup described in detail earlier.[4] A temperature difference of about 1–1.5 K was maintained across two ends of the sample and the thermo emf was measured on a Keithley 181 nanovoltmeter. Electrical contacts to the sample were made by first sputtering gold on the ends using a suitable mask and subsequently applying Ag paint. Stable contacts with negligible contact resistance were achieved in this way. Four-probe resistivity measurements were also made on the same sample on which thermopower measurements were done.

The measured resistance for the sample $[R(T)/R(230)]$ in the temperature range 65–180 K is shown in Fig. 2. The slope of resistivity versus temperature curve first starts changing at 140 K and $d\rho/dT$ shows a dip at 125 K, which may be due to a charge-density-wave (CDW) transition. The magnitude of resistivity increase between 180 and 60 K is typically of the same order (2.5–3 times) as observed in other samples of this compound.

The measured thermoelectric power (S) is small and negative (~ -1.3 μV/K) in the temperature range 125–210 K in conformity with metallic behavior, as de-

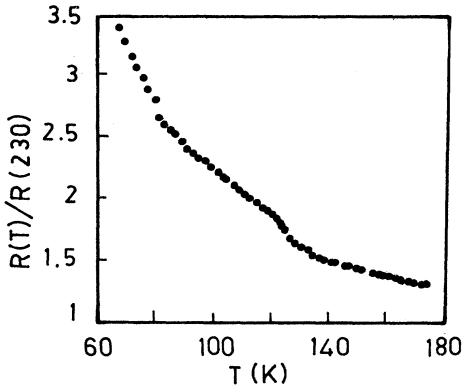

FIG. 2. Temperature dependence of normalized resistance $R(T)/R(230)$ measured along the c axis. The CDW onset temperature is 125 K.

duced from resistivity measurements.[3] Below 125 K, $|S|$ starts decreasing rapidly to even smaller values and becomes positive below 115 K. This behavior is similar to that of the purple bronze, $K_{0.9}Mo_6O_{17}$,[5] molybdenum oxide bronze η-Mo_4O_{11},[6] and other systems where there is only a partial nesting of the Fermi surface at T_p and the transition to higher resistivity is described as a metal-to-metal transition. The understanding of these systems is not as simple as that of the canonical systems such as TaS_3 and $(TaSe_4)_2I$, where the conductivity behavior changes from metallic to insulating due to the opening of a CDW gap at the Fermi surface.[7,8]

In quasi-low-dimensional systems, where there is only a partial nesting of the Fermi surface below T_p, one expects to observe the combined effect of two types of behavior:

(i) Electrical and thermal transport from electron and hole carriers created by thermal excitation of electrons across the CDW gap in directions in which there is Fermi-surface nesting.

(ii) Metallic transport from those regions of the Fermi surface which still lie in partly filled bands. The thermopower behavior for each of these contributions is distinctly different.

In the first case the thermopower behavior is like that of semiconductors and if one retains the familiar nomenclature of E_c and E_v as the bottom of the conduction band and top of the valence band, respectively, the expression for thermopower is[9]

$$S=\frac{k}{e}\left(\frac{1-b}{1+b}\frac{E_c-E_v}{2kT}+\frac{1}{1+b}A_v-\frac{b}{1+b}A_c\right), \quad (1)$$

where $b=\sigma_e/\sigma_c$ and the constants A_v, A_c depend on the actual density of states and mobilities in the valence and conduction bands, but can be assumed to be temperature independent. If we make a simplifying assumption that the temperature-independent second and third terms are approximately the same magnitude (i.e., $A_v \simeq A_c$ and $b \simeq 1$) these terms will not contribute appreciably to S and expression (1) reduces to a simple form

$$S=\frac{k}{e}\left(\frac{1-b}{1+b}\frac{E_c-E_v}{2kT}\right). \quad (2)$$

The justification for this assumption will be given later. The temperature dependence of the thermopower contribution from those parts of the Fermi surface which get nested as a result of CDW formation is therefore expected to be inversely proportional to temperature with a constant of proportionality related to the CDW gap.

In the second case, the thermopower is metallic and is of the form[10]

$$S=-\frac{\pi^2k^2T}{3e}\left(\frac{\partial}{\partial E}\ln(E)\right)_{E=E_F}, \quad (3)$$

which gives for a spherical Fermi surface

$$S=-\frac{\pi^2k^2T}{3e}\left(\frac{1}{A}\frac{\partial A}{\partial E}+\frac{1}{l}\frac{\partial l}{\partial E}\right)_{E=E_F}, \quad (4)$$

where A is the area of the Fermi surface and l is the mean free path. Even when the Fermi surface is not spherical, it has been suggested that to a first approximation one can divide the Fermi surface into two or more essentially spherical regions and the general expression can be written as

$$S=-\frac{\pi^2k^2T}{3e}\frac{\partial}{\partial E}\left(\sum_i l_iA_i\right)\Big/\sum_i l_iA_i, \quad (5)$$

where l_i and A_i are the mean free paths and surface areas corresponding to these regions. If $\partial A/\partial E$ and $\partial l/\partial E$ are positive, as is often the case for normal Fermi surfaces (the area of the Fermi surface increases with increasing E and the more energetic the electron the less likely it is to be scattered, giving a longer mean free path), expression (4) gives a negative thermopower for metals with a linear temperature dependence.

In a system such as $La_2Mo_2O_7$ where both metallic and semiconducting behaviors are present, one should then be able to express the thermopower in the form

$$S=-\alpha T+\beta/T, \quad (6)$$

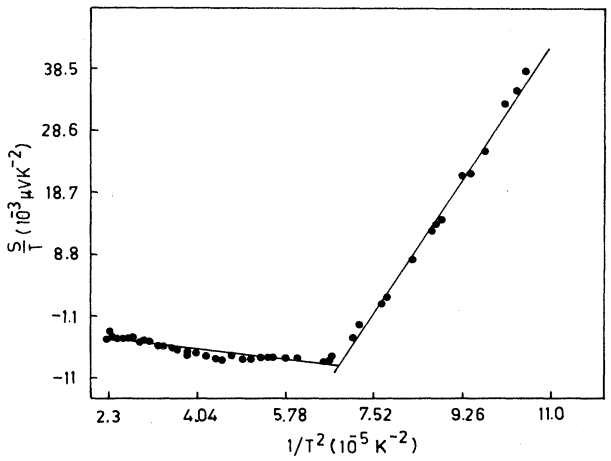

FIG. 3. Temperature dependence of thermoelectric power $S(T)$ plotted in the form S/T vs $1/T^2$ to separate the metallic and CDW contributions. The slope β and intercept α, as defined in Eq. (6), are estimated from this plot. The curve crosses zero at $T=115$ K.

and get an estimate of metallic- as well as the semiconductor-type contribution by plotting S/T versus $1/T^2$. Figure 3 shows such a plot from the $La_2Mo_2O_7$ system. The proportionality constant for metallic contribution comes out to be 2.7×10^{-3} $\mu V/K^2$ above $T_p=125$ K and 105×10^{-3} $\mu V/K^2$ below T_p. This large increase in the coefficient α below T_p can be explained as a result of the loss of portions of the Fermi surface area due to nesting as well as a decrease in mean free path consequent to the opening of the CDW gap and additional scattering by the lattice modulation [see Eq. (4)].

The slope β obtained from thermopower data changes from -0.97×10^2 μV above T_p to 12.64×10^2 μV below T_p. The change in magnitude as well as sign are significant. The coefficient β is related to the gap $\Delta=E_c-E_v$ and $b=\sigma_e/\sigma_h$ according to Eq. 2

$$\beta=\frac{k}{e}\left(\frac{1-b}{1+b}\frac{\Delta}{2k}\right). \tag{7}$$

The slope of thermopower data therefore gives an estimate of the quantity $[(1-b)/(1+b)](\Delta/e)$ as 2.5 meV below the Peierls transition. This small value is consistent with our earlier assumption of $b\simeq1$ because typical CDW gaps obtained in other materials are larger (typically 10^{-2}–10^{-1} eV).

Above T_p, the slope is small and negative but nonzero. This implies a semiconductive type behavior above T_p. The explanation for this can be found by looking at band-structure calculations of $La_2Mo_2O_7$ carried out by Whangbo and Canadell.[11] These calculations show that there are two partially filled d-block bands in this material labeled σ_+ and δ_1. The bottom of the next higher band δ_2 lies above but very close to the Fermi level (0.018 eV above). This would lead to excitation of electrons from the δ_1 to the δ_2 band even above T_p and a thermopower behavior typical of carriers excited across a gap. The slope is negative, as expected for electrons.

In conclusion, we find that the temperature dependence of thermopower can be consistently described by an expression of the type $S=-\alpha T+\beta/T$ for CDW systems that have a partial Fermi-surface nesting below the Peierls transition. The metallic and semiconductive contribution can be separated by plotting S/T vs $1/T^2$. This analysis should also be applicable to other similar systems.

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