Frequency-Dependent Thermoelectric Power in $K_{0.3}MoO_3$

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We have measured the frequency dependence of the thermoelectric power, S, in the charge-density-wave state of $K_{0.3}MoO_3$. A strong frequency dependence with both real and imaginary components was observed, and we interpret our finding in terms of a two-fluid model. We also discuss the criteria of observability of this novel phenomenon in other materials where the electrical conductivity is frequency dependent.

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The electrical transport properties of the charge-density-wave (CDW) ground state have been thoroughly explored in various inorganic linear-chain compounds.[1] The electrical conductivity, σ, is both frequency and electric field dependent, and the behavior has been analyzed by assuming a two-fluid model where the current is carried by both the condensed and uncondensed electrons. This two-fluid model has been successful in analyzing the main features of the nonlinear conductivity. However, Hall-effect measurements[2] in the nonlinear conductivity region indicate the breakdown of such a two-fluid model and point to deviations from a description which assumes two independent current-carrying entities.

The nonlinear electrical conductivity is also accompanied by changes of the other transport coefficients. The thermoelectric power was found to be electric field dependent,[3] and has also been analyzed first by assuming a two-fluid picture with the condensate carrying electrical current but no heat. Subsequent experiments, extending the applied electric field range to high fields, demonstrated that the heat carried by the condensate is proportional to the heat generated by the CDW transport.[4] Such a process requires the boil-off of condensed electrons, and consequently violates the assumptions of the two-fluid model. In the high-temperature-gradient (instead of high electric field) limit nonlinear phenomena were observed,[5] and successfully interpreted in a two-fluid model as due to nonlinear CDW currents induced by the high thermoelectric fields of the normal carriers.

In this paper we report our experiments on the frequency-dependent thermoelectric power, S, in the material $K_{0.3}MoO_3$. At low temperatures, where the electrical conductivity is frequency dependent in the low audio spectral range, we find that S is also frequency dependent, and has both in-phase and out-of-phase components, which we call ReS and ImS, respectively. Aside from being the first observation of a frequency-dependent thermoelectric effect in any solid, our experiments can also be analyzed in terms of two contributions to both the conductivity and the thermoelectric power. We also discuss the observability of the phenomenon in various materials where the conductivity is frequency dependent.

$K_{0.3}MoO_3$ undergoes a CDW transition at $T_P = 180$ K.[6] Below T_p, the conductivity has all the signatures of a dynamical charge-density-wave transport. The low-frequency conductivity (a quantity directly related to our experiments) has been explored earlier.[7] The conductivity becomes frequency dependent at progressively lower and lower frequencies with decreasing temperature, mainly due to the progressive freezing out of the normal—and thus frequency-independent—component to the electrical conduction. The thermoelectric power has also been investigated by employing conventional techniques. S increases upon undergoing the CDW transition, then displays a maximum around 30 to 40 K, and decreases below this temperature. This behavior is characteristic of $S(T)$ measured in other materials with a CDW ground state.[8]

We have employed an ac technique to measure the frequency dependence of the thermoelectric power in the range of 0.1 to 20 Hz. To produce the time-varying temperature gradient, we have used the following setup. The two ends of a long, thin $K_{0.3}MoO_3$ single crystal (length: 3 mm, cross section: 700×75 μm) were attached to the tungsten spirals of two subminiature light bulbs as heaters by GE varnish. A differential thermocouple, consisting of 7-μm-diam Chromel and Constantan wires was glued to the sample surface opposite to the heaters to monitor the temperature gradient along the sample. Two copper-plated electrode contacts were applied to measure the thermal voltage and the conductivity of the sample. The heaters were driven by digitally synthesized sinusoidal currents shifted by $\pi/2$ in phase with respect to each other, so that the total heating power was constant while the temperature gradient varied sinusoidally. The amplitude of the temperature difference between the sample ends was typically 0.1 K or smaller. The thermal voltages on the sample and on the thermocouple were recorded by a digital oscilloscope. The magnitude and phase of the sample thermoelectric power were inferred by comparison of the recorded signals.

At room temperature no reliable data were obtained above 5 Hz because of the thermal inertia of the system. With decreasing temperature, however, the thermal inertia decreased as monitored by the diminishing phase shift between the heater current and the thermocouple signal. Below 50 K, the thermocouple signal was frequency independent in the whole frequency range investigated (0.1 to 20 Hz).

In Fig. 1 the temperature dependence of the magnitude of the thermoelectric power, $|S|$, is shown at three selected frequencies: 0.1, 1, and 20 Hz (the thermopower is negative at all temperatures below the CDW transition). In the temperature range of 30 to 50 K, the thermoelectric power is frequency independent, and its magnitude agrees with previous measurements. We consider this observation as a further verification of the experimental arrangement we have employed. Below 30 K, a strong frequency dependence develops. At the lowest frequency, 0.1 Hz, S further increases with decreasing temperature down to the lowest temperature investigated. At higher frequencies, however, S reaches a maximum between 20 and 30 K, below which it drops rapidly. Together with the frequency variation of S, the phase of the thermal voltage lags behind the temperature gradient. Instead of a single real value, the thermoelectric power is now characterized by an in-phase component, ReS, and an out-of-phase component, ImS.

In Fig. 2, the frequency dependence of ReS and ImS are shown at two different temperatures. The 22.1-K data show a crossover from a regime of frequency independent ReS, and small, increasing ImS at low frequencies, to a strongly decreasing ReS and ImS at high frequencies. The crossover frequency is approximately 2 Hz. At 19.5 K the crossover is at a lower frequency and, in the measured frequency range, the data are well characterized by a power law, $S(\omega)\propto(i\omega)^{-\alpha}$, with $\alpha=0.36$.

We have also measured the frequency-dependent conductivity of the sample at the same frequencies and temperatures. No frequency dependence has been observed in the temperature range where the thermoelectric power is frequency independent, but a frequency-dependent conductivity is found at temperatures where S is frequency dependent. For later comparison, in Fig. 3 we show the inverse of the conductivity, $\sigma(\omega)^{-1}$, at the temperatures of the data of Fig. 2. At the higher temperature, $\sigma(\omega)^{-1}$ shows the same crossover-type behavior as S with the same crossover frequency, while at the lower temperature the conductivity is again well described by the power law $\sigma(\omega)^{-1}\propto(i\omega)^{-\alpha}$, with the same exponent.

The starting point of our analysis is a two-fluid model of the normal (uncondensed) and CDW electrons. In this model the total conductivity and thermoelectric power are

$$\sigma=\sigma_n+\sigma_{\mathrm{CDW}}, \tag{1a}$$

$$S=\frac{S_n\sigma_n+S_{\mathrm{CDW}}\sigma_{\mathrm{CDW}}}{\sigma_n+\sigma_{\mathrm{CDW}}}, \tag{1b}$$

where the subscripts n and CDW refer to the normal and CDW contributions, respectively. The frequency dependence of the conductivity is attributed to the CDW component, $\sigma_{\mathrm{CDW}}(\omega)$, with no contribution at zero frequency. The normal component, σ_n, is frequency indepen-

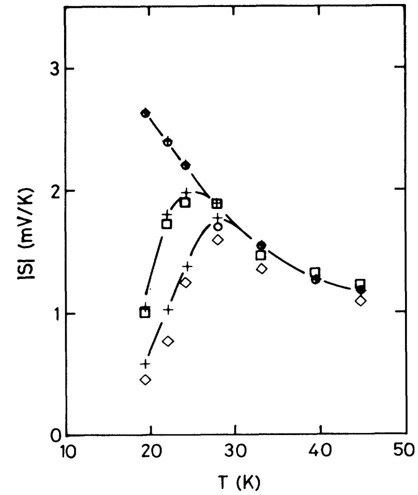

FIG. 1. Temperature dependence of the magnitude of thermoelectric power at different frequencies: Circles, $\omega/2\pi=0.1$ Hz; squares, $\omega/2\pi=1$ Hz; diamonds, $\omega/2\pi=20$ Hz. Note that the thermoelectric power is negative at all temperatures in the CDW state. The crosses are the prediction of Eq. (1b) with $S_{\mathrm{CDW}}=0$, $\sigma_n=\sigma(0.1\text{ Hz})$, $S_n=S(0.1\text{ Hz})$.

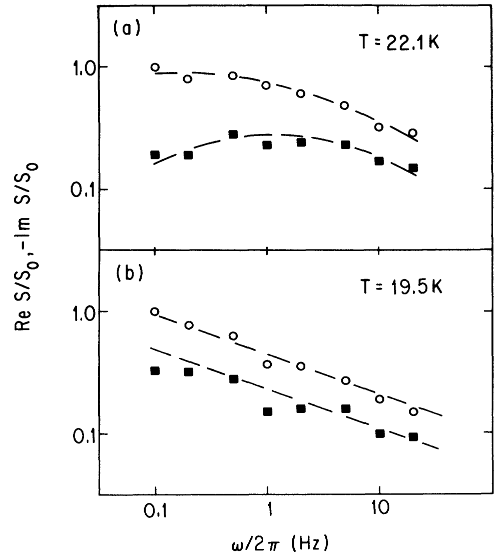

FIG. 2. Frequency dependence of the real part (circles) and imaginary part (squares) of the thermoelectric power, S, normalized to the real part measured at $\omega/2\pi=0.1$ Hz, S_0. (a) $T=22.1$ K, $S_0=-2.35$ mV/K; the dashed lines are a guide to the eye. (b) $T=19.5$ K, $S_0=-2.6$ mV/K; the dashed lines are the power law $S\propto(i\omega)^{-\alpha}$ with $\alpha=0.36$.

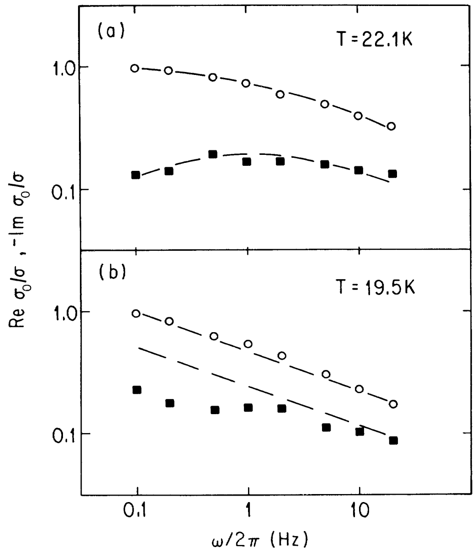

FIG. 3. The frequency dependence of the inverse conductivity, $\sigma(\omega)^{-1}$, at the same temperatures as in Fig. 2: Real part, circles; imaginary part, squares. Both quantities are normalized to the real part measured at $\omega/2\pi=0.1$ Hz, σ_0. (a) $T=19.5$ K, $\sigma_0=6.6\times10^{-5}\ \Omega^{-1}\text{cm}^{-1}$, the dashed lines are a guide to the eye. (b) $T=22.1$ K, $\sigma_0=7.9\times10^{-6}\ \Omega^{-1}\text{cm}^{-1}$, the dashed lines are the power law $\sigma^{-1}\propto(i\omega)^{-\alpha}$ with $\alpha=0.36$, as in Fig. 2.

dent. Thus the dc thermoelectric power is simply that of the normal electrons. With increasing frequency, however, $\sigma_{\text{CDW}}(\omega)$ increases, and becomes comparable to the normal conductivity σ_n. At these frequencies the thermoelectric power given by (1b) is also expected to become frequency dependent.

In order to analyze our experimental results, we assume that there is no direct CDW contribution to S ($S_{\text{CDW}}=0$), and the only source of the frequency dependence is $\sigma_{\text{CDW}}(\omega)$ in the denominator of Eq. (1b). As $S_n\sigma_n$ is independent of frequency, $S(\omega)$ and $\sigma(\omega)^{-1}$ should go hand in hand. This is precisely what is observed (see Figs. 2 and 3) demonstrating the validity of this approach. The close covariation of both the real and imaginary parts of $S(\omega)$ and $\sigma(\omega)^{-1}$ proves that the main source of the frequency dependence of the thermoelectric power is a frequency-dependent contribution to the conductivity coming from the response of the charge-density waves. In this picture the thermal voltage developed by one fluid (normal electrons) is shunted by the current carried by the other one (CDW's). As a further verification of the above picture, we also show the prediction of Eq. (1b) with the assumption of $S_{\text{CDW}}=0$. Again, there is a good agreement with the $|S|$ data measured at different temperatures.

The assumption of $S_{\text{CDW}}=0$ implies that the alternating CDW current contributes to the charge transport only, but not to the heat transport. Previous studies have shown that in the high-field, nonlinear regime, the dc CDW current does carry entropy,[4] in apparent conflict with our conclusion. However, the mechanism of entropy production may be fundamentally different for a pinned mode which oscillates about the equilibrium position, and for a condensate which executes large-amplitude translational motion. Consequently, the different conclusions arrived at by conducting the experiments under different circumstances are *a priori* not contradictory.

Our analysis relies on the applicability of the two-fluid model described by Eq. (1). Within this framework, the thermoelectric power of each fluid is frequency independent, and the resulting S varies with frequency due to the frequency dependence of the conductivity. In other materials, however, where the electric current is carried by one type of carrier, a possible frequency-dependent conductivity does not lead automatically to a frequency-dependent thermoelectric power. For single-particle transport, the Peltier coefficient, $\Pi=ST$, the ratio of the heat and charge transported by the carrier, is expected to be frequency independent in the first approximation. In a more detailed picture, S may vary with ω depending on the scattering mechanisms, density of states, etc., but no $S(\omega)\sigma(\omega)=\text{const}$ law is expected in general.

In conclusion, we have reported the first observation of a frequency-dependent thermoelectric power in any solid. The observation is related to the frequency-dependent conductivity which occurs in the range of our experiments. Crucial to the observation appears to be a two-fluid description with the measured S being the weighted average of the thermoelectric coefficients of the condensed and uncondensed electrons, each of them giving a frequency-independent contribution. These assumptions account well for the frequency dependence of both the real and imaginary parts of the thermoelectric power.

Aside from charge-density-wave materials, other solids also may display frequency-dependent conduction at low frequencies. Our analysis suggests that if the frequency-dependent conductivity is due to one type of carrier, such as in most materials where $\sigma(\omega)$ is due to disorder effects, S is not necessarily frequency dependent. Thermoelectric measurements in some of such materials would be of great interest.

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[1] For a recent review see *Electronic Properties of Inorganic Quasi-One-Dimensional Materials,* edited by P. Monceau (Reidel, Dordrecht, 1985).

[2] S. N. Artemenko, E. N. Dolgov, A. N. Kruglov, Yu. I.

Latshyev, Ya. S. Savitskaya, and V. V. Frolov, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 258 (1984) [JETP Lett. **46**, 891 (1984)].

[3] J. P. Stokes, A. N. Bloch, A. Jánossy, and G. Grüner, Phys. Rev. Lett. **52**, 372 (1984).

[4] G. Mihály, G. Kriza, and G. Grüner, Solid State Commun. **68**, 993 (1988).

[5] W. Beyerman, L. Mihály, and G. Grüner, Phys. Rev. Lett. **56**, 1489 (1986).

[6] For a review of the properties of $K_{0.3}MoO_3$ see C. Schlenker and J. Dumas, in *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures,* edited by J. Rouxel (Reidel, Dordrecht, 1986), p. 135.

[7] R. J. Cava, R. M. Fleming, P. Littlewood, E. A. Rietman, L. F. Schneemeyer, and R. G. Dunn, Phys. Rev. B **30**, 3228 (1984); Wei-yu Wu, L. Mihály, G. Mozurkewich, and G. Grüner, Phys. Rev. B **33**, 2444 (1986).

[8] R. Allgeyer, B. H. Suits, and F. C. Brown, Solid State Commun. **43**, 207 (1982); D. C. Johnston, J. P. Stokes, P. L. Hsieh, and G. Grüner, J. Phys. (Paris), Colloq. **44**, C3-1749 (1983); B. Fisher, Solid State Commun. **43**, 227 (1983).