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Thermopower and the electron-phonon interaction in high-T_c superconductors

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The temperature dependence of metallic diffusion thermopower arising from electron-phonon enhancement is calculated for high-T_c superconductors, in particular La-Sr-Cu-O. The potential usefulness of thermopower is demonstrated by a similar calculation for high-resistivity Chevrel superconductors, which gives an excellent description of their total thermopower and provides evidence for a normal electron-phonon interaction. An analysis of diffusion thermopower in present measurements on metallic high-T_c superconductors is prevented by phonon drag or other effects; measurements on more disordered samples are needed to permit a comparison with our calculations and help determine the role of the electron-phonon interaction in these systems.

One of the most interesting and controversial questions concerning the new high-T_c superconductors is the role (if any) played by the electron-phonon interaction in producing the remarkable superconducting behavior. On the one hand, some theorists start from the premise that a wholly new electronic mechanism is required, and ascribe the linear temperature dependence of the normal-state resistivity often seen above the transition temperature T_c to mechanisms different from the usual electron-phonon scattering.[1,2] On the other hand, recent isotope effect measurements suggest that the superconductivity may involve the electron-phonon interaction,[3] and some aspects of transport measurements appear consistent with ordinary metallic behavior.[4–7]

It is therefore worthwhile to make use of all possible probes of the electron-phonon interaction in these materials. It has been known for some years[8] that the electron-phonon interaction enhances metallic diffusion thermopower at low temperatures, but normally this effect is obscured by the presence of an additional contribution owing to the phonon-drag effect. However, electron and phonon mean-free paths are sufficiently small in amorphous metals[9] and high-resistivity Chevrel compounds[10] to essentially eliminate phonon drag, leaving the electron-phonon enhancement of thermopower clearly visible.[11,12] In fact, we see [13] for the first time the full decay with temperature of the electron-phonon enhancement. A great advantage of our analysis of electron-phonon enhancement is that it does not require the magnitude of the diffusion thermopower to be calculated theoretically, which is extremely difficult.[10]

In this Rapid Communication we investigate thermopower as a potential probe of the electron-phonon interaction in high-T_c superconductors, making calculations of the expected diffusion thermopower for different Eliashberg functions $\alpha^2F(E)$. To demonstrate the utility of thermopower analysis when certain conditions are met (namely, the absence of phonon-drag, magnetic, and nonmetallic effects), we make a similar calculation for Chevrel compounds. We obtain excellent agreement with the experimental diffusion thermopower using an electron-phonon interaction of the size indicated by a McMillan-type equation, which provides evidence for a normal electron-phonon interaction in these compounds rather than more exotic models such as that proposed by Yu and Anderson.[14]

We suggest an analogous analysis for the new superconductors, which, like the sintered Chevrel-phase superconductors,[15] have very high resistivities above their transition temperature T_c. It is pointed out that the thermopower will be highly nonlinear at low temperatures if the electron-phonon interaction is large, even in the absence of phonon drag. Some comments are made on current thermopower measurements on high-T_c superconductors, and the need for measurements on more disordered systems to permit comparison with our calculations is pointed out.

Because it depends approximately on the derivative of a conductivitylike function at the Fermi level, diffusion thermopower is enhanced[8] at low temperatures by the $(1+\lambda)$ factor, where λ is the electron-phonon interaction parameter, even though conductivity itself is not. The calculation of the temperature dependence of metallic diffusion thermopower, including additional effects arising from velocity and relaxation-time renormalization and from higher-order diagrams (the Neilsen-Taylor effect), gives [13]

$$S_d = S_b[1+a\lambda\bar{\lambda}_s(T)] \; , \tag{1}$$

where S_b is the bare diffusion thermopower, a is a constant (equal to unity in the absence of velocity and relaxation time renormalization and higher-order diagram effects), and $\bar{\lambda}_s(T)$ is the normalized temperature-dependent enhancement of thermopower:

$$\bar{\lambda}_s(T) = \frac{\int_0^\infty dE\, E^{-1}\alpha^2F(E)G_s(E/k_BT)}{\int_0^\infty dE\, E^{-1}\alpha^2F(E)} \; . \tag{2}$$

Here $G_s(y)$ is the universal function evaluated previously.[13]

When one scattering mechanism dominates, and if the density of states does not vary too sharply near the Fermi level, the bare thermopower S_b will be approximately linear in temperature T for nonmagnetic metals. The other important requirement for the observation of the electron-phonon enhancement effect in thermopower is the absence of the phonon-drag term, which in normal crystals is the dominant contribution to thermopower at intermediate temperatures. Since crystalline thermopower rarely bears any resemblance to simple linear behavior and is notoriously difficult to interpret, we spend some time demonstrating that the situation in metals with short electronic mean-free paths is much simpler.

The necessary conditions are well satisfied in nonmagnetic glassy metals, and the measured thermopowers on these systems[16] are almost all in good agreement with predictions from (1) and (2). Further, the size of the enhancement effect at low temperatures is approximately equal to $(1+\lambda)$ with λ estimated from the superconducting transition temperature (where observed) using the McMillan formula.[11,12] This leads to the conclusion that the constant a is approximately unity and the energy renormalization effect is normally dominant (although this is not the case when S_b is very small because the absolute size of the enhancement effect is then also very small[13]).

Another class of material in which the conditions for the observation of the electron-phonon enhancement of thermopower are met are the high-resistivity Chevrel-phase compounds[15] $Cu_{1.8}Mo_6S_{8-y}Se_y$ and $Cu_{1.8}Mo_6S_{8-y}Te_y$. These systems provide a very nice example, because one can see the progressive suppression of a negative phonon-drag peak in $Cu_{1.8}Mo_6S_{8-y}Se_y$ as residual resistivity is increased by increasing the Se content, leaving for $y=6$ and 7 a positive diffusion thermopower that is linear except for a relatively large enhancement at low temperatures.[10] For these systems, the condition for the absence of phonon drag is approximately $\rho_0 > 0.85\rho_{RT}$, where ρ_0 is the "residual" resistivity (the value just above T_c) and ρ_{RT} the room-temperature resistivity, in which case structural scattering dominates the resistivity and the relative temperature dependence is small.

The input parameters for the calculation of thermopower enhancement are the electron-phonon parameter λ and the Eliashberg function $\alpha^2F(E)$. We make the calculation for the system $Cu_{1.8}Mo_6S_5Te_3$ (the other high-resistivity systems show similar behavior[10,15]). Following the results from glassy metals, especially in view of the relatively large size of thermopower in these systems, the energy renormalization effect is taken as dominant,[10] i.e., $a \approx 1$. If normal electron-phonon theory is applicable, λ can be estimated from the transition temperature $T_c = 4.76$ K using the McMillan formula with the usual Coulomb repulsion parameter $\mu^* = 0.13$ and a Debye temperature $T_D = 210$ K as estimated for $Cu_{1.8}Mo_6SSe_7$ from specific-heat measurements.[15] The result is $\lambda = 0.71$. Alternatively, one can use Fischer's general expression[17] for Chevrel compounds to obtain $\lambda = 0.69$. Thus we take $\lambda = 0.7$. For the shape of $\alpha^2F(E)$, we use the phonon density of states $F(E)$ measured[18] at low temperature in $Cu_2Mo_6S_8$, with α^2 constant or varying as $E^{-1/2}$ as suggested by Lachal, Junod, and Muller.[19] As shown in Fig. 1, the calculated thermopower is not too sensitive to the shape of $\alpha^2F(E)$, the most important parameter being λ.

Figure 1 also shows that the calculated thermopower enhancement is in excellent agreement with the experimental data, which suggest that the usual electron-phonon theory relating λ and T_c works well, and so provides no support for the local phonon model proposed by Yu and Anderson[14] for these materials. We emphasize that the size of λ is indicated rather directly by the ratio of thermopower slopes at low and high temperatures, which is independent of the absolute size of thermopower. Thus the comparison of calculated and observed *enhancement* effects in Fig. 1 is without adjustable parameters. Additional discussion of Chevrel compounds is given in an earlier paper,[10] in which fits were made using Debye-type models for the phonons.

Obviously it would be of great interest to investigate whether the diffusion thermopower of the new high-T_c superconductors follows the same conventional metallic pattern as the Chevrel superconductors. If so, one could estimate the size of electron-phonon coupling by a similar analysis. If not, the inadequacy of the conventional electron-phonon theory would be demonstrated.

We therefore show in Fig. 2 calculations of the diffusion thermopower of high-T_c superconductors using our conventional metallic equations (the calculation is for the normal state—the thermopower in the superconducting state is zero). Two shapes were used for $\alpha^2F(E)$: First, that calculated by Weber[20] for La-Sr-Cu-O for $\lambda = 2.5$, and second, the measured[21] phonon density of states $F(E)$ in $La_{1.85}Sr_{0.15}CuO_4$ with α^2 implicitly taken as constant [$F(E)$ for $YBa_2Cu_3O_7$ is similar,[21] so given the weak sensitivity to the details of $\alpha^2F(E)$, our calculations are also applicable to the Y-based superconductors]. For compar-

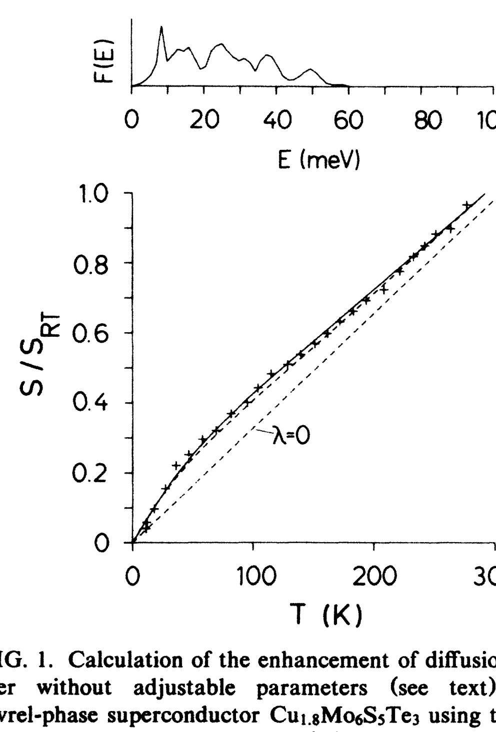

FIG. 1. Calculation of the enhancement of diffusion thermopower without adjustable parameters (see text) for the Chevrel-phase superconductor $Cu_{1.8}Mo_6S_5Te_3$ using the experimental phonon density of states $F(E)$ for $Cu_2Mo_6S_8$ (Ref. 18) (top) and taking α^2 as constant (solid line) or varying as $E^{-1/2}$ (upper dashed line). The crosses show the experimental data from Ref. 15. S_{RT} is the room-temperature value of the thermopower (9.5 μV K^{-1}).

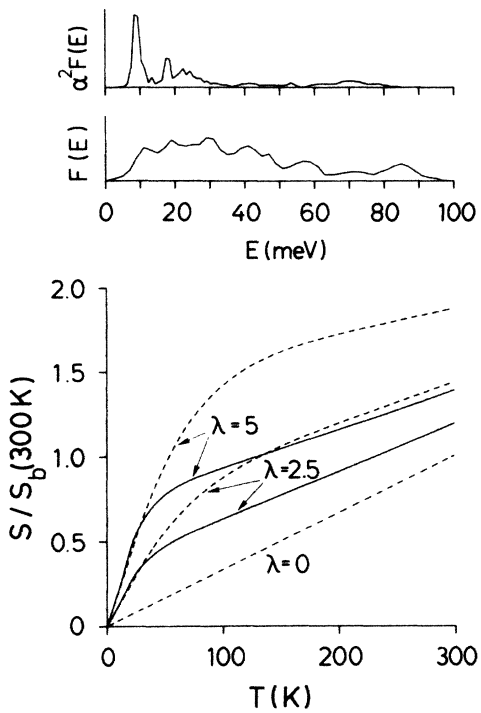

FIG. 2. Calculation of the diffusion thermopower in the normal state of high-T_c superconductors, for different values of the electron-phonon coupling parameter λ. The full lines are for an Eliashberg function $\alpha^2F(E)$ of Weber (Ref. 20) (top), and the dashed lines for $\alpha^2F(E)$ having the same shape as the experimental phonon density of states $F(E)$ in La-Sr-Cu-O (Ref. 21) (middle). S_b is the bare thermopower in the absence of the electron-phonon interaction.

ison, curves for the *same* shape of $\alpha^2F(E)$ are given for both $\lambda=2.5$ and $\lambda=5$.

Clearly, for large values of λ the diffusion thermopower itself becomes highly nonlinear, and the high-temperature part extrapolates to a nonzero value at zero temperature. Because of the greater weight at low energies in Weber's $\alpha^2F(E)$, the enhancement decays more quickly as temperature increases. The effect of velocity and relaxation time renormalization and higher-order diagram effects, if present, would be simply to change the apparent size of λ without changing the temperature dependence of the thermopower.[13]

Further measurements on high-T_c superconductors with shorter mean-free paths are needed before we can compare our calculations with experiment, since present measurements do not allow a determination of the *diffusion* thermopower. Unlike lightly doped $La_{2-x}Sr_xCuO_4$, highly doped samples (e.g., $x=0.25$) do show usual metallic behavior: a relatively small thermopower with a positive peak around 70 K typical of phonon drag and a negative thermopower at high temperatures indicating a negative diffusion thermopower.[4] (It is interesting that the unexpected observation by Uher, Kaiser, Gmelin, and Walz[4] of *positive* Hall coefficient but *negative* diffusion thermopower agrees with the band-theory predictions of Allen, Pickett, and Krakauer[22] for conduction in the xy plane, the dominant conduction direction.) The size of the thermal resistivity[5] suggests a degree of disorder intermediate between that of amorphous metals and normal crystals, which is also consistent with the size of the resistivity T dependence relative to the "residual" resistivity. An investigation of the size of the thermopower peak as a function of disorder would be of considerable interest: If it is phonon drag, it should decrease in size as disorder increases, leaving ultimately a diffusion thermopower that can be compared to our calculation. Note that if there is a sharply varying density of states in the vicinity of the Fermi level, the Mott formula is no longer valid for the evaluation of S_b and the thermopower is no longer linear (especially at high temperatures) even in the absence of the electron-phonon interaction. However, in the strongly disordered systems of interest for comparison with our calculation, density-of-states singularities will tend to be smeared out, and the expected strong anisotropy in crystalline samples[22] will tend to be suppressed.

Turning now to $YBa_2Cu_3O_7$, we find a considerable sample dependence in the thermopower data, and no clear interpretation suggests itself except that the magnitude is metallic. The striking increase of thermal conductivity[5,23] below T_c demonstrates the crucial importance of the electron-phonon interaction for the phonon heat current, so it is not unlikely to play a role in the electrical resistivity and thermopower. The observed sign of the thermopower is positive (but not always[23]). A small peak has been seen above T_c (again not always[24]), possibly a phonon-drag peak truncated at a temperature near 90 K by the onset of of the superconductivity,[5] although the sharpness in some observations suggests instead an unusual precursor effect of the superconductivity.[5,25] Above about 150 K, the temperature variation of S is small, and it usually extrapolates to positive values at zero temperature (which would be consistent with an enhanced positive diffusion thermopower). A downturn in S is seen in some measurements[5,25] above about 240 K, the origin of which is obscure. It may be that the cancellation of larger thermopower contributions from different bands or directions makes interpretation difficult, or other effects in strongly correlated systems come into play. Nevertheless, measurements on samples with increased disorder (e.g., by irradiation) would be of interest to check whether a simpler thermopower similar to our calculation emerges for analysis. (If the behavior differs from our calculation, this would also be an important conclusion indicating a clear difference from the Chevrel superconductors.) If T_c is reduced as disorder increases, it would still be helpful in understanding the origin of the superconductivity to investigate the electron-phonon interaction in these lower-T_c samples, which would have the advantage that any electron-phonon enhancement would be seen to lower temperatures. In view of the controversy over the origin of the linear resistivity behavior, it would also be of interest to check whether the temperature dependence of resistivity in more disordered systems disappears as in amorphous metals.

If other enhancements are present,[26] the electron-phonon enhancement may still be distinguishable from its decay with temperature on the scale of the Debye temperature.

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