

Electron-phonon interaction and thermopower nonlinearities in Chevrel-phase compounds

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We show that previously reported measurements for the Chevrel compounds $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ and $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Te}_y$ provide evidence for electron-phonon enhancement of thermopower, when scattering is sufficiently large to suppress phonon drag. This enhancement effect is similar to that hitherto seen in glassy metals, and is in agreement with theoretical calculations. The apparent sizes of the enhancement ($\lambda \lesssim 1$) are consistent with estimates from the McMillan formula using usual parameter values, in contrast to the unusually large values of λ and Coulomb repulsion μ^* recently suggested for similar systems.

I. INTRODUCTION

The electron-phonon interaction in the *A15* and Chevrel-phase compounds has always been of particular interest because of their high superconducting transition temperatures. Recently, the unusual properties of these materials have led to novel theoretical suggestions. Anderson *et al.*¹ suggested that localization enhanced the Coulomb repulsion μ^* , leading to the general degradation of superconducting transition temperature T_c as resistivity increases that is observed experimentally. Though not directly related to the work of Anderson *et al.*, a proposal was made by Schachinger *et al.*² that the properties of the Chevrel compound $\text{Cu}_2\text{Mo}_6\text{S}_8$ could be accounted for by a model involving a large value of μ^* (about 0.6) and a correspondingly large electron-phonon enhancement λ (about 2.2), in contrast to the earlier model³ with more conventional values for these parameters ($\mu^* \sim 0.1$ and $\lambda \sim 1$).

In another development, Yu and Anderson⁴ proposed a local-phonon model of strong electron-phonon interaction, involving very large values of the electron-phonon coupling λ , that could account for the saturation of resistivity and temperature dependence of susceptibility above about 200 K in strong electron-phonon coupling compounds. Matsuura and Miyake⁵ pointed out the similarity of the unusual properties of these materials to those of heavy-fermion systems. They suggested a heavy-fermion band could arise in the *A15* and Chevrel compounds from many-body correlations between periodic two-level systems (instead of the usual localized spins) and conduction electrons. The origin of the periodic two-level systems in these compounds was suggested to be the double-well potentials in the strong-coupling model of Yu and Anderson.⁴ The value of the electron-phonon coupling constant λ , however, was suggested to be only of order unity.

It is of interest, therefore, to make use of all possible experimental probes of the electron-phonon interaction. We show in this paper that the thermopower of high-resistivity Chevrel-phase compounds, like that of amorphous metals, yields rather directly information about electron-phonon enhancement.

Opsal *et al.*⁶ suggested that the electron-phonon interaction enhances the diffusion thermoelectric power of

metals at low temperatures, the size of the enhancement factor being the usual $(1 + \lambda)$ mass enhancement as seen, for example, in low-temperature specific heat. Unfortunately, the presence of a large phonon drag contribution to thermopower has up to now precluded direct confirmation of the enhancement effect in crystalline materials, but Opsal *et al.*⁶ found some indirect evidence for the effect in the magnetothermopower of aluminum. In addition, Crisp and Henry,⁷ in separating the measured thermopower of dilute silver alloys into diffusion and phonon drag components using a two-band model, inferred that at least one of the characteristic diffusion thermopowers appeared to be nonlinear at low temperatures, while Jäckle⁸ showed that the low-temperature thermopower of amorphous SnCu films was too large to be explained within the free-electron model without enhancement.

However, the first direct evidence for the electron-phonon enhancement of thermopower was the low-temperature "knee" seen by Gallagher⁹ in the thermopower of glassy metals, in which the phonon drag contribution is suppressed by the strong disorder scattering.⁸ This enhancement effect is now well established as a general feature of nonmagnetic glassy metals⁹⁻¹⁴ and amorphous films.¹⁵ It is sometimes not fully appreciated that thermopower in systems with large structural scattering is very much simpler than in low-resistivity crystalline metals, not only owing to the suppression of phonon drag, but also because the dominance of structural scattering removes almost completely nonlinearities arising from changes in the balance of scattering with temperature. Thus, for example, trace magnetic impurities have no discernible effect, in strong contrast to the case of pure metal thermopower. In addition, the beauty of the electron-phonon enhancement effect in thermopower is that it is seen directly as the ratio of slopes at low and high temperatures in the same data set, this ratio being essentially independent of the absolute values of the slopes.

We show here that the measurements of Vasudeva Rao *et al.*¹⁶ on the Chevrel compounds $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ and $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Te}_y$ provide the first direct evidence of electron-phonon enhancement of thermopower in crystalline systems. These measurements provide further evi-

dence that the *positive* knee seen in the thermopower when scattering of electrons is strong is not simply a vestige of a large phonon-drag peak, since the phonon-drag contribution in these compounds appears to be a large *negative* peak that is reduced as scattering increases.

The crystal structure of $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ is triclinic between 5 and 270 K, comprising distorted Mo_6S_8 "building blocks" with two Cu atom positions per unit cell in the interstices (not all occupied).¹⁷ The residual resistivities ρ_0 (the resistivity just above the superconducting transition temperature) of Chevrel compounds such as $\text{Cu}_x\text{Mo}_6\text{S}_8$ are large (at least $100 \mu\Omega \text{ cm}$); these resistivities correspond to electron mean free paths of the order of 20–50 Å or less, and as temperature increases the resistivity shows saturation effects typical of systems in which the mean free path is approaching the lattice spacing.^{18,19} The effects are even more pronounced²⁰ as Se is partially substituted for S to form $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$. The absolute resistivity is difficult to determine for sintered pellets as used by Sankaranarayanan *et al.*,²⁰ but these authors tabulate values of ρ_0/ρ_{RT} , where ρ_{RT} is the room-temperature resistivity, that indicate approximately the relative size of the structural scattering of electrons (and also very approximately of phonons, in the absence of thermal resistivity data). Data for the $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ compound are of limited value since phase transformations occur at 120 and 170 K.

II. THERMOPOWER NONLINEARITIES

Examples of the thermopower nonlinearities seen by Vasudeva Rao *et al.*¹⁶ in Chevrel-phase compounds are shown in Fig. 1. For $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ there is a large negative peak typical of those ascribed to phonon drag. The size of this peak is progressively reduced as Se replaces S, i.e., as y increases in the compounds $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$. This effect is shown in Fig. 2, where we have plotted the maximum deviation ΔS of the thermopower from the line joining the origin ($S=0, T=0$) to the measured thermopower around room temperature. This decrease is not surprising in view of the fact that the residual resistivity ratio ρ_0/ρ_{T} of these compounds increases strongly as y increases from 0 to 3, as also shown in Fig. 2. Thus as the scattering of electrons and of phonons by structural irregularities increases, the phonon heat current is reduced and there is a reduction in momentum transferred to the electrons, i.e., of the phonon drag effect.

What is initially more surprising is that the disappearance of the phonon drag peak leads to a linear thermopower only at higher temperatures,¹⁶ with a *positive* deviation ΔS from this linear behavior at temperatures around 40 K. However, this behavior is strongly reminiscent of the knee in the thermopower of glassy metals due to electron-phonon enhancement, and we suggest that this is the origin of the positive deviations ΔS in the Chevrel compounds. Obviously the correlation between ΔS and ρ_0/ρ_{RT} shown in Fig. 2, with positive values of ΔS occurring only in those compounds with high residual resistivity ratios (i.e., small phonon drag effects), supports our explanation. The data for $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ with $y=7$ are similar to those for $y=6$ shown in Fig. 1, while the data

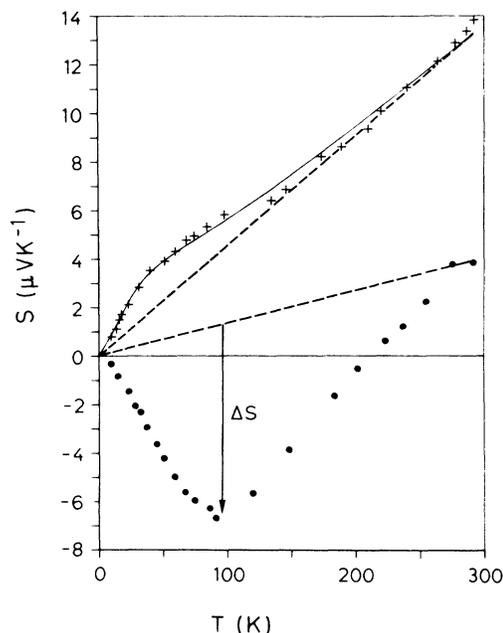


FIG. 1. Thermopower S as a function of temperature T (from Ref. 16) for $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ (dots), showing the maximum deviation ΔS from a line joining the origin to points near room temperature, and for $\text{Cu}_{1.8}\text{Mo}_6\text{S}_2\text{Se}_6$ (crosses) fitted to our theoretical expression [Eq. (1)] for electron-phonon enhancement (solid line). Fitting parameters are listed in Table I.

for $y=3, 4,$ and 5 show possible evidence of a slightly increased slope at low temperatures.¹⁶ The enhancement effect is also seen in $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Te}_y$ Chevrel compounds with $y=2, 3,$ and 4 , as indicated by the example in Fig. 3; in these compounds the residual resistivity ratio ρ_0/ρ_{T} is also very large,²¹ of order 0.9.

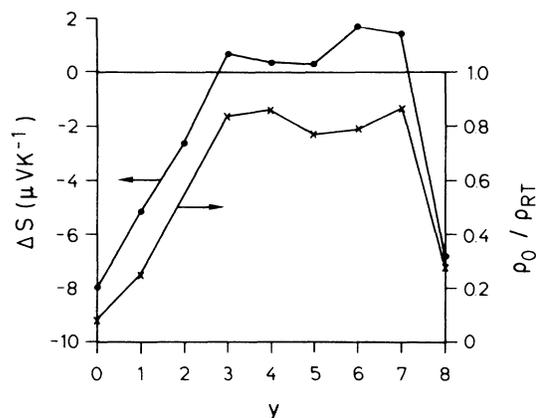


FIG. 2. Maximum deviation ΔS of the thermopower, as defined in Fig. 1 and the text, of $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ compounds, using data from Ref. 16. Also shown are ratios of the resistivity ρ_0 just above the superconducting transition temperature to room-temperature resistivity ρ_{RT} , as tabulated in Ref. 20.

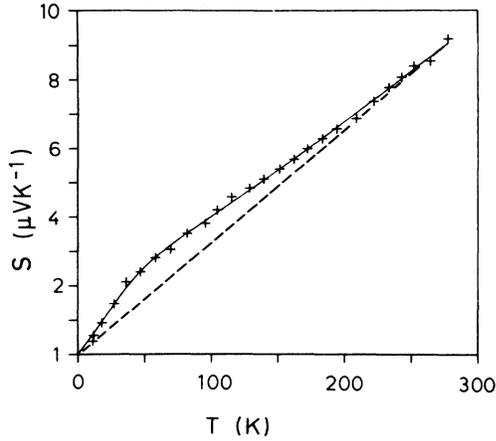


FIG. 3. Thermopower of $\text{Cu}_{1.8}\text{Mo}_6\text{S}_5\text{Te}_3$ (crosses) from Ref. 16, with a fit to our Eq. (1) (solid line). Fitting parameters are given in Table I. The dotted line shows linear behavior.

III. ANALYSIS OF ELECTRON-PHONON ENHANCEMENT

To investigate this suggestion quantitatively, we have fitted the data of Vasudeva Rao *et al.*¹⁶ to the theoretical expression for the electron-phonon enhancement of diffusion thermopower S_d :²²

$$S_d = [1 + a\lambda\bar{\lambda}_s(T/T_D^*)]X_b T, \quad (1)$$

where X_b is the bare thermopower parameter S_b/T (S_b being the bare diffusion thermopower, i.e., the value in the absence of electron-phonon enhancement, that is usually approximately linear in T in nonmagnetic systems), a is a constant discussed below, λ is the usual mass enhancement due to energy renormalization by phonons, and $\bar{\lambda}_s(T/T_D^*)$ is the normalized temperature-dependent enhancement of thermopower:²²

$$\bar{\lambda}_s \left[\frac{T}{T_D^*} \right] = \int_0^\infty dE \frac{\alpha^2 F(E)}{E} G_s \left[\frac{E}{k_B T} \right] / \int_0^\infty dE \frac{\alpha^2 F(E)}{E}. \quad (2)$$

Here, $\alpha^2 F(E)$ is the Eliashberg function that describes the interaction of electrons and phonons, $F(E)$ being the den-

sity of phonon states as a function of energy E and α^2 the electron-phonon coupling factor, $G_s(y)$ is the standard function we have defined previously,²² and k_B is Boltzmann's constant. $\bar{\lambda}_s(T/T_D^*)$ starts from the value unity at zero temperature, and may or may not show a small peak as temperature increases, depending on the energy dependence of $\alpha^2 F(E)$ at low energies. At temperatures of the order of T_D^* , the effective Debye temperature for the $\alpha^2 F(E)$ distribution, $\bar{\lambda}_s(T/T_D^*)$ has decreased to small values and the thermopower reverts to its unenhanced linear behavior.

The constant a in Eq. (1) takes the value unity if only the usual mass enhancement due to energy renormalization is present, but velocity and relaxation time renormalization,²² and Nielsen-Taylor higher-order diagram effects,²³ may also make a contribution and change the value of a . These effects in the presence of strong elastic scattering have a similar temperature dependence to the energy renormalization effect, so it is reasonable to take a as a temperature-independent constant.

The fits of the data in Figs. 1 and 3 to Eq. (1) show that the electron-phonon enhancement effect can give a good explanation of the positive knee seen in the thermopower. The parameter values obtained for these fits, and for similar fits for other concentrations, are listed in Table I. The theoretical enhancement shapes used were those we have calculated previously^{14,23} for a Debye-like model in which $\alpha^2 F(E)$ varies as E^n up to a sharp cutoff at $k_B T_D^*$, with $n=1, 2$, or 3 , and for a smoothed $\alpha^2 F(E)$ shape. The calculated enhancement shape is insensitive to the shape of $\alpha^2 F(E)$ at higher energies (the main effect is simply a change in T_D^*), but its low-temperature behavior does depend on the behavior of $\alpha^2 F(E)$ at low energies, i.e., on the exponent n . We found that an E^3 variation for $\alpha^2 F(E)$ gave a somewhat better fit than E or E^2 , but the difference in fit quality was not large. Accordingly, the parameter values in Table I are for the $n=3$, Debye-like spectrum, with very approximate uncertainties estimated from the variation of fit parameter values with $\alpha^2 F(E)$ shape and change of data weighting.

It is tempting to regard these E^3 preferences, like similar behavior in glassy metals,^{11,12,14} as some of the first evidence for the prediction of Keck and Schmid²⁴ that $\alpha^2 F(E)$ should vary as E^3 at low energies when electron scattering is strong. However, caution should be exercised, since this result is crucially dependent on the values of S/T at very low temperatures. This ratio is very

TABLE I. Values of the bare thermopower parameter X_b , effective Debye temperature T_D^* , and effective enhancement $a\lambda$ for the fits of Eq. (1) to the data of Vasudeva Rao *et al.* (Ref. 16). Also listed are values of the electron-phonon coupling parameter λ calculated from the McMillan formula (e.g., Ref. 12) using experimental superconducting transition temperatures (Ref. 26) and Coulomb repulsion $\mu^* = 0.13$.

Compound	X_b (nV K ⁻²)	T_D^* (K)	$a\lambda$	λ_{calc}
$\text{Cu}_{1.8}\text{Mo}_6\text{S}_2\text{Te}_2$	32±2	330±80	0.5±0.1	0.6
$\text{Cu}_{1.8}\text{Mo}_6\text{S}_5\text{Te}_3$	31±1	260±50	0.6±0.1	0.7
$\text{Cu}_{1.8}\text{Mo}_6\text{S}_6\text{Te}_4$	40±1	250±50	0.5±0.1	0.6
$\text{Cu}_{1.8}\text{Mo}_6\text{S}_2\text{Se}_6$	44±2	190±40	1.0±0.2	0.7
$\text{Cu}_{1.8}\text{Mo}_6\text{S}_1\text{Se}_7$	46±2	180±40	0.8±0.2	0.7

difficult to measure accurately as T tends to zero, and there is the possibility of a perturbing influence of electron-electron correlations at low temperatures.²⁵ At this stage, therefore, we say simply that our analysis is consistent with the result of Keck and Schmid. Fortunately, our analysis should not be seriously affected by incipient localization, since its effect is mainly to increase thermopower magnitude with little effect on the relative temperature dependence.²⁵ The quality of the fits, at least for the compounds including Te, argues against the presence of a remaining phonon drag contribution.

We now discuss briefly the values of the fit parameters in Table I. The values for the effective Debye temperature T_D^* of the $\alpha^2 F(E)$ distribution are of the correct order of magnitude: Vasudeva Rao *et al.*¹⁶ found a Debye temperature of 210 K for $\text{Cu}_{1.8}\text{MoSSe}_7$ from specific-heat measurements between 25 and 65 K.

The sizes of the bare thermopower X_b are very large. For this reason, we would expect the energy renormalization effect to dominate over the effects of velocity and relaxation time renormalization²² and higher-order diagrams.²³ There is some evidence for these effects when the bare thermopower is small,²² but the parameter a is about 1 for glassy metals with larger values of X_b ,¹⁴ so unless these effects are dramatically larger in the Chevrel compounds (with even larger X_b), a should also not vary much from 1. Thus the values of $a\lambda$ in Table I should be reasonable estimates of λ . We see that our deduced values of $a\lambda$ are consistent with values of λ calculated from T_c values in the McMillan formula¹² with the conventional value of 0.13 for μ^* .

IV. CONCLUSION

We conclude that there is direct evidence for the electron-phonon enhancement of the diffusion thermopower in crystalline-metals, but that the effect is only visible when structural-scattering is large enough to suppress phonon drag. The data of Vasudeva Rao *et al.*¹⁶ for $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ Chevrel compounds provide a rather neat demonstration of the suppression of a large negative phonon drag peak by structural scattering as y increases, leaving the small positive enhancement effect.

We find that in $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ and $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Te}_y$ the electron-phonon enhancement λ is of approximately the size expected from the McMillan formula with the conventional value 0.13 for the Coulomb repulsion μ^* . There is no evidence for very large values of λ (and so of μ^*) similar to those suggested by Schachinger *et al.*² for $\text{Cu}_2\text{Mo}_6\text{S}_8$ ($\lambda \sim 2.2$ and $\mu^* \sim 0.6$): our results are more similar to the earlier model for $\text{Cu}_2\text{Mo}_6\text{S}_8$ of Lachal *et al.*³

The superconducting transition temperature T_c of $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ and $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Te}_y$ shows the strong reduction as residual resistivity ratio increases (i.e., as mean free path decreases) that is a general feature of the *A15* and Chevrel compounds: the value of T_c for $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ is 10.8 K, but this is reduced²⁶ to about 4 K for the high-resistivity compounds we have analyzed. According to Anderson *et al.*,¹ such a reduction in T_c can arise from an increase in μ^* , while Belitz²⁷ derives a generalized McMillan equation with an extra term due to electron-electron interactions that is the main cause of the decrease in T_c ; in both cases, the value of λ is postulated not to decrease significantly from the clean limit reference as disorder increases: if we take $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ as the "clean" reference for our case, we have $\lambda \sim 1.1$. Our results for $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ are inconclusive, but for $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Te}_y$ (for which our fits are better), the thermopower enhancement size ($\lambda \sim 0.5$) suggests that the decrease in T_c relative to $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ is associated with a decrease in λ . Such behavior has also been inferred from tunneling experiments on disordered Nb_3Sn by Geerk *et al.*²⁸ This decrease of λ could possibly arise from changes in the phonon spectrum as Te is added, but our result is also consistent with the suggestion of Meisel and Cote²⁹ that the decrease of electron-phonon coupling at low energies as electron mean free path is reduced causes a reduction in T_c . This decrease of electron-phonon coupling also causes the E^3 variation of $\alpha^2 F(E)$ at low energies²⁴ that we have found gives the best fit to the temperature dependence of the thermopower data.

Because in the usual quasiparticle picture thermopower depends rather generally on the energy derivative of conductivity,⁶ it gives directly the size and temperature dependence of the renormalization of electron energy by the electron-phonon interaction, i.e., of the mass enhancement. Our analysis suggests that to be viable, theories such as the local-phonon model of Yu and Anderson⁴ or the heavy-fermion model of Matsuura and Miyake⁵ need to be able to simulate normal quasiparticle energy renormalization with conventional parameter values.

Further measurements, particularly of the thermopower of highly disordered *A15* compounds, would be of great interest—the existing measurements of Sarachik *et al.*³⁰ for V_3X compounds are for samples with residual resistivities from 5 to 35 $\mu\Omega$ cm, too small to eliminate the effect of phonon drag.

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