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Enhanced Seebeck coefficient from carrier-induced vibrational softening

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Through their electron-lattice interactions, localized carriers reduce vibrational stiffness constants in their surroundings. States with a large electronic polarizability (e.g., multiatomic localized states and states of a singlet bipolaron formed of degenerate electronic orbitals) induce exceptionally large softening. This carrier-induced softening augments the Seebeck coefficient of solids whose carriers hop between these localized states through two separate effects. One enhancement is due to a localized carrier inducing an increase in a solid's vibrational entropy. The other contribution is proportional to the vibrational energy transferred with a carrier as it hops. Both softening contributions are independent of the carrier density. The magnitudes and temperature dependencies of these contributions to the Seebeck coefficient indicate the electronic polarizabilities of the localized states and the vibrational modes to which they are coupled. Measured softening enhancements of Seebeck coefficients are sometimes large enough (e.g., >200 μV/K measured at 300 K in boron carbides) to significantly increase the efficiency of thermoelectric energy conversion. [S0163-1829(99)02109-8]

I. INTRODUCTION

A localized carrier generally induces displacements of the equilibrium positions of the atoms that surround it. As a result, simplified models often presume that the effect of a localized carrier on the atoms that surround it is only to displace the atoms' equilibrium positions.[1] In particular, these models assume (1) that the solid's atomic vibrations are strictly harmonic and (2) that the electronic energy of a localized carrier varies only linearly with atomic displacements. Beyond these simplifications, however, a localized carrier generally shifts the stiffness constants (and thereby the frequencies) of vibrational modes to which it is coupled. Carrier-induced changes of local stiffness result both (1) from vibrational anharmonicity and (2) from nonlinear dependencies of the electronic energy of a self-trapped carrier on atomic displacements.

Indeed, anharmonicity of a vibrational mode means that the stiffness constant for that mode depends on the mode's displacement. Thus, with vibrational anharmonicity a carrier-induced change of a mode's equilibrium value is accompanied by a change of the mode's stiffness. However, this effect is typically modest. In particular, even for the relatively large carrier-induced atomic shifts associated with small-polaron formation, stiffness changes are estimated to be $<20\%$.[2]

Localized carriers soften the vibrational modes to which they are coupled because the carrier's electronic energy generally depends nonlinearly on atomic displacements. Indeed, localized carriers soften the vibrational modes to which they are coupled even when the one-electron *potential* is presumed to vary linearly with changing atomic positions.[3] This carrier-induced local lattice softening is associated with the redistribution of the charge of the localized carrier that occurs as atoms change positions. For this reason the carrier-induced lattice softening is proportional to the electronic polarizability of the localized carrier.[3] Carrier-induced softening is greatest for vibrational modes with wavelengths comparable to the spatial extent of the localized electronic carrier.

An explicit but simple example of carrier-induced softening illustrates the effect of a carrier on two intramolecular modes of a simple two-center molecule.[4] Carrier-induced softening occurs as the carrier ''sloshes'' between the two portions of the molecule in response to asymmetric intramolecular vibrations. The magnitude of the softening depends on the ratio of the transfer energy associated with the intramolecular electronic motion to the lowering of the one-electron potential energy when a carrier is confined to one of the molecule's two centers. Carrier-induced softening can be nearly complete, 100%, when these two energies are close to one another. This model of carrier-induced vibrational softening was advanced to explain why cuprates' vibrations soften and soft local modes appear when carriers are introduced by doping. The Holstein model,[1] in which there is no carrier-induced softening, is obtained in the limit of vanishing intramolecular electronic transfer, vanishing electronic polarizability.

Carrier-induced vibrational softening is also a general feature of a singlet bipolaron formed from a pair of carriers that occupy *degenerate* orbitals.[5] The bipolaron's stabilization as a singlet results from atomic displacements that break the spatial symmetry associated with the orbital degeneracy. The nonlinear variation of the electronic energy of the singlet pair with symmetry-breaking atomic displacements results because the Coulomb repulsion between carriers that share a common orbital, U, differs from that between carriers in different orbitals, u. This nonlinear variation of the singlet energy with symmetry-breaking atomic displacements softens the associated symmetry-breaking vibrations.

This paper addresses the effects of carrier-induced softening on the Seebeck coefficients of solids whose charge carriers hop between localized states. Carrier-induced softening produces two distinct contributions to the Seebeck coefficient. Both contributions are independent of the carrier concentration. One contribution is due to a localized carrier inducing an increase in a solid's vibrational entropy. The other contribution is proportional to the vibrational energy transferred with a carrier as it hops. The magnitudes and temperature dependences of these enhancements indicate the electronic polarizabilities of the localized states and identify the energies of the softened vibrational modes. In this manner, carrier-induced softening's effect on the Seebeck coefficient probes hopping carriers' localized electronic states and the vibrations to which they are coupled.

Furthermore, carrier-induced softening's augmentations of Seebeck coefficients are sometimes large enough (e.g., >200 μV/K at 300 K in boron carbides)[6,7] to significantly increase the efficiency of thermoelectric energy conversion. As such, carrier-induced softening suggests that additional unexpectedly good thermoelectrics may be found among systems for which hopping carriers occupy states with large electronic polarizabilities.

II. GENERAL FORMALISM

The Seebeck coefficient α, is usually obtained by measuring the electromotive force ΔV, induced across a sample by the imposition of the temperature differential, $\Delta T{:}\alpha \equiv \Delta V/\Delta T$. Equivalently, the Seebeck coefficient is the entropy transported per charge carrier divided by the carrier's charge, q.[8] The Seebeck coefficient may be expressed as the sum of two contributions: $\alpha \equiv \alpha_{\text{presence}} + \alpha_{\text{transport}}$.[9] Here $q\alpha_{\text{presence}}$ is the change of the system's entropy produced by adding a charge carrier. This contribution is independent of the means by which a carrier is transported through a material. The other contribution $\alpha_{\text{transport}}$ is the net energy transferred in moving a carrier divided by qT, where T is the temperature. This contribution depends on the mechanism of charge transport.

The change of the system's entropy induced by the addition of a charge carrier may be expressed in terms of the change of the system's internal energy ΔU:

$$\alpha_{\text{presence}} = (\Delta U - \mu)/qT, \tag{1}$$

where μ is the carriers' chemical potential. The dependences of ΔU and μ on the carrier density and the temperature reflect the carriers' interactions. To display individual physical phenomena that contribute to α_{presence}, α_{presence} is rewritten as the sum of contributions to the carrier-induced entropy change:

$$\alpha_{\text{presence}} = (\Delta S_{\text{mixing}} + \Delta S_{\text{spin}} + \Delta S_{\text{vibrations}})/q, \tag{2}$$

where the three terms correspond to changes of (1) the entropy-of-mixing, (2) the spin entropy, and (3) the vibrational entropy upon adding a carrier of charge q. The first two contributions are well known.[10]

The entropy-of-mixing contribution is usually dominant in lightly doped semiconductors. In these circumstances the change of the entropy-of-mixing upon adding a carrier to a system is large because there are very few carriers per thermally available state. Simple formulas result when the thermal energy k_BT exceeds the width of the carriers' band since then all of the band's N states are thermally available. For example, when only single occupancy of a site is permitted:

$$\alpha_{\text{mixing}} = \Delta S_{\text{mixing}}/q = (k_B/q)\ln[(1-c)/c], \tag{3}$$

where k_B is the Boltzmann constant and $c \equiv n_c/N$, where n_c is the number of carriers.[10]

The contribution to the Seebeck coefficient that results from a carrier's presence altering the system's spin entropy also becomes simple in the absence of intersite magnetic interactions. Then the spin contribution for a carrier confined to a single magnetic site is

$$\alpha_{\text{spin}} = \Delta S_{\text{spin}}/q = (k_B/q)\ln[(2S+1)/(2S_0+1)], \tag{4}$$

where S_0 and S are the net spins of the magnetic site in the absence and presence of the carrier, respectively.[11] However, Eq. (4) should be applied cautiously. In particular, calculation of α_{spin} for magnetic semiconductors in the presence of intersite exchange interactions indicates that Eq. (4) is only obtained at temperatures well above ($\approx$ ten times) the magnetic ordering temperature.[12] At lower temperatures, carrier-induced changes of the spin entropy associated with intrasite exchange, depicted in Eq. (4), are largely offset by carrier-induced changes of the spin entropy associated with intersite exchange.[12]

Furthermore, even in nonmagnetic semiconductors Seebeck coefficient measurements of hopping carriers do not report observing the simplest spin-entropy contribution, $\alpha_{\text{spin}} = (k_B/q)\ln(2)$.[13,14] Here, as in magnetic semiconductors, the spin degree of freedom may be suppressed by interactions between spins that overwhelm the thermal energy k_BT.

III. SOFTENING CONTRIBUTIONS TO THE SEEBECK COEFFICIENT

A polaron forms when an electronic carrier is bound within the potential well produced by the equilibrium positions of the atoms surrounding the carrier being displaced from their carrier-free equilibrium positions to equilibrium positions consistent with the presence of the bound electronic carrier. This situation (self-trapping) requires that the self-trapped carrier move more rapidly within the potential well that binds it than do the atoms whose displacements produce the potential well. In particular, the binding energy of the self-trapped carrier must exceed the characteristic phonon energy $E_{\text{self-trapped}} > \hbar\omega$.

Self-trapping is described by the adiabatic approach. In the adiabatic approach the electronic carrier responds to the potential produced by atoms as if it were static and the potential energy that governs atomic motion is augmented by the electronic energy of the carrier. Consider for example Holstein's molecular crystal model, a periodic array of molecules with each molecule's motion described by a single deformational coordinate that vibrates harmonically.[1] When a self-trapped carrier occupies a particular molecule, motion of that molecule is described by the adiabatic Hamiltonian:

$$H_{\text{adiabatic}} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + \frac{M\omega^2 x^2}{2} + E(x), \tag{5}$$

where $E(x)$ is the electronic energy of the carrier as a function of the molecule's deformational coordinate x, whose harmonic vibrations are characterized by the reduced atomic mass M and vibrational frequency ω. Holstein takes the electronic energy to be a linear function of x: $E=-Ax$. However, the electronic energy is not generally linear.[3–5] A carrier-induced change in the stiffness of the occupied site occurs when the electronic energy is nonlinear. For example, if $E(x)=-(Ax+Bx^2/2)$, occupation of the molecule reduces its stiffness from $M\omega^2$ to $M\omega^2-B$. This extension of the Holstein model can be generalized to realistic molecules that have a set of deformational modes $\{x_i\}$, rather than just one.[15]

Carrier-induced softening of vibrational frequencies produces a change of vibrational entropy. Since the entropy of a sum of oscillators of frequencies ω_i is

$$S_{\text{vibrations}}=-k_B\sum_i \{\ln[2\sinh(\hbar\omega_i/2k_BT)] -(\hbar\omega_i/2k_BT)\coth(\hbar\omega_i/2k_BT)\}, \qquad (6)$$

carrier-induced changes of the vibrational frequencies of $\Delta\omega_i$ contribute

$$\alpha_{\text{vibrations}}=\left(\frac{k_B}{q}\right)\sum_i\left(\frac{-\Delta\omega_i}{\omega_i}\right)\left[\frac{(\hbar\omega_i/2k_BT)}{\sinh(\hbar\omega_i/2k_BT)}\right]^2 \qquad (7)$$

to α_{presence}. This contribution rises with increasing temperature from zero to a temperature-independent value of $\alpha_{\text{vibrations}}=(k_B/q)\Sigma_i(-\Delta\omega_i/\omega_i)$ when $k_BT\gg\hbar\omega_i$. Thus, the magnitude of $\alpha_{\text{vibrations}}$ is governed by the sum of the carrier-induced fractional shifts of the frequencies of the vibrational modes.

Carrier-induced softening also produces a heat-transport contribution to the Seebeck coefficient for transport by phonon-assisted hopping, $\alpha_{\text{transport}}$. In this process an electronic carrier moves between sites in response to motions of those atoms that determine the electronic energies associated with occupation of each of the two sites. The rate for this process depends on (1) the electronic-energy functions associated with a carrier occupying initial and final sites [e.g., the two $E(x)$ functions associated with occupation of initial and final sites] as well as (2) the parameters that characterize atomic motions about each site. Carrier-induced softening affects a hopping rate by altering the atomic motions about the occupied site.

To calculate $\alpha_{\text{transport}}$ I first recall from Ref. (9) that $\alpha_{\text{transport}}\equiv E_T/qT$, where E_T is the net flow of vibrational energy that accompanies a phonon-assisted hop from an initial site to a final site:[9,16]

$$E_T=\frac{k_BT^2}{2}\left[\frac{\partial\ln(R_{1,2}/R_{2,1})}{\partial T_1}-\frac{\partial\ln(R_{1,2}/R_{2,1})}{\partial T_2}\right]_{T_1=T_2=T}. \qquad (8)$$

Here $R_{1,2}$ (and $R_{2,1}$) are the rates for hops from site 1 to site 2 (and from site 2 to site 1), while site 1 is at temperature T_1 and site 2 is at temperature T_2.

The phonon-assisted rate for a carrier hopping between sites with separate vibrational baths (in which a carrier's presence may alter local stiffness and vibrational frequencies) is obtained by straightforward modification of available expressions.[17] The ratio of the jump rates is

$$\frac{R_{1,2}}{R_{2,1}}=\frac{\int_{-\infty}^{\infty}dt\,\exp[G(1,2{:}t)]\cos[F_2(1,2{:}t)+\Delta_{12}t/\hbar]}{\int_{-\infty}^{\infty}dt\,\exp[G(2,1{:}t)]\cos[F_2(2,1{:}t)+\Delta_{21}t/\hbar]}, \qquad (9)$$

where

$$G(1,2{:}t)\equiv\sum_q[\Gamma_{q,1}^c\coth(\hbar\omega_q/2k_BT_1) +\Gamma_{q,2}\coth(\hbar\omega_q/2k_BT_2)][\cos(\omega_qt)-1], \qquad (10)$$

and

$$F_2(1,2{:}t)\equiv\sum_q[\Gamma_{q,1}^c+\Gamma_{q,2}]\sin(\omega_qt), \qquad (11)$$

and Δ_{12} is the difference between final and initial site energies (including lattice-relaxation energies) for a carrier that hops from site 1 to site 2. Here the functions $\Gamma_{q,1}$ ($\Gamma_{q,2}$) and $\Gamma_{q,1}^c$ ($\Gamma_{q,2}^c$) describe the coupling of the electronic state at site 1 (and site 2) to vibrations of frequency ω_q when unoccupied or occupied by a carrier, respectively. As detailed below, these coupling functions indicate both (1) the dependences of the electronic energy of the state that a carrier occupies or would occupy on vibrational parameters, and (2) the frequencies and stiffness of these vibrational parameters.

These coupling functions are now modeled so as to permit consideration of the effects of disorder and of carrier-induced softening. For simplicity, a carrier localized at a site is presumed to be coupled to only a single vibrational mode. Disorder and carrier-induced softening affect the coupling functions in different ways. With disorder both the electron-lattice interactions at sites 1 and 2 [e.g., $E_1(x_1)$ and $E_2(x_2)$] and the frequencies of the vibrations to which carriers are primarily coupled, ω_1 and ω_2, can differ from one site to the other. By contrast, carrier-induced softening will alter the vibrational parameters of a site only when it is occupied by a carrier. Parameters that are shifted by the presence of a carrier are herein designated by the index "c." Then the coupling functions at occupied and unoccupied sites are written as

$$\Gamma_{q,1}^c=(E_{b,1}^c/\hbar\omega_q)\,\delta_{\omega_q,\omega_1^c},\quad \Gamma_{q,2}^c=(E_{b,2}^c/\hbar\omega_q)\,\delta_{\omega_q,\omega_2^c}, \qquad (12a)$$

and

$$\Gamma_{q,1}=(E_{b,1}/\hbar\omega_q)\,\delta_{\omega_q,\omega_1},\quad \Gamma_{q,2}=(E_{b,2}/\hbar\omega_q)\,\delta_{\omega_q,\omega_2}, \qquad (12b)$$

respectively. This notation is chosen to make contact with prior studies. In particular, $E_{b,1}^c$ and $E_{b,2}^c$ are the small-polaron binding energies (lowerings of the solid's net energy) for a carrier occupying sites 1 and 2, respectively. By contrast, $E_{b,1}$ and $E_{b,1}$ are these binding energies in the absence of carrier-induced softening.

Now, following the well-established procedures, rates appropriate to multiphonon hopping are obtained by replacing $\sin\omega_qt$ by ω_qt and $\cos\omega_qt$ by $1-(\omega_qt)^2/2$ in Eqs. (10) and (11) and then performing the t integrations of Eq. (9):[17]

$$\ln\left(\frac{R_{1,2}}{R_{2,1}}\right)=\frac{[E^c_{b,2}+E_{b,1}+\Delta_{21}]^2}{2[E^c_{b,2}\hbar\omega^c_2\coth(\hbar\omega^c_2/2k_BT_2)+E_{b,1}\hbar\omega_1\coth(\hbar\omega_1/2k_BT_1)]}-\frac{[E^c_{b,1}+E_{b,2}+\Delta_{12}]^2}{2[E^c_{b,1}\hbar\omega^c_1\coth(\hbar\omega^c_1/2k_BT_1)+E_{b,2}\hbar\omega_2\coth(\hbar\omega_2/2k_bT_2)]}. \tag{13}$$

Inserting Eq. (13) into Eq. (8) yields

$$E_T=\frac{[E^c_{b,1}+E_{b,2}+\Delta_{12}]^2[E^c_{b,1}(\hbar\omega^c_1)^2\,\mathrm{csch}^2(\hbar\omega^c_1/2k_BT)-E_{b,2}(\hbar\omega_2)^2\,\mathrm{csch}^2(\hbar\omega_2/2k_BT)]}{8[E^c_{b,1}\hbar\omega^c_1\coth(\hbar\omega^c_1/2k_BT)+E_{b,2}\hbar\omega_2\coth(\hbar\omega_2/2k_BT)]^2}+\frac{[E^c_{b,2}+E_{b,1}+\Delta_{21}]^2[E^c_{b,2}(\hbar\omega^c_2)^2\,\mathrm{csch}^2(\hbar\omega^c_2/2k_BT)-E_{b,1}(\hbar\omega_1)^2\,\mathrm{csch}^2(\hbar\omega_1/2k_BT)]}{8[E^c_{b,2}\hbar\omega^c_2\coth(\hbar\omega^c_2/2k_BT)+E_{b,1}\hbar\omega_1\coth(\hbar\omega_1/2k_BT)]^2}. \tag{14}$$

In the high-temperature (semiclassical) limit in which vibrations may be treated classically, $k_BT>\hbar\omega_1,\hbar\omega_2,\hbar\omega^c_1,\hbar\omega^c_2$, Eq. (14) becomes

$$E_T=\frac{[E^c_{b,1}+E_{b,2}+\Delta_{12}]^2[E^c_{b,1}-E_{b,2}]}{8[E^c_{b,1}+E_{b,2}]^2}+\frac{[E^c_{b,2}+E_{b,1}+\Delta_{21}]^2[E^c_{b,2}-E_{b,1}]}{8[E^c_{b,2}+E_{b,1}]^2}. \tag{15}$$

Examination of Eq. (15) verifies that without carrier-induced softening, $E^c_{b,1}=E_{b,1}$ and $E^c_{b,2}=E_{b,2}$, vibrational energy is only transported in hops between inequivalent sites:[9] e.g., $E_T=(\Delta/2)[(E_{b,1}-E_{b,2})/(E_{b,1}+E_{b,2})]$ at high temperatures, where $\Delta\equiv\Delta_{12}=-\Delta_{21}$.

By contrast, with carrier-induced softening vibrational energy is even transported in hops between equivalent sites. To obtain this result, observe that carrier-induced softening lowers the energy of the occupied site. Thus, $\Delta_{21}=\Delta_{12}=E^c_b-E_b$ for hops between equivalent sites, where $E^c_b\equiv E^c_{b,1}=E^c_{b,2}$ and $E_b\equiv E_{b,1}=E_{b,2}$. In the absence of disorder it is convenient to define $\omega_c\equiv\omega^c_1=\omega^c_2$ and $\omega\equiv\omega_1=\omega_2$. Then, E_T for hops between equivalent sites may be written as

$$E_T=(E^c_b)^2\frac{[E^c_b(\hbar\omega_c)^2\,\mathrm{csch}^2(\hbar\omega_c/2k_bT)-E_b(\hbar\omega)^2\,\mathrm{csch}^2(\hbar\omega/2k_BT)]}{[E^c_b\hbar\omega_c\coth(\hbar\omega_c/2k_BT)+E_b\hbar\omega\coth(\hbar\omega/2k_BT)]^2}. \tag{16}$$

As the temperature is raised from absolute zero, E_T increases from zero to $E_A[(E^c_b-E_b)/(E^c_b+E_b)]$, where $E_A\equiv(E^c_b)^2/(E^c_b+E_b)$ is the hopping activation energy. The high-temperature limit of E_T is the difference between the contributions to E_A from occupied and final sites.[6,10]

The hopping activation energy E_A is the minimum strain energy required to bring the electronic energies of initial and final sites into coincidence.[2,5,10] In the absence of carrier induced softening, $E^c_b=E_b$ and $E_A=E_b/2$. In this situation equal contributions to the minimum strain energy come from deformation about the hop's initial and final sites. In the opposite limit, very strong carrier-induced softening, $E^c_b\gg E_b$, $E_A\rightarrow E^c_b$. In this regime the primary contributions to the net minimum strain energy are from deformations about the initially occupied site since it is significantly softened.

A simple expression for E_T is obtained when one observes that the binding energy varies inversely with the local stiffness, $E_b\propto 1/M\omega^2$, and one considers the limit of a small fractional carrier-induced frequency shift, $(\omega-\omega_c)/\omega\equiv(-\Delta\omega/\omega)\ll 1$. In particular, as E_b and E^c_b approach one another Eq. (16) becomes

$$E_T=E_A\left(\frac{-\Delta\omega}{\omega}\right)\frac{(\hbar\omega/k_BT)}{\sinh(\hbar\omega/k_BT)}, \tag{17}$$

where $E_A=E_b/2$.

For simplicity the preceding calculation of E_T has only considered carrier-induced softening of a single vibrational mode. Beyond this simplification, E_T is the sum of contributions from each shifted vibrational mode. Then, the net carrier-induced softening contribution to the Seebeck coefficient, obtained by adding Eq. (7) to the multimode generalization of Eq. (17), is

$$\alpha_{\mathrm{softening}}=\alpha_{\mathrm{vibrations}}+E_T/qT=\left(\frac{k_B}{q}\right)\sum_i\left(\frac{-\Delta\omega_i}{\omega_i}\right)\times\left[F_{\mathrm{vibrations}}(\Theta_i/T)+\frac{E_{A,i}}{k_B\Theta_i}F_{\mathrm{transport}}(\Theta_i/T)\right], \tag{18}$$

where $\Theta_i\equiv\hbar\omega_i/k_B$,

$$F_{\mathrm{vibrations}}(\Theta_i/T)\equiv\left[\frac{(\Theta_i/2T)}{\sinh(\Theta_i/2T)}\right]^2, \tag{19}$$

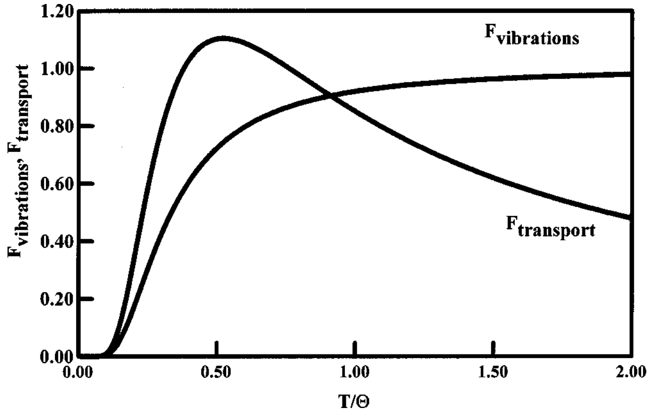

FIG. 1. $F_{\text{vibrations}}(\Theta/T)$ and $F_{\text{transport}}(\Theta/T)$ plotted against T/Θ.

and

$$F_{\text{transport}}(\Theta_i/T) \equiv \frac{\Theta_i}{T} \frac{(\Theta_i/T)}{\sinh(\Theta_i/T)}. \tag{20}$$

IV. DISCUSSION

The temperature dependences of the two contributions to the square brackets of Eq. (18) differ from one another. As illustrated in Fig. 1, with rising temperature $F_{\text{vibrations}}(\Theta/T)$ rises monotonically from zero toward a near constant value at sufficiently high temperatures. By contrast, Fig. 1 shows that $F_{\text{transport}}(\Theta/T)$ is a peaked function of temperature that vanishes at both the low- and high-temperature limits. In general $\alpha_{\text{softening}}$ is the sum of contributions with different phonon temperatures, Θ_i having temperature dependences like those of the two functions, $F_{\text{vibrations}}(\Theta/T)$ and $F_{\text{transport}}(\Theta/T)$, illustrated in Fig. 1. Thus, $\alpha_{\text{softening}}$ will peak as a function of temperature on the scale of a vibrational temperature.

A crude underestimate of $\alpha_{\text{softening}}$ may be obtained by replacing the square-bracketed term of Eq. (18) by unity. Then $\alpha_{\text{softening}} \approx (k_B/q)\langle N_s(-\Delta\omega/\omega)\rangle$, where the final factor denotes the average product of the number of softened vibrational modes N_s and their fractional softening. The first factor, $k_B/q \approx 86$ μV/K for $q=|e|$, is the characteristic scale of the Seebeck coefficient. The second factor determines the magnitude of $\alpha_{\text{softening}}$.

A small Seebeck enhancement would result if only a single mode were to be softened, $N_s=1$, and its softening were only the small value characteristic of that arising from vibrational anharmonicity, $(-\Delta\omega/\omega) \approx 0.1$:$\langle N_s(-\Delta\omega/\omega)\rangle \approx 0.1$. In particular, carrier-induced softening would then only enhance the Seebeck coefficient by less than 10 μV/K.

However, a carrier in a molecularlike state will generally soften many vibrational modes. In particular, carrier-induced softening generally occurs for vibrational modes whose wavelengths are comparable to the molecular-state diameter. Furthermore, due to the generally large electronic polarizability of large-radius states, their carrier-induced softening can be much larger than that produced by vibrational anharmonicity. In these instances $\langle N_s(-\Delta\omega/\omega)\rangle$ can be substantially greater than unity. Thus, significant enhancements of the Seebeck coefficient from carrier-induced softening are expected when the carriers are in molecular orbitals encompassing many atomic sites.

Recent measurements of the Seebeck coefficients of boron carbides as functions of carrier density and temperature (9–900 K) are consistent with the existence of large enhancements of boron carbides' Seebeck coefficients resulting from carrier-induced softening.[7] Boron carbides, $B_{12+x}C_{3-x}$ for $0.1<x<1.5$, are composed of 12-*atom* icosahedral units upon which carriers are believed to form singlet bipolarons and between which carriers are thought to hop.[5,6] Boron carbides' carrier densities are large (0.1 to 0.5 bipolarons per site). Thus the mixing contribution to the Seebeck coefficient, α_{mixing} should be quite small: zero at $x=1$.[6] Nonetheless, boron carbides' Seebeck coefficients are surprisingly large (>200 μV/K at 300 K for $x=1$).[7] Consistent with carrier-induced softening, the Seebeck enhancements are nearly independent of carrier concentration and are peaked functions of temperature. These temperature dependences are well described by sums of contributions having the forms depicted in Fig. 1.[7]

The large enhancements of boron carbides' Seebeck coefficients greatly increase their thermoelectric figures-of-merit. As a result, boron carbides are unexpectedly efficient high-temperature thermoelectrics.

Significant enhancements of Seebeck coefficients (and thermoelectric figures of merit) through carrier-induced softening may occur in other systems where carriers move between molecular units. To determine whether the Seebeck coefficients are enhanced requires obtaining the carrier densities as well as the Seebeck coefficients. In addition, measurements should be performed over a significant range of carrier densities and temperatures to determine if an enhancement is independent of carrier density and is a peaked function of temperature.

Large increases of the Seebeck coefficient of molecular-like systems from carrier-induced softening could render these systems useful as efficient thermoelectrics. Such a circumstance would provide an avenue for the development of thermoelectrics.

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