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Aftab Alam, Rajiv K. Chouhan, and Abhijit Mookerjee

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Thermal conductivity and diffusion-mediated localization in $\text{Fe}_{1-x}\text{Cr}_x$ Alloys

Aftab Alam*

Division of Materials Science and Engineering, Ames Laboratory, Ames, Iowa 50011, USA

Rajiv K. Chouhan¹, and Abhijit Mookerjee²

¹ *Department of Materials Science, S.N. Bose National Centre for Basic Sciences, JD-III Salt Lake City, Kolkata 700098 and*

² *Advanced Materials Research Unit and Department of Materials Science,
S.N. Bose National Centre for Basic Sciences, JD-III Salt Lake City, Kolkata 700098*

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We apply a Kubo-Greenwood type formula combined with a generalized Feynman diagrammatic technique to report a first principles calculation of the thermal transport properties of disordered $\text{Fe}_{1-x}\text{Cr}_x$ alloys. The diagrammatic approach simplifies the inclusion of disorder-induced scattering effects on the two particle correlation functions and hence renormalizes the heat current operator to calculate configuration averaged lattice thermal conductivity and diffusivity. The thermal conductivity $\kappa(T)$ in the present case shows an approximate quadratic T -dependence in the low temperature regime ($T < 20$ K), which subsequently rises smoothly to a T -independent saturated value at high T . A numerical estimate of mobility edge from the thermal diffusivity data yields the fraction of localized states. It is concluded that the complex disorder scattering processes, in force-constant dominated disorder alloys such as Fe-Cr, tend to localize the vibrational modes quite significantly.

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I. INTRODUCTION

The study of phonon excitations and the associated thermal transport properties is an important field of research in disordered alloys. In certain materials, disorder mediated scattering can shrink the typical mean free path (MFP) of phonons to such a level that wavelength and MFP no longer remain sharp concepts, and the usual textbook phonon gas model for thermal conductivity breaks down. From the theoretical perspective, the development of a reliable quantum mechanical theory to predict such properties in random alloys is a difficult task mainly because of two problems : (i) one needs a microscopic description of inter-atomic force constants with an intrinsic off-diagonal disorder and (ii) one has to configuration average a two-particle correlation function within a Kubo-type formula. The effects of dominant off-diagonal force constant disorder in alloys can be quite unusual, as we have shown earlier.¹ Most theories of thermal transport, developed in the past few decades however, are either based on the single-site coherent potential approximation (CPA),² the perturbation-based approach simulating the Peierls-Boltzmann equation (PBE)³ or atomistic models with a large unit cell and periodic boundary conditions.⁴ CPA, being a single-site mean-field approximation, is inadequate for treating multi-site off-diagonal disorder arising out of force constants and is reported, for example, to inadequately explain experimental life-time data on simple Ni-Pt alloys.⁵ The perturbative simulation approach, although rigorously derived, is limited in applicability to model lattices alone and has not been tested on realistic materials. The atomistic models are computationally expensive due to the large unit-cell size, non-self-consistent and suffer from the finite size errors.

In a recent paper⁶ we have developed a theoretical approach to calculate the configuration averaged lattice thermal conductivity and diffusivity for random alloys. This formalism combined a Kubo-Greenwood approach with a generalized Feynman diagrammatic technique to explicitly incorporate the effect of disorder induced scattering. We showed that disorder scattering renormalizes both the phonon propagators as well as the heat currents. These corrections are related to the self-energy and vertex corrections. Unlike the single-site CPA, this approach explicitly takes into account the fluctuations in masses (diagonal), force constants and heat currents (off-diagonal disorder) between different ion-cores and incorporates the sum rule relating the diagonal element of the force constant to the off-diagonal ones.

We find that the disorder induced scattering effects on the thermal conductivity, $\kappa(T)$, is relatively large in the low frequency regime. $\kappa(T)$ shows a quadratic T -dependence in the low temperature range, where only low energy vibrations are excited, and then smoothly rises to a T -independent saturated value at high T . Thermal diffusivity manifests the effect of disorder in a more dramatic fashion, and gives an idea about localization. Based on our calculation on $\text{Fe}_{1-x}\text{Cr}_x$ alloys, a large fraction ($> 90\%$) of vibrational eigenstates are found to be localized with the maximum localization near 50-50 composition, where the disorder scattering is maximum, as expected.

II. THERMAL TRANSPORT

For disordered materials, the lattice thermal conductivity requires the configuration average of the response

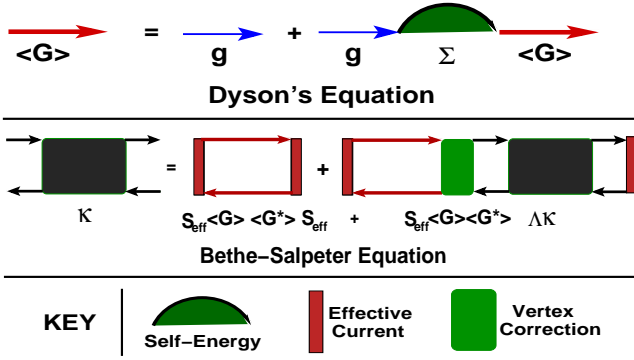


FIG. 1. (Color Online) (Top row) Dyson's Equation due to scattering diagrams for the single particle averaged Green's functions for disordered alloys. (Middle Row) Bethe-Salpeter equation for the response functions in disordered alloys. (Bottom Row) Key to diagrams. $\langle \mathbf{G} \rangle$ is the averaged disorder renormalized Green's function, $\langle \kappa \rangle$ is the two-particle correlation function related to Thermal conductivity, Σ is the self energy and \mathbf{S}_{eff} is the disorder-renormalized effective current.

functions of the kind (see Ref. 6),

$$\langle \langle \kappa(z_1, z_2, T) \rangle \rangle = \int \frac{d^3 \mathbf{k}}{8\pi^3} \text{Tr} \left[\langle \langle \mathbf{S}(\mathbf{k}, T) \mathbf{G}(\mathbf{k}, z_1) \mathbf{S}(\mathbf{k}, T) \mathbf{G}(\mathbf{k}, z_2) \rangle \rangle \right], \quad (1)$$

where \mathbf{S} is the heat current operator and \mathbf{G} is the phonon propagator. $\langle \langle \rangle \rangle$ denotes configuration averaging.

The right hand side of Eq. (1) involves the configuration average of four random functions whose fluctuations are correlated. Unlike the configuration average of a single particle Green function $\langle \langle \mathbf{G}(\mathbf{k}, z) \rangle \rangle$, which can be calculated via a perturbative self-consistent Dyson's equation (shown diagrammatically in the 1st row of Fig. 1), the average of a two-particle correlation function such as that in Eq. (1) is non-trivial. The zeroth order approximation for such an average is the one which assumes the fluctuations between all four random functions to be uncorrelated, and expresses the average of the product as the product of the averages (as in the so called Virtual Crystal Approximation (VCA)). The inherent correlation, however, requires the contributions from averages taken in pairs, triplets and all four random functions. Such disorder induced corrections can be calculated very efficiently within a Feynman diagrammatic technique (details have been discussed in Ref. 6), which renormalizes both the phonon propagators as well as the heat currents to provide a mathematical expression for $\langle \langle \kappa \rangle \rangle$ with an *effective* heat current \mathbf{S}_{eff} related to the self-energy of the propagators (shown by 1st diagram on right hand side of the middle row of Fig. 1). The last term in the middle row gives the contribution from the so called vertex correction arising out of the correlated propagation. For a harmonic solid, thermal diffusivity has a similar expression as $\langle \langle \kappa \rangle \rangle$ except the product of five random functions instead of four. A similar diagrammatic procedure has been used earlier by us⁶ to calculate the

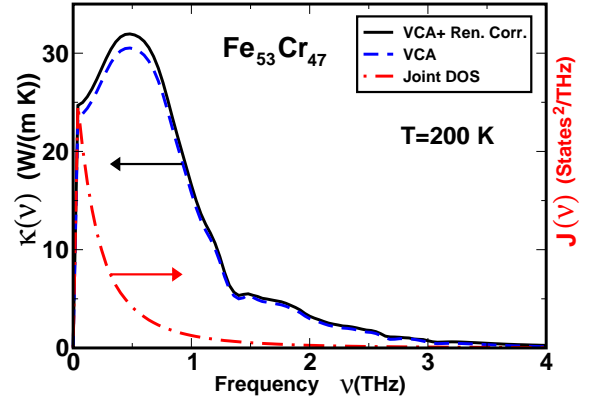


FIG. 2. (Color Online) Frequency dependence of Thermal conductivity and Joint density of states for $\text{Fe}_{53}\text{Cr}_{47}$ alloy at $T = 200$ K. Solid line shows the result including all disorder-induced corrections + the vertex correction (middle row of Fig. 1) and dashed line including the VCA average alone.

configuration averaged thermal diffusivity as given by,

$$\langle \langle D(\nu) \rangle \rangle = \frac{1}{\pi^2} \int d\nu' \int \frac{d^3 \mathbf{k}}{8\pi^3} \text{Tr} \left[\langle \langle \mathbf{S} \mathbf{G}(\mathbf{k}, \nu') \mathbf{S}(\mathbf{k}) \mathbf{S} \mathbf{G}(\mathbf{k}, \nu') \mathbf{S}(\mathbf{k}) \mathbf{S} \mathbf{G}(\mathbf{k}, \nu) \rangle \rangle \right].$$

III. COMPUTATIONAL DETAILS

The above theoretical approach for the thermal transport of disordered materials is combined with a first-principles Quantum-ESPRESSO (QE) calculation⁷ of the force-constants. QE is a linear response based method: namely the density functional perturbation theory (DFPT).⁸ The dynamical matrix for the phonon excitation of a system is obtained from the ground state electron charge density and its linear response to a distortion of the ion-core geometry. We refer the reader to a recent article⁹ for further computational details on $\text{Fe}_{1-x}\text{Cr}_x$ alloys. This alloy, being a basic ingredient of stainless steel, is a technologically important structural material, dominated by force-constant disorder and hence should serve as a critical test of our theory for the thermal transport properties.

IV. RESULTS AND DISCUSSION

In Fig. 2, we display the frequency dependence of lattice thermal conductivity $\kappa(\nu)$ and the scaled joint density of states $J(\nu)$ at $T = 200$ K for the $\text{Fe}_{53}\text{Cr}_{47}$ alloy. It is obvious from the figure that the transition rate τ (related to the heat current operator) is strongly dependent both on the initial and final energies throughout the phonon spectrum i.e. $\kappa(\nu, T) \neq |\tau(\nu, T)| J(\nu)$, where $J(\nu)$ (shown by dot-dashed line in Fig. 2) is given by

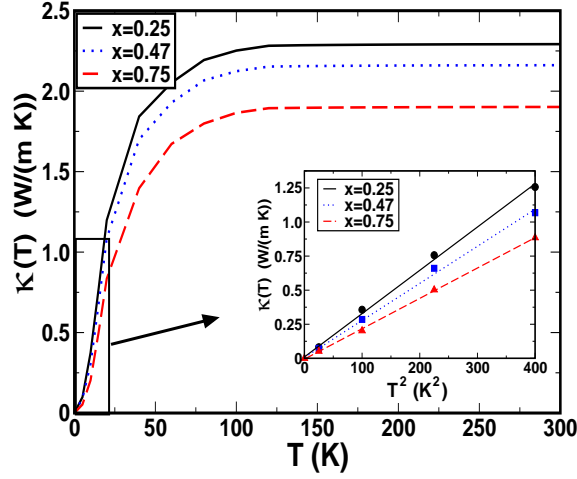


FIG. 3. (Color Online) Temperature dependence of Thermal conductivity (κ) for three $\text{Fe}_{1-x}\text{Cr}_x$ alloys. Inset shows the quadratic T -dependence of κ in the low T -range.

$$\langle\langle J(\nu) \rangle\rangle = \int d\nu' \int \frac{d^3\mathbf{k}}{8\pi^3} \text{Tr} [\Im m \langle\langle \mathbf{G}(\mathbf{k}, \nu') \rangle\rangle \Im m \langle\langle \mathbf{G}(\mathbf{k}, \nu' + \nu) \rangle\rangle].$$

The effect of disorder-induced renormalized corrections (black solid lines) to the zeroth order virtual-crystal-approximation (VCA) (blue dashed line) thermal conductivity is not significant, and becomes negligibly small beyond $\nu = 2.7$ THz. The traditional single site mean-field approximation is, therefore, expected to describe well the multiple scattering phenomenon associated with the high frequency mode, deviating only in the low frequency range where the higher order corrections become important. Notably, both $\kappa(\nu)$ and $J(\nu)$ curve has a dip at a very small energy ($\nu \simeq 0$). Such a dip reflects the missing intraband contribution (κ^{II}) to the conductivity. The origin of this dip is a natural outcome of a smooth convolution of two Green matrices $\mathbf{G}(\mathbf{k}, \nu')$ and $\mathbf{G}(\mathbf{k}, \nu' + \nu)$ (or two smooth DOS). A similar dip has also been reported by Feldman *et al.*⁴ in amorphous Si and $\text{Si}_{1-x}\text{Ge}_x$ alloys. Unlike our case ($\kappa(\nu) \rightarrow 0$ as $\nu \rightarrow 0$), this dip in their calculation stands at a finite value as $\nu \rightarrow 0$. These authors have introduced an arbitrary Lorentzian broadening of the delta functions in their Kubo-Greenwood expression for κ , while in our calculation this arises naturally through the disorder induced broadening of the spectral function $\Im m[\mathbf{G}(\mathbf{k}, \nu)]$. An extrapolation of our $\kappa(\nu)$ -curve (see Fig. 2) from a value just above $\nu = 0$ to a value at $\nu = 0$ yields an estimate of the dc thermal conductivity, which comes out to be 24.7 W/(m K) for the present $\text{Fe}_{53}\text{Cr}_{47}$ alloy at $T = 200$ K. Literature survey shows a lack of available experimental data for concentrated $\text{Fe}_{1-x}\text{Cr}_x$ alloy, however there exist some on the dilute Cr-alloys.¹⁰ For example κ_{expt} for $x = 0.25\%$ Cr is ~ 22 W/(m K), with

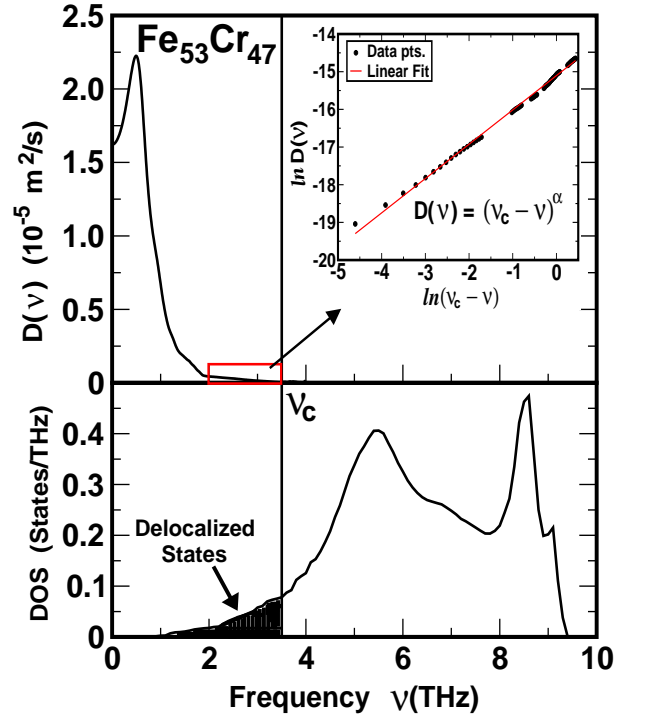


FIG. 4. (Color Online) Thermal diffusivity (top) and DOS (bottom) vs. phonon frequency (ν) for $\text{Fe}_{53}\text{Cr}_{47}$ alloy. Inset shows an approximate linear ν -dependence of $D(\nu)$ above 2 THz. ν_c locates the mobility edge and area under the shaded region gives an estimate of the fraction of delocalized states.

which we shall compare our theoretical estimate below.

Figure 3 shows the temperature dependence of thermal conductivity for three $\text{Fe}_{1-x}\text{Cr}_x$ alloys. Note that $\kappa(T)$ behaves quadratically (see inset) in the low temperature regime ($T < 20$ K) where only low-energy vibrations are excited. As the temperature is increased further, the T -dependence of κ becomes much milder and eventually reaches a T -independent saturated value. The origin of such a high T -saturation is not very well described by most previous theories. Within a harmonic approximation, such a saturation mainly arise from the T -dependence of Einstein specific heat piece of the conductivity expression.⁴ The intrinsic harmonic diffusion of higher energy delocalized vibrations are mostly responsible for the relevant dominant mechanism in this regime. Another qualitative explanation can be that : the phonon-phonon scattering in this high T -range becomes so strong that the phonon MFPs reach a minima, and further enhancing the disorder scattering by raising temperature would not cause any further reduction in the MFP, hence resulting in a T -independent thermal conductivity. This, however, is just a physically plausible explanation based on the MFP and is not intended to reflect a known outcome of the proposed theory itself. One can also notice an overall reduction of κ with increasing disorder (x), as expected. Such effect usually reflect the scattering arising out of the difference in masses, radii

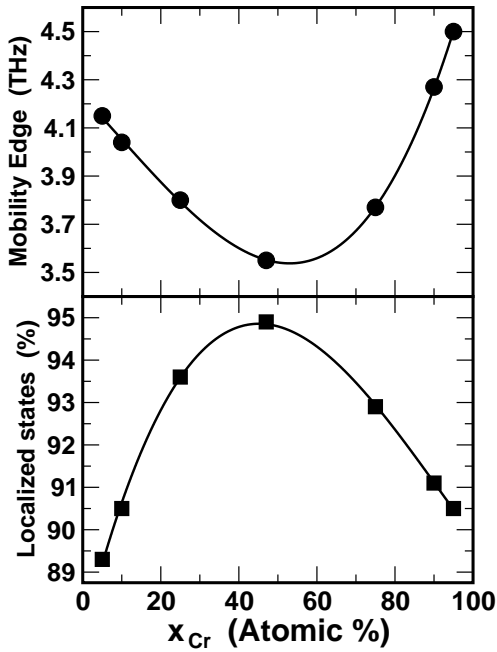


FIG. 5. Mobility edge (top) and the percentage of localized states (bottom) vs Cr-concentration for $\text{Fe}_{1-x}\text{Cr}_x$ alloy.

and force constants between the host lattice atoms and impurities. In the present $\text{Fe}_{1-x}\text{Cr}_x$ alloy, however, this scattering is mainly dominated by a large difference of force constants between Fe and Cr atoms in the alloy, while their masses and radii are almost similar. As far as the comparison goes, looking at the solid black curve of Fig. 3 for $x=0.25\%$ Cr, one can notice the saturated value of thermal conductivity (room temperature value) to be 22.8 W/(m K) which is in good agreement with the experimental value of 22 W/(m K) .

Next, we examine the effect of disorder scattering on the vibrational eigenstates and hence the localization of the phonon modes based on a thermal diffusivity calculation. In Fig. 4, we show the thermal diffusivity (top panel) and the phonon density of states (bottom panel) vs frequency for the $\text{Fe}_{53}\text{Cr}_{47}$ alloy. Above $\nu \simeq 2 \text{ THz}$, $D(\nu)$ decreases smoothly (approximately linear in ν) with a critical frequency $\nu_c = 3.55 \text{ THz}$, where $D(\nu)$ vanishes to within a very small level of noise. This regime is shown, for clarity, as a log-log plot within the inset of the top panel. The calculated critical exponent $\alpha \simeq 1.011$ agrees with the scaling and other theories of Anderson localization.¹¹ The critical frequency ν_c locates the mobility edge above which the diffusivity strictly goes to zero in the infinite size limit, and the allowed vibrational states above (below) this frequency remain localized (de-localized). This is shown by the area under the shaded (unshaded) region in the bottom panel which gives an estimate of the percentage of delocalized (localized) states.

The location of mobility edge (ν_c) and the percentage of localized states (calculated from the area under the curve in Fig. 4) with varying Cr-content in $\text{Fe}_{1-x}\text{Cr}_x$

alloy is shown in Fig. 5. Such a non-monotonous variation of the fraction of localized states is an artifact of the varying band-width of the phonon spectrum with x . Unlike the mass dominated $\text{Si}_{1-x}\text{Ge}_x$ alloys⁴ which show an increasing percentage of localized states, towards the upper end of the phonon spectrum, with increasing Ge-concentration, the Fe-Cr alloys show maximum localization at $x_{Cr} = 47 \%$. Such a maximal localization may be due to the dominance of the force constant disorder in the present alloy which causes an enhanced disorder scattering at $x = 47 \%$ and hence localize the vibrational modes maximally.

An alternative way of estimating the fraction of localized (delocalized) states is to calculate the so called “inverse participation ratio” $1/p_\gamma$ defined as, $1/p_\gamma = \sum_\mu \int (d^3k/8\pi^3) \epsilon_\gamma^\mu(\mathbf{k})$, where $\epsilon_\gamma^\mu(\mathbf{k})$ is the μ th Cartesian component of the normalized polarization vector of the γ th mode. p_γ measures the number of atoms on which γ th vibrational mode has significant amplitude. $1/p_\gamma \rightarrow 0$ for delocalized mode, but remains finite for localized modes. Although this procedure provides a quick assessment of localization, it suffers from a shortcoming which arises quite often from the existence of an unexpected *few* localized modes in the low frequency regime as discussed earlier.^{4,12} This is mainly due to a sensitive dependence of p_γ on the boundary condition used in the concerned model. In other words, finite-size theory (even for large model systems) cause an unphysical gap at the bottom of the spectrum, and the states closest to this gap may be or appear to be localized. The same states in a macroscopic sample, however, may not be localized but propagating (or may be resonant).^{4,12} The percentage of localized (de-localized) states calculated using the area above (below) ν_c of DOS curve and using p_γ may differ, if calculated from such finite-size theories. However, being a k -space based formulation, our theory does not suffer from such differences and is free from the unexpected errors arising from the existence of few localized modes in the low energy regime.

V. SUMMARY

In summary, we combine a generalized Kubo-Greenwood type formula with the linear-response based QE calculation to make a first principles prediction of the thermal conductivity and diffusivity of disordered Fe-Cr alloys. The effect of disorder-induced scattering on κ is found to decrease with increasing phonon energy. Thermal conductivity shows a quadratic T -dependence in the low T -regime, increasing smoothly to a T -independent saturated value at high T . Thermal diffusivity provides an estimate of the location of mobility edge, which subsequently gives an idea about the disorder-induced localization in the system. Vibrational modes in the present $\text{Fe}_{1-x}\text{Cr}_x$ alloy are maximally localized at $x = 47 \%$, where the effect of disorder scattering is maximum.

VI. ACKNOWLEDGMENTS

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* emails: aftab@ameslab.gov, abhijit@bose.res.in

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