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Dear *Physical Review B* Editor:

We have submitted the manuscript titled “Evaluation of the virtual crystal approximation for predicting alloy vibrational mode properties and thermal conductivity” by Jason M. Larkin and Alan J. H. McGaughey for consideration for publication in *Physical Review B*.

We recently received correspondence indicating that our submitted manuscript did not meet the criteria of the Physical Review B journal. These criteria state that the submitted manuscript should, “be of high quality and scientific interest, be recognized as an important contribution to the literature, and be of particular interest to our readers.” We believe that, due to the length and rigor of our manuscript, it is not obvious that the criteria are satisfied. We believe that a full referee review is necessary to determine if our manuscript meets the criteria stated. We highlight below the ways in which our manuscript satisfies these requirements. Note that reference numbers correspond to those used in our submitted manuscript.

New Understanding of Physics

We believe that our manuscript demonstrates a new understanding of the physics of thermal transport in disordered lattices. Our results demonstrate an important connection between the modeling of disordered lattices and amorphous materials. [1,2,11,35,86] The high-scatter limit of mode thermal diffusivity that is used in models of disordered materials has not been verified theoretically.[1,2,80,86]

In our manuscript, we demonstrate that the high-scatter limit of thermal diffusivity is important for the thermal modeling of the disordered lattices (e.g., alloys) and amorphous phase of Lennard-Jones argon, which are materials with important contributions from the whole spectrum of vibrational modes. For low-frequency dominated materials, such as Stillinger-Weber silicon with thermal conductivities significantly larger than the high-scatter limit, the high-scatter limit of mode diffusivity is unimportant.

In VC-ALD, the disorder in the alloy is treated as a perturbation. The perturbative disorder model was originally developed to model isotopic solids where the disorder

is weak.[11] The limits of the VC-ALD method have not been determined. We are able to determine the limits of the VC-ALD approach using computationally-inexpensive empirical potentials and self- consistently treating the disorder explicitly and as a perturbation. We are not aware of any such previous study. Our results indicate that while VC-ALD is generally an accurate method for low-frequency dominated materials, care must be taken when modeling alloys with low thermal conductivities, where significant underprediction of thermal conductivity is likely.

Scientific Interest

The breakdown of the VC-ALD method has gone unnoticed by previous studies because: (I) these studies were limited to the VC-ALD method because of computationally-expensive DFT calculations.[12,18-27] (ii) these studies have focused on low-frequency dominated materials.[12,18-27] (iii) these studies did not compare predictions with experiment.[21,22,26]

While our work uses empirical potentials, we provide a self-consistent study of thermal transport in these systems. The use of empirical potentials versus computationally-expensive DFT calculations was necessary to observe the breakdown of the VC-ALD method. Our study includes two example materials which demonstrate the applicability and breakdown of the VC-ALD method, and we believe the results are of general use for the study of any disordered lattice.

We believe several results of our work are of significant scientific interest. The following calculations we performed are novel additions to the literature:

1) To model the disordered lattices explicitly, we used Normal Mode Decomposition (NMD). NMD has been performed previously on the perfect crystal, disordered lattice and amorphous phases.[53,60-62] In this work, we use NMD to predicting the lifetimes of a disordered lattice using VC-NMD, where the normal modes of the Virtual Crystal (VC) are used as an approximation. This has not been before.

2) To model the disorder explicitly, we use the Allen-Feldman (AF) theory of diffusons. The Allen-Feldman theory of diffusons has been previously applied only to amorphous phases.[16,17,35,36,74] We use the AF theory to show that the lower-limit of diffusivity of high-frequency modes in a disordered lattice is the high-scatter limit, in contrast to the VC-ALD method. Identification of this high-scatter limit of mode diffusivity was essential for identifying the breakdown in the VC-ALD method. The high-scatter limit of diffusivity is usually assumed, without theoretical justification, in models for disordered and amorphous materials.[1,2,80,83] Our study gives self-consistent justification for the use of the high-scatter limit of diffusivity.

3) We measure the structure factor for modes in a disordered lattice, which has only been done previously for modes in amorphous materials.\cite{PRB articles} The structure factors measurements help to understand the underprediction of the VC-predicted group velocity as the representative velocity scale for mode diffusivities in the disordered lattice. While previous studies have attempted to predict the group velocity of modes in disordered systems, there is no theoretical justification for the methods used.[60-62] We believe the measurement of the structure factor is a significant contribution to understanding how to predict the correct velocity scale for mode diffusivities in disordered systems.[]

Work Quality

We believe our work is of high quality. We present a self-consistent study of the VC approximation using five different method (VC-ALD, VC-NMD, Gamma-NMD, AF theory, and Green-Kubo). We study the thermal transport of Lennard-Jones argon in 3 solid phases of the materials: perfect crystal, disordered lattice, and amorphous phase. By using three phases, we demonstrate that applicability of the different methods for predicting the thermal conductivity and mode-properties:

1) Molecular Dynamics-based Green-Kubo: suitable for modeling all three phases. The GK method does not predict the mode properties.

2) Phonon based VC-ALD and VC-NMD: suitable for the perfect crystal and disordered lattices with the high-scatter limit correction.

3) The AF theory of diffusons: suitable for the high-frequency modes of the disordered lattice and all modes of the amorphous phase.

We are unaware of any other study which uses all five of these methods self-consistently on the same material system.

Contribution to the Literature

Due to their low thermal conductivities, alloys are currently an active area of research, notably in the thermoelectric energy conversion field. The ability to predict alloy thermal conductivity is critical in narrowing down a large materials design space. Recent papers [e.g., *PRL* **106**, 045901 (2011), *PRL* **109**, 095901 (2012), *PRB* **85**, 184303 (2012)] have used the VC-ALD method to make such predictions.

We believe this work will make an important contribution to the literature because the high-scatter limit adjustment is of interest to the study of low-thermal conductivity alloys. Thermoelectric energy generation materials, such as PbTe/Se alloys,[21,22,49] maximize their efficiency by minimizing their thermal conductivity. The search for lower thermal conductivity alloys will require the modeling of even

lower-thermal conductivity alloys, where the high-scatter limit we have proposed should be considered.

Interest to Physical Review Readers

Of our 90 references, 43 of them are from the Physical Review journals (Letters, B, and E). We believe we have made a significant contribution to the Physical Review literature by extending the results found in these 43 publications. We believe this work should be published in Physical Review B.

We suggested the following reviewers:

Davide Donadio
Group Leader
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Junichiro Shiomi
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Their names appear on nine of the publications that we reference in our manuscript, five of which are published in Physical Review Letters or B.[21-23,28,29,53,60-62] We believe they will be fair judges of the significance of our work.

We look forward to your response.

Sincerely,

Alan McGaughey