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March 22, 2013

Dear *Physical Review B* Editor:

On March 23, 2013, we 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 received correspondence on March 29, 2013 indicating that our manuscript was not suitable for *Physical Review B*. The correspondence stated that a 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 may not be immediately obvious that these criteria are satisfied. We believe that a full referee review is necessary to determine if our manuscript meets the stated criteria. We highlight below how we believe that our manuscript satisfies these requirements. Please note that reference numbers correspond to those used in the submitted manuscript.

New Understanding of Physics

Our manuscript provides original insight into the physics of thermal transport in disordered lattices (i.e., isotopic solids and alloys). Notably:

1. The first rigourous test of the virtual crystal (VC) approximation when used in anharmonic lattice dynamics (ALD) calculations. The VC-ALD technique has been used in a number of recent papers published in PRB and PRL (REFS), but its limits have not been assessed. 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]. We determined 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 materials whose thermal conductivity is dominated by low-frequency vibrational modes, care must be taken when modeling alloys with low thermal conductivities, where significant underprediction of thermal conductivity is likely.

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2. The indentification of important connections between the modeling of disordered lattices and amorphous materials [1,2,11,35,86]. We demonstrate that the high-scatter limit of thermal diffusivity typically used in modeling amorphous materials is directly relevant to the modeling of disordered lattices. Application of the VC approximation leads to vibrational mode diffusivities that are non-physical and the high-scatter limit provides a simple, physically-sound approach for correcting these predictions.

Scientific Interest

The breakdown of the VC-ALD method has gone unnoticed in previous computational work because these studies: (i) were limited to the VC-ALD method because of computationally-expensive DFT calculations, so that validation was not possible [12,18-27], (ii) focused on materials where the thermal conductivity is dominated by low-frequency vibration modes [12,18-27], and/or (iii) did not always compare their predictions with experimental measurements [21,22,26].

In our work, *we provide a self-consistent study of thermal transport in disordered lattices using a set of complementary computational tools based in molecular dynamics simulations and lattice dynamics calculations*. The use of empirical potentials versus computationally-expensive DFT calculations allowed us to perform the molecular dynamics simulations that were necessary to observe the breakdown of the VC-ALD method. Our study includes two test materials that demonstrate the applicability and breakdown of the VC-ALD method. *The conclusions are of general use for the study of any disordered lattice.*

The following calculations that we performed are novel additions to the literature:

1) *Virtual Crystal + Normal Mode Decomposition.* To model disordered lattices explicitly, we (and others) used normal mode decomposition (NMD) on the fully disordered supercell. This approach is limited in that the group velocity cannot be extracted so that thermal conductivity cannot be predicted. The novel contribution of our work is the use of NMD to predict the lifetimes of a disordered lattice using VC-NMD, where the normal modes of the Virtual Crystal (VC) are used as an approximation.

2) *Allen-Feldman Theory on Disodered Lattice.* To model the disorder explicitly, we also use the Allen-Feldman (AF) theory of diffusons. This theory has only previously been applied 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, which incorrectly predicts that the limiting value is zero. 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 its use.

3) *Structure Factor of Disordered Lattice to Predict Group Velocities.* We calculated the structure factor for modes in a disordered lattice, which has previously only been done for modes in

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amorphous materials. \cite{PRB articles} The structure factor predictions help us to understand that the VC-predicted group velocities are an underprediction of 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]. The structure factor provides a rigorous manner to estimate group velocities and is a significant contribution to understanding how to predict the correct velocity scale for mode diffusivities in disordered systems. []

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Work Quality

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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 three solid phases of the materials: perfect crystal, disordered lattice, and amorphous phase. By using three phases, we demonstrate the applicability of the different methods for predicting the thermal conductivity and mode-properties:

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

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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 that uses all five of these methods self-consistently on the same material system. *Our work provides clear guidelines for others on what tools are appropriate for different solid state systems.*

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Contribution to the Literature

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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.

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Interest to Physical Review Readers

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

We suggested the following reviewers:

Davide Donadio
Group Leader
Max Planck Institute for Polymer Research
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Junichiro Shiomi
Associate Professor
Mechanical Engineering, University of Tokyo
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Xiulin Ruan
Assistant Professor
Mechanical Engineering, Purdue University
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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 *Physical Review B* [21-23,28,29,53,60-62]. We believe that they will be fair judges of the significance of our work.

We look forward to your response.

Sincerely,

Alan McGaughey

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