A description...

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Dear *Physical Review B* Editor:

We are submitting 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*.

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 anharmonic lattice dynamics and the virtual crystal approximation (an approach we call VC-ALD) to make such predictions.

In VC-ALD, the disorder in the alloy is treated as a perturbation. The limits of this approach have yet to be determined. In our work, we use computationally-inexpensive empirical potentials to assess the virtual crystal approximation by 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, care must be taken when modeling alloys with low thermal conductivities, where significant underprediction of thermal conductivity is likely.

Reference numbers correspond to those used in our submitted manuscript. Note that a majority of the articles we reference are from Physical Review (Letters or B).  
  
1) We have identified the breakdown of the VC-ALD method, specifically the phonon-defect scattering theory of Tamura, whose original theory was developed to treat weak disorder in isotopic lattices.  We believe that this breakdown has gone unnoticed by other studies using VC-ALD because they have focused on low-frequency dominated materials or have not carefully compared with experiment.\cite{lots of PRB articles} These previous studies were limited to the use of VC-ALD because of expensive Density Functional Theory (DFT) calculations. Using computationally-inexpensive empirical potentials, our study uses five different methods (VC-ALD, VC-NMD, Gamma-NMD, Allen-Feldman (AF) theory, and Green-Kubo (GK)) to self-consistently study the effect of disorder explicitly and as a perturbation.

We do not believe that the use of empirical potentials reduces the impact of our study. It is necessary given the computationally-expensive methods we have used. Our study includes 2 example materials which demonstrate the applicability and breakdown of the VC-ALD method, and we believe the results are generally useful for the study of any disordered lattice.   
  
2) The application of the AF theory of diffusons to a disordered lattice has not been done before.\cite{lots of PRB articles}  The AF theory application allowed us to identify the high-scatter limit for vibrational diffusivity in a disordered lattice, which was essential for identifying the breakdown in the VC-ALD method.  This high-scatter limit of diffusivity is usually assumed, without theoretical justification, in models for disordered and amorphous materials.\cite{PRB articles}  
  
3)  The measurement of the structure factor for modes in a disordered lattice, which has only been done previously for amorphous materials.\cite{PRB articles} This allowed us to identify the underprediction o the VC-predicted group velocity as the representative velocity scale for mode diffusivities in the disordered lattice. 

We suggest the following reviewers:

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We look forward to your response.

Sincerely,

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