Poster Presentation

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Lattice thermal expansion of complex oxides with intrinsic anharmonicity

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The lattice thermal expansion of crystalline solids cannot be adequately modeled by Grüneisen approximation using either Einstein single harmonic frequency or Debye frequency spectrum because a true phonon spectrum does not follow either of the two kinds. The Debye model misfits to many observations due to the fact that real solids comprises of axial anisotropy, lattice waves with dispersion at the Brillouin zone boundaries, low/high frequency optical vibrations in excess of the Debye spectrum. The actual frequency distribution is a complicated function of frequency instead of a simple parabolic Debye spectrum. The frequency distribution can be simplified using power series [1] leading to singularities before and after the Debye cutoff frequency. Using multiple Debye or Einstein oscillators, or their mixtures, is also common practice to better describe the lattice expansion, however, these models extremely suffer from intrinsic anharmonicity in particular at high temperatures. It was demonstrated that even the noble monoatomic solids required inclusion of anharmonic terms in the harmonic model to better explain the observed values [2]. Worse even, when anharmonicity becomes dominant due to formation of vacancies and defects, anomalies of hard/soft modes or change of stereochemical activities of lone electron pairs (LEPs) as function of temperature. Herein we approach an extended Grüneisen approximation that includes harmonic, quasiharmonic and intrinsic anharmonic potentials to describe the internal energy of the crystal as function of temperature. The model has been applied to several complex oxides with LEPs ($Bi_2Ga_4O_9$ [3]) along with axial negative thermal expansion ($PbFeBO_4$) and rigid-unit-modes ($KAsW_2O_9$) reported here. The metric parameters were obtained from quality data collected from temperature-dependent neutron and X-ray powder diffractions.

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