



Phonons and anomalous thermal expansion behaviour in crystalline solids



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ABSTRACT

Anomalous thermal expansion behaviour of several open frame-work compounds has been extensively investigated using the techniques of inelastic neutron scattering and lattice dynamics. These compounds involve increasing level of structural complexity and flexibility, which leads to increased values of thermal expansion coefficients approaching colossal values. In several compounds, neutron inelastic scattering experiments have produced quantitative estimates of the anharmonicity of phonons over a range of low energies, and thereby explained the observed thermal expansion quantitatively. The anharmonicity is found to be an order of magnitude larger than that in usual materials. Lattice dynamical calculations have correctly predicted the observed anharmonicity in the neutron experiments and revealed the overall nature of phonons involved. In compounds showing negative thermal expansion, the phonons responsible have rather low energies up to 10 meV. In most compounds, the anharmonic phonons span all over the Brillouin zone, while in some cases the specific phonons are limited to certain wave-vectors. The nature of specific phonons responsible for anomalous behavior is found to be different in all these compounds. These phonons generally involve transverse vibrations, librations and internal distortions of the polyhedral units. The paper reviews recent advances in the understanding of anomalous thermal expansion behaviour.

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1. Introduction

Compounds that contract upon heating over a certain temperature range are exceptional. Such materials find extremely useful technical applications in composites. Compensating the usual (positive) thermal expansion of ordinary materials by contracting compounds allows tailoring the thermal expansion behavior of the ensemble. The technological relevance of these compounds and their composites principally derives from their ability to withstand thermal shock without any damage. The negative thermal expansion (NTE) phenomenon typically originates [1–39] from the presence of low-energy anharmonic vibrations of atoms.

The phenomenon of negative thermal expansion (NTE) is well known in nature, most notably in water around its melting point. Amongst solids, invar, which is an alloy of Fe and Ni, has very low or negative volume thermal expansion coefficient depending on its composition. The popular semiconductor materials silicon and germanium also exhibit the NTE behavior at low temperature. However, the discovery of large negative thermal expansion (NTE) in ZrW₂O₈ [40] over a wide range of temperatures has led to extensive research in this area [1–25,28,34,36,40–99]. Over the last two decades anomalous thermal expansion behavior has been found in large number [12,63,70,75,79,83,84,87,100–112] of open frame work compounds. These compounds find applications in forming the composites with tailored thermal expansion coefficients useful for applications such as in fiber optics, coatings, electronics, and mirror substrates to tooth fillings.

NTE has been found in framework oxides [40,100,101] with M–O–M (M = metal) linkages. For example, ZrW₂O₈ has a NTE coefficient of $-27 \times 10^{-6} \text{ K}^{-1}$ at 300 K. Further, the NTE coefficients of compounds with M–CN–M linkages was found to reach a much higher value of $-51 \times 10^{-6} \text{ K}^{-1}$ for Zn(CN)₂ [102] at 300 K. Apparently, the linkage between two neighboring

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