JCCM_Sept05_03

Rubber like Thermal Expansion, Elastic Constants and Compressibility in some Crystalline Solids

Authors: F. R. Drymiotis et al.
Phys. Rev. Letters, vol. 93, 025502-1-4 (2004);

Authors: C. Pantea et al., arXiv.org/cond-mat/0509220

Recommended with a Commentary by Chandra Varma, Bell laboratories and University of California, Riverside.

These two papers are interesting because they provide a fresh and novel impetus to study the everlasting problems of anharmonic systems.

Most crystalline solids expand and their elastic constants decrease on warming. This is understood as arising from cubic anharmonicity and the two effects are related to each other through the Gruneisen constant. A few crystalline solids do contract on warming but their elastic constants also increase; this is also consistent with anharmonic perturbation calculations if the quartic anharmonicity dominates over the cubic anharmonicity. This behavior is markedly different from polymeric solids, like rubber, which contract anomalously (almost linearly with temperature) on warming and whose elastic constants simultaneously increase. Polymeric solids are modeled by bonds of fixed length with zero stiffness for bond-bending at their contact. The contraction on increasing temperature is understood as a purely entropic effect at the bond-angles.

It was quite a surprise to discover, a few years ago, crystalline solids in which the volume decreases with increasing temperature linearly; In ZrW_2O_8, this happens from about 20 K to the highest measured temperature of about 500 K. This has posed the question: Can anharmonic perturbation theory explain this, even in principle. The two papers recommended above give persuasive evidence that this is not possible and that alternate starting points more like the theory of rubber elasticity and thermodynamics are required to understand these crystalline solids.

In ZrW_2O_8 at ambient temperature is a cubic (this is itself a surprise) perovskite solid down to the lowest temperature consisting of octahedra and tetrahedra linked together at corners. The bond angles and the bond lengths of the octahedra and the tetrahedra are more than an order of magnitude stiffer than the bond-angles linking them. They have been modeled as units with fixed volume and shape linked together with weak bonds, i.e. as three-dimensional analogs of the one-dimensional polymeric rubber. Such models, in which anharmonicity is modeled by rigid constraints do give thermal contraction on warming. But their full investigation and applications to get the right elastic properties of solids is a hard unfinished problem. It is very interesting that starting from such models, the conventional anharmonic perturbation theory results cannot be obtained in any limit and vice-versa.

In the first of the papers quoted above, the elastic constants are measured as a function of temperature; they behave conventionally, i.e. they decrease on warming which is contrary to what anharmonic perturbation calculations would give for a solid whose volume decreases on raising the temperature. The elastic constants actually decrease linearly in the same temperature region where the volume contracts; between 20 K and 300 K, the decrease is more than 30%. The Poisson ratio is also measured and is similar to that of ordinary solids. The second paper is motivated by the well-posed question, does the bulk modulus soften under pressure? This would be expected from the change of elastic constants with temperature: since the compressibility must remain positive the volume must decrease under pressure, just as it does on increasing the temperature. The authors find that it is indeed so and in fact can fit their observations quantitatively knowing the change in volume with temperature and the change in volume under pressure. This paper is a judicious combination of phenomenology and experimental techniques, but it ought to be noted that the elastic properties of a solid are not given correctly by the constrained lattice models that these experiments support because that requires developments of methods in which one can calculate by expanding about the absolute rigid enforcement of constraints.

Some inelastic Neutron scattering experiments measuring the vibrational spectra of such solids as a function of temperature have not been very helpful in understanding the thermal contraction, in my opinion, because they have been analyzed through conventional methods. Further experiments which probe anharmonicity in solids such as ultrasonic attenuation and thermal conductivity as well as experiments on the elastic limit of such solids would be quite worthwhile.