Nuclear Resonant X-ray Scattering at Pressure and Temperature: Applications to Thermophysics

Brent Fultz, Stefan Lohaus, and Pedro Guzman
Dept. of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA 91125

Nuclear resonant inelastic x-ray scattering (NRIXS) is well established as an important probe of phonon spectra of materials. Especially with guidance from *ab initio* computation, NRIXS spectra have proved reliable for obtaining the vibrational entropy (which is usually the dominant source of entropy of solid materials). An advantage of NRIXS over inelastic neutron scattering is that the sample volume is sufficiently small to permit measurements on materials under pressure in diamond anvil cells.

The equation of state $V(P,T)$ (volume, pressure, temperature) comes from partial derivatives of the free energy $G = H - TS$, so the entropy S is a key quantity for understanding the temperature dependence of V. Two important parts of S can be determined from NRS experiments – the vibrational entropy, S_{vib}, and the magnetic entropy, S_{mag}. Measuring these as functions of pressure opens new experimental approaches to understanding thermophysical properties.

An example is thermal expansion, $\beta = V^{-1}\, \partial V/\partial T$. Consider the rigorous Maxwell relation $\partial V/\partial T = -\, \partial S/\partial P$. For invar, with near-zero thermal expansion, NRIXS can test if the pressure dependence of S_{vib} and S_{mag} sum to zero. We recently measured the phonon partial DOS of ^{57}Fe in ^{57}Fe-36%Ni, the hyperfine magnetic field of ^{57}Fe, and the lattice parameter at two temperatures (300 and 410 K) at pressures to 15 GPa. The interesting part is below about 4 GPa, where the magnetization is being squeezed out, and an increasing magnetic disorder gives an increasing S_{mag}. Simultaneously, S_{vib} is decreasing as the phonons stiffen under pressure. We are still analyzing the results, but preliminary work shows a rather good cancellation of the changes of S_{vib} and S_{mag}. Their sum is nearly constant with pressure. This seems to account for the $\partial S/\partial P = 0$ that is required by thermodynamics if $\beta = 0$. Other contributions such as electronic entropy are not so significant.

It is important to put this work in the context of modern materials physics. Today the effects of pressure on phonon spectra can be calculated by *ab initio* methods with some reliability at 0 K, but calculations with simultaneous pressure and temperature remain a challenge. NRIXS measurements with control over simultaneous temperature and pressure can provide a large part of the free energy, $G(P,T)$, helping to test modern computational methods. Another thermophysical property amenable to such research is the temperature dependence of the elastic constants. The elastic constants at 0 K are well understood today, but their temperature-dependence is not simple to understand.

Invar is a special case, with its interesting behavior at low temperatures and relatively low pressures. In general, useful studies on the origins of thermophysical properties will require NRS measurements at higher T and P. Such work can begin to address the less understood cross-terms that scale with the product PT, which depends on how intrinsic phonon anharmonicity changes with P, or equivalently, how Grüneisen parameters change with T.