	Experiment title: Determination of the elastic moduli of Mo at high pressures with inelastic x-ray scattering.	**Experiment number**: HS-2447
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Report:

Molybdenum is a body centered cubic transition metal whose high-pressure behavior has attracted considerable experimental and theoretical interest.[1-7] The structure of molybdenum has been characterized by both static and shock compression over a wide range of pressure and temperature and thus, molybdenum is of great use as a secondary pressure standard[8,9]. Furthermore, Mo has likely the largest Kohn anomaly of any transition metal (along {001}) with an ~37% softening from q=0.6 to the zone edge. Yet, in static compression experiments, the bcc structure has been shown to be stable to least 272 GPa[3]. Thus, molybdenum makes an excellent target to study the effects of pressure on electron phonon coupling and the evolution of elasticity in bcc metals in general and, it is also an extremely useful material to test modern theoretical approaches to predicting physical and transport properties in condensed materials. Indeed, first principles equation of state calculations have been carried out over a wide range of pressure and temperature[5]. Furthermore, molybdenum is one of four metals, whose reduced shock isotherms were used to calibrate the ruby florescence pressure scale. However, as pointed out by Duffy and Wang (1998), the effective shear strength of both the dynamic and static compression curves is an important source of error in the ruby pressure scale. Thus, there has recently been much interest in determining the shear strength and elastic moduli of molybdenum under high-pressure conditions. Much of the impetus for the reinvestigation of molybdenum is motivated by the well-established discrepancy between the shock and static equations of state. We have recently used inelastic x-ray scattering on ID28 to overcome this limitation and have measured the phonon dispersions in molybdenum to pressures of ~40 GPa. In conjunction with this work, we have also used high pressure X-ray diffraction to determine the hydrostatic room temperature equation of state of Mo. This data together with the low q portion of the dispersion curves have been used to determine the pressure evolution of full elastic tensor to 37 GPa. Further, at these extreme pressures, we find a dramatic decrease in the anomalous dispersion along many of the branches most notably the LA [100] suggesting decreased electron–phonon coupling upon compression. In conjunction with the experimental work we have used density functional theory[11,12] to calculate the quasi-harmonic phonon spectrum of molybdenum up to pressures of 37 GPa (figure 1), where second derivatives of the total energy were calculated with respect to atomic displacements using a variational approach from which the dynamical matrix and phonon spectrum were calculated (Daniel Orlikowski, Pers. Comm., 2005) .[13,14] This was made possible through the ABINIT project[15], which is a robust, plane-wave DFT code using a fast Fourier transform to convert the wave-function between real and reciprocal space.[16]

The calculations are well converged for the phonon spectrum with respect to several parameters. We used a norm-conserving Troullier-Martins pseudo-potential[17] with 6 valence electrons ($4d^5$ $5s^1$) within the generalized gradient approximation (GGA)[18] for the exchange correlation function. The kinetic energy cut-off was determined to be 25 Ha and a 24x24x24 Monkhorst-Pack fc-point grid[19] was found to give converged total energy results. For the phonon spectrum, 29 irreducible q-points were used for the interpolation of the interatomic force constants. Total energies were converged to within 1e-16 Ha for the ground state and 5e-7 Ha for a given *q-point.* A Gaussian broadening scheme of the electron density of states was used. With this scheme, we found a sensitivity in the phonon calculation specifically for the edge phonons along [ζ,0,0]. After several tests, a broadening value $r = 0.01$ Ha was determined to give more consistent results relative to the entire calculated phonon spectrum. The smaller broadening values yielded significantly lower phonon values at the zone-edge. However, with any of the tried broadening values, the calculated spectrum itself along symmetry lines was not as sensitive and therefore the phonon calculation is considered converged for $r = 0.01$ Ha. The calculations were performed at the experimentally determined volumes. Overall, the calculated phonon spectrums compare very favorably with the experiment[20-22] along the symmetry lines. Our new data together with the theoretical calculations suggest that band broadening on compression likely results in decreasing electron-phonon coupling thus leading to a reduction in the phonon anomalies. This normalization of the phonon spectra may explain the extreme pressure stability of the bcc phase in this material.

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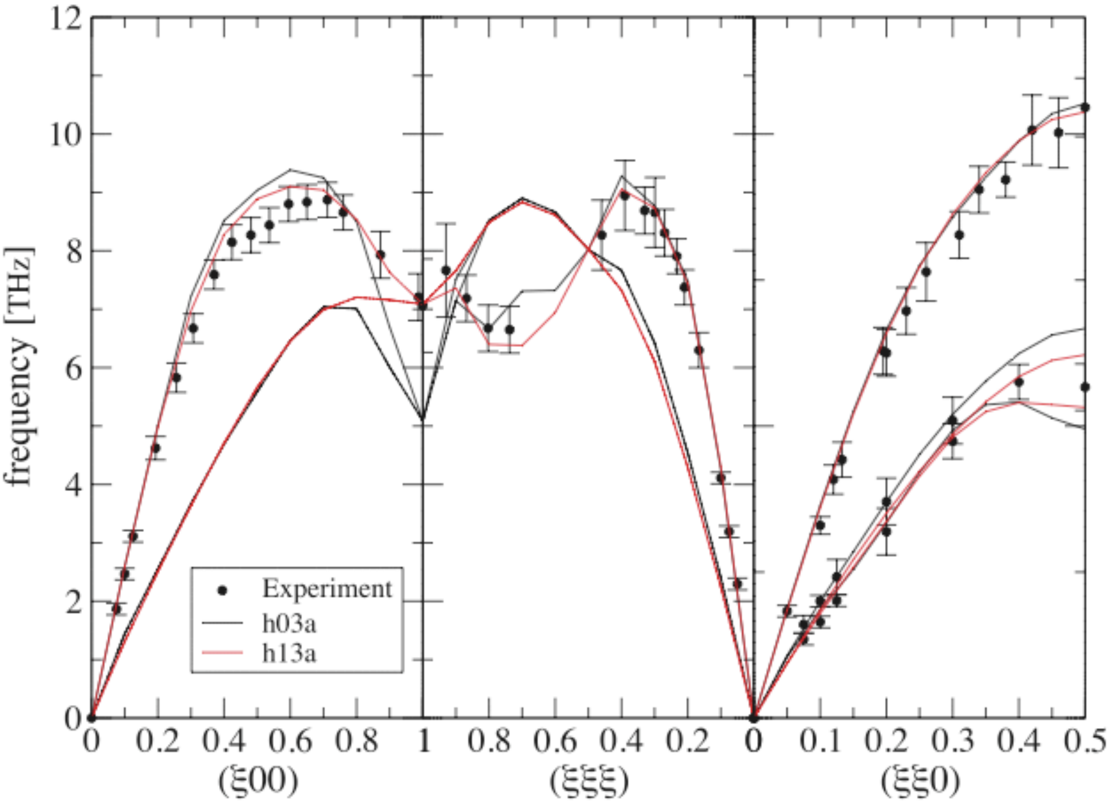

Fig. 1 The phonon spectrum along the symmertry lines compared to experimental (solid circles). The calculation was performed at Ω=94.08 a.m.^{3}/atom (~37 GPa)