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2001 J. Phys.: Condens. Matter 13 7847

(http://iopscience.iop.org/0953-8984/13/34/323)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 7847–7858 PII: S0953-8984(01)27055-6

Inelastic x-ray scattering at ultrahigh pressures

Ho-kwang Mao[1], **Chichang Kao**[2] **and Russell J Hemley**[1]

[1] Geophysical Laboratory and HPCAT, Carnegie Institution, 5251 Broad Branch Road NW, Washington, DC 20015-1305, USA
[2] National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, USA

Received 24 July 2001
Published 9 August 2001
Online at stacks.iop.org/JPhysCM/13/7847

Abstract

Inelastic x-ray scattering (IXS) provides high-pressure research with an arsenal of analytical capabilities for key measurements that were previously unattainable, and high-pressure research provides IXS with numerous applications where the technique has unique advantages over other methods. High-pressure investigations can now be conducted using non-resonant IXS, resonant IXS, nuclear resonant IXS and x-ray emission spectroscopy with energy resolutions of 100 meV to 1 eV for electronic transitions and 1 to 10 meV for phonon studies. By pressure-tuning materials over a wide range, we are able to investigate fundamental properties of the electron gas, strongly correlated electron systems, high-energy electronic excitations and phonons in energy and momentum space. The results have important implications for a variety of materials problem applications as well as providing basic information for understanding the deep interior of the Earth and other planets.

1. Interdisciplinary high-pressure sciences

Extreme pressure conditions radically alter the properties of materials. Studies of such states of matter have important implications for a wide range of problems, from chemistry and materials science [1], to fundamental physics [2], to Earth and planetary sciences [3]. Exploration of the pressure variable has revealed new classes of materials. Rare gases, normally classified as chemically inert, combine with other elements under pressure [4-6]. Normally unreactive metals also relinquish their inertness to form new alloys with other elements [7]. Silicon–oxygen tetrahedral frameworks, the basis of rock-forming minerals, are destroyed and replaced by altogether different structures at pressures equivalent to those found deep within the Earth [8]. Carbon rings, basic structural units of organic chemicals and biomaterials, become unstable and are replaced by diamond-like structures. Carbon forms tetrahedral frameworks, and carbon dioxide crystallizes into a quartz-like superhard material [9, 10]. Since most of the matter in the solar system exists under extreme pressures, the flurry of new findings is changing our understanding of the nature and evolution of the planets [11, 12]. New non-crystalline states appear [13, 14], high-temperature superconductivity is enhanced [15], insulating solids

undergo novel transitions to metals [16] and superconductors [17] and there is the prospect for observing entirely new physical phenomena.

What has made this new field of research possible is the sustained development of a broad range of high-pressure techniques based on the diamond cell. Numerous types of cell are in use but all consist of a pair of gem diamonds that pressurize the sample contained inside a small chamber formed within a metal shim, or gasket, placed between the tips of the anvils. Invented over 35 years ago [18], this device has undergone several generations of evolution, especially during the last decade. Now, sample temperatures in excess of those at the surface of the sun ($T > 7000$ K) (see review [19]) as well as ultralow temperatures down to ten millikelvin [20, 21] can be achieved—while samples are under high pressure. Hand in hand with these developments in pressure generation, there have been extensive advances in research techniques for obtaining accurate measurements of physical and chemical properties of the samples contained within these high-pressure devices. With this concurrent advancement in pressure generation and analytical techniques, the new diamond cell provides a powerful vehicle for reaching extreme pressure conditions, as well as a wide, clear window for comprehensive in-depth investigations. For instance, the development of electrical conductivity and magnetic susceptibility [22] microprobes has led to measurement of the record-high superconducting temperature (164 K) [23] and the discoveries of the high-pressure chalcogen superconductors (among which sulphur becomes a record-high elemental superconductor at 17 K and 1.5 Mbar (150 GPa) [17]). The developments of laser [24, 25], optical and infrared spectroscopies [26, 27], which probe vibrational, electronic and magnetic states in molecules and solids at high pressures, has led to the discoveries of quantum and classical orderings of solid hydrogen [28] and symmetrization of ice [29, 30]. The developments of synchrotron x-radiation for diffraction, scattering and spectroscopy has helped to characterize samples under extreme conditions [31–33] and led to discoveries of myriad new phenomena [34, 35] and new classes of materials [4, 10, 14, 36].

2. Studies of material dynamics by inelastic x-ray scattering at high pressures

High-pressure research has only fully utilized the elastic scattering (diffraction) component of the synchrotron source for static structural investigation. At the forefront of synchrotron techniques are those exploiting the enormous potential of inelastic x-ray scattering (IXS) for high-pressure dynamics research. In IXS, an incident x-ray photon with energy E_1, wavevector $\boldsymbol{\kappa}_1$ and polarization $\boldsymbol{\varepsilon}_1$ is scattered by the sample and altered into a photon with energy E_2, wavevector $\boldsymbol{\kappa}_2$ and polarization $\boldsymbol{\varepsilon}_2$. The energy transfer is $E_1 - E_2$, and the momentum transfer is $4\pi \sin(\theta/2)/\lambda$ where θ is the scattering angle. Experimentally, IXS measures the dynamic structure factor, $S(\boldsymbol{q}, \omega)$, which covers an extremely wide variety of electron and phonon dynamics. With the x-ray wavelength comparable to the scale of the wavevector, dispersion over the entire Brillouin zone can be probed. Complementary to inelastic scattering of light, electrons and neutrons, IXS is relatively new and is only becoming a realistic experimental tool with the arrival of the extremely brilliant, high-energy synchrotron sources. For materials at ambient conditions, the most basic properties suitable for IXS studies were determined decades ago by other methods. The frontier of IXS research has shifted to a number of 'exotic' properties (e.g. phonons at mesoscopic wavelengths [37, 38]). At megabar pressures, however, other methods are often rendered unusable or very restrictive. Techniques employing electron, ultraviolet or soft x-ray beams require a high-vacuum environment, in direct contradiction to the high-pressure environment in which the pressure vessel totally blocks the beam. Inelastic neutron scattering requires mm to cm samples that are limited to pressures below 20 GPa [39]. Consequently, even the most fundamental properties of the simplest materials, such as the

electronic band structure of silicon or phonon dispersion of iron or ice, could not be measured at high pressure until very recently. Free of these limitations, IXS holds the promise of fulfilling the technological development essential to the full exploration of the interdisciplinary high-pressure sciences.

3. High-energy electronic excitations at high pressure

The stationary states of the Schrödinger equation for electrons are clearly functions of volume and hence alterable by pressure. Pressure has drastic effects on the energy and dispersion of electronic bands. Such effects are manifested as bands that cross the Fermi surface causing pressure-induced insulator-to-metal transitions. However, observations in the past have been limited to a narrow energy window. Many electronic levels, including some of the most intriguing pressure-induced changes, occur outside the intrinsic band gap (5 eV) of the diamond window, and are thus inaccessible by conventional optical probes. For example, for the vast range of compression of hydrogen from a molecular solid to proposed metallic states, the density increases by more than a factor of ten [33, 40]. A conducting state has been observed in high-temperature fluid hydrogen [41]. In low-temperature solid hydrogen the electronic states are predicted to change from initially free-molecular-like levels, to a wide-gap insulator with bound excitons, to indirect band-gap closure, and eventually to an alkali-metal-like free electron gas (following structural transitions). The fascinating process has been the focus of a large number of theoretical calculations over the past 70 years [42–46], but the electronic transitions, particularly the band structure and excitons in the insulating state, are largely outside the optical observation window.

Using a high-energy x-ray beam for excitation, IXS spectroscopy provides access to probe high-energy electronic levels. Schell *et al* [47] successfully demonstrated the first measurement of a 21.9 eV electronic excitation in solid helium at 61.5 MPa and 4.3 K. Several major experimental challenges, however, need to be overcome before IXS can be applied to megabar pressure samples routinely. First, the double differential scattering cross section of IXS is very small. Second, all the available x-rays need to be focused on to the sample, whose size is on the order of 10–50 μm. Third, for IXS measurements with 100 meV to 1 eV resolution obtained by available x-ray analysers, the x-ray energy is typically between 8 and 10 keV. At these x-ray energies, the absorption of diamond is very high. The first two difficulties have been resolved to a large extent by the recent improvements in both flux and brightness in sources and the development of micro-focusing optics. The third difficulty is avoided by the use of a Be gasket (figure 1) and a panoramic scattering geometry (figure 2), which allows the x-ray beam to enter and exit the diamond anvil cell mainly through the Be gasket [48, 49]. The combination of these advances enables us to begin IXS experiments using diamond cells.

4. Compression of electron gas in 'simple metals'

The electron gas of simple metals is one of the oldest and most studied many-body problems in condensed-matter physics. However, the dynamic structure factor $S(\boldsymbol{q}, \omega)$ of a three-dimensional electron gas is well defined only for a hypothetical metallic density $r_s < 1$ where the random phase approximation (RPA) applies and for $r_s > 20$ where 'Wigner lattice' ordering occurs [50]. For real metals in which r_s typically falls between 2 and 6, lattice effects are important, and the RPA must be modified by a controversial local field correction factor $g(\boldsymbol{q})$. IXS has proven to be the ideal tool for experimentally studying the full dynamic response

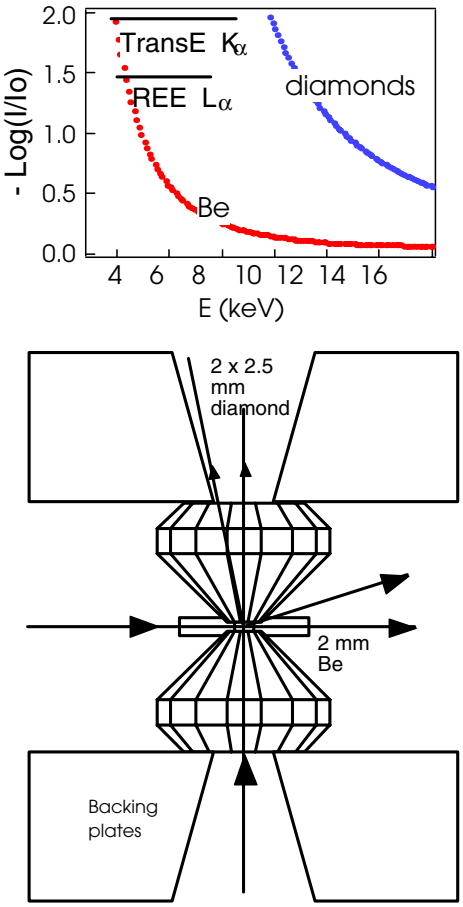

Figure 1. Transmission of x-ray in the axial geometry through the diamonds and radial geometry through the Be gasket.

function of the electron gas and has been applied to simple metals including Li, Na, Al and Be [51–57]. Each metal has a discrete r_s value at ambient pressure. Comparison of the electron gas in these systems is also partially affected by their different core electrons. To further our understanding of the electron gas, pressure provides a variable for continuously tuning the band structure of real metals over a wide range of r_s, thus showing the overall picture of the electron gas at different densities.

Recently, we have performed an IXS study of collective excitations of valence electrons in a diamond cell. Specifically, the plasmon energy of Na was measured as a function of density or pressure. As the pressure increased from ambient to 26.5 kbar (2.65 GPa), the plasmon energy of Na increased from 6.35 eV to 7.19 eV. The sample size was about 0.5 mm (diameter) $\times$ 0.1 mm (thickness), the incident x-ray energy used was 10 keV and the scattering angle was 6°. Measurements up to 15 kbar were carried out at X21 hybrid wiggler beamline at the National Synchrotron Light Source (NSLS), and the measurement at 26.5 kbar was performed at 13-ID of GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) of the Advanced Photon Source (APS). In both cases the incident photon flux of about 5×10^{10} photons s^{-1} was measured, and the total energy resolution of the

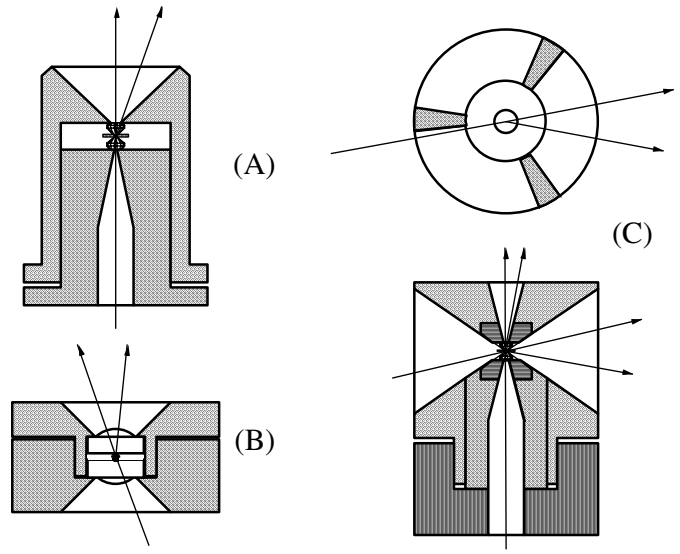

Figure 2. X-ray scattering geometry in various types of diamond cell. (A) Scattering through narrow openings of the diamond cell axis; (B) axial scattering through Be seats; (C) panoramic scattering through Be gasket and axial scattering.

experiment was about 1 eV. The difference in data quality is due to a set of micro-focusing Kirkpatrick–Baez (KB) mirrors [58] that were used at GSECARS to reduce the beam size to 10 μm $\times$ 10 μm, thus essentially removing the effect of Be background. Figure 3 shows measured inelastic x-ray scattering spectra of Na. The background due to inelastic scattering from the Be gasket has been removed by fitting the raw data with a single Lorentzian and a third order polynomial background. The dashed lines in figure 3 show the best-fit Lorentzian lineshape using fitted parameters. The measured values agree well with the RPA calculation.

The experiment demonstrates the power of pressure to tune various properties. For instance, Hong and Lee [59] derived an analytic expression for the dynamic structure factor $S(\boldsymbol{q}, \omega)$ for the electron gas. The asymptotically exact solution is only valid at one particular electron density of $r_s = 3.5$, but no real metal at ambient conditions has this density. Lithium ($r_s = 3.25$) is the closest for comparison [51], and Na ($r_s = 3.93$) is significantly higher. Figure 4 shows the equation of state of Na determined by x-ray diffraction at ambient temperature and the large range of electron densities (r_s) of the experiment. With slightly higher pressures of 45 kbar, we will be able to test the behaviour at the predicted singular point at $r_s = 3.5$.

5. Dynamic response of strongly correlated electronic systems

Strongly correlated electronic systems display rich phenomena ranging from magnetic ordering to superconductivity. As a result, they have attracted particular attention in condensed matter physics. Competition among the Mott–Hubbard interaction energy U, the ligand field energy Δ, the 3d bandwidth W and the ligand–metal hybridization interaction T lead to complex electronic, magnetic and phonon behaviour, which is strongly manifested in the pressure dimension. Understanding electron correlation effects in strongly correlated electronic systems remains one of the major challenges in solid state physics. In one limit, semi-empirical

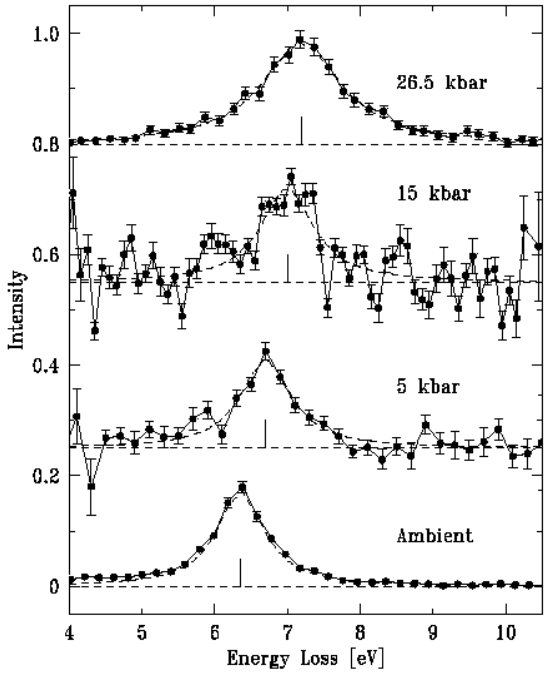

Figure 3. Plasmon of Na measured with IXS as a function of pressure in a diamond cell.

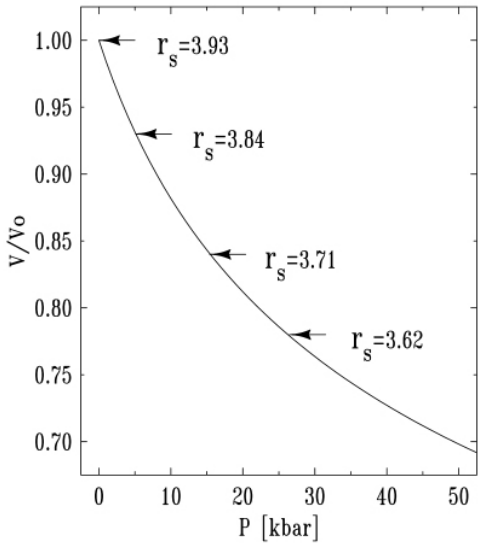

Figure 4. Pressure–volume (r_s) relation of Na at ambient temperature.

model Hamiltonians, which can be solved analytically or numerically, are constructed to study these systems [60]. In the other limit, first-principles electronic structure calculations are being extended to these systems by introducing new theoretical schemes to include electron correlations [61]. Megabar pressures can be used to modify properties at different energy

scales, such as the on-site Coulomb energy, charge transfer energy and crystal-field splitting, that also drive the large number of phase transitions induced by pressure in these systems. Combining IXS with megabar pressure thus provides a unique opportunity to systematically study the effect of these parameters in combination with theory, and to study the origin of the large number of phase transitions and the associated changes in their electronic structures.

It has also been found that for narrow-band solids, such as transition-metal and rare-earth compounds, resonant inelastic x-ray scattering can be used to probe specific elementary excitations [62, 63]. In these experiments on highly correlated electron systems, the incident x-ray energy is tuned through an absorption edge of the sample to exploit the resonant condition in the scattering [64, 65]. For example, large resonant enhancement of charge transfer excitations was observed in NiO [66]. A configuration-interaction cluster model of NiO can be used to interpret the scattering cross section and the strong incident energy dependence. This interpretation has been confirmed by the observation of charge transfer excitations in several high-T_c related compounds [67, 68]. Recently, polarization and momentum dependent measurements on these compounds have also been reported [69, 70].

There have also been a growing number of resonant inelastic scattering (RIXS) studies of core excitations [71–74]; i.e. the final states of the inelastic scattering process in these studies are localized, shallow core excitations. It should be noted that these shallow core excitations are the same excitations routinely probed by soft x-ray absorption spectroscopy, and are rich in multiplet structures for these highly correlated electronic systems. In fact, the high-energy scale parameters of the highly correlated systems are routinely derived from fitting these spectra with model calculations. For magnetic samples, excitation with circularly polarized x-rays can also provide information on spin-resolved electronic structure [75–77].

We have also explored high-resolution x-ray emission spectroscopy (HRXES) [78] for the study of strongly correlated electronic systems at high pressure. In HRXES, deep-core electrons in the sample are excited by x-rays. The core holes then decay through radiative processes and produce fluorescent photons. The energies of the fluorescent photons are analysed with sub-eV energy resolution of the emission spectral lineshape to provide information on the filled electronic states of the sample. The final state of the fluorescent process is a one-hole state, identical to the final state of the photoemission process. Photoelectron spectroscopy is an important tool for studying large chemical shifts in the core-level binding energies and the valence band density of states, but requires a vacuum environment incompatible with high pressures. HRXES provides an alternative tool and solves the problem for *in situ* measurements at high pressure.

In HRXES, the incident beam can be broadband; it is sufficient for x-rays of high enough energy to penetrate the pressure vessel and excite the emission of the sample. Only the element specific emission x-rays must exit the vessel, reducing half of the absorption problem. With the low end of the high-pressure energy window extended down to 4 keV by the high-strength beryllium gasket [48], all elements above Ca ($Z = 20$) can be studied at high pressures by a suitable choice of analyser crystals. In particular, the important 3d and 4f emissions will now be open for high-pressure research. This covers the transition elements and rare-earth elements with specific electric, magnetic and optical properties crucial for a wide range of applications in materials sciences and technology. For instance, transition-element ions, with their variable valence and magnetic states, control major geochemical and geophysical processes, such as oxidation, reduction, chemical differentiation, elasticity, geomagnetism, conductivity and radiation heat transfer. Magnetic collapse in transition-metal monoxides has been predicted from first-principles computations at pressures of the lower mantle and core [79]. We have studied high-pressure HRIXS of iron oxides and sulphides at the NSLS and APS. High-resolution Kβ emission of ferrous ion in troilite shows a high-spin to low-spin

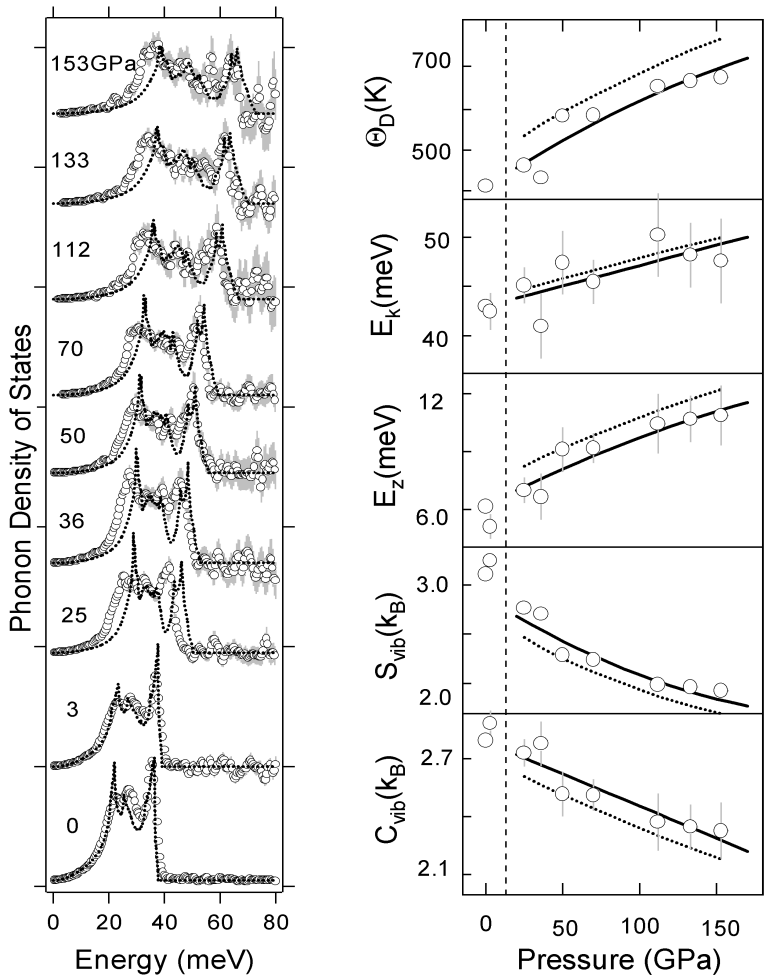

Figure 5. Left: phonon DOS of iron. Right: thermodynamic parameters of iron as a function of pressure. Symbols, error bars, and solid curves are the NRIXS experimental results; thin dashed curves are from *ab initio* theory [94].

transition at 4 GPa coinciding with the FeS I–II structural transition [80]. Likewise, a high-spin to low-spin transition occurs in haematite at 50 GPa. Wüstite, on the other hand, remains high spin to pressures as high as 140 GPa [81]. High-resolution Kγ emission spectra of these minerals reveal their oxygen bonding characteristics. The results place important constraints on models of the deep mantle and cores of terrestrial planets.

6. Phonon vibrational dynamics at high pressures

The effect of pressure on phonon dynamics reveals a wealth of information on fundamental interatomic interactions, propagation of elastic waves, mechanical stability of solids, phase transition mechanisms, vibrational energies and thermodynamic parameters. Raman and infrared spectroscopies have been used extensively for high-pressure studies of dynamics (for example see [82–84]), but momentum resolution is not straightforward partly because the

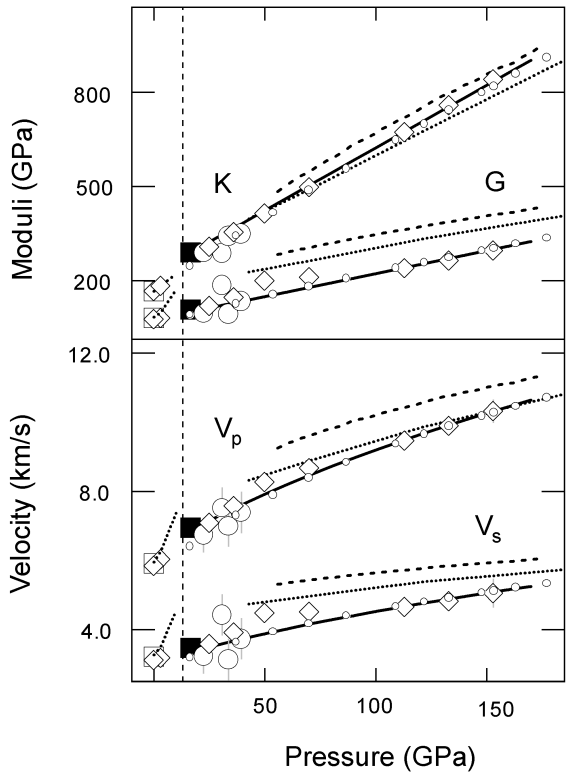

Figure 6. Aggregate elasticity of Fe at high pressures; open [95] and full [49] squares, ultrasonic data; circles, RXD data with Au stress calibration [49]; small circles, RXD extrapolation based on constant K/G [49]; diamonds, present NRIXS results; full curves, curve-fitting through the ultrasonic and the NRIXS data; dotted curves, calculated from the slope at the gamma point of the present *ab initio* theoretical phonon dispersion curves; dashed curves, *ab initio* calculations of Steinle–Neumann *et al* [96]. The vertical line at 13 GPa separates bcc Fe and high-pressure hcp Fe.

stressed diamond anvils changes the polarization of the probing light beam. Phonon studies for the full range of $\boldsymbol{q}$ are normally carried out by inelastic neutron scattering (INS), which requires centimetre-size samples currently impossible for ultrahigh-pressure research. Phonon dispersion study of single-crystal diamond has demonstrated that the resolution of IXS could be on a par with INS in its coverage of full momentum space [85]. With the optimized size of the focused x-ray beam and sample, similar quality of data has been obtained on single-crystal argon [86] at high pressures. This opens tremendous opportunities for complete characterization and tuning phonon dynamics over a large range of density.

Phonon densities of state (DOS) can be obtained by IXS measurement of polycrystalline samples integrated through the entire Brillouin zone. The acoustic velocity is directly derived from the dispersion of the acoustic phonon energy [87]. Studies of phonon DOS can be greatly simplified if the element involved has a nuclear resonant Mössbauer effect. For instance, the nuclear resonant inelastic x-ray scattering (NRIXS) method developed for the Mössbauer isotope ^{57}Fe has produced DOS measurements of bcc-Fe at ambient conditions identical to the INS results [88]. We successfully extended the NRIXS technique to high pressure and obtained the DOS of hcp-Fe up to 153 GPa [89]. The high-pressure vibrational dynamics of

iron has attracted particular attention among physicists and geophysicists because iron is an archetypal transition element [90, 91] and is a dominant component in the cores of the Earth and other terrestrial planets (Mars, Venus, Mercury). Many important dynamic, thermodynamic and elastic properties, including vibrational kinetic energy (E_k), zero-point vibrational energy (E_Z), vibrational entropy (S_{vib}) and vibrational heat capacity (C_{vib}), Debye temperature (Θ_D), Grüneisen parameter (γ), thermal expansivity (α), longitudinal velocity (V_P), shear velocities (V_S), bulk modulus (K) and shear modulus (G) are derived from the phonon DOS (figures 5 and 6). These properties are essential for interpreting seismological observations [92, 93] and numerical modelling of planetary cores, but have previously eluded direct experimental study and have been dependent solely upon theoretical calculations.

7. Conclusions

The handful of examples demonstrate the potential of the IXS as a powerful tool for probing materials dynamics at high pressures. With the full integration of the high pressure and the IXS instrument, we expect an order of magnitude improvement in the signal-to-background ratio. In addition, with the recent development of synchrotron sources, we expect to have 2×10^{13} photons s^{-1} within 1 eV bandwidth. The more than two orders of magnitude gain in flux and one order in sampling discrimination can be used for ultrahigh-pressure studies of smaller samples or higher-Z elements with high-energy resolutions. Fundamental behaviour of the electron gas, strongly correlated electronic systems and phonon dynamics can be investigated over an extended pressure range, in principle to multimegabars (e.g. > 300 GPa). In addition to the importance to basic physics and materials sciences, knowledge of high-pressure behaviour is important for exploring the properties of Earth and planetary interiors.

Acknowledgments

The recent experiments described above were performed with the help of J Shu and J Hu. This work was supported by the NSF, NASA, DOE and the W M Keck Foundation. We thank NSLS and APS for providing synchrotron radiation.

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