Review Article

meV-resolved inelastic X-ray scattering

Introduction

Inelastic X-ray scattering with meV-resolution (IXS) allows investigation of atomic dynamics in condensed matter systems, including phonons in crystalline materials, and various excitations in glasses, liquids, and low-dimensional materials. The meV and (nm to) Å scales probed by IXS are exactly the scales relevant to understanding the equilibrium dynamics of most condensed matter systems. Thus, there is a general need to probe excitations on these scales as a basic spectroscopy, including for investigation of *superconductivity, thermal transport, thermoelectricity, ferroelectricity, multi-ferroicity, metal-insulator transitions, viscosity, fragility, relaxations and dispersion in disordered materials, behavior near critical points, localized modes in clathrates or cage compounds, elasticity, etc*. Further, atomic dynamics have a role in many phase transitions, both as related to the previous list of properties, and as generally relevant to structural changes and, e.g., the appearance of precursors to charge density waves. There is increasing interest in the interaction of phonons with other systems, including electron-phonon coupling (e.g., Kohn anomalies, Peierls instabilities, and generalizations there-of), magnon-phonon coupling, and interaction with other quasi-particles. Other recent topics of interest include the topology of phonon dispersion bands (e.g., Dirac points) and phonons carrying angular momentum. All of these drive an interest in – even a necessity of – probing equilibrium atomic dynamics at meV scales.

IXS offers two notable advantages relative to the main alternative technique, inelastic neutron scattering (INS). In particular, the high flux and brilliance of modern X-ray sources means IXS can probe small (~10 micron scale) samples, allowing measurements of sample volumes some 7, or more, orders of magnitude smaller than those needed for INS. This is important for investigating new materials, where the few cubic mm size single-crystals needed for INS are often not available, for measuring samples in extreme, e.g., high pressure, conditions, or for measuring thin films. It also offers generally "easy access" in that the first step for a potential IXS user is "find a good quality ~0.1–1 mm size sample crystal" as opposed to "grow (or assemble) a few cubic mm of perfect crystal" as needed for INS. A more subtle opportunity with IXS is improved investigation of disordered materials: kinematic limits in neutron scattering, where the energy of the neutron probe is comparable to that of the phonon, do not affect IXS, allowing substantially improved data quality with IXS for disordered materials. A more detailed review of IXS, including a thorough comparison to INS with a focus on crystalline systems can be found in [1,2] while a recent overview of work on disordered materials in Japan can be found in [3]. It is worth emphasizing that the spectrometers at SPring-8 BL35XU [4] and SPring-8 BL43LXU [5] (see Fig. 1), after many years of effort [6-9], now lead the field, providing better resolution, higher flux, more analyzers, and generally better stability/reliability than is available at other facilities [1,2]. Figure 2 gives an overview of possible operating conditions.

Fig. 1. SPring-8 meV-IXS Spectrometers. Top: BL35XU in ~2000 while the lower panels are recent photos of the spectrometer arms at BL35XU (middle) and BL43LXU (bottom).

Eulerian Cradle Single Crystals Thin films	2.5 – 800 K (closed cycle systems)
No Eulerian Cradle Polycrystal Powders Liquids, Glasses	<1900 K (furnace) <3000 K (laser heated DAC) <7 T (cryomagnet) <1500 K <300 bar (gas pressure for liquids)

Resolution FWHM (meV)	X-ray Energy (keV)	Reflection Si (nnn)
2.8	17.79	(9 9 9)
1.2	21.75	(11 11 11)
1.1	23.72	(12 12 12)
0.7	25.70	(13 13 13)
0.35	29.66	(15 15 15)

Fig. 2. Table of the IXS operating conditions. Resolutions vary from 2.8 to 0.35 meV, depending on details. The resolution in the table is the value after optimization at BL43LXU while BL35XU now operates only at the (9 9 9) and (11 11 11) with slightly worse resolution than listed. Focused beam sizes at the sample are ~80 microns at BL35XU, and ~50 microns at BL43LXU, however these can be reduced to 20 and 5 microns, respectively, by KB mirrors that are customed designed for IXS. Additional information may be found at https://beamline.harima.riken.jp/en/bl_info/bl43lxu_info_en.html https://beamline.harima.riken.jp/bl43lxu/ and http://www.spring8.or.jp/wkg/BL35XU/instrument/lang-en/INS-0000001392/instrument_summary_view

High Pressure Science

One area of longstanding work at SPring-8 has been the use of IXS to measure elastic properties, especially the speed of sound, of materials under high pressure and, sometimes, at high temperature, in diamond anvil cells (DACs). This information is critical to interpret seismological measurements of the earth: the only directly measured information about the earth's interior is the local sound velocity and the density, as determined by seismology and is, e.g., encoded in the Preliminary Reference Earth Model (PREM) [10]. Thus, in order to investigate the material composition, temperature, and structure of the earth's interior, one must compare the model velocity and density values, e.g., PREM, with lab measurements of reference systems: surprising as it may be, IXS provides one of the better ways of measuring sound velocities of samples under extreme pressure. Therefore, in 2007 RIKEN's Materials Dynamics Laboratory began a program to make these measurements possible, focusing internal manpower on the subject and initiating collaboration with external groups. The program has now broadened, and has been able to achieve ever higher pressures and temperatures, with, most recently the attainment of pressures comparable with the earth's inner core [11].

One notes that while measurements of acoustic modes are conceptually simple (measure the dispersion and determine the slope in the long-wavelength, Q→0, limit), practically they are extremely challenging as one must isolate the signal from a few microns of sample encased in several mm of diamond. They have required the development of specialized instrumentation, beyond the already challenging task of preparing samples in DACs at pressures up to 300 GPa. Recent critical improvements have included the development of a multilayer reverse KB setup to achieve a 5 micron spot size [9] (now the smallest beam available for meV-IXS world-wide) and a Soller screen to improve the signal to noise [9]. The multilayer KB was a relatively early multilayer focusing element at SPring-8 and pushed the limits of the multilayer deposition control. The "reverse" designation refers to the fact the setup focuses more strongly in the vertical than in the horizontal, as is needed to overcome the impact of upstream optics and achieve a round beam on the sample.

The operation of the Soller screen is shown in Fig. 3. If one wanted to collect only a single scattering angle, a slit would be sufficient to remove most the background from the diamonds. More generally, one would like a series of parallel foils, a Soller slit, to permit collection of a larger solid angle. However, Soller slit fabrication is extremely difficult when the needed spacing between channels is ~0.05 mm. Instead, the Soller screen employs two screens with laser cut holes and some dead space between adjacent channels. This, unfortunately, reduces the number of analyzer columns at BL43LXU from

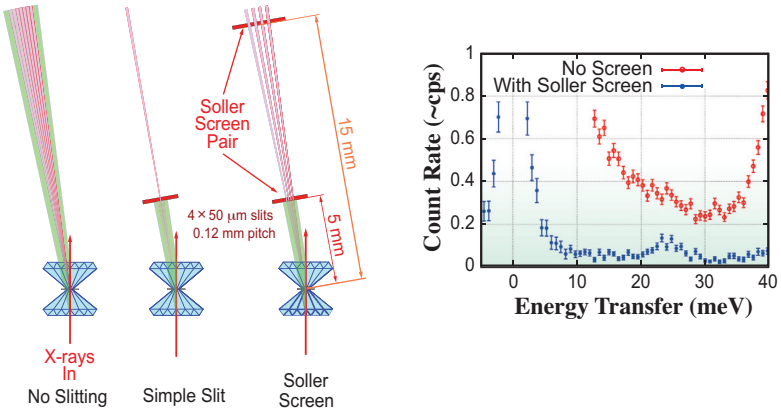

Fig. 3. Soller screen. Left Panel: Conceptual setup for the Soller screen compared to no slitting, or a simple single slit. The Soller screen reduces the background (green) from the diamonds, while still allowing the scattering from the sample to reach the analyzers. Right Panel: Improved data quality with the Soller screen – the peak at 24 meV is the desired signal and is essentially buried in the background from the diamonds without the screen.

7 to 4, but reduces the background from the diamonds and allows one to observe the signal (see Fig. 3). When measuring a single spectrum requires 1 to 2 days, as is often needed at pressures > 150 GPa, the factor of 4 improvement relative to simple slit is critical, reducing the time for a measurement at one pressure to 2 or 3 days from, e.g., 1–2 weeks.

The high pressure setup has been used to investigate many materials, include solid iron at up to 3000 K and 160 GPa [12], solid iron at room temperature to 300 GPa [11] and various iron compounds, usually in the range of 20 to 150 GPa [13-18]. Also, as described on p. 102 (Submission by Ikuta *et al.*) of this issue, some measurements have recently allowed the creation of a new primary pressure scale to pressures in excess of 220 GPa, the first such scale available to multi-megabar pressures[19]. We have also begun investigating glasses under pressure [20-22].

Another extremely difficult class of DAC experiments has been investigations of liquids at high pressure and temperature. This is important as the outer core of the earth is liquid. Work has included both pure iron and iron-compounds [23-27]. In these experiments one has the added difficulty of maintaining the sample stably over the several-hour time scale of the measurements, as liquids easily migrate in the cell. Measurements were possible by essentially creating a sapphire cell *inside* the DAC to confine the liquid [23]. Even so, these are very challenging experiments and pressures have, so far, been limited to < 100 GPa.

The work described above used polycrystalline samples, but there has also been a lot of effort to make measurements on single crystal samples, as this allows determination of the complete elasticity tensor. An efficient way to do this using the 2D analyzer arrays at SPring-8 was published in 2008 [28] and the method has since been extended to multiple materials [29-34]. Notably, however, crystal quality can sometimes degrade significantly at higher pressures, so that the maximum pressure successfully used in single crystal work is about 50 GPa. None the less, the method gives relatively precise values for most elastic constants.

Liquids

As noted above, IXS is a particularly good technique to investigate disordered materials as IXS allows access to atomic dynamics at mesoscale correlation lengths (say 1–10 nm^{-1}) that cannot be matched by neutron scattering. We do not review that work here, as a recent publication [3] discussed such work at SPring-8. However, we mention one example where IXS allowed the resolution of a long-standing controversy about the mesoscale dynamics of water. In particular, high-quality data with sub-meV energy resolution and excellent momentum transfer resolution was obtained at BL43LXU. Careful data treatment then showed that, despite two separate groups suggesting that there was an anomalous extra mode in water, in fact, the lineshape could be well explained by including a bipolar interaction between the quasi-elastic scattering of the water and the acoustic mode [35] (see Fig. 4). This contribution, reminiscent of a Fano profile seen in Raman scattering, was fully expected from theory, but had been neglected in earlier analyses.

Thin Films

Thin film measurements are interesting because there are a variety of materials that are essentially only available in thin-film form – including "bulk" materials that are stabilized by the substrate, or materials where one is creating some sort of periodic or semi-periodic layered structure as may be especially interesting for thermal engineering. However, the obvious problem is that the samples are thin, with an exceptionally thick film being ~1 micron thick, and more typical thicknesses being ~100 nm or less. Then, for IXS, one typically employs a grazing incidence geometry, where the beam is incident nearly parallel to the surface as this helps to increase the path in the sample and hence the signal. While this limits the range of momentum transfers that can be measured, it does allow measurements to take place. However, such work requires both rather careful calculations that properly take account of the tilting of the incident X-ray beam by upstream focusing elements (e.g., [36]), and additional stages and specialized setups to deal with proper alignment at grazing incidence. This work has largely been done at BL35XU. The first published thin film work

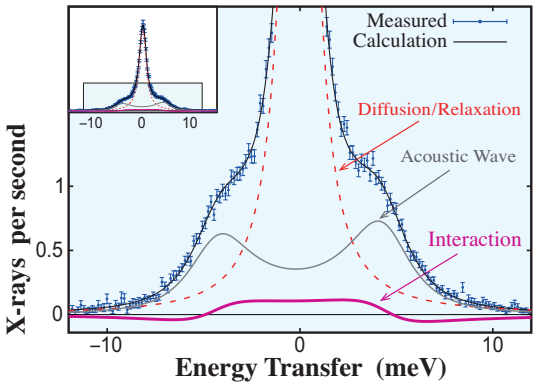

Fig. 4. Interaction contribution in water. Spectrum at Q = 2.5 nm^{-1} with ~0.9 meV resolution expanded to show the various contributions. The inset shows the full spectrum. Fits without the interaction added a weak mode at low energy that is not needed when the correct, interacting, lineshape is used. After [35].

was done to investigate the phonon structure InGaAs/GaAsP quantum well structures [37] with later work investigating "bulk" ScN [38] and a HfN/HfSc superlattice [39]; work is continuing.

Complex Materials: IXS/Structural Complementarity

As noted above there are many types of complex materials (ferroelectrics, superconductors, CDW materials, clathrates/cage compounds, frustrated materials, etc.) where IXS is a useful probe of material properties – as is often made easier because the sample size for IXS can be small. These measurements are too large a topic to review here, and instead we refer the reader to [1,2] and references therein. However, there is an increasing tendency to simultaneously investigate the detailed structural characteristics as seen in diffuse scattering and the phonon behavior in parallel studies. While, broadly speaking, this is unsurprising, as IXS essentially probes the excited states of structure, it is worth mentioning specifically as we see this as a growing trend. In particular, work recently investigated the detailed orbital shapes and anomalous phonon dynamics FeV_2O_4 [40] and other work in showed the impact of lone pair electrons in dynamics of InTe [41] (See also the article on p. 64 by Zhang and Iversen). In the specific context of SPring-8, we believe the combination of single crystal diffraction measurements at BL02B1 with IXS measurements at BL35XU or BL43LXU will be increasingly powerful.

Future Plans for IXS at SPring-8

Future plans for IXS are expected to proceed in several directions, aside from a constant improvement in sample environments. Most immediately, the area detectors that have been shown to be extremely useful at BL43LXU [42,43] will be installed also at BL35XU, permitting easier attainment of higher resolution. This will be matched, funding permitting, by modification temperature control system that should both improve the stability from the ~1 mK rms observed at BL35XU to the <0.2 mK observed at BL43LXU, and improve the resolution [7]. Meanwhile, especially at BL35XU, we will continue to optimize the setup for investigating thin films. We also expect to integrate single crystal diffraction measurements, and especially thermal diffuse scattering (TDS) measurements, more fully with the IXS setups. Finally, the very recent success [44] in achieving 0.35 meV resolution at BL43LXU will allow IXS studies of disordered materials at very low momentum transfers, $0.5 < Q < 1.0$ nm^{-1}, a regime that is important for the understanding the crossover from long-wavelength continuum dynamics to the microscale, but has never been directly probed previously by any method.

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