SPring-8 meV-IXS Program Overview

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SPring-8 has had a meV-resolution IXS program for just over 2 decades, now with two IXS spectrometers one at BL35XU[1] and one at BL43LXU[2]. The table summarizes many of the relevant capabilities. This talk will discuss the status of the beamlines and the opportunities available, as well as the main programs now in progress. An overview of IXS and different spectrometers and beamlines can also be found in [3].

	BL35XU	**BL43LXU**
Administration	JASRI (~50/50 IXS/NRS)	RIKEN (10-15% JASRI)
Momentum Transfer	~1-100 nm^{-1} (at 21.7 keV)	
2D Analyzer Array	12 Channels: 4(H) x 3(V)	28 Channels: 7(H) x 4(V)
Operating Resolution (Analyzer dependent)	1.3 meV at 21.75 keV (2.8 meV at 17.79 keV)	(0.8 meV at 25.7 keV) 1.3 meV at 21.75 keV 2.8 meV at 17.79 keV
Beam Spot Size (Diameter, FWHM)	~80 um Standard ~18 um Possible	~50 um Standard ~5 um Possible
Typical Setups	Single Crystal Work (2-800K) Disordered Materials (Liquids, Glasses, *etc.*) High Pressure Diamond Anvil Cells (DACs)	
Note: other specialized setups may be available in collaboration with user groups.		
Specializations	Thin Films At Grazing Incidence	High Pressure DAC [5] Masks for Low Q<~1 nm^{-1} High Field (7T) Magnet
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Both beamlines have 2-dimensional analyzer arrays that are particularly efficient for investigating the dispersion of transverse modes [3]. Both beamlines also use backscattering monochromators that provide extremely good (e.g. ~0.1 meV/week) stability for the energy zero. Recent work investigating the resolution function [4] has improved fitting for glasses.

After the reduction in beamtime due to the BL35 "upgrade", BL35/IXS will try to focus primarily on 1.3 meV resolution work, with a specialization for grazing incidence setups for thin films. BL43LXU continues to run a robust setup for work with DACs (pressures up to ~300 GPa) mostly with 2.8 meV resolution, while the work-horse instrument for crystal dynamics runs at 1.3 meV resolution, and, in special cases, sub-meV resolution can be used for targeted measurements.

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Determination of single crystal elasticity and equation of states based on meV-IXS

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Abstract

Single crystal elasticity is one of basic physical properties for materials. We have presented a method to determine this property precisely based on meV-IXS spectra (Fukui et al., 2008). This technique can be adapted to a tiny sample with irregular shape or opacity because hard x-ray as a probe of meV-IXS can be easily focused down to micron size and has a relatively high penetrability, and because its refractive index of x-ray is almost unity independently to a type of materials. The wavelength of the x-ray probe also enable us to determine the crystal orientation of the sample using the same measurement instrument for meV-IXS.

The high penetrability of x-ray is also effective for samples under extreme conditions. Simultaneous measurement of a molar volume and an elasticity of a material yields an equation of states (EoS) of the material independently to other pressure standards by numerically integration of a bulk modulus. We have measured single crystal elasticity of pressure-standard materials and demonstrated to establish absolute pressure scales (Yoneda et al, 2017; Kamada et al., 2019; Fukui et al. 2020). We review how to establish EoSs based on single crystal elasticity as well as some tips to determine single crystal elasticity from meV-IXS spectra.

Reference

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IXS measurements in extreme conditions: A multi-megabar primary pressure scale and the structure of the Earth's core

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Abstract:

Elucidating precise information about the Earth interior is one of the long-standing propositions of the Earth science. However, because we cannot directly go and/or see to the Earth's interior, our knowledge on the Earth's core is based on comparison of laboratory measurements with seismological observations, informed by meteorite composition, and indications of the Earth's core temperature. One of the most interesting topics of such works is the density deficit issue, which is the suggestion that Earth's inner core must contain light elements because the density of the inner core determined from seismological Earth model is lower than the density of pure iron determined from laboratory measurements and/or theoretical work: the density deficit of the inner core has been considered ~4%. However, such conclusion is based on a pressure scale to evaluate laboratory-based measurements. the accurate pressure scale is a prerequisite to high-pressure physics and is critical for relating laboratory-based measurements to actual geological conditions and seismological observations. Also, the pressure scale is one of the most fundamental topics for the condensed-matter physics. However, despite significant effort, there remain large discrepancies in the available scales at the multi-megabar pressures of the Earth's core, and indeed these differences tend to become even larger (approaching a factor of two) as pressures increase. The uncertainty of the pressure scales makes it difficult to estimate the composition of the Earth's core, and in particular, has impact on the possible amount of light elements therein and/or the temperature estimation of the Earth's core. We report here the first primary pressure scale extending to the multi-megabar pressures of Earth's core by measuring longitudinal and transverse acoustic phonon velocities using inelastic x-ray scattering from a rhenium sample in a diamond anvil cell. Our new pressure scale agrees with previous primary scales at lower pressures and also shock compression experiments, but it is lower than previous secondary and theoretical scales at Earth's core pressures: previous scales have overestimated laboratory pressures by at least 20% at 230 GPa. Our new scale suggests the density deficit of the inner core is ~9%, doubling the light-element content of the inner core.

Effect of symmetry breaking on phonons in noncentrosymmetric magnets

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Symmetry breaking has been a fundamental concept in condensed matter physics related to the emergence of novel electronic states. In particular, spatial-inversion symmetry (SIS) and time-reversal symmetry (TRS) breaking lift the spin degeneracy of the electronic state. Therefore, novel spin-related electric phenomena such as Edelstein effect and the anomalous Hall effect emerge in symmetry-broken-materials. Here we have investigated the effect of SIS and TRS breaking on phononic bands in a chiral magnet MnSi using high-resolution inelastic X-ray scattering and first-principles calculations[1]. We find a momentum-transfer-dependent (q-dependent) splitting between transverse phonon bands having angular momentum parallel or antiparallel to q. This is an indication of the phononic version of spin-momentum locking owing to the SIS breaking. On the other hand, we observed no significant impact from TRS breaking induced by a magnetic field. This suggests the effect of time-reversal symmetry breaking is small or is restricted to a very low energy regime in this material, possibly due to small spin-orbit interaction. To observe the large impact of magnetism in phononic dispersion, some rare-earth compounds having larger spin-orbit coupling seems promising.

[1] Y. Nii *et al.*, *Submitted*.

Nematic Correlation Length in Iron-Based Superconductors Probed by Inelastic X-Ray Scattering

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Nematicity is ubiquitous in electronic phases of high-T_c superconductors, particularly in the Fe-based systems. We used inelastic x-ray scattering to extract the temperature dependent nematic correlation length ξ from the anomalous softening of acoustic phonon modes in FeSe, underdoped $Ba(Fe_{0.97}Co_{0.03})_2As_2$, and optimally doped $Ba(Fe_{0.94}Co_{0.06})_2As_2$. In all cases, we find that ξ is well described by a power law $(T-T_0)^{-1/2}$ extending over a wide temperature range. Combined with the previously reported Curie-Weiss behavior of the nematic susceptibility, these results point to the mean-field character of the nematic transition, which we attribute to a sizable nematoelastic coupling that is likely detrimental to superconductivity.

Determination of Phononic Bandgap and Phonon Anomalies in Epitaxial Metal/Semiconductor Superlattices with Inelastic X-ray Scattering

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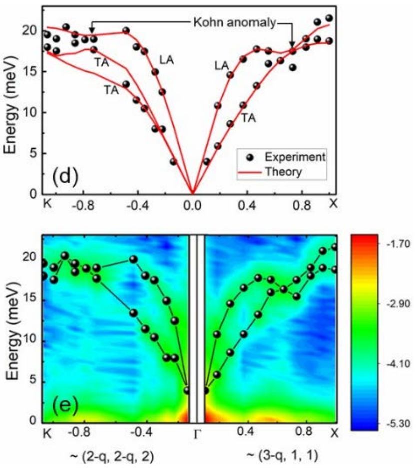
Epitaxial metal/semiconductor superlattice heterostructures with lattice-matched abrupt interfaces and suitable Schottky barrier heights are attractive for thermionic emission-based waste-heat to electrical energy conversion, hot electron-based solar-to-electrical energy conversion and for the demonstration of the thermal hyper-conductivity in solid-state devices. HfN/ScN is one of the earliest demonstrations of epitaxial single-crystalline metal/semiconductor heterostructures and has attracted significant interest in recent years to harness its excellent properties into device applications. Though the understanding of the mechanism of thermal transport in HfN/ScN superlattices is extremely important for practical applications, not much attention has been devoted to measure their phonon dispersion and related properties.

In this work, we employ non-resonant meV-resolution inelastic X-ray scattering to determine the momentum-dependent phonon modes in epitaxial metallic HfN and lattice-matched HfN/ScN metal/semiconductor superlattices. HfN exhibits a large phononic bandgap (~ 40 meV) and Kohn anomaly in the longitudinal and transverse acoustic phonon modes at q~0.73 along the [100] and [110] directions of the Brillouin zone due to the nesting of the Fermi surface by the wave vector (q). The in-plane [100] acoustic phonon dispersion of the HfN/ScN superlattices is found to be dominated by the HfN phonons, while the optical phonons exhibit both ScN and HfN characteristics. First-principles density functional perturbation theory modeling is performed to explain the experimental phonon spectra and temperature-dependent thermal conductivity are measured with a pump-probe spectroscopic technique. These results will help understand the phonons in HfN and HfN/ScN metal/semiconductor superlattices for thermionic energy conversion.



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Acoustic dispersion in liquids with Peierls distortions

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So far, we have conducted inelastic X-ray scattering (IXS) experiments on liquid Bi [1], liquid GeTe [2], liquid Sb [3], and liquid $Ge_2Sb_2Te_5$ [4] using the spectrometer at BL35XU/SPring-8. We have observed the dynamic structure factor $S(Q,E)$ and investigated the excitation energy associated with the collective motion of atoms. Bi, Sb, and GeTe, which have a crystal structure with Peierls distortion, have a local structure in which shorter and longer bonds appear alternately even on melting. $Ge_2Sb_2Te_5$ has a rock salt structure with pores, but in the liquid state, it is thought to have a local structure with Peierls distortion like the other liquids. When $S(Q,E)$ is analyzed using a model function consisting of a quasi-elastic component and two inelastic excitation components, the Q dependence of the excitation energy of the longitudinal acoustic mode in these liquids shows a flat-topped curve. The second excitation energy shows values smaller than the excitation energy of the longitudinal acoustic mode and we have regarded this low-energy excitation as the excitation originating from transverse waves in the liquids and have called it a transverse acoustic mode.

In this talk, we will mainly present the results of liquid phase-change material $Ge_2Sb_2Te_5$. $Ge_2Sb_2Te_5$ has been applied to a nonvolatile memory because of fast phase change between crystalline and amorphous states. We found that $S(Q,E)$ of ternary liquid $Ge_2Sb_2Te_5$ contains the third inelastic excitation component. The third excitation energy at the flat-topped Q region agrees with the energy at the corresponding Q in liquid GeTe. Because it is inferred that the vibration frequencies of the Sb-Te pair are different from those of the Ge-Te pair, the result suggests that they are observed separately. More interestingly, the third excitation energy behaves like an optical mode with decreasing Q towards 0. The destination seems to correspond to the vibration energy of four-fold coordinated Ge sites with an octahedral order in the amorphous state obtained by ab initio molecular dynamics (AIMD) simulations. The result suggests that four-fold coordinated Ge sites in the amorphous state are originated from those in the liquid state. These results indicate that $S(Q,E)$ obtained by IXS can provide important information on structural properties in the liquids.

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Real-space analyses of liquid dynamics using high energy-resolution inelastic X-ray scattering

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The conventional approach to the study of the liquid dynamics is to measure the dynamic structure factor, $S(Q, \omega)$, where Q and $E=\hbar\omega$ are the momentum transfer and energy transfer, by inelastic X-ray or neutron scattering and to fit models in Q-ω space to interpret the data. For the systems which lack periodicity in their atomic structures, analyses in reciprocal space are sometimes powerless in describing their structure and dynamics and the real-space analyses can provide their local information as has been demonstrated in the structural analyses using pair-distribution function. Recent progress in inelastic X-ray scattering makes it possible to obtain inelastic scattering spectra over a wide range of Q and E with a high Q- and E-resolution within a reasonable amount of time. The wide Q- and E-ranges make it possible to calculate the self-part and the distinct-part of the Van Hove function–spatial and temporal correlation function [1]–via Fourier transform of $S(Q, \omega)$ over ω and Q [2]. With this approach, we have studied spatial and temporal correlations of molecular motion in liquids [2–4]. In this presentation, our recent efforts in understanding the real-space local motion in liquids using the Van Hove function will be presented.

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Liquid-like and gas-like components in the dynamics of supercritical water

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In recent years, interest in supercritical water has been growing because of its importance in biological and geological sciences and because of its wide application in biochemical industries. Underlying many of these applications is the large tunability of the density and solvation properties of supercritical water near its critical point. A thorough physical understanding of these properties is needed in order to further exploit them to facilitate a variety of chemical processes. However, while the thermodynamics of supercritical fluids is relatively well-understood, with the "Widom line" indicating a rapid crossover between liquid-like and gas-like states in the supercritical region, details of their microscopic dynamics are less clear. This reveals a lack of experimental data and theoretical understanding of the dynamics of supercritical fluids.

Therefore, in this work, we study the molecular-scale dynamics in sub- to supercritical water with meV-resolved inelastic x-ray scattering measurements and molecular dynamics simulations. Contrary to commonly used models, we observe that the longitudinal current correlation spectra contain not one, but two main components: a low-frequency, gas-like component and a high-frequency, liquid-like component. Our analysis shows that, while the gas-like component is associated with free-particle motion, the liquid-like component arises from the O—O stretching mode between hydrogen-bonded molecules, which is reminiscent of the longitudinal acoustic mode in ambient water. With increasing temperature, the hydrogen-bond network diminishes and the spectral weight shifts from the liquid-like to the gas-like component, leading to a dynamical transition. The ratio between the two components can be used to describe quantitatively the microscopic dynamics of supercritical water, with a rapid crossover around the Widom line, thus drawing a connection between the dynamics and the thermodynamics of the system. The changing ratio between the components can also be used to explain the thermodynamic state dependence of physicochemical properties such as the dielectric constant, which has important implications for industrial applications of supercritical water. Further simulation results on other systems indicate that this two-component behavior is not specific to water and its hydrogen-bonding network, but a general phenomenon among supercritical fluids.