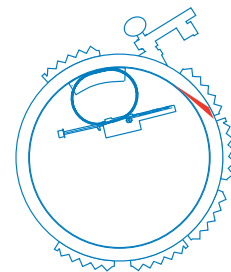


ADVANCES IN HIGH-ENERGY-RESOLUTION X-RAY SCATTERING AT BEAMLINE 3-ID



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Inelastic x-ray scattering is a powerful and important tool for the study of collective excitations in condensed matter systems. The technique measures the dynamic structure factor, which leads to an understanding of electron or atomic correlations in space and time. At moderate energy resolutions (few hundred meV), electron correlations can be studied in metallic systems, strongly correlated electron systems, etc.

At ultra-high energy resolution (a few μeV to meV) the dynamic correlations of ion cores (phonons) can be studied using the inelastic x-ray scattering technique in systems where traditional methods such as neutron scattering may be less applicable. These include ultra-high-resolution nuclear-x-ray-inelastic-scattering to derive partial phonon density of states from disordered systems, thin films, nano-particles, etc. The ultra-high-energy-resolution x-ray experiments will also focus on the dynamics in glasses and liquids.

High-energy-resolution scattering capabilities developed at the Advanced Photon Source (APS) to perform these investigations are the focus of this article, and they directly benefit from the high brilliance of APS undulator sources.



Beamline 3-ID at the APS is one of the strategic instruments used by the Synchrotron Radiation Instrumentation Collaborative Access Team (SRI-CAT). This beamline is dedicated to high-energy-resolution x-ray scattering studies. With optics suitable for $\Delta E/E$ ranging from 10^{-5} to 10^{-13} in the 6-30 keV range, the beamline is equipped with some unique instrumentation developed specifically for the production of x-rays with meV and neV band-pass. Experiments in 1997 have focused on the development of new high-energy-resolution monochromators (shown above) and analyzers based on crystal optics and timing techniques. Applications of

the newly developed techniques include the first sub-meV x-ray spectrometer to record iron phonon density of states in iron metal and in Fe_3Al as a function of order-disorder phase transformation; vibrational dynamics measurements in iron thin films and multilayers and interfaces; observation of partial phonon density of states in Sn and Eu compounds; and measurement of phonon dispersion relations as a function of momentum transferred in diamond and chromium.

The general approach followed when conducting high-energy-resolution experimentation at APS beamline 3-ID was to unify the monochromatiza-

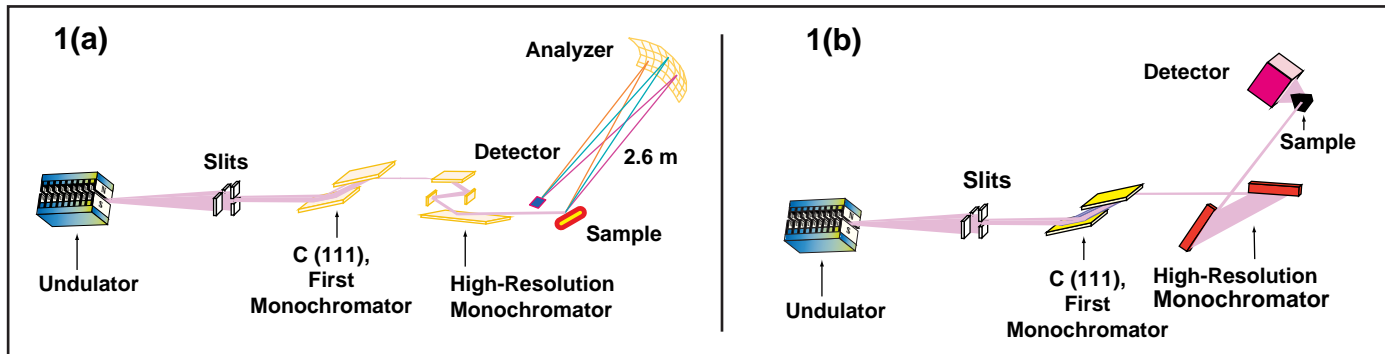


FIG. 1. The schematic layout for high-energy-resolution inelastic x-ray scattering as implemented at the 3-ID beamline of SRI-CAT. 1(a) The inelastic x-ray spectrometer that consists of an “in-line,” nested, 2-channel-cut design high-resolution monochromator followed by a curved crystal analyzer. 1(b) The inelastic nuclear resonant scattering spectrometer that consists of two flat-crystal monochromators followed by a fast detector with nano-second resolution for time discrimination. An in-line monochromator as shown in 1(a) is also available for several isotopes for coherent or incoherent nuclear resonant scattering.

tion process and develop different styles of analyzers. The inelastic x-ray scattering setup using an “in-line” monochromator and curved crystal backscattering is shown in Fig. 1(a), and the configuration for inelastic nuclear resonant scattering is shown in Fig. 1(b).

HIGH-ENERGY-RESOLUTION MONOCHROMATORS

The underlying principle in high-energy-resolution monochromatization is to employ an optimum combination of asymmetrically cut single-crystal reflections to create the desired energy bandpass, angular acceptance, and overall efficiency or throughput. Several different software packages have been developed to optimize certain parameters, such as the choice of reflection planes, the degree of asymmetry, and energy resolution.¹ These programs include calculation of modified DuMond dia-

grams²; accurate three-dimensional (angle-energy-reflectivity) throughput calculations of multiple-crystal systems, including the source divergence and bandpass³; and the complete treatment of multi-beam excitations in single crystals, including exact backscattering.⁴

A summary of crystal monochromators developed is given in Table I. The choice of energy is dictated by specific nuclear resonance or exact backscattering geometry. The nuclear resonance provides a unique way of analyzing energy exchange of photons with phonons by tuning the incident beam energy around the nuclear resonance energy and exciting the resonance via phonon exchange, which then leads to extraction of momentum-integrated partial density of states. The back-scattering geometry, on the other hand, provides the possibility of measuring phonon dispersion relations using single

TABLE I. Crystal monochromators available at the high-energy-resolution beamline 3-ID as of October 1997.

E (keV)	Description	ΔE (meV)	ph/sec/ ΔE /100 mA Measured Flux	Notes
8.4	Si (333) Si (444)	15	N/A	2-nested channel cuts
13.841	Si (422) Si (884)	5.5	5×10^9	2-nested channel cuts
14.413	Si (422) Si (10 6 4)	5.6	1.1×10^{10}	2-nested channel cuts
14.413	Si (975) Si (975)	0.84	6×10^8	2-flat crystal
14.413	Si (975) Si (975)	0.66*	3×10^8	2-flat crystal
21.50	Si (440) Si (15 11 3)	1.0	2×10^8	2-flat crystal
23.880	Si (400) Si (12 12 12)	3.4	8×10^8	2-flat crystal

* The monochromators differ in the asymmetry used in preparing the crystals.

crystals. It is worthwhile to note that the energy bandpass of 0.66 meV at 14.413 keV with 3×10^8 photons/sec represents the highest photon flux with the lowest $\Delta E/E$ achieved so far, using the flat-crystal concept described in^{1,5,6}.

HIGH-ENERGY-RESOLUTION ANALYSIS TECHNIQUES

Analysis of the energy spectrum of inelastically scattered x-rays with sufficient resolution and efficiency continues to be a challenge. The conflicting aspects of this method stem from the divergent nature of the scattered x-rays and the limited angular acceptance of crystals used as analyzers. The problem becomes particularly serious when the required resolution drops below 10 meV in the 6-30 keV range. The established method, originally introduced in the early 1980s,⁷ involves the use of near-backscattering geometry from high-order Bragg reflections. In order to improve the total solid angle subtended by the analyzer, the thin crystal would be bent to a spherical shape with several-meters radius of curvature. This, accompanied by several different procedures to reduce or eliminate bending stress,^{8,9} provides a reasonable solution to an immediate problem.

We have developed a new procedure for use in preparing 10-cm-diameter diced analyzers comprising approximately 8,000 crystals. With respect to earlier methods, we take a new approach to reducing the strain on the curved analyzer. We use a Pyrex wafer as substrate to position the 8,000 crystals. Then, the Pyrex-epoxy-silicon "sandwich" is pressed into a concave substrate with a 2.6-m bending radius.¹⁰

the use of backscattering geometry provides an opportunity to measure phonon frequency-momentum dispersion relations along high-symmetry crystallographic directions from single-crystal samples. Figure 2 shows an example of a phonon dispersion in diamond along the [111] direction. Figure 3 demonstrates the capability for studying phonons in transition metals.

The unique nature of the beamline 3-ID spectrometer lies in the use of a tunable, in-line nested high-resolution monochromator¹¹⁻¹³ to make energy scans instead of the traditional route employing temperature scans of the monochromator or the analyzer. There are several advantages to the in-line geometry. First, there is no need to scan the entire spectrum to find the dispersion of a particular phonon mode as a function of scattering angle, since it achieves energy analysis by tuning the angle of the monochromator crystals with respect to the beam ($0.5 \mu\text{rad}/\text{meV}$ for the inner crystal Si (884) and $0.03 \mu\text{rad}/\text{meV}$ for the outer crystal Si (422)). This saves considerable time in data collection, where one can jump from the elastic peak to the

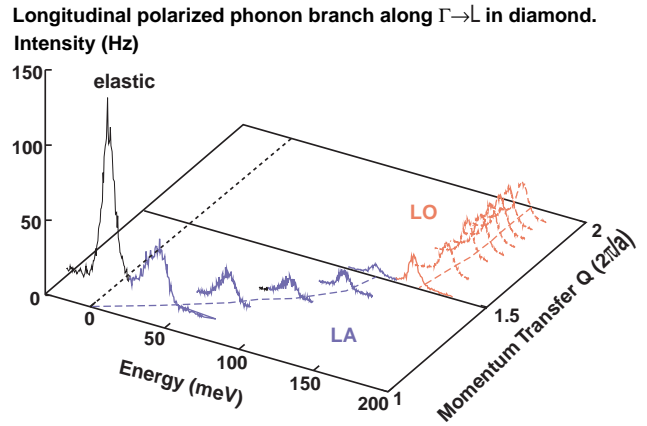


FIG. 2. Spectra at different momentum transfers representing longitudinal acoustic and optic modes in diamond along the [111] direction (L). The measurements were carried out using the Si(777) reflection of the analyzer at a Bragg angle of 89.97° with a total energy resolution of 7.5 meV. These data prove that there is no measurable overbending in the optical mode as predicted by ab-initio calculations.

Longitudinal acoustic phonons along $\Gamma \rightarrow H$ in chromium

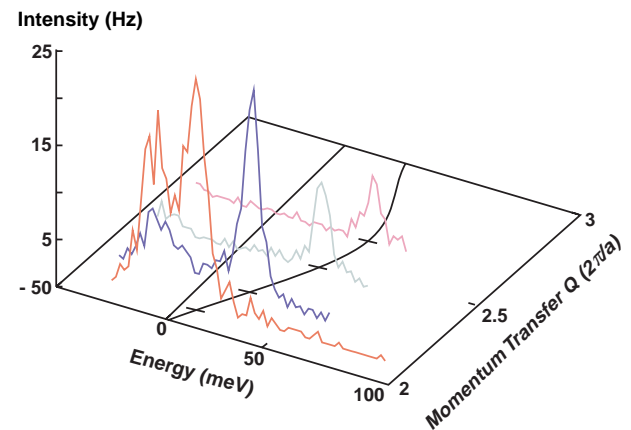


FIG. 3. Studies of phonons in chromium, demonstrating the performance of the instrument for high-resolution inelastic x-ray scattering.

phonon peak directly. The second advantage is the flexibility in beamline optics, which enables this type of scattering study in many beamlines that are suitable for x-ray diffraction. It does not dictate the beamline optics design the way backscattering monochromators would, and it reduces the total length of the beam, minimizing the effects of beam movement. Finally, the in-line monochromators are tunable over several hundred eV, and they form a basis for inelastic scattering studies from other elementary excitations, like plasmons, where the energy resolution can be a fraction of eV, and yet excitations may extend over a larger energy range. *cont'd on page 14*

FIG. 4. Monochromator designs in 3-ID: (a) A nested, 2-channel-cut, high-energy-resolution, high-angular-acceptance monochromator to provide monochromatic x-rays parallel to the incident x-ray beam. The first and last reflection faces are usually of lower order silicon reflections to provide the angular acceptance, while the inner crystal is cut such that higher order reflections provide the desired energy resolution. The angle-energy-reflectivity relation shown on the right-hand side is calculated for Si (422) (10 6 4) reflections at 14.413 keV. (b) Two highly asymmetrically cut silicon crystals optimized to achieve sub-meV energy resolution at an x-ray energy of 14.413 keV. The very high asymmetry angle used for the first reflection results in a grazing angle of 0.46° and consequently is most efficient when used with undulator sources that produce beams of small spatial extent. The measured energy resolution from this design is $660 \mu\text{eV}$ ($\Delta E/E = 4.6 \times 10^{-8}$). A similar concept has been used to achieve 3.4-meV resolution at 23.880 keV, and 1 meV at 21.541 keV. The contour plots on the top correspond to 50% of peak reflectivity.

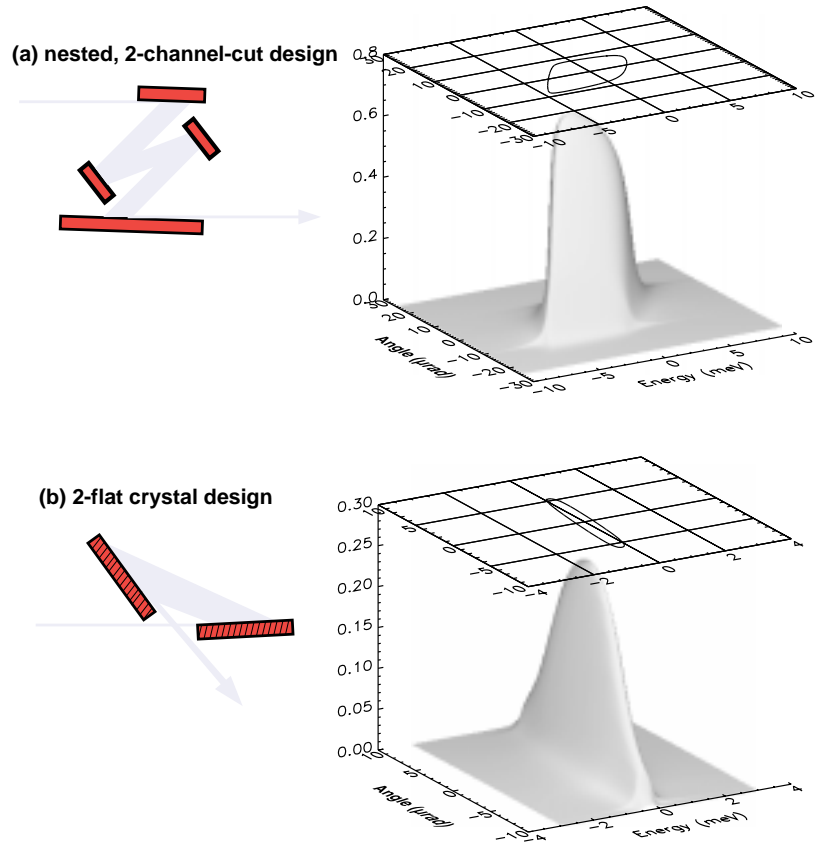
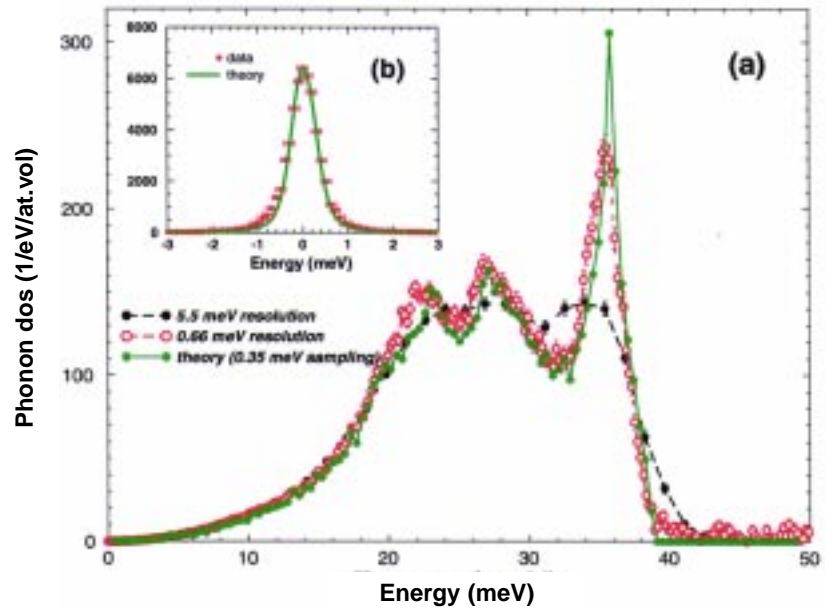


FIG. 5. (a) The phonon density of states of iron measured by inelastic nuclear resonant scattering. The black-filled circles were measured using a 5.5-meV nested monochromator, while the red, empty circles were measured with 0.66-meV resolution, 2-bounce flat crystals. The theory curve is calculated from experimentally determined force constants via fitting the coherent neutron scattering data (courtesy of B. Fultz). (b) The inset shows the resolution function of the 0.66-meV monochromator as measured with coherent nuclear forward scattering. The theoretical calculation includes the brilliance function of the incident beam coupled to the dynamical diffraction equations. The low dispersion points corresponding to higher density of states at 23 and 28 meV are the two transverse acoustical modes, while the peak at 37 meV is the longitudinal acoustic mode. A direct knowledge of phonon density of states is essential in the calculation of classical thermodynamic quantities like heat capacity, entropy, and thermal conductivity.



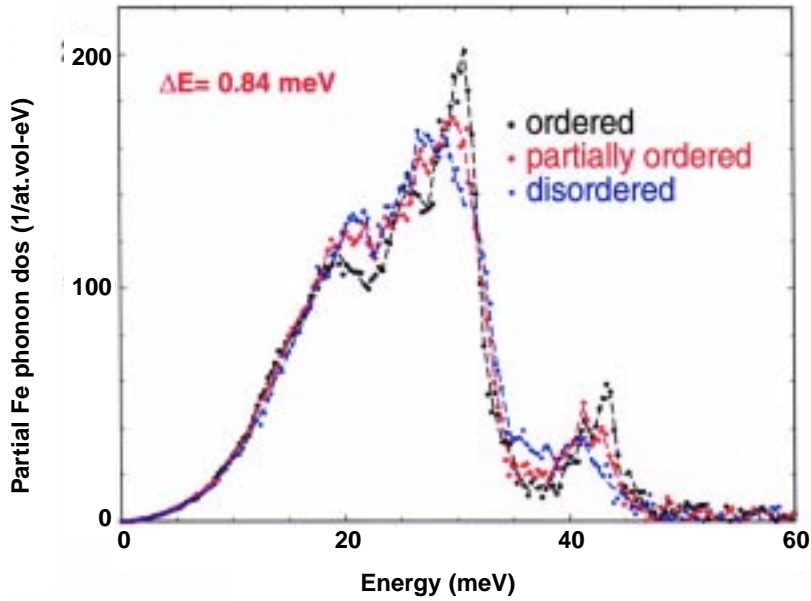


FIG. 6. Partial phonon density of states of Fe in Fe_3Al system as a function of order-disorder transformation. The systematic changes in the spectra indicate the effect of chemical short-range order on the vibrational dynamics of the alloy. The optical modes at 43 meV are due to Fe atoms with Al near neighbors. The sensitivity of phonon density of states to local ordering is somewhat of a surprise, given the general understanding that interatomic forces are of long range in metals. (Work done in collaboration with Prof. B. Fultz, California Institute of Technology.)

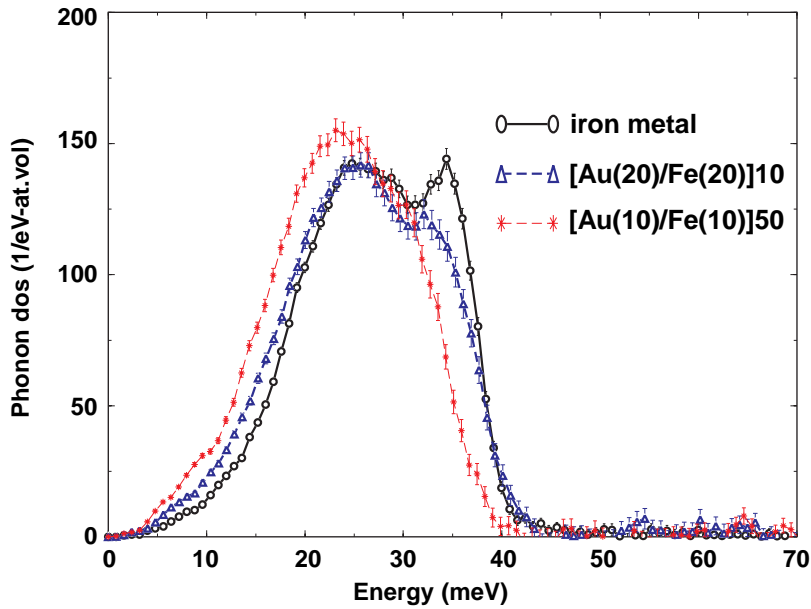


FIG. 7. Phonon density of states of Fe in an Fe/Au multilayer with varying thicknesses. As the layer thickness decreases, the softer modes below 25 meV appear to gain. Also note the disappearance of the longitudinal acoustic mode at 36 meV. Similar trends were observed with decreasing thickness in pure iron films. (Work in progress, in collaboration with S. Bader of Argonne National Laboratory.)

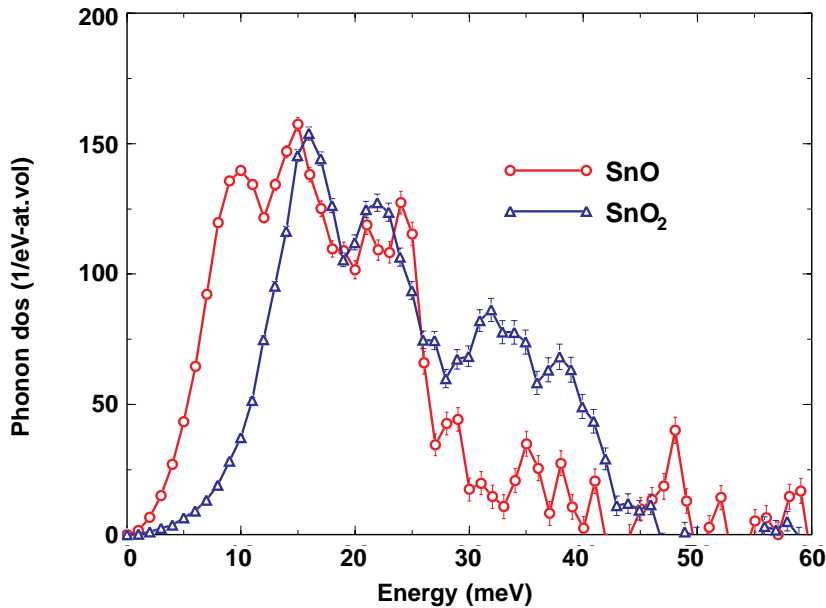


FIG. 8. Partial phonon density of states of Sn in two oxides, SnO and SnO_2 . The experiments allowed an accurate determination of Lamb-Mössbauer factors. For SnO the probability of recoil-free fraction of absorption and emission of 23.880 keV x-rays is 0.318 ± 0.041 , and for SnO_2 the same probability is 0.627 ± 0.09 .

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The inelastic scattering technique described above requires the use of single crystals. In order to study polycrystalline materials, powder samples, and, in particular, thin films, alternative methods must be developed. One such alternative is the use of nuclear resonance as an energy analysis technique. This approach was introduced in 1994,¹⁴⁻¹⁶ and it relies on tunable high-energy-resolution monochromators and the presence of suitable isotopes in the sample under analysis. This technique provides unequalled capability in terms of measuring partial phonon density of states in any medium, solid or liquid, crystalline or amorphous, bulk or thin films — even monolayers at an interface. It also allows extraction of phonon density of states directly from the data without the knowledge of crystal structure. New developments at the APS with respect to this technique are: (A) the resolution with which it can be carried out, (B) the media to which it can be applied, and (C) the isotopes for which optics have been produced.

(A) As shown in Table 1, we have developed the first sub-meV monochromator for lattice dynamic measurements. The dispersive, asymmetrically cut Si (975) crystals, shown in Fig. 4, yielded 0.66 meV ($\Delta E/E = 4.5 \times 10^{-8}$) resolution and 3×10^8 photons/sec at 14.4 keV. By using this monochro-

mator, phonon density of states of Fe metal has been measured and compared to theory derived from single-crystal neutron scattering measurements (Fig. 5).⁵ We have also made use of this monochromator to study the effect of order-disorder in an Fe₃Al system (Fig. 6).¹⁷

(B) We have demonstrated that this method can be utilized to study the effect of reduced dimensionality on vibrational modes. In this instance, we measured phonon density of states of nanocrystalline iron,¹⁸ and in thin films of Fe/Au multilayers, as shown in Fig. 7.

(C) It is our goal to widen the application of inelastic nuclear resonant scattering to other isotopes. Toward this end, we have built monochromators for ¹¹⁹Sn and ¹⁵¹Eu isotopes. The first results on Sn are shown in Fig. 8, in which the partial phonon density of states of SnO is compared to SnO₂. The ¹¹⁹Sn resonance was observed in September 1997. The resolution achieved was 3.4 meV at 23.878 keV ($\Delta E/E = 1.4 \times 10^{-7}$). The ¹⁵¹Eu resonance was observed in November 1997 with 1 meV resolution at 21.548 keV ($\Delta E/E = 4.6 \times 10^{-8}$).

The results presented here represent a small fraction of the work carried out at SRI-CAT. We encourage those with an interest in applying some of these methods to contact us directly. ○

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