

Sn-119 Nuclear Resonant Scattering Program at Advanced Photon Source Sector 30  
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In 2014, Sn-119 nuclear resonant scattering program at Advanced Photon Source moved from Sector 3 to Sector 30 for the much better flux there, providing enhanced performance for Sn NRS studies.

It shares the same undulators and high-resolution monochromator with the high energy-resolution inelastic x-ray scattering (HERIX) program already at Sector 30. Since 2015, general user proposals (GUPs) have been accepted and experiments conducted with continuing and guaranteed beamtime allocation each APS run cycle. Overview of the instrumentation and research done will be presented, as well as some perspectives for development.

## **Nuclear Resonant Scattering at extreme pressure and temperature**

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Activities of Nuclear Resonant Scattering at 3ID, APS are summarized, especially under the condition of high-pressure and extreme temperature. The outlook of the potential development upon the APS storage ring upgrade will be discussed during the talk.

# Nuclear Resonant X-ray Scattering at Pressure and Temperature: Applications to Thermophysics

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Nuclear resonant inelastic x-ray scattering (NRIXS) is well established as an important probe of phonon spectra of materials. Especially with guidance from *ab initio* computation, NRIXS spectra have proved reliable for obtaining the vibrational entropy (which is usually the dominant source of entropy of solid materials). An advantage of NRIXS over inelastic neutron scattering is that the sample volume is sufficiently small to permit measurements on materials under pressure in diamond anvil cells.

The equation of state  $V(P,T)$  (volume, pressure, temperature) comes from partial derivatives of the free energy  $G = H - TS$ , so the entropy  $S$  is a key quantity for understanding the temperature dependence of  $V$ . Two important parts of  $S$  can be determined from NRS experiments – the vibrational entropy,  $S_{\text{vib}}$ , and the magnetic entropy,  $S_{\text{mag}}$ . Measuring these as functions of pressure opens new experimental approaches to understanding thermophysical properties.

An example is thermal expansion,  $\beta = V^{-1} \partial V / \partial T$ . Consider the rigorous Maxwell relation  $\partial V / \partial T = -\partial S / \partial P$ . For invar, with near-zero thermal expansion, NRIXS can test if the pressure dependence of  $S_{\text{vib}}$  and  $S_{\text{mag}}$  sum to zero. We recently measured the phonon partial DOS of  $^{57}\text{Fe}$  in  $^{57}\text{Fe}$ -36%Ni, the hyperfine magnetic field of  $^{57}\text{Fe}$ , and the lattice parameter at two temperatures (300 and 410 K) at pressures to 15 GPa. The interesting part is below about 4 GPa, where the magnetization is being squeezed out, and an increasing magnetic disorder gives an increasing  $S_{\text{mag}}$ . Simultaneously,  $S_{\text{vib}}$  is decreasing as the phonons stiffen under pressure. We are still analyzing the results, but preliminary work shows a rather good cancellation of the changes of  $S_{\text{vib}}$  and  $S_{\text{mag}}$ . Their sum is nearly constant with pressure. This seems to account for the  $\partial S / \partial P = 0$  that is required by thermodynamics if  $\beta = 0$ . Other contributions such as electronic entropy are not so significant.

It is important to put this work in the context of modern materials physics. Today the effects of pressure on phonon spectra can be calculated by *ab initio* methods with some reliability at 0 K, but calculations with simultaneous pressure and temperature remain a challenge. NRIXS measurements with control over simultaneous temperature and pressure can provide a large part of the free energy,  $G(P,T)$ , helping to test modern computational methods. Another thermophysical property amenable to such research is the temperature dependence of the elastic constants. The elastic constants at 0 K are well understood today, but their temperature-dependence is not simple to understand.

Invar is a special case, with its interesting behavior at low temperatures and relatively low pressures. In general, useful studies on the origins of thermophysical properties will require NRS measurements at higher  $T$  and  $P$ . Such work can begin to address the less understood cross-terms that scale with the product  $PT$ , which depends on how intrinsic phonon anharmonicity changes with  $P$ , or equivalently, how Grüneisen parameters change with  $T$ .

# Time-domain synchrotron Mössbauer spectroscopy at extreme conditions

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Time-domain synchrotron Mössbauer spectroscopy (SMS) (aka. nuclear forward scattering) utilizes a synchrotron radiation source to excite the nuclei. The brilliant and focused synchrotron X-ray beam makes the technique compatible with complex sample environment such as high pressure and low temperature. After APS-U due to the change from 24- to 48-bunch timing mode, shorter lived isotopes are more favorable such as  $^{151}\text{Eu}$  ( $\tau_{1/2} = 9.7$  ns) and  $^{161}\text{Dy}$  ( $\tau_{1/2} = 28.2$  ns). In this talk I will discuss two case studies in  $\text{EuFeAs}_2$  and Dy metal to investigate the magnetic phase diagram under high pressure and low temperature in diamond anvil cell.

Divalent Eu-based intermetallic compounds exhibit rich magnetic properties due to the strong local magnetic moment. In Eu-based pnictide superconductors, peculiar coexistence of two collective phenomena, magnetic order from Eu ions and bulk superconductivity from Fe-As layers, makes these systems ideal platforms to investigate the competition of magnetism and superconductivity. Aiming to establish the microscopic P-T phase diagram of recent 112-type iron-pnictides  $\text{EuFeAs}_2$  high-pressure SMS experiments in  $^{151}\text{Eu}$  and  $^{57}\text{Fe}$  have been performed in the parent as well as Ni-doped compounds. We have found that application of pressure completely suppresses the itinerant electron magnetism from the Fe sublattice and the local magnetism in Eu ions. The suppression of local magnetism is associated with a significant increase of mean valence in Eu ions.

In the case of Dy metal, the local-moment magnetism has been studied under high pressure up to 141 GPa using SMS. With increasing pressure Dy's magnetic ordering temperature changes drastically. At 10 K the hyperfine magnetic field of Dy remains almost constant with increasing pressure up to 141 GPa, showing the robustness of the local magnetism. At about 120 GPa magnetic ordering temperature increases sharply to  $\sim 280$  K and drops at higher pressure, in good agreement with the Doniach scenario.

## NRIXS on High Valent Iron Complexes Relevant to Small Molecular Activation

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High valent Iron-oxo/hydroxo (Fe=O/Fe-OH) species have been identified as the key reactive intermediates to carry out numerous oxidative transformations in biology, such as oxidative oxygenation and halogenation reactions. Some of these transformations are key chemical steps in many biological pathways, such as DNA/RNA repair, gene regulation, O<sub>2</sub> sensing, and natural product biosynthesis. In order to design synthetic catalysts that can harvest the strong oxidizing power from the iron-oxo/hydroxo species in a controlled fashion, it is necessary to obtain a thorough molecular level description of the Fe=O/Fe-OH moiety and its interactions with the supporting ligands, as well as with the local environment. In the past decades, experimental and theoretical efforts have brought significant progress on the understandings of electronic structure and reactivity relationships of Fe=O/Fe-OH species. However, detailed spectroscopic studies on Fe=O/Fe-OH moieties that are in different oxidation states but supported by similar ligand systems having tunable hydrogen bonding interactions are rare. By using synchrotron radiation based <sup>57</sup>Fe Nuclear Resonant Inelastic X-ray Scattering (<sup>57</sup>Fe NRIXS) together with <sup>16</sup>O/<sup>18</sup>O isotope labeling, we have revealed the vibrational signatures of Fe=O and Fe-OH moieties in a series of mono-iron synthetic complexes in different oxidation states (Fe<sup>III</sup> or Fe<sup>IV</sup>), and showed that subtle changes of the hydrogen bonding interactions to the Fe=O/Fe-OH moieties can significantly affect their vibrational features. Based on these vibrational data and density functional theory (DFT) calculations, we will discuss the electronic effects of the iron oxidation state, the supporting ligand, and the local environment to the bonding interactions of Fe=O/Fe-OH moieties. We will also extend our discussion to a series of high valent (Fe<sup>IV</sup> or Fe<sup>V</sup>) iron-imido (Fe=NR) complexes, which are supported by *N*-heterocyclic carbene ligand and exhibit parallel chemical reactivities as those of Fe<sup>IV</sup>=O species. <sup>57</sup>Fe NRIXS data revealed the vibrational features associated with Fe<sup>IV</sup>=NR/Fe<sup>V</sup>=NR moieties in these complexes. Based on these observations, a comparison between Fe<sup>IV</sup>=NR and Fe<sup>V</sup>=NR, and Fe<sup>IV</sup>=O units will be given.

# NUCLEAR RESONANT SCATTERING PROGRAM AT HPCAT

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Thanks to the high brightness third generation synchrotron sources and development of tunable monochromators with sub-meV resolution, nuclear resonant X-ray scattering has become a relatively new method since late 90s and widely used to study materials under extreme conditions. Nuclear resonant X-ray scattering can be divided into two methods: nuclear resonant inelastic X-ray scattering (NRIXS) and nuclear forward scattering (NFS).[1]

Typical beam size at sample position is  $\sim 4$  (V) x  $6$  (H)  $\mu\text{m}^2$  at FWHM and the flux for NRS experiment is  $\sim 1 \times 10^9$  ph/s at 16 ID-D of HPCAT.[2] The 2-meV high resolution monochromator (HRM) is used for  $^{57}\text{Fe}$  nuclear resonance at 14.414keV and consists of two channel cut silicon crystals (Si (4 4 0) and Si (9 7 5)). We can now routinely measure NRIXS under high pressures using panoramic DAC and two or three APD detectors in close proximity. In addition to the pressure dependent studies at room temperature, we have two cryostats coupling with membrane control, online ruby system to do NFS experiment under low temperature and high pressure.

In this presentation, we will give summary on the nuclear resonant scattering program at HPCAT and present several science highlights in last a few years to demonstrate HP NRS applications in geophysics, condensed matter physics and materials science [3-6]. Future plans after APS-U will also be discussed.

This work is performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operations are supported by DOE-NNSA's Office of Experimental Sciences. The Advanced Photon Source is a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

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# Evaluation of Synchrotron Based NRS Data

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The discovery of nuclear resonant scattering (NRS) using a synchrotron radiation source by *Gerdau et al.* in 1985 [1] was followed by intense development that was fuelled by availability of third-generation synchrotron facilities: the ESRF in Grenoble, France; the APS in Argonne, USA; the SPring-8 in Hyogo, Japan, and more recently PETRA III in Hamburg. A variety of NRS were explored during the earlier period and some have survived the test of practicality and are in use today for applications such as the study of vibrational and magnetic properties of condensed matter under extreme conditions. In this presentation, specific evaluation software for a selection of NRS techniques is discussed with emphasis on their potential for applicability and availability to users.

The scheme in Figure 1 illustrates how four classes of NRS are distinguished: coherent elastic (I); incoherent elastic (II); incoherent inelastic (III). Each class has seen development of specific tools as shown in Table I that have been used in a variety of applications, and superior brightness and focused spectral flux density of third-generation synchrotron radiation facilities has permitted scientists to develop applications with ever smaller samples under increasingly extreme conditions.

Early nuclear resonant scattering studies showed that synchrotron radiation experiments with nuclear resonances greatly benefitted from a new, translational approach: time resolved instead of energy resolved measurements, the latter familiar to traditional Mössbauer spectroscopy. This advance resulted from the time structure of synchrotron radiation, which is emitted as a sequence of very short x-ray pulses of typically less than 100 ps duration. Energy spectroscopy in the  $\mu\text{eV}$  to  $\text{neV}$  range is possible by analysis of the time-decay pattern of x-rays scattered off or transmitted through samples containing a suitable nuclear resonant isotope. The measurement and analysis of such time spectra constitutes the main part of the NFS/SMS, GINRS, NBS/NLS, NLE, and SRPAC methods. NRIXS on the other hand, integrates time spectra but nevertheless requires time discrimination.

Nuclear resonant scattering science continues to evolve with enhanced instrumentation, improvement of synchrotron radiation sources, development of nuclear resonant methods, and new applications. Almost always scientific results rely critically on tested and easily accessible evaluation software, such as the CONUSS and PHOENIX programs [3]. Continuous maintenance of software and proper hands-on training to potential users are very important to optimize user experience.

Table I: Nuclear resonant scattering tools and classes. Abbreviations: Nuclear Resonant Inelastic X-ray Scattering (NRIXS); Nuclear Resonant Vibrational Spectroscopy (NRVS); Nuclear Forward Scattering (NFS); Synchrotron Mössbauer Spectroscopy (SMS); Grazing Incidence Nuclear Resonant Scattering (GINRS); Nuclear Bragg/Laue Scattering (NBS/NLS); Nuclear Lighthouse Effect (NLE); Synchrotron Radiation Perturbed Angular Correlation (SRPAC); traditional Mössbauer Spectroscopy (MS).

tool	I	II	III
NRIXS/NRVS	-	-	X
NFS/SMS	X	-	-
GINRS	X	-	-
NBS/NLS	X	-	-
NLE	X	-	-
SRPAC	-	X	X
MS	-	X	X

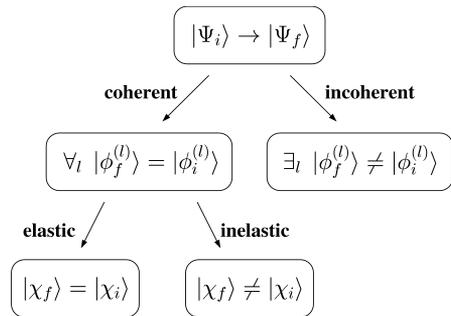


Figure 1. Classification of scattering processes. The quantum state of the scatterer  $|\Psi\rangle$  is factorized into quantum states of the atom cores  $|\phi\rangle$  and vibrations  $|\chi\rangle$ . (adapted from [2])

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