Wednesday, May 13
Facility-specific Workshops

APS Workshop 9
Workshop on Sn-119 Nuclear Resonant Scattering at the APS

Location: Bldg. 402, Room E1100/E1200

Organizers: Michael Hu and Bogdan Leu (APS)

The purpose of this workshop is to inform the broader general user community about the development of a new capability at Sector 30 regarding the use of the 119Sn nuclear resonance. The workshop will bring together experts in the field with potential new users to identify specific needs and develop plans to implement those requirements.

The nuclear resonant scattering studies performed at Sector 3 and Sector 16 in the last two decades have proved valuable in studying diverse materials, including porphyrins, proteins, enzymes and inorganic catalysts, superconductors, clathrates, thermoelectrics, metallic alloys, and earth-bound minerals under extreme pressures. Measurement of element-selective phonon density of states and extraction of numerous thermal and elastic constants motivated many new areas of research.

Similarly, measurement of nuclear forward scattering in the time domain with nanosecond resolution led to better understanding of electronic properties, such as valence and magnetism, in samples and under conditions that render these measurements impossible in the laboratory. For example, magnetism has been measured in monolayers or under pressures exceeding 1 Mbar.

Thus, the interest in nuclear resonant studies has grown to a point where it is necessary to optimize beamlines for different isotopes and to create more opportunities. One such opportunity presents itself at Sector 30. The working energy of the HERIX spectrometer at Sector 30 (23.7 keV) and the 119Sn nuclear resonance (23.88 keV) can be reached with the same monochromator. The combination of this cryogenically cooled, high-resolution monochromator with 1 meV resolution and a newly installed short-period undulator (1.72 cm) creates an ideal condition for such measurements. The available flux is better by almost an order of magnitude than at similar facilities around the world. Recent tests and scientific output [1] have demonstrated this capability at Sector 30.

Tin-based nuclear resonance studies are of interest to a variety of groups working with such materials as newly discovered superconductors, thermoelectric materials, clathrates, Sn-halides, porphyrins, and organometallic compounds. The combination of access to the 119Sn resonance with capabilities such as microfocusing for nanomaterial studies and infrastructure for high-pressure measurements should make the new technique highly attractive for new users.

Reference

[1] B.M. Leu et al., "Vibrational dynamics of the host framework in Sn clathrates," *Phys. Rev. B* **90**, 104304 (2014), DOI: http://dx.doi.org/10.1103/PhysRevB.90.104304.

8:30 – 8:35 Welcome & Introductory Remarks

8:35 – 9:05 Ercan Alp (Argonne National Laboratory)
Sn-based Nuclear Resonant Scattering Studies: Past and Present

9:05 – 9:45	John Tse (University of Saskatchewan) *Chemical Bonding and Lattice Dynamics of Sn Compounds from 119-Sn Mossbauer*
9:45 – 10:25	Raphael Hermann (Forschungszentrum Juelich) *Highly Anisotropic Lattice Dynamics in* $[(SnSe)_{1.04}]_m$-$[MoSe_2]_n$ *Ferrecrystals*
10:25 – 10:35	Break
10:35 – 11:15	Mathieu Roskosz (Univ. des Science et Tech. de Lille) *Tin Isotopes: The Next Probe of Planetary Differentiation and Core Formation*
11:15 – 11:55	W. Robert Scheidt (University of Notre Dame) *Tin Porphyrins 1969–2014*
11:55	Wrap-up and concluding remarks

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Sn-based Nuclear Resonant Scattering Studies: Past and Present

E.E. Alp, W. Bi, J. Zhao, M.Y. Hu, T.S.Toellner, and B. Leu

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^{119}Sn is the second most popular Mössbauer isotope after ^{57}Fe. This is partly due to long lifetime of its parent isotope ^{119m}Sn (250 days), relatively simple M1 transition from 3/2 to 1/2 state, reasonably long lifetime (18.3 nsec or 25.7 neV), and low transition energy (23.88 keV). Sn was among the first metals extracted (around 3500 BC). In modern times, Sn has found wider use in organotin compounds, transparent conductors, catalysis, protective coatings, float-glass production, and more recently in dye-sensitized solar cells, perovskites, Li-ion batteries, and tin chalcogenides as thermoelectric materials. Sn is also shown to be amenable to form two-dimensional topological insulators.

In this talk, I will introduce the Sn-based Mössbauer work done at the synchrotron radiation sources, their information content, and give a description of the new capability at Sector 30 beamline.

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Chemical Bonding and Lattice Dynamics of Sn compounds from 119-Sn Mossbauer

John S. Tse

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In this presentation, I will present a general introduction on how 119-Sn Mossbauer spectroscopy can provide useful chemical information and lattice dynamics of Sn nuclei in a variety compounds. Special emphases will be on system that cannot be easily amenable to laboratory Mossbauer spectrometers, such as thin films and under extreme conditions.

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Highly Anisotropic Lattice Dynamics in $((SnSe)_{1.04})_m$-$(MoSe_2)_n$ Ferecrystals

Raphaël P. Hermann

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The highly anisotropic lattice dynamics properties in SnSe based ferecrystals obtained from nuclear resonance inelastic x-ray scattering by the ^{119}Sn Mössbauer resonance will be discussed. Ferecrystals and related misfit layered compounds exhibit extremely low lattice thermal conductivity. These materials multilayer materials exhibit turbostratic disorder between the two constitutent layers stacked in the direction perpendicular to the substrate, here *m* unit-cells of SnSe and *n* of $MoSe_2$. By measuring the density of phonon states for Sn with the beam in plane with the layers and perpendicular to the layers, highly contrasting speed of sound and force constants are found for the (*m*,*n*)=(1,1) system. Further, a comparison of systems with (*m*,*n*)=(1,1) and (4,1) reveals the importance of interface effects in determining the lattice dynamics properties. Overall the ferecrystals are ideal in revealing properties of phonons under confinement.

Benedikt Klobes, Michael Hu, Matt Beekman, and David C. Johnson are acknowledged for the fruitful collaboration. The Advanced Photon Source at Argonne National Laboratory is acknowledged for provision of synchrotron radiation facilities at Sector 3.

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Tin Isotopes: The Next Probe of Planetary Differentiation and Core Formation

Mathieu Roskosz

UMET, CNRS, University of Lille, France

Terrestrial planets (including Mars and the Moon) are differentiated into metallic cores and silicate mantles and crusts. This layered structure provides some of the most important properties of these planets such as a magnetic field that deflects the solar wind and plate tectonics. Understanding the thermodynamical conditions (P, T, fO_2) that prevailed during this differentiation is thus a major question in Earth sciences. The elemental concentrations of siderophile (iron-loving) elements in the Earth's mantle have been intensively studied. Based on this approach, it is now widely accepted that the upper mantle abundances have been set by metal-silicate equilibrium in an early magma ocean. However, the redox conditions and their evolution during planetary formation are still highly controversial.

A new approach of this question is based on the isotopic composition of siderophile elements (mainly Si and Fe). However, a quantitative analysis of data collected on natural samples requires knowing accurately the way isotopes partition between coexisting phases (iron-based metal alloys, silicates and sulfides in particular). The so-called *fractionation factor* can be determined experimentally but it requires drastic equilibrium conditions that are barely achievable at the high pressures and temperatures of interest. In the case of iron and tin these experimental difficulties can be overcome if fractionation factors are indirectly measured using a synchrotron-based inelastic spectroscopy. The determination of these factors is achieved by measuring phonon excitations using a kind of inelastic x-ray scattering based on special Mössbauer nuclei (NRIXS).

In this context the recent analytical developments make possible to analyze the isotopic compositions of tin in natural samples. So far, this system has never been successfully explored from a geochemical point of view. Though some attempts were made in the past, the chemical separation of tin from other elements present in rocks was a real issue that is being solved these days. Now, we have a unique opportunity to develop the tin isotope geochemistry. There are very few places in the world with sufficient x-ray intensity, proper high-resolution optics, and nanosecond time resolved detectors with high efficiency to measure ^{119}Sn-specific properties of materials. The APS beamlines (Sector 3 and Sector 30) have developed proper crystal optics suitable for this purpose.

Here I will present known aspects of the physical and coordination chemistry of tin in geomaterials, how they should control tin isotopes fractionation and how Sector 30 will help us, in the coming years, to provide the mandatory fractionation factors to make Sn isotopes the new probe of the early evolution of the Moon, the Earth and Mars.