7th North American Mössbauer Symposium

January 11-12th, 2013
at the University of Texas at Austin

Organizing Committee

Dr. Jung-Fu Lin, University of Texas at Austin
Dr. Esen Ercan Alp, Argonne National Laboratory
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Dedicated to
Dr. Dean Taylor
Los Alamos National Laboratory

7th North American Mossbauer Symposium
University of Texas at Austin, January 11-12, 2013, Austin, TX
Program at Barrow Conference Room, JGB/GEO 4.102

January 10, 2013, Thursday
19:00-21:00   Reception Dinner at the Carillon of the AT&T Center

January 11, 2013, Friday
8:30-9:00   Registration & Breakfast at Holland Family Center (JGB/GEO 2.102)

(Session Chair: C. Johnson)
9:00-9:15   Welcome remarks: J.F. Lin, R. Kukkadapu, E. E. Alp
9:15-9:45   **Dean Taylor (LANL)**
                    50 years in Mössbauer Spectroscopy
9:45-10:15   **Wolfgang Sturhahn (Caltech)**
                    Synchrotron radiation based Mössbauer techniques

10:15-10:45   Coffee Break at Holland Family Center

(Session Chair: J. F. Lin)
10:45-11:15   **Lars Bocklage (HASYLAB-DESY, Germany)**
                    Probing spin waves in microstructures via nuclear resonant scattering
11:15-11:45   **V. Struzhkin (Geophysical Laboratory-CIW)**
                    Quantum critical point and spin fluctuations in lower mantle ferropericlase
11:45-12:15   **Moshe Pasternak (Tel Aviv University, Israel)**
                    Pressure induced spin-crossover and *Mott-Hubbard* transitions
12:15-12:30   5 poster introductions, 3 minutes each

12:30-13:30   Lunch at Holland Family Center

(Session Chair: E. E. Alp)
13:30-14:00   **Brent Fultz (Caltech)**
                    Anharmonic phonons and thermodynamics
14:00-14:30   **Nicolas Dauphas (U. of Chicago)**
                    NRIXS moments and applications in isotope geochemistry
14:30-15:00   **Michael Hu (Argonne National Laboratory)**
                    Anharmonicity studies with nuclear resonant inelastic x-ray scattering

15:00-15:30   Coffee Break at Holland Family Center

(Session Chair: R. Kukkadapu)
15:30-16:00   **Poster Review** (Posters are in display at Holland Family Center)
16:30-17:00   **Thomas Toellner (Argonne National Laboratory)**
                    Improving nuclear resonant scattering measurements
17:00-17:30   **Raphael Herman (Jülich Forschung Zentrum, Germany)**
                    Nuclear inelastic scattering above 30 keV

19:00-21:00   Texas BBQ Dinner at Scholz Garten
                    1607 San Jacinto Blvd., Austin TX 78701; (512) 474-1958

January 12, 2013, Saturday
8:30-9:00   Breakfast at Holland Family Center

(Session chair: V. Struzhkin)
9:00-9:30   **Catherine McCammon (Bayerisches Geoinstitut, Bayreuth, Germany)**
              Mössbauer spectroscopy along the geotherm
9:30-10:00   **Caitlin Murphy (Geophysical Laboratory, CIW)**
              Thermoelasticity of hcp-iron at 171 gigapascals
10:00-10:30   **Bin Chen (U. of Michigan)**
              Elastic and acoustic properties of Fe_7C_3 up to megabar pressures

10:30-11:00   Coffee Break at Holland Family Center

(Session Chair: M. Hu)
11:00-11:30   **Chang-Qing Jin (Institute of Physics, CAS, China)**
              Magnetic phase transitions in BeFe2As2 ferropnictide at high pressure
11:30-12:00   **Wenli Bi (UIUC-COMPRES and ANL)**
              Valence and magnetic state in Europium under extreme pressure
12:00-12:30   **Charles Johnson (U of Tennessee Space Institute)**
              Superparamagnetism of Europium Sulfide nanoparticles

12:30-13:30   Lunch at Holland Family Center
(Session Chair, Thomas Toellner)
13:30-14:00   **Zhu Mao (University of Texas at Austin)**
              Spin and valence state of iron in lower mantle silicates
14:00-14:30   **Yuming Xiao (HP-CAT, CIW)**
              Nuclear resonant scattering under high pressure at HP-CAT
14:30-15:00   **Timothy Sage (Northeastern University)**
              Probing biomolecular structure and elasticity eith ^{57}Fe
15:00-15:30   Coffee Break at Holland Family Center

(Session Chair, Jiyong Zhao)
15:30-16:00   **Sally Tracy (Caltech)**
              Evidence for polaron-ion correlations in Li_xFePO_4 from nuclear resonant
              scattering
16:00-16:30   **Lisa Mauger (Caltech)**
              Anharmonic phonon behavior in α-iron at high temperatures
16:30-17:00   **Rama Balasubramanian (Roanoke College)**
              Investigations on the role of nanocatalysts in the formation of nanotubes

17:00-18:30   **Mineral Physics Lab Tour (Afu Lin; JGB 6.308)**
              Campus Tour (Nikki Seymour; leaving at Holland Center at 17:30)

*19:00-21:00   **Symposium Banquet at Iron Cactus***
              606 Trinity Street, Austin TX 78701; (512) 472-9240

January 13, 2013, Sunday
9:30-~12:00   Austin Excursion (Texas Capital, Mt. Bonnell, Colorado River)
(Meet/leave at 9:30 am at University Avenue side of the AT&T Center)

FIFTY-FOUR YEARS OF HAVING FUN WITH THE MÖSSBAUER EFFECT

R. Dean Taylor

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The author will review his research activities since the discovery of the Mössbauer Effect, the early days when almost any equipment development or science result was a new discovery. Science funding in the sixties was abundant and switching to this new intriguing discipline was easy. Publication of Mössbauer Effect papers soon became so prolific that PRL considered a temporary ban, just to catch up.

Development of suitable cryogenic and electronic equipment played an important role in making this new discipline available to essentially everyone. Physics lab courses soon included simple ME demonstrations.

Several series of local and international meetings focussed on the ME soon evolved, along with a ME bibliography service. Most of these basic and industrial applications Conferences still exist today.

The new ME attracted scientists from many different disciplines and served as a melting pot for a wealth of ideas often uniquely suitable to some of the wide range of high resolution features available from a nuclear probe located in a solids environment.

My background was low temperature physics, emphasizing the two-fluid properties of ^{3}He and ^{4}He and their mixtures and of the state properties of the heliums and of tritium and its mixtures with deuterium and ^{3}He. I soon became an electrical engineer, mechanical engineer, radiochemist, and much more. The drudgery of data acquisition using SCA's, EPUT counters, and single velocity transducers was soon superseded by use of MCA's, feed-back loudspeaker-type transducers, mag-tape readouts, and pc computers.

We confirmed Mössbauer's discovery in ^{191}Ir and soon showed ^{67}ZnO to be ME active. These experiments were followed by low-temperature "brute-force" nuclear polarization of magnetized ^{57}Co in ^{56}Fe metal using adiabatic demagnetization, then ^{3}He pumping, and finally a home-built dilution refrigerator that reached 0.030 K. We had an accurate but very clumsy milli-K thermometer.

Other early experiments included a study of the temperature dependence of the hyperfine field of Fe metal, the ME of Fe using the 6.3-keV internal conversion x-rays, the elliptical polarization of magnetized iron, the ME of ^{181}Ta in Ta and W, and the lattice dynamics and localized moments of ^{57}Fe (^{57}Co) in various metallic elements. Coexistence of magnetism and superconductivity was first shown by ME.

Our first ME measurements at high pressures were on a ^{57}Co in Fe metal source placed in a DAC (diamond anvil cell) reaching pressures of 22 GPa, sufficient to transform cubic Fe to non-magnetic hcp Fe. There was no ordering down to 0.030K and no magnetically induced moments.

It was about this time (1981) that Moshe Pasternak spent a sabbatical with me and this has led to months' long visits every year since. The program also benefitted from 1-2 postdocs in years up until my retirement in 1990. But my retirement was just a change of paycheck. My vocation became my "hobby", an adventure that LANL has reasonably supported for 23 years. And Pasternak's visits continue to be productive and exciting.

Our collaboration has strongly supported temperature and high pressure studies to the 100 GPa region involving ME, resistivity, synchrotron radiation XRD, and DAC cell development. Most of the studies have involved ^{57}Fe ME using ^{57}Co in Rh "point sources" in a series of studies designed to understand the complex transformational behaviour in Fe compounds. ^{129}I ME studies have contributed, *e.g.*, the Mott transition in NiI$_2$, until US source preparation was no longer practical.

A fling into the area of gamma-ray lasers with Gil Hoy yielded little substantive except positive evidence for a ME in 40-sec ^{109}Ag, first observed at LANL and later at Old Dominion.

SYNCHROTRON RADIATION BASED MÖSSBAUER TECHNIQUES

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The discovery of nuclear resonant scattering 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. A variety of nuclear resonant techniques were explored during this 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, a selection of nuclear resonant scattering techniques is reviewed with emphasis on their potential for applicability.

With the scheme in Figure 1, we distinguish four classes of nuclear resonant scattering: coherent elastic (I);
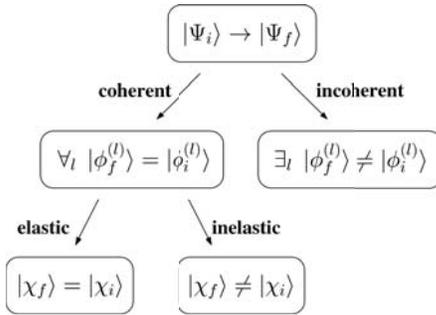
Figure 1. Classification of scattering processes. The quantum state of the scatterer $|\Psi\rangle$ is factorized into quantum states of the atom cores $|\phi\rangle$ and vibrations $|\chi\rangle$. (adapted from [2])

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.

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

The superior brightness and focused spectral flux density of third-generation synchrotron radiation facilities is evident from the comparison shown in Table II and has permitted scientists to develop applications with ever smaller samples under increasingly extreme conditions.

Table II: Comparison between a modern synchrotron radiation source and a commercially available ^{57}Co source with 100 mCi activity. Losses due to x-ray optics are included in the synchrotron data. (adapted from [2])

Property	SR	^{57}Co	unit
Spectral flux	3×10^{12}	2.5×10^{10}	ph/s/eV
Brightness	10^{22}	2.5×10^{13}	ph/s/eV/sr
Spectral flux density	5×10^{18}	2×10^{11}	ph/s/eV/m^2
focused	7×10^{21}	-	ph/s/eV/m^2
Beam size (V x H)	0.4 x 2	10 x 10	mm^2
focused	10 x 10	-	μm^2
Polarization	100	0	%

Early nuclear resonant scattering studies showed that synchrotron radiation experiments with nuclear resonances greatly benefitted from a new approach: time resolved instead of energy resolved measurements familiar to traditional Mössbauer spectroscopy. This novel approach resulted from the particular properties 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 μeV to 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. In a class I process, such as nuclear forward scattering, the different nuclear transitions are excited simultaneously by a synchrotron x-ray. Following the excitation, these transitions behave as a set of oscillators with slightly different frequencies. At the instant of excitation in phase, the differences in phase between oscillators quickly increase and lead to a sequence of destructive and constructive interferences. This results in intensity oscillations in the time spectra, the so called "quantum beats."

Nuclear resonant scattering continues to evolve with the development of new instrumentation, improvement of synchrotron radiation sources, and development of new nuclear resonant methods. In particular, speculation about the potential impact of nuclear resonant scattering at x-ray laser facilities remains tempting.

[1] E. Gerdau, R. Ruffer, H. Winkler, W. Tolksdorf, C.P. Klages, J.P. Hannon, Phys. Rev. Lett. 54, 835-838 (1985)
[2] W. Sturhahn, J. Phys.: Condens. Matter 16, S497-S530 (2004)

PROBING SPIN WAVES IN MICROSTRUCTURES VIA NUCLEAR RESONANT SCATTERING

L. Bocklage[1], K. Schlage[1], H.-C. Wille[1], C. Swoboda[2], G. Meier[2], and R. Röhlsberger[1]

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Nuclear resonant scattering (NRS) is employed to investigate dynamical effects like diffusion, phonons or relaxation processes [1]. The inherent sensitivity to dynamics on the time scale of the lifetime of the nucleus suits NRS to study magnetization dynamics. Spin waves are collective excitations of the magnetization in ferromagnetic materials based on the precession of magnetic moments. The properties of spin waves can be tuned by the material or the geometry of the investigated elements paving the way to functional spin wave applications. With respect to spin waves NRS features intrinsic advantages. By using isotope probe layers, the sub-nanometer resolution will enable to study depth profiles of spin waves within films and the microscopic model of NRS will help to extract the dynamic magnetization.

We present first results of NRS on permalloy ($Ni_{80}Fe_{20}$) microstructures excited by a radio-frequency magnetic field. The measurements are performed at beamline P01 at PETRA III (DESY). The 14.4 keV resonance of ^{57}Fe is used as probe in the isotope enriched permalloy film. The dynamic external magnetic field drives the magnetization at the resonance frequency of the stripe at 1.45 GHz and excites a standing spin wave along the width of the element. Here, we observe a distinct change in the measured time spectra.

NRS measurements under grazing-incidence on a permalloy stripe of 800 µm length, 10 µm width and 30 nm thickness are shown in Fig. 1. The magnetization in the stripe is parallel to the incident wave vector and the time spectrum exhibits a pronounced beating pattern as expected in this geometry. At high amplitudes of the driving field (~1 mT) the oscillations almost completely vanish (see Fig. 2) showing the strong impact of the spin wave on the time spectra. The temporal period of the spin wave is about a nanosecond and much smaller than the lifetime of the nucleus. Thus the nucleus experiences an average hyperfine field. As shown in Fig. 2 the average field almost completely results in a single resonance [2].
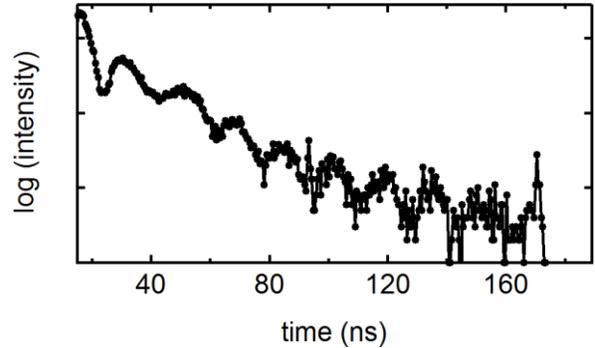
Figure 1. Time spectrum of a permalloy ($Ni_{80}Fe_{20}$) stripe without excitation.
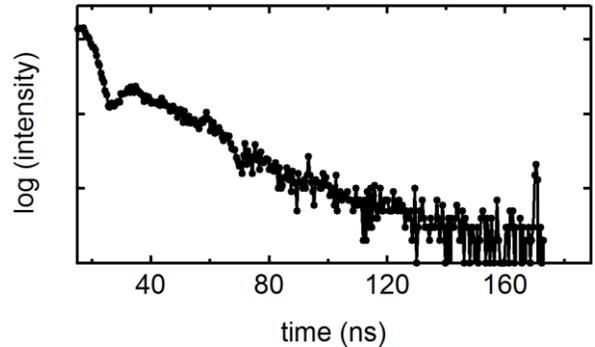
Figure 2. Time spectrum of a permalloy stripe excited by a microwave field at ferromagnetic resonance.

[1] R. Röhlsberger, Springer Tracts In Modern Physics 208, 2004.
[2] M. Blume and J. A. Tjon, Phys. Rev. **165**, 446 (1968).

QUANTUM CRITICAL POINT AND SPIN FLUCTUATIONS IN LOWER MANTLE FERROPERICLASE

I. S. Lyubutin[2], V. V. Struzhkin[1], A. A. Mironovich[3], A. G. Gavriliuk[1-3], P. G. Naumov[1], J. F. Lin[4], S. G. Ovchinnikov[5,6], S. Sinogeikin[7], P. Chow[7], Y. Xiao[7], and R. J. Hemley[2]

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Ferropericlase, (Mg,Fe)O is one of the most abundant minerals in the Earth's lower mantle. The high-spin (HS) to low-spin (LS) transition in the Fe^{2+} ions can dramatically alter the physical and chemical properties of (Mg,Fe)O in the deep mantle, thereby changing our understanding of the Earth's deep interior. To establish a fundamental understanding of the ground electronic state of iron, the electronic and magnetic states of Fe^{2+} in $(Mg_{0.75},Fe_{0.25})O$ have been investigated by transmission (TMS) and synchrotron (NFS) Mössbauer spectroscopy at high pressures and low temperatures (down to 5 K). The results show that the ground electronic state of Fe^{2+} at the critical pressure P_c of the spin transition and close to T=0 is determined by a quantum critical point P_q (T = 0, P_c). At this critical point, the energy difference between the HS and LS states (an energy gap for the spin fluctuation) is zero. The deviation from T=0 leads to the thermal excitation of the HS or LS state, suggesting a strong influence on the magnetic and physical properties of the material. Combining these observations with theoretical calculations, the results indicate that the existence of the quantum critical point at zero temperature affects not only the low-temperature physical properties, but also the strong temperature/pressure-dependent properties at conditions relevant to the middle layer of the Earth's lower mantle.

Figure 2. Magnetic phase diagram of ferropericlase $(Mg_{0.75},Fe_{0.25})O$ at high pressures and low temperatures. The dashed blue line separates the regions of the HS paramagnetic and antiferromagnetic phases between 0 and 50 GPa. Above 56 GPa, the diagram shows the LS diamagnetic phase which appears due to the HS → LS crossover. A quantum critical point appears in the diagram at T = 0 and $P = P_c$ which can be explained in terms of the geometric phase of the topological origin that is considered as an order parameter in the spin crossover phenomena [1] (33). In the shaded (red) area, the HS and LS states coexist due to the thermal fluctuations between the electronic HS and LS states. In the upper part of this area (shaded red), the region of the coexisting HS and LS states is extended to high temperatures relevant to the lower mantle conditions [calculated from the Ref. [2] (31) experimental data]. The dash line in this area indicates the position of maximum magnetic susceptibility χ forferropericlase.

[1] Ovchinnikov SG (2005) The mechanism of the electronic transition in ferroborates under high pressure. *J. Phys.: Cond. Matter* 17:S743-S751.
[2] Lin JF*, et al.* (2007) Spin transition zone in Earth's lower mantle. *Science* 317:1740-1743.

Figure 1. Representative low-temperature synchrotron Mössbauer spectra of $(Mg_{0.75},Fe_{0.25})O$ at 38 GPa (a) and 55 GPa (b). High-frequency quantum beats indicate a magnetic ordering of Fe^{2+} ions in the HS state, whereas the low-frequency quantum beats indicate the paramagnetic state of Fe^{2+} ions in the HS state. Absence of the quantum beats indicates the occurrence of the diamagnetic state of the LS Fe^{2+} ions. Solid lines are calculated data.

Mössbauer studies in pressure induced spin-crossover and *Mott-Hubbard* transitions in ferric-oxides leading to unusual structural phase transitions.

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Extensive high-pressure studies carried out in $M^{3+}FeO_3$ ($M \equiv$ B, Al, Ga, *RE*) ferric oxides and Goethite (FeOOH) [1,2] led to the discovery of an unusual kind of isostructural *zeroth-order* phase transition characterized by a sharp volume collapse with no hysteresis. This kind of transition, with no change in space group, followed either a pressure induced collapse of the *Mott-Hubbard* correlation gap, accompanied by insulating-metal transition (e.g., GaFeO₃), or from the spin crossover ($S=5/2 > S=1/2$) in Fe^{3+}. Both these electronic transitions result in substantial shortening of the Fe-O bonding responsible for the large volume contraction. Those cases will be contrasted with the HP transition in hematite which undergo a *bona fide* 1st order phase transition [3]

Measurements have been carried out combining ^{57}Fe Mössbauer spectroscopy, powder and single-crystal X-ray diffraction, *k*-edge based spectroscopy, and R(P,T).

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∗ HS > LS in Fe-metal as manifested by the discontinuous increase in $\rho_s(0)$
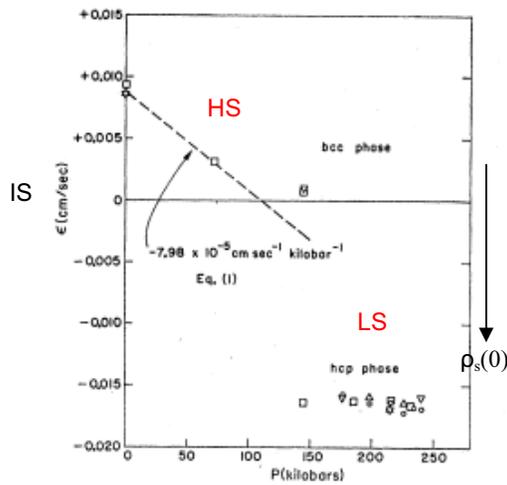
PHYSICAL REVIEW   VOLUME 135, NUMBER 6A   14 SEPTEMBER 1964

Mössbauer Effect in Iron under Very High Pressure*†

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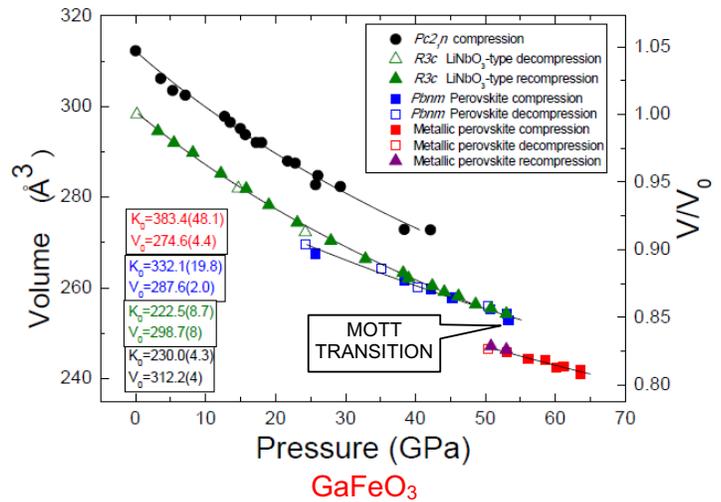
1. R. Arielly, et al..Phys. Rev. B **84**, 094109 (2011).
2. G.Kh. Rozenberg et al. Europhys. Lett. **71** (2), 228 (2005).
3. M. P. Pasternak et al. Phys. Rev. Letters. **82**, 4663 (1999).

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Keywords: ferric oxides, electronic/structural phase transitions, XRD diffraction, ^{57}Fe Mössbauer spectroscopy

Anharmonic Phonons and Thermodynamics

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Measurements of nuclear resonant inelastic x-ray scattering (NRIXS) on materials under pressure give detailed information on how phonon frequencies of a material change with volume, and changes in the phonon contribution to the free energy. Likewise, NRIXS measurements on materials at elevated temperatures show significant changes of the phonon spectrum. We also perform inelastic neutron scattering (INS) measurements, and combining the datasets allow us to obtain the total phonon DOS, and the two phonon partial DOS curves of a binary alloy [1,2]. The combinations of four measurements (NRIXS, T), (NRIXS,P), (INS,T), (INS,P) have not been practical, but subsets of them have given a more complete picture of high temperature thermodynamics.

In general, only part of the temperature-dependent phonon thermodynamics can be attributed to the thermal expansion. Especially at high temperatures, anharmonic contributions to the phonon entropy can be a significant fraction of a k_B per atom. Our group has been assessing non-harmonic behavior from phonon-phonon interactions with inelastic neutron scattering and sometimes with density functional theory computations. We showed that the dominant effects in fcc metals were the kinematical requirements of energy and momentum conservation, not the wavevector-dependence of the cubic anharmonicity [3,4]. A kinematical model with both cubic and quartic perturbations was used to assess phonon shifts and broadenings measured with Raman spectroscopy on rutile TiO_2 and SnO_2. On the other hand, highly anharmonic materials such as ScF_3 are inappropriate for perturbation theory, and offer interesting challenges for measuring entropy by inelastic scattering methods.

I will review a few principles of thermodynamics at high pressure and high temperatures, and point out problems that stem from the use of Grueneisen parameters, especially when Grueneisen parameters have opposite signs for phonon modes measured at elevated pressure or elevated temperature. Approaches to reconciling this apparent discrepancy will be described, and some experimental challenges are outlined. There are theoretical challenges as well, especially for extracting the vibrational entropy from spectra of anharmonic phonons.

[1] J.A. Munoz, et al., Phys. Rev. Lett. 107, 115501 (2011).
[2] M.S. Lucas, et al., Phys. Rev. B 82, 144306 (2010).

[3] X. Tang, C-W. Li, B. Fultz, Phys. Rev. B, 82, 184301 (2010).

[4] X. Tang and B. Fultz, Phys. Rev. B 84, 054303 (2011).

NRIXS MOMENTS AND APPLICATIONS IN ISOTOPE GEOCHEMISTRY

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Iron isotope geochemistry is a rapidly growing field with applications ranging from low temperature aqueous systems to planet forming processes [1]. Critical inputs in iron isotope studies are equilibrium fractionation factors between coexisting phases. Traditionally, these have been estimated by performing equilibration experiments, whereby two phases are allowed to equilibrate isotopically in the laboratory under controlled T-P conditions, and the Fe isotopic composition of the coexisting phases are measured. This method is difficult to implement as equilibration between phases can be limited by slow exchange kinetics at low temperature and the results can be ambiguous.

A very useful feature of iron isotope systematics is that the reduced partition function ratio that gives equilibrium fractionation factors can be derived from NRIXS measurements [2,3]. Using independent approaches, Polyakov et al. [2] and Dauphas et al. [3] showed how this value could be calculated from the even moments of the iron partial phonon density of states (PDOS). We also established mathematically relationships between the even moments of g and the centred moments of S [3,4] (g is the PDOS while S is the excitation probability function):

$$m_2^g = \frac{R_3^S}{E_r}$$

$$m_4^g = \frac{R_5^S - 10 R_2^S R_3^S}{E_r}$$

$$m_6^g = \frac{R_7^S + 210 \left(R_2^S\right)^2 R_3^S - 35 R_3^S R_4^S - 21 R_2^S R_5^S}{E_r}$$

Using S rather than g has several advantages. The most important one is that the odd moments of S are largely insensitive to background subtraction when the acquisition range is symmetric, while the moments of g are not. Furthermore, error estimations with S are more straightforward than with g because the uncertainties at all energies are independent. For applications in iron isotope geochemistry, we use the values calculated from S as these are more accurate and more precise than those calculated from g.

We have measured the NRIXS spectra of silicate glasses of basaltic to rhyolitic compositions synthesized under variable oxygen fugacities (from IW to air). The goal of this work is to understand the cause of iron isotopic fractionation in igneous rocks and to investigate iron coordination environment in magmas/glasses. We have also acquired conventional Mössbauer and XANES spectra for Fe^{3+}/Fe_{tot} and structural characterizations. At high temperature, equilibrium isotopic fractionation is proportional to differences in the force constants of coexisting phases, which is given by the 3rd moment of S [5]. The force constants of iron in basalt, andesite, and dacite increase linearly with increasing Fe^{3+}/Fe_{tot} ratio. The force constants of iron in rhyolitic glasses also increase with increasing oxidation state but the trend is shifted from less silicic magmas. A similar shift is also observed for the centroid energy in XANES. We use the trends to estimate the force constant of Fe^{2+} and Fe^{3+} in the various glasses. In basalt, andesite, and dacite, the force constants of Fe^{2+} and Fe^{3+} are ~180 and 360 N/m, respectively. In rhyolite, the force constant of Fe^{3+} is similar to less silicic glasses but that of Fe^{2+} is higher (~280 N/m). We have used these measurements to calculate the iron isotopic fractionation during partial mantle melting to make oceanic crust and during magma differentiation to make granites and rhyolites. The predicted values agree well with the isotopic compositions of rocks measured by multi-collector inductively coupled plasma mass spectrometry. We are currently assessing whether iron isotopic fractionation can be used to estimate redox conditions in modern and ancient terrestrial rocks.

[1] N. Dauphas, O. Rouxel, Mass Spectrometry Reviews, 25, 515, 2006.
[2] V.B. Polyakov, S.D. Mineev, R.N. Clayton, G. Hu, K.S. Mineev, Geochimica et Cosmochimica Acta 69, 5531, 2005.
[3] N. Dauphas, M. Roskosz, E.E. Alp, C.K. Sio, F.L.H. Tissot, M. Hu, J. Zhao, L. Gao, R.V. Morris, Geochimica et Cosmochimica Acta 94, 254, 2012.
[4] M.Y. Hu, T.S. Toellner, N. Dauphas, E.E. Alp, J. Zhao, Physical Review B, submitted, 2012.
[5] H.J. Lipkin, Physical Review B, 52, 10073, 1995.

Anharmonicity studies with nuclear resonant inelastic x-ray scattering

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Abstract

The interpretation of NRIXS measurements has been done mostly in the context of quasi harmonic approximation. Phonon density of states and dynamic properties like mean kinetic energy and mean force constant can be derived. Going beyond the harmonic lattice model, we show that the anharmonic terms in the lattice potential can be measured. This opens up the NRIXS method to study anharmonicities in materials. Given any specific model of lattice potentials, one can calculate the moments of a would-be measured NRIXS spectrum. This may be used to restrict and adjust models of lattice potentials. We will present new results and re-analysis of some previous ones in light of this anharmonic consideration.

IMPROVING NUCLEAR RESONANT SCATTERING MEASUREMENTS

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Nuclear resonant scattering can be used to provide elastic and thermodynamic information of host materials containing a nuclear resonant isotope via the technique of nuclear resonant vibrational spectroscopy (NRVS). It also provides important information on the local chemical environment of the resonant isotope via the technique of synchrotron Mössbauer spectroscopy (SMS). Both of these scattering techniques often require narrow energy-band filtering of synchrotron radiation to limit the X-ray load on the detection system and allow observation of the nuclear resonant signal. Typically, meV-bandwidth X-ray monochromators are used to perform both classes of measurements. In addition, in the case of NRVS, the spectral distribution of the incident beam as produced by the X-ray monochromator becomes an important contributor to the quality of the data and directly determines both the energy resolution of the data, as well as the lowest energy lattice excitation that can be resolved. Being able to resolve $0.1\,\mathrm{meV}$ features in the data would impact many research fields that use NRVS, but this level of resolution poses many obstacles.

First attempts to improve energy bandwidths to $0.1\,\mathrm{meV}$ ($\mathrm{E/dE}>10^8$) at hard X-ray energies proved difficult due to crystal fabrication and were accompanied by low spectral efficiency and poor wavelength stability [1, 2]. Recent progress at the Advanced Photon Source on a prototype, ultra-high-energy-resolution monochromator (UHRM) using active-feedback control and cryogenic stabilization has resulted in an order of magnitude improvement in efficiency and two orders of magnitude improvement in stability. In this talk, I will present the current status of this prototype UHRM along with prospects for extending the design to other nuclear resonant energies and other energy resolutions.

An additional development aimed exclusively at the technique of SMS involves combining a microfocused X-ray beam with high-speed shutters to completely suppress the enormous electronic charge scattering that accompanies nuclear resonant scattering. This alternative approach would mitigate the need for a high-resolution monochromator for SMS measurements and has the potential for both improving counting rates and extending the capabilities of SMS. The results of a demonstration experiment [3] and the implications of high-speed shuttering for SMS measurements will be discussed.

References

[1] Toellner, T.S., Hu, M.Y., Sturhahn, W., Bortel, G., Alp, E.E. & Zhao, J. (2001), J. Synchrotron Rad. **8** 1082 (2001).

[2] Yabashi, M., Tamasaku, K., Kikuta, S. & Ishikawa, T., Rev. Sci. Instrum. **72**, 4080 (2001).

[3] T.S. Toellner, E.E. Alp, T. Graber, R.W. Henning, S.D. Shastri, G. Shenoy, and W. Sturhahn, J. Synchrotron Rad., **18** 183, (2011).

Nuclear Inelastic Scattering above 30 keV

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Measurements of the partial density of phonon states with inelastic nuclear resonance scattering have recently passed their 15th anniversary[1]. Monochromatization in the meV range is required in order to properly resolve the phonon spectrum. Obtaining such resolution becomes very challenging for nuclear resonances above 30 keV[2], as an energy resolution $\Delta E/E$ better than 3.10^{-8} is required. With the use of a single crystal sapphire backscattering monochromator we have been successful in carrying out measurements with the antimony-121 37.2 keV[3], tellurium-125 35.4 keV[4] and xenon-129 39.9 keV[5] nuclear resonances. Nuclear inelastic scattering measurements on several compounds with ~1 meV resolution will be presented.

The phonon properties obtained mostly in thermoelectric bulk antimonides and tellurides as well as in similar compounds with confined geometry such as nanowires and thin films will be reviewed. In bulk thermoelectric materials, the specific dominating mechanisms that limit the thermal conductivity have been identified for several antimonide Zintl phases such as $Yb_{14}MnSb_{11}$ and Zn_4Sb_3 [6]. For skutterudite compounds, for the first time, the study of the unfilled $FeSb_3$ [7] was possible and direct comparison with the lattice dynamics in filled skutterudites reveals that besides the presence of rattling modes, an overall very soft framework might also contribute to the low thermal conductivity e.g. in $YbFe_4Sb_{12}$ [8].

Recently tellurium-125 nuclear inelastic scattering measurements have been carried out with improved resolution and the results obtained on bulk Bi_2Te_3 and Sb_2Te_3 [9] and binary IV-VI tellurides [10] will be presented , as well as the first experimental insights in the specificity of lattice dynamics in nanoscaled thermoelectrics obtained both by inelastic neutron and nuclear inelastic scattering, notably in Bi_2Te_3 nanowires, in $FeSb_2$, ZnSb, and NiSb nanopowders, in LAST-*m*, $Pb_mAgSbTe_{2+m}$, phases, with $6<m<18$, and in nanostructured Si [11]. First results of high pressure nuclear inelastic scattering carried out with the antimony-121 and tellurium-125 nuclear resonances will be discussed.

The latest developments have enabled measurements with the xenon-129 nuclear resonances and phonon spectra will be presented for solid Xe and a xenon hydrate clathrate.

[1]   Seto M. et al., Phys. Rev. Lett. 74, 3828 (1995);
        Sturhahn W. et al., Phys. Rev. Lett. 74, 3832 (1995);
        Chumakov A. et al., Europhys. Lett. 30, 427 (1995).
[2]   Sergueev I. et al., J. Synchr. Rad. 18 802 (2011).
[3]   Wille H.-C. et al., Phys. Rev. B 76, 140301(R) (2007).
[4]   Wille H.-C. et al., Europhys. Lett. 91, 62001 (2010).
[5]   Klobes B. et al., in prep. (2013).
[6]   Moechel A. et al., Phys. Rev B 84, 184303 (2011).
[7]   Moechel A. et al., Phys. Rev B 84, 064302 (2011).
[8]   Moechel A. et al., Phys. Rev B 84, 184306 (2011).
[9]   Bessas D. et al., Phys. Rev B 86, 224301 (2012).
[10]   Bauer Pereira P. et al., Phys. Stat. Solidi B,
        DOI 10.1002/pssb.201248412 (2012).
[11]   Claudio T. et al., J. Mater. Sci.
        DOI 10.1007/s10853-012-6827-y(2012).

MÖSSBAUER SPECTROSCOPY ALONG THE GEOTHERM

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Iron is both the most abundant element in the Earth and the only major element with multiple electronic configurations (valence and spin state). ^{57}Fe Mössbauer spectroscopy measured in the energy domain remains one of the best methods to determine iron valence and the nature of spin transitions in lower mantle phases, but since both pressure and temperature can profoundly influence electronic properties, mantle and core phases are best studied *in situ* under high pressure and high temperature conditions. Up until now measurements at high P,T using a diamond anvil cell could only be made using external heating and hence were limited to a maximum of around 800 K. Higher temperatures are possible through laser heating; however conventional radioactive sources have limited intensity and essentially no possibilities for focusing in a laboratory setting.

To overcome these limitations we have developed an energy domain Synchrotron Mössbauer Source (SMS) on beamline ID18 at the European Synchrotron Radiation Facility (ESRF), enabling rapid collection of high quality energy domain Mössbauer spectra. Combined with a portable double-sided laser heating system, SMS spectra can be collected on iron-containing phases at P,T conditions up to those near the Earth's core in less than one hour. Complementary data are provided by nuclear forward scattering (NFS) spectra measured at the same P,T conditions in the time domain.

In this presentation we will describe SMS and NFS studies performed on beamline ID18 at ESRF on the lower mantle phases $(Mg,Fe)(Si,Al)O_3$ perovskite and $(Mg,Fe)O$ using a laser heated diamond anvil cell. We will address data analysis and interpretation of the spectra, and discuss their implications for properties and dynamics of the Earth's interior.

THERMOELASTICITY OF HEXAGONAL CLOSE-PACKED IRON TO 171 GIGAPASCALS

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Iron is an important component of minerals throughout the Earth, and it is thought to be the main constituent in Earth's core. Existing experiments suggest that the hexagonal-close packed phase of iron (hcp-Fe) is stable at core conditions. Therefore, firmly establishing the high-pressure thermoelastic and thermodynamic properties of hcp-Fe is essential for understanding Earth's iron-rich core.

We probed hcp-Fe's total phonon density of states (DOS) at eleven compression points between 30 and 171 GPa (1.7 Mbar) at 300 K, using nuclear resonant inelastic x-ray scattering (NRIXS) and *in situ* x-ray diffraction (XRD) experiments performed at Sector 3-ID-B of the Advanced Photon Source at Argonne National Laboratory [1–4]. A neon pressure medium was loaded for a subset of our experiments, in order to create a quasihydrostatic sample enviornment. In addition, we collected XRD before and after each NRIXS dataset to determine the sample volume *in situ*. Finally, our long data collection times resulted in a high statistical quality dataset that, in turn, allowed for unique analyses of hcp-Fe's thermoelastic and thermodynamic properties.

For example, we obtain hcp-Fe's volume-dependent vibrational free energy (F_{vib}) and entropy (S_{vib}) from the integrated total phonon DOS and our *in situ* XRD measurements. The volume dependence of F_{vib} provides hcp-Fe's harmonic vibrational thermal pressure (Table I), which we combine with theoretically calculated electronic and anharmonic components [5] to determine its total thermal pressure to Earth's core conditions (Figure 1) [2]. In addition, our measured volume dependence of S_{vib}—together with an established equation of state (EOS) for hcp-Fe [5]—gives its thermal expansion coefficient at 300 K [4]. Finally, we use the volume-dependence of hcp-Fe's total phonon DOS to determine its vibrational Grüneisen parameter (γ_{vib}), which relates thermal pressure to thermal energy per unit volume [3]. Using a common parameterization for the volume dependence of γ_{vib}, we constrain its value at pressures corresponding to Earth's core (Figure 2).

These three parmaeters are interrelated and provide information about hcp-Fe's thermal EOS. In turn, this allows us to constrain the amount of light elements that must be present in Earth's solid inner core via comparison with seismic observations of its density [2].

[1] W. Sturhahn et al., *Hyperfine Interactions*, 125, 149–172, 2000.
[2] C.A. Murphy et al., *Phys. Earth Planet. Int.,* 188, 114–120, 2011.
[3] C.A. Murphy et al., *Geophys. Res. Lett.,* 38, L24306, 2011.
[4] C.A. Murphy et al., *J. Geophys. Res.,* under review, 2012.
[5] A. Dewaele et al., *Phys. Rev. Lett.*, 97, 215504, 2006.

Table I: Vibrational thermodynamic parameters for hcp-Fe from its total phonon DOS.

V (cm^3/mol) [1]	P (GPa)[1]	F_{vib} (meV/atom)[2]	P_{vib}^{h} (GPa)[2]
5.92(2)	30(2)	19.8(6)	2.31(6)
5.81(1)	36(2)	22(1)	2.34(6)
5.56(1)	53(2)	29(1)	2.43(6)
5.36(1)	69(3)	34.1(8)	2.49(6)
5.27(2)	77(3)	35.7(5)	2.52(6)
5.15(2)	90(3)	39.2(7)	2.56(6)
5.00(2)	106(3)	42.9(8)	2.60(6)
4.89(2)	121(3)	46.7(7)	2.64(6)
4.81(2)	133(4)	48.8(9)	2.67(6)
4.70(2)	151(5)	51.1(9)	2.70(6)
4.58(2)	171(5)	55.9(1.4)	2.74(6)

[1]*Sample volumes (V) were measured with in-situ XRD and converted to pressures (P) using the Vinet EOS for hcp-Fe reported in [5].*
[2]*We determined hcp-Fe's vibrational free energy (F_{vib}) from the integrated phonon DOS [1], and used its volume dependence to obtain hcp-Fe's harmonic vibrational thermal pressure (P_{vib}^{h}) at 300 K [2].*
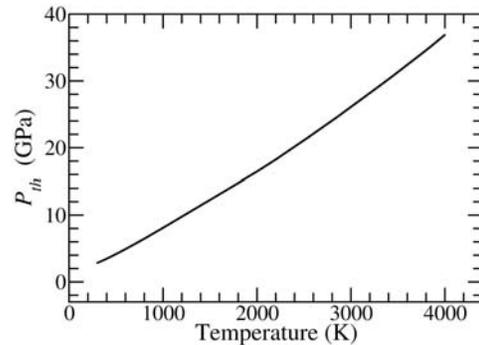
Figure 1. Total thermal pressure (P_{th}) for hcp-Fe at a pressure of 151 ± 5 GPa, accounting for electronic and anharmonic effects [2; 5].
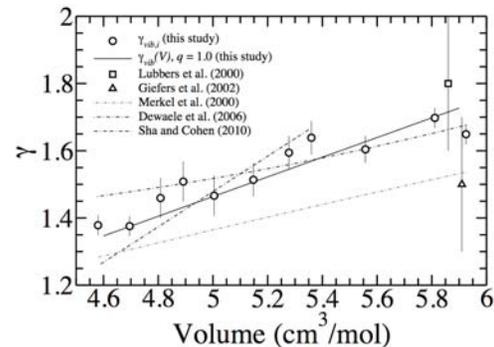
Figure 2. Volume dependence of the vibrational and total Grüneisen parameters for hcp-Fe from theoretical calculations and experiments [3].

ELASTIC AND ACOUSTIC PROPERTIES OF FE$_7$C$_3$ UP TO MEGABAR PRESSURES

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Carbon is considered a principal light element in the Earth's iron-rich core, mainly because of its strong affinity for iron during core-formation differentiation and its competency in explaining the density deficit of the core [1]. The iron carbide phases, Fe$_3$C or Fe$_7$C$_3$, have both been proposed as a major constituent in the Earth's inner core [1-4]. However, recent studies on melting relations of the iron-carbon binary system at high pressures suggested that Fe$_7$C$_3$ is likely to be a more important crystallizing phase than Fe$_3$C at core conditions [5,6]. To test the hypothesis of an Fe$_7$C$_3$-dominant inner core, we have determined the density and sound velocities of Fe$_7$C$_3$ up to core pressures and evaluated the effects of pressure-induced magnetic transitions, from synchrotron-based single-crystal X-ray diffraction (XRD), synchrotron Mössbauer spectroscopy (SMS) and nuclear resonant inelastic X-ray scattering (NRIXS) measurements in diamond anvil cells at 300 K.

From our single-crystal XRD measurements of Fe$_7$C$_3$ at 300 K up to 167 gigapascals (GPa), two discontinuities in the compression curve have been identified, first of which at 7.0-7.5 GPa corresponds to a ferromagnetic to paramagnetic transition and manifests as the disappearance of fast oscillations in the SMS Spectra at pressure above 7 GPa [7]. The second discontinuity near 53 GPa results in softening of Fe$_7$C$_3$, presumably caused by a high-spin to low-spin transition of iron. The fit to the compression data between 7 and 53 GPa by the Birch-Murnaghan equation of state (EOS) yields $K_0 = 201(\pm12)$ GPa, $K' = 8.0(\pm1.4)$, and $V_0 = 184.69(\pm0.16)$ Å^3, and the fit to the data between 53 and 167 GPa yields $K_0 = 307(\pm6)$ GPa, $K' = 3.2(\pm0.1)$, and $V_0 = 182.87(\pm0.38)$ Å^3. The densities of Fe$_7$C$_3$ at inner core conditions have been calculated from the EOS parameters for Fe$_7$C$_3$ determined at pressures between 53 and 167 GPa and existing thermoelastic parameters [4,8,9] and compared with seismic data, which suggests a volume fraction of Fe$_7$C$_3$ from 62 to 95% in the inner core or a carbon content of 5.1-7.9% by weight for an iron-carbon core scenario.

We have also conducted NRIXS measurements of Fe$_7$C$_3$ up to 150 GPa at 300 K and determined its Debye sound velocity (V_D) from the low-energy region of the partial phonon density of state (DOS). From the EOS and V_D, shear (V_S) and compressional (V_P) velocities have been derived for Fe$_7$C$_3$ up to 150 GPa. The V_S of Fe$_7$C$_3$ softens at pressures above 70 GPa, possibly due to the high-spin to low-spin transition of iron. The extrapolated V_P and V_S compared with seismic data also strongly support the Fe$_7$C$_3$-dominant inner core scenario, rendering Earth's core the largest reservoir of carbon in Earth.

[1] B. J. Wood, Earth Planet. Sci. Lett. **117**, 59 (1993).
[2] L. Gao, B. Chen, J. Wang, E. E. Alp, J.-C. Zhao, M. Lerche, W. Sturhahn, H. P. Scott, F. Huang, Y. Ding, S. V. Sinogeikin, C. C. Lundstrom, J. D. Bass, and J. Li, Geophys. Res. Lett. **35**, L17306 (2008).
[3] L. Gao, B. Chen, J. Zhao, E. E. Alp, W. Sturhahn, and J. Li, Earth Planet. Sci. Lett. 309, 213 (2011).
[4] Y. Nakajima, E. Takahashi, N. Sata, Y. Nishihara, K. Hirose, K. Funakoshi, and Y. Ohishi, Am. Mineral. 96, 1158 (2011).
[5] Y. Nakajima, E. Takahashi, T. Suzuki, and K.-I. Funakoshi, Phys. Earth Planet. Inter. 174, 202 (2009).
[6] O. Lord, M. Walter, R. Dasgupta, D. Walker, and S. M. Clark, Earth Planet. Sci. Lett. 284, 157 (2009).
[7] B. Chen, L. Gao, B. Lavina, P. Dera, E. E. Alp, J. Zhao, and J. Li, Geophys. Res. Lett. 39, L18301 (2012).
[8] H. K. Mao, Y. Wu, L. C. Chen, and J. F. Shu, J. Geophys. Res. 95, 21737 (1990).
[9] C. T. Seagle, A. J. Campbell, D. L. Heinz, and G. Shen, J. Geophys. Res. 111, B06209 (2006).

Magnetic phase transitions of BaFe$_2$As$_2$ ferropnictide at high pressure

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The discovery of LaFeAsO[1] superconductors ignites the world wide fever for iron based superconductors [2~8] that include "1111"[1], "122"[6], "111"[8], "11"[7] systems etc., opening a new era for studies of superconductivity. Generally speaking, iron based superconductors are developed from parent state that takes a spin density wave (SDW) antiferromagnetic order [2]. Either chemical doping or pressure will suppress SDW leading to the appearance of superconductivity. Comparing with chemical doping, pressure is a pure physical manner without introducing disorder or impurities. One of key topics of iron based superconductors is to understand the relationship among magnetic ordering, crystal structure symmetry breaking & superconductivity. Taking the 122 system as an example, we studied systematically the pressure induced phase transitions in BaFe2As2 based on synchrotron Mössbauer spectroscopy combined with X-ray diffraction. The results revealed that the ferropnictide BaFe$_2$As$_2$ undergoes a paramagnetic to antiferromagnetic transition, coupled with a tetragonal to orthorhombic `symmetry breaking`. It is found that while coincide at the ambient condition, pressure separates the two transitions effectively. Our results indicate that a pressure induced nematic mesoscopic phase likely precedes macroscopic orthorhombic antiferromagnetic order, highlighting the important role of local magnetic moment in inducing superconductivity.

References:

1.Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc.130, 3296(2008).

2 Kenji Ishida, Yusuke Nakai, and Hideo Hosono, J. Phys. Soc. Jpn. 78 (2009) 062001

3. G.R.Stewart Rev. Mod. Phys. 83, 1589 (2011)

4. D.C.Jonston Advances in Physics 59, 803 (2010)

5, C. Day, Physics Today 62, 36 (2009)

6. M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008)

7. Hsu F-C, Luo J-Y, Yeh K-W, Chen T-K, Huang T-W, Wu P M, Lee Y-C, Huang Y-L, Chu Y-Y, Yan D-C and Wu M-K, 2008 Proc. Natl Acad. Sci. USA 105 14262

8. X.C.Wang, Q.Q. Liu, Y.X. Lv, W.B. Gao, L.X.Yang, R.C. Yu, F.Y.Li, C.Q. Jin, Solid State Communications 148, 538(2008)

Valence and Magnetic State in Europium at Extreme Pressures

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Changes in the valence state and magnetic properties of Eu metal under extreme pressures have been studied using x-ray absorption near-edge spectroscopy, x-ray magnetic circular dichroism and synchrotron Mössbauer spectroscopy to understand the pressure-induced superconductivity of Eu metal at pressures above 75 GPa. Contrary to previous reports about Eu's valence state, Eu is found to remain nearly divalent to the highest pressures reached (87 GPa) with magnetic order persisting up to 50 GPa at low temperatures. Density functional theory has been applied to give insight into the pressure-induced changes in both Eu's electronic structure and Mössbauer isomer shift.

MöSSBAUER SPECTRA AND SUPERPARAMAGNETISM OF EUROPIUM SULFIDE NANOPARTICLES

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We have studied nanoparticles of EuS using Mössbauer spectroscopy at low temperatures and compared them with bulk samples. EuS was the first non-metallic ferromagnet to be discovered. It is a narrow-gap semiconductor, with E_g = 1.65 eV and T_c = 17 K.

Nanoparticles were synthesized using a colloidal synthetic approach, and suspended in concentrated methanolic suspensions in an argon environment to suppress surface oxidation. As a further precaution to prevent oxidation they were immediately loaded into the cryostat. The nanoparticles are fairly monodisperse and TEM images gave their average diameter as 20 nm.

The Mössbauer spectra (Fig. 1) showed that about 25% of the europium was present as Eu^{3+}, despite the protective surfactant coating. As the temperature was lowered they showed the line broadening and splitting characteristic of superparamagnetism. The low temperature value of the hyperfine field was 298 kG, and the blocking temperature was about T_B = 12 K. Using

$$kT_B = aKV$$

where a = 0.22, the magnetic anisotropy K was estimated to be 180 Jm^{-3}

T_B was too close to T_c to allow an accurate measurement of K from the linear temperature variation of the hyperfine field due to collective magnetic excitations [1].

The results for T_B and K are discussed in comparison with the values given by Zhao *et al* [2] from magnetization and susceptibility measurements;

The superparamagnetic behavior of the nanoparticles can be contrasted with the sharper lines in the Mössbauer spectra of bulk EuS (Fig.2), measured at the same temperatures.

Fig. 2. Mössbauer spectra of bulk EuS.

[1]   S. Mφrup, *J. Mag. Mag. Mat.* **37** 39 (1983)
[2]   F. Zhao, H-L Sun and S. Gao, *Small* **2** 244 (2006
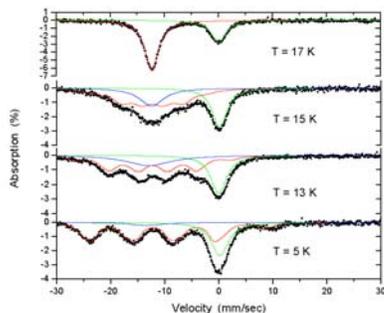
.Fig. 1. Mössbauer spectra of EuS nanoparticles.
    Note the Eu^{3+} at ~ 0 mm/s

SPIN AND VALENCE OF IRON IN LOWER-MANTLE SILICATE PEROVSKITE AND POST-PEROVSKITE BY SYNCHROTRON MÖSSBAUER SPECTROSCOPY

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Fe-bearing silicate perovskite (Pv) and post-perovskite (PPv), (Al-(Mg,Fe)SiO$_3$), is expected to be the most abundant mineral in the Earth's lower mantle (from 24 to 136 GPa, and from 1900 to 4000 K). Experimental studies on the spin and valence states of iron on Pv and PPv at P-T conditions of the lower mantle is thus essential for understanding the properties of the region.

In this presentation, we will discuss the spin and valence states of Fe in lower-mantle Pv and PPv studied using synchrotron Mössbauer spectroscopy in a high-pressure diamond anvil cell. The spin states of Fe in Pv have attracted extensive research interest in the past few years [1-4]. In Pv, Fe^{2+} can occupy the large psudo-dodecahedral site (A site) and has been found to exhibit extremely high quadrupole splitting (QS) at lower-mantle pressures [2,3]. Combined with theoretical studies, such high QS of Fe^{2+} in Pv observed from Mössbauer measurements represents a significant lattice distortion of the lattice sites caused by the atomic site change. Fe^{2+} in Pv in the Earth's lower mantle is thus most likely in the high-state (HS) state. In contrast to Fe^{2+}, Fe^{3+} can occupy the smaller octahedral site (B site), and has been shown to experience an increase in QS with pressure as a result of the HS to low-spin (LS) transition. The pressure-induced spin transition of Fe^{3+} and the atomic site change of Fe^{2+} can affect a number of physical and chemical properties of Pv, providing new insights into the properties of the Earth's lower mantle [2,3].

Silicate-Pv is expected to transform to PPv in the Earth's D" region. Due to the extremely high pressure and temperature of the D" region, the experimental studies on the spin and valence states of Fe in PPv is much more challenging. The exact spin and valence states of iron in PPv remain highly debated. Similar to that observed in Pv from Mössbauer studies, Fe^{2+} in the larger lattice sites also exhibits extremely high QS (>3.5 mm/s) and may remain in the HS state at the pressure of the lowermost mantle. On the other hand, the Fe^{3+}, which occupies the smaller octahedral site is likely in the LS state [1,4]. Since Earth's lower mantle likely contains approximately 5% aluminous, we have also examined the potential compositional effect of Al on the spin and valence states of Fe in Pv and PPv using direct Mössbauer measurements.

Here we will present and review recent results on the spin and valence states of iron using high pressure-temperature Mossbauer results, focusing on the consequences of the transitions in terms of their implications to deep-Earth geophysics, geochemistry, and geodynamics [1].

[1] J. F. Lin, S. Speziale, Z. Mao, H. Marquardt, Effects of the electronic spin transitions of iron in lower-mantle minerals: implications to deep-mantle geophysics and geochemistry, *Rev. Geophys.*, 2012 (submitted).
[2] J. F. Lin, E. E. Alp, Z. Mao, T. Inoue, C. McCammon, Y. Xiao, P. Chow, and J. Zhao, Electronic spin and valence states of iron in the lower-mantle silicate perovskite by synchrotron Mössbauer spectroscopy, *Am. Miner.*, 97, 592-597, 2012.
[3] Z. Mao, J. F. Lin, H. P. Scott, H. C. Watson, V. B. Prakapenka, Y. Xiao, P. Chow, C. McCammon, Iron-rich perovskite in the Earth's lower mantle, *Earth Planet Sci. Lett.*, 309, 179-184, 2011.
[4] Z. Mao, J. F. Lin, C. Jacobs, H. C. Watson, Y. Xiao, P. Chow, E. E. Alp, and V. B. Prakapenka, Electronic spin and valence states of Fe in CaIrO$_3$-type silicate post-perovskite in the Earth's lowermost mantle, *Geophys. Res. Lett.*, 37, L22304, 2010.

NUCLEAR RESONANT SCATTERING UNDER HIGH PRESSURE 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 spectroscopy has become a relatively new spectroscopic method since late 90s and widely used to study materials under extreme conditions. Nuclear resonant X-ray spectroscopy can be divided into two methods: nuclear resonant inelastic X-ray scattering (NRIXS) and nuclear forward scattering (NFS).[1]

NRXIS is a technique in which energy gain or loss through a scattering process involving phonon excitations is monitored via excitation of a Mössbauer resonance. From NRIXS, partial density of states (pDOS) can be acquired and important dynamic, thermodynamic, and elastic information such as vibrational kinetic energy, vibrational entropy, Debye temperature and sound velocities can be derived.

Nuclear forward scattering, also known as synchrotron Mössbauer spectroscopy, can give information on spin state, valence state and magnetic ordering of samples. Compared to conventional Mössbauer spectroscopy using a radioactive source, NFS has big advantages in studies under high pressure due to the small beam size and high intensity X-ray which third generation synchrotron source can provide.

At HPCAT, the spectroscopy line consists of IDA with a newly installed liquid nitrogen cooled Si (1 1 1) double crystal monochromator with ~1eV energy resolution, transport lines; IDC with an interchangeable high-resolution monochromator at ~2meV energy resolution and two 1-meter K-B mirrors; and IDD, the experiment station, with a 2.7 meter 0-90 degree horizontal spectrometer and a dedicated XES setup. [2] Typical beam size at sample position is ~25(V) x 50 (H) μm^2 at FWHM when using meter-long KB mirrors, smaller beam size (4x5 μm^2) can be achieved by using a pair of 200mm KB mirrors.

The 2-meV high resolution monochromator (HRM) is used for ^{57}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 in last a few years and present some new results on NFS of ferrocene and Fe-based superconductors.

Figure 1. Resolution function of the HRM
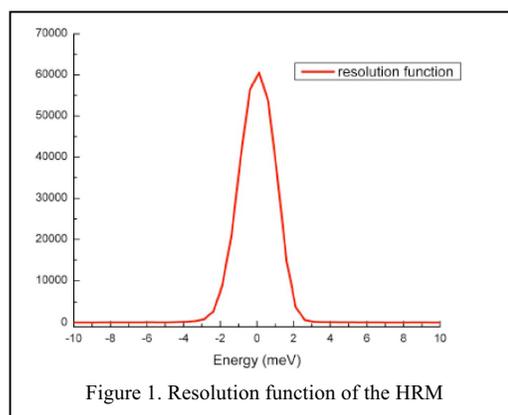
[1] W. Sturhahn, J. Phys. Condens. Matt., 16, 497-530, 2004.
[2] G.Y. Shen et al, High Pressure Research, 28, 145-162, 2008.

PROBING BIOMOLECULAR STRUCTURE AND ELASTICITY WITH ^{57}FE

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Iron-containing proteins are indispensable to the life, regulation, aging, and death of the cell. Cellular metabolism depends on enzymes containing Fe and other metals and contributes to global biogeochemical cycles that exchange atmospheric pools of oxygen and nitrogen with biologically useable forms of these elements.

Measurements of resonant nuclear absorption by ^{57}Fe at synchrotron facilities selectively reveal vibrational motion of individual iron atoms within proteins containing thousands of other atoms. Quantitative comparison of the resulting information on vibrational amplitudes and directions, as well as frequencies, with quantum chemical predictions identifies vibrations of all Fe-ligand bonds and also provides a detailed test of the predicted electronic structure. I will present recent applications to enzymes that contain iron within a planar heme group.

Figure 1. Mutational redesign of myoglobin introduces a second nonheme metal binding site near the heme, yielding engineered proteins Cu$_B$Mb and Fe$_B$Mb that mimic the catalytic sites of heme-copper oxidase and nitric oxide reductase enzymes, respectively.
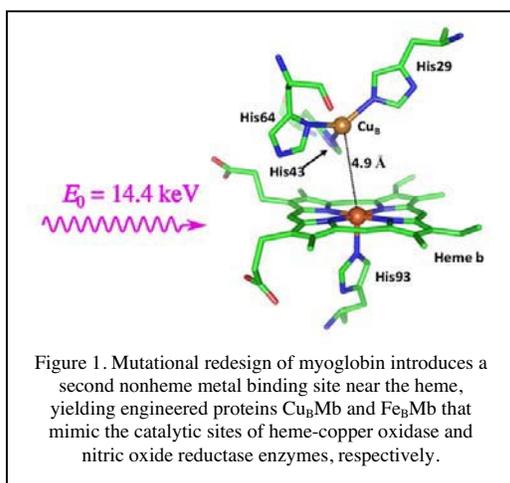
One question of current interest is how a nearby nonheme metal site controls the reaction of the heme with nitric oxide (NO). NO inhibits the heme-copper site that consumes oxygen in cellular respiration, but is metabolized to produce the greenhouse gas nitrous oxide (N_2O) in closely related bacterial enzymes with iron in the nonheme site. Protein engineering mimics the catalytic site (Fig. 1) and enables selective metal replacement at either heme or nonheme site, opening the door to detailed spectroscopic investigation of reaction intermediates that are too unstable to characterize in the natural enzyme. In addition, recent results demonstrate that vibrational dynamics of heme and nonheme irons can be probed independently (Fig. 2).

Finally, averaged force constants, derived directly from the experimentally determined vibrational density of states (VDOS), quantify important aspects of structure and elasticity even when individual vibrational modes cannot be resolved and identified. Fe-ligand vibrations make the primary contribution to the *stiffness*, an effective force constant which measures the average strength of nearest neighbor interactions, while low frequency oscillations of the protein determine the *resilience*, a distinct force constant that probes the elasticity of the iron environment.

Table I: The stiffness and resilience, averaged force constants derived from vibrational measurements, quantitatively measure distinct elastic properties of heme and nonheme sites.

	force constant (pN/pm)	
	stiffness	resilience
Mb(II)	189 ± 20	21.2 ± 1.3
Fe(II)$_B$*Mb(II)	182 ± 9	20.3
*Fe(II)$_B$Mb(II)	155.± 6	20.1

Figure 2. Selective incorporation of ^{57}Fe enables independent measurement of vibrational dynamics of iron at both heme and nonheme sites.
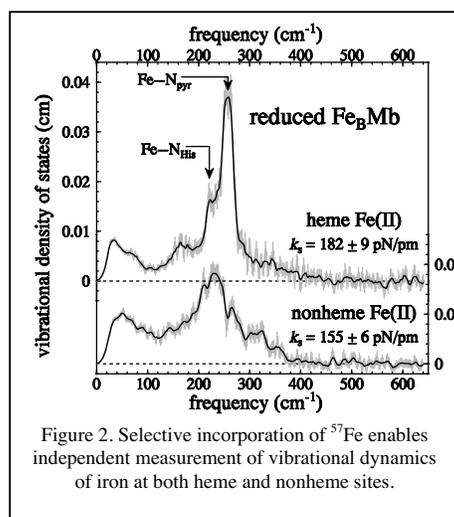
EVIDENCE FOR POLARON-ION CORRELATIONS IN Li_xFePO_4 FROM NUCLEAR RESONANT SCATTERING

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$LiFePO_4$ is an important new material for electrodes of rechargeable Li-ion batteries. It offers low cost, low toxicity, thermal stability and high energy density. The conductivity mechanism in $LiFePO_4$ is small polaron hopping. There is a keen interest in understanding the transport of Li ions and electrons within the lattice and improving the intrinsic electrical conductivity in Li_xFePO_4. Valence fluctuations of Fe^{2+} and Fe^{3+} were studied in a solid solution of Li_xFePO_4 by nuclear resonant forward scattering of synchrotron x-rays at elevated temperatures in a diamond-anvil pressure cell. The spectra acquired at different temperatures and pressures were analyzed for the frequencies of valence changes using the Blume-Tjon model of a system with a fluctuating Hamiltonian. The polaron hopping frequencies were analyzed to obtain activation energies and activation volumes. There was a large suppression of hopping frequency with pressure, giving an activation volume for polaron hopping that was large and positive, $5.8\pm0.7Å^3$. This large value indicates correlated motions of Li^+ ions and polarons. It is plausible that the activation volume for polaron hopping is effectively enhanced by the electron-ion binding energy. Electrical conductivity requires decoupling of the ion and polaron motions, so their correlated motion may also suppress electrical conductivity in $LiFePO_4$.

ANHARMONIC PHONON BEHAVIOR IN α-FE AT HIGH TEMPERATURES

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The high temperature thermodynamics of Fe are of great interest to both fundamental and applied science. The magnetic properties of bcc Fe have a strong influence on its thermodynamics, such as its unusual polymorphism, but the fundamentals of these relationships are not well understood. The evolution of phonon dynamics with temperature in the bcc α-Fe phase can provide insight.

The phonon density of states of bcc ^{57}Fe was measured from 23K up through the 1185K fcc phase transition using Nuclear Resonant Inelastic X-ray Scattering at the Advanced Photon Source. At higher temperatures all phonons shift to lower energies (soften) with thermal expansion. Near the 1043K Curie temperature, low energy transverse modes soften more rapidly suggesting strongly anharmonic behavior preceding the α-Fe to γ-Fe structural transition. This softening greatly exceeds that predicted by the quasiharmonic model which incorporates softening related to thermal expansion.

The interatomic force constants for Fe were obtained by iteratively fitting a Born von-Karman model to the experimental phonon spectra. Temperature trends in these force constants are used to interpret the thermal softening of the different phonon modes. The unusually large phonon anharmonicity of bcc Fe at elevated temperatures is discussed in terms of the temperature dependences of the first and second-neighbor interatomic force constants. The vibrational entropy is calculated from the density of states measurements and its contribution to the high temperature thermodynamics of bcc Fe is discussed.

Figure 1. ^{57}Fe density of states at a range of temperatures.
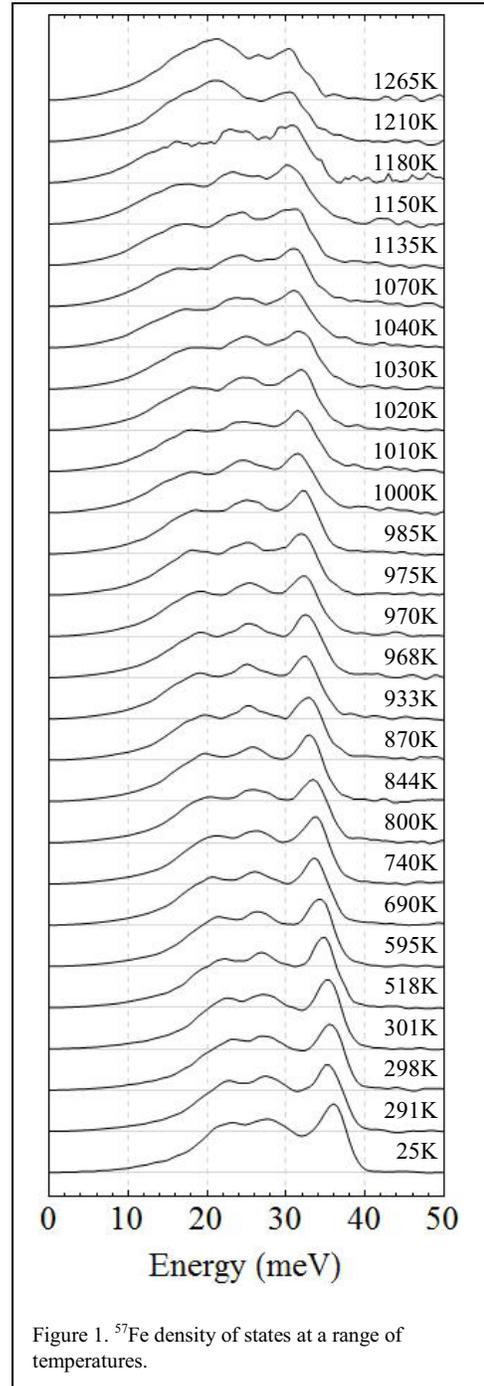
Investigations on the role of nanocatalysts in the formation of nanotubes

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It is very well known that the study of hyperfine magnetic interactions using Mössbauer spectroscopy is very useful in determining the morphological and magnetic properties of nanophase iron oxides. This talk will feature a broad overview of the determination of the morphology of nanophase materials with a specific focus on the growth of carbon nanotubes and our latest results. Carbon nanotubes are cylindrical nanostructures with hexagonal networks of carbon atoms with interesting electronic and mechanical properties. CNT synthesis route involving the catalytic decomposition of hydrocarbons on metal particles have been widely popular. We have shown that single wall carbon nanotubes (SWNT) of diameters less than 2 nanometers can be grown directly from nanophase catalyst particles such as maghemite γ-Fe_2O_3, goethite and chromium substituted goethite on a Silicon substrate using the conventional CVD process. The sizes of SWNT were measured using Atomic Force Microscopy. The average tube diameter was measured to be 1.0 ± 0.2 nm. FTIR and X-ray diffraction measurements were performed to characterize the catalyst iron oxide. Scanning Electron Microscopy measurements revealed that the catalyst oxide particles formed in clusters of 100 nm diameters. While SWNT grown with goethite and Cr-goethite formed as nanowires, the SWNTs grown with maghemite showed spontaneous Y-branching, as shown in the figure. Transmission Mössbauer (TMS) measurements at room temperature of maghemite and chromium goethite showed the presence of superparamagnetic doublet, characteristic of nanophase iron oxides. Room temperature TMS spectrum of goethite catalyst was magnetic. TMS spectra at 77K of maghemite and chromium goethite particles showed some superparamagnetic behavior with blocking temperature just below ~270K. With the growth of single wall nanotubes, our results show that the superparamagnetic state of maghemite nanocrystals play a crucial role in the formation of Y branches in long uniform tubular structures. The crystallographic, morphological and magnetic properties of the catalyst metal powders and the properties of the resulting SWNTs will be presented.

Spontaneous Y-branching observed in SWNTs grown with nanophase maghemite
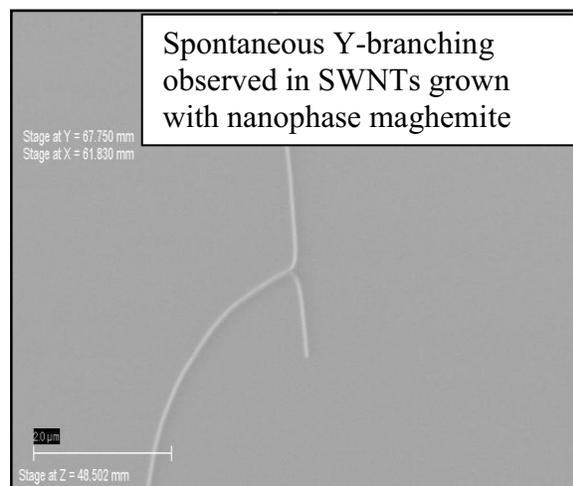
Magnetic and structural transition of $SrFe_2As_2$ under high pressure and low temperature

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Superconductivity in the iron-based compounds arises from the antiferromagnetically ordered spin density wave (SDW) where Fe2+ spin arrange in a stripe type with spin parallel along the strip but anti parallel between the neighbor stripe. High pressure can be an effective method to suppress the SDW state in order to induce the superconductivity, which has been recently observed in the AFe_2As_2 compounds such as for $CaFe_2As_2$, $SrFe_2As_2$ or $BaFe_2As_2$.

We measured nuclear resonant forward scattering (NFS) of synchrotron radiation and x-ray diffraction of $SrFe_2As_2$ at high pressures and low temperatures. The structural and magnetic transitions are coupled at high pressures, but are strongly suppressed to zero at a critical pressure around 4.8 GPa. At 13 K, our XRD results shown that the orthorhombic phase decreases as pressure increasing, while the tetragonal phase is enhanced. A combination of orthorhombic and tetragonal phases was observed between 4.2 and 4.8 GPa, at which pressure range, the magnetic and nonmagnetic phases coexist at 15 K obtained by our NFS results.

References:

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3290 (2008).

[2] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008).

[3] M. Tegel, M. Totter, V. Weib, F. M. Schappacher, R. Pottgen, and D. Johrendt, J. Phys.: Condens. Matter 20, 452201 (2008).

SPIN TRANSITIONS AND SPIN-SPIN INTERACTIONS IN EARTH'S MANTLE

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Earth's mantle is the most voluminous layer of the planet, being subjected to extreme pressures up to 136 GPa and temperatures up to ~3500 K. Based on a pyrolitic compositional model, the lower mantle is mainly made of ferropericlase ((Mg,Fe)O), aluminous silicate perovskite (Al-(Mg,Fe)SiO$_3$), and calcium silicate perovskite (CaSiO$_3$). Silicate perovskite transforms into silicate post-perovskite structure just above the core-mantle region, the D" layer. The existence of iron in the lower-mantle minerals can affect a broad spectrum of the minerals' physical and chemical properties.

In this talk, I will address the pressure-induced electronic spin-pairing transitions of iron and their associated effects on the physical properties of host phases in lower-mantle minerals including ferropericlase, silicate perovskite, and post-perovskite at high pressures and temperatures [1]. The spin crossover of Fe^{2+} in ferropericlase occurs over a wide pressure-temperature range extending from the middle part to the lower part of the lower mantle. Furthermore, a high-spin to low-spin transition of Fe^{3+} in the octahedral site of perovskite occurs at pressures of 15-50 GPa [2]. In post-perovskite the octahedral-site Fe^{3+} remains in the low-spin state at the pressure conditions of the lowermost mantle. These changes in the spin and valence states of iron as a function of pressure and temperature have been reported to affect physical, chemical, rheological, transport properties of the lower-mantle minerals. These effects of the spin transition can thus significantly affect our understanding of the deep Earth. I will present and evaluate the consequences of the transitions in terms of their implications to deep-Earth geophysics, geochemistry, and geodynamics [1].

The electrons of ferrous and ferric iron ions that occupy some of the lattice sites in mantle minerals become slightly polarized in the presence of the Earth's magnetic field. Using recent deep-Earth geophysics and geochemistry results, we have developed a model of the polarized electron spin density within the Earth [3]. We have examined possible long-range spin-spin interactions between these spin-polarized geoelectrons and the spin-polarized electrons in recent particle physics experiments [3]. Based on these results, we propose that multiple field observations of the particle physics experiments at various points on the Earth and with different detector orientations could discriminate between the various possible spin-spin potentials [3]. Once the potential is well understood, similar measurements could be used to probe the Earth's iron concentration and its spin and valence states as a function of depth. Such information might eventually help reconcile seismic observations and mineral physics data with geochemical models.

[1] **J. F. Lin**, S. Speziale, Z. Mao, H. Marquardt, Effects of the electronic spin transitions of iron in lower-mantle minerals: implications to deep-mantle geophysics and geochemistry, *Rev. Geophys.,* 2012 (submitted).

[2] **J. F. Lin**, E. E. Alp, Z. Mao, T. Inoue, C. McCammon, Y. Xiao, P. Chow, and J. Zhao, Electronic spin and valence states of iron in the lower-mantle silicate perovskite by synchrotron Mössbauer spectroscopy, *Am. Miner.*, 97, 592-597, 2012.

[3] L. R. Hunter, J. E. Gordon, S. Peck, D. Ang, and **J. F. Lin**, Using the Earth as a polarized electron source to search for long-range spin-spin interactions, *Science*, Research Article, 2012 (in press).

NRIXS under high pressures and low temperatures

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Nuclear Resonant Inelastic X-ray Scattering (NRIXS) is a powerful technique that gives us information about the vibrational properties of a crystal lattice. We take advantage of the accessible nuclear resonant transition of ^{57}Fe, probing how excitation of the nucleus is modified by available vibrations (phonons). Recently, a high-pressure and low-temperature cryostat system to allow temperature as low as ~10 K with miniature diamond anvil cell and Be windows have been designed for Nuclear Resonant IXS of ferropnictides at Sector 3 of the Advanced Photon Source. The system will allow for measuring projected phonon density of states of iron in ferropnictides at the Superconducting Dome region. These results will provide new insights in understanding the intrinsic properties of the ferropnictide compounds as a function of pressure at the temperature range where the SDW or superconductivity is expected to occur.

Figure 1. Miniature diamond anvil cell for the high pressure and low temperature NRIXS system.
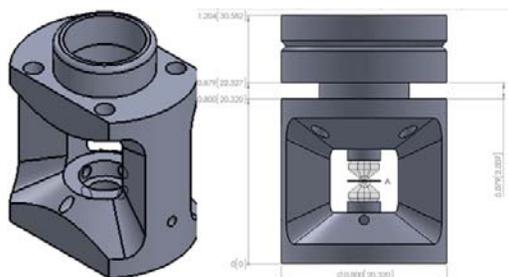
Figure 2. High-pressure and low-temperature cryostat system with miniature diamond anvil cell and Be windows for NRIXS.
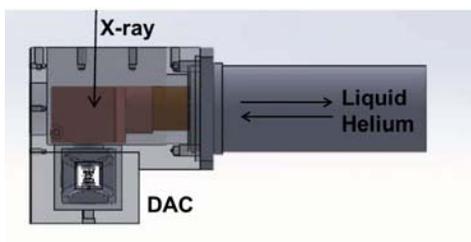
Figure 3. High-pressure and low-temperature cryostat system with two APD detectors collecting data.
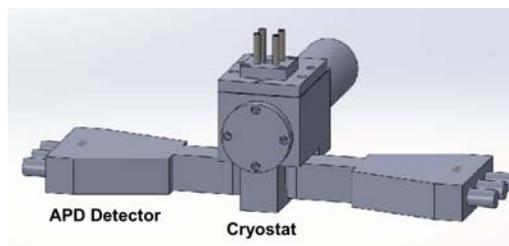
[1] Y. Kamihara, T.Watanabe, M.Hirano and H. Hosono, J. Am. Chem. Soc.130, 3296 (2008).
[2] O. Dwlaire, M. S. Lucas, A. M. Dos Santos, A. Subedi, A. S. Sefat, M. A.Mcguire, L. Mauger, J. A. Mulloz, C. A. Tulk, Y. Xiao, M. Somayazulu, J. Y. Zhao, W. Struhahn, E. E. Aip, D.J. Singh, B. C. Sales, D. Mandrus, and T. Egami, Phys. Rev. B 81, 094504 (2010).
[3] W. Uhoya, A. Stemshorn , G. Tsoi, and Y. K. Vohra, Phys. Rev. B 82, 144118 (2010).

EFFECTS OF MICROBIAL REDOX TRANSFORMATION OF CLAY MINERALS ON CONTAMINAT ATTENUATION

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Keywords: Radionuclides, Reduction, Contaminants

Topic: Applications in Soils, Mineralogy, Geology and Archaeology

The U.S. Department of Energy (DOE) faces the challenge of cleaning up groundwater plumes contaminated by nitrate and various radioactive metals. The mobility of these constituents in contaminated aquifers is governed, in part, by Fe-mineralogy of the sediment. Therefore, there is particular interest in understanding the role of Fe(II)-minerals, such as magnetite, Fe-carbonates, Fe-sulfides, and Fe(II)-clays, as well as Fe(II) adsorbed onto oxides/clays, in reduction of oxidized soluble contaminates to sparingly soluble phases, e.g., $Tc(VII)_{aq}$ to $Tc(IV)$.

The oxidation sate of Fe in clays is constantly cycled in sedimentary environments. However, the relative effect of such cycling under abiotic and biotic conditions is not well known.

Two studies were carried out to gain insights into the role of clay Fe on contaminant attenuation. In the first study, nontronite clay subjected to multiple cycles of biotic reduction and air oxidation were subjected to Tc(VII) reduction. In the second study, microbially reduced nontronite was oxidized by Fe(II) oxidizing and nitrate reducing bacteria. Detailed studies indicated that oxidation of Fe(II) is reversible but the extent of oxidation decreases with cycling. Also, the studies indicated that reactivity of Fe species towards contaminant varies with cycling. Details characterization and reactivity of the sediments will be discussed.

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