SYNCHROTRON-BASED SPECTROSCOPIC TECHNIQUES: MÖSSBAUER AND HIGH-RESOLUTION INELASTIC SCATTERING

JENNIFER M. JACKSON*
Seismological Laboratory, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA (USA)

Abstract We summarize recent developments in selected synchrotron-based spectroscopy methods like nuclear resonant forward scattering ("synchrotron Mössbauer spectroscopy"), nuclear resonant inelastic x-ray scattering ("NRIXS"), and momentum-resolved inelastic x-ray scattering ("IXS"). The inelastic methods provide specific vibrational information, e.g., the phonon density of states, and in combination with diffraction data permits the determination of sound velocities under high pressure and high temperature. The Mössbauer method gives hyperfine interactions between the resonant nucleus and electronic environment like isomer shifts, quadrupole splittings, and magnetic fields, which provide important information on valence, spin state, and magnetic ordering. Both nuclear resonant methods use a nuclear resonant isotope as a probe and can be applied under high pressure and high temperature. The physical mechanism of the scattering processes will be discussed and several high-pressure high-temperature examples will be given.

Keywords: Synchrotron Mössbauer spectroscopy, valence states, inelastic x-ray scattering, phonon density of states, sound velocities

1. Synchrotron Mössbauer Spectroscopy (SMS)

Conventional Mössbauer spectroscopy as well as SMS are based on the often appreciable probability that the resonant nuclei absorb x-rays without participation of lattice vibrations, i.e., recoilless. Similar to conventional

* E-mail: jackson@gps.caltech.edu

E. Boldyreva and P. Dera (eds.), *High-Pressure Crystallography: From Fundamental Phenomena to Technological Applications*, DOI 10.1007/978-90-481-9258-8_5,
© Springer Science + Business Media B.V. 2010

Mössbauer spectroscopy (MBS), the SMS method permits us to determine distortions of electronic charges at the position of the ^{57}Fe nuclei. The configuration of the electron shell and the deviation of the local environment from cubic symmetry expresses itself in two parameters that are accessible to SMS measurements, the splitting of the excited nuclear state caused by an electric-field-gradient tensor (quadrupole splitting) and a shift of the nuclear states caused by the s-electron density in the nuclear volume (isomer shift).

The comparison of the different experimental approaches of more traditional methods of MBS and SMS reduces to an evaluation of the properties of the used radiation source. Synchrotron radiation and γ-rays emitted by a radioactive source have very different properties. However, both types of sources permit Mössbauer experiments aiming at the extraction of hyperfine parameters, e.g., quadrupole splittings and isomer shifts. Synchrotron radiation is emitted in short (<100 ps) intense pulses that repeat periodically. On the other hand, the emission of photons from radioactive sources is random in time. The situation is inverted if we analyze the energy bandwidths, which are on the order of millielectronvolt for monochromatized synchrotron radiation but only about the natural line width (Γ = 4.66 neV for the 14.4125 keV resonance of the ^{57}Fe isotope) for a suitable radioactive source. This reciprocal behavior strongly suggests that the experimental techniques should be similarly reciprocal, i.e., energy-resolved spectroscopy with radioactive sources (MBS) and time-resolved spectroscopy with synchrotron radiation (SMS). Figure 1 illustrates the spectra of a material for which the iron nuclei experience a quadrupole splitting, Δ. In conventional MBS, we observe two dips separated by Δ in the energy-dependent transmission through the material. The time-dependent transmission that is observed in SMS shows oscillations with a period of $2h/\Delta$, where h is Planck's constant. In both cases, we directly obtain the quadrupole splitting from the data. Isomer shifts are only observable in a relative sense; in the case of MBS, with respect to the source emission line, and in the case of SMS, with respect to a reference absorber that must be inserted into the beam path. In comparison to the traditional Mössbauer spectroscopy, the high brilliance of the synchrotron radiation reduces the synchrotron Mössbauer data collection times tremendously, allows easier access for high-pressure studies, and reduces pressure gradients in the observed data.

For SMS measurements, the energy bandwidth of the excitation source should be as small as practicably achievable with reasonable efficiency. The high-resolution monochromator is tuned to the nuclear transition energy and kept as stable as possible. X-rays that are transmitted through the sample

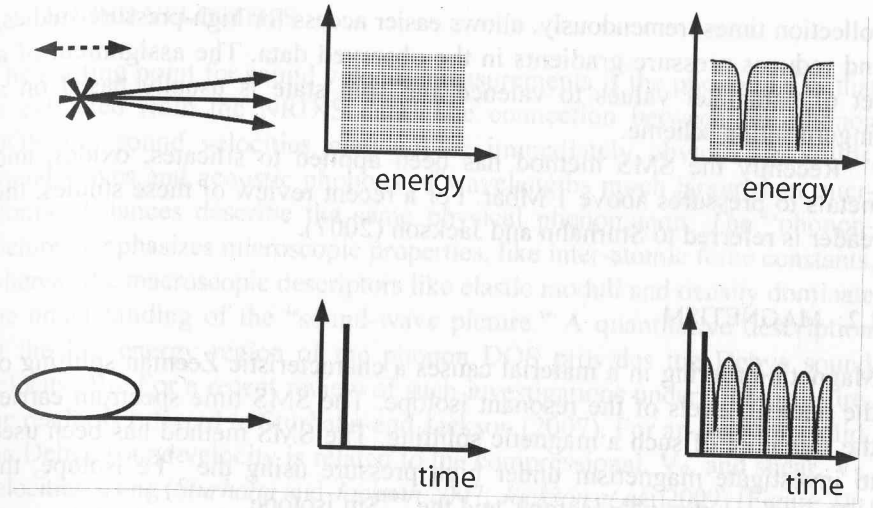

Figure 1. Reciprocal properties of radioactive sources (*top*) and synchrotron radiation (*bottom*) lead to reciprocal experimental techniques (From *Jackson et al.* (2005)).

excite the resonant nuclei coherently and are observed with an avalanche photo diode detector that is placed far enough away from the sample to avoid contamination from incoherent scattering. The delayed events are mapped as a function of elapsed time between arrival of a synchrotron radiation pulse and detection of transmitted x-ray photon – this constitutes the time spectrum of the nuclei in the sample. The delayed transmitted intensity can be expressed in terms of the nuclear contribution to the index of refraction of the sample. The reader is referred to *Sturhahn* (2000, 2004) for more details on SMS and details of data evaluation. At present, there are three facilities capable of such measurements: the European Synchrotron Radiation Facility in Grenoble (France), the Advanced Photon Source in the Chicago, IL area (USA), and the Super Photon Ring in Kansai (Japan).

1.1. VALENCE AND SPIN STATE

Most of the minerals and polymorphs expected in Earth's interior are believed to incorporate low concentrations of Fe^{2+} and/or Fe^{3+} of about 10 at% or less. They are not expected to be magnetically ordered in Earth's lower mantle because of the low Fe content and the elevated temperatures. However, valence and spin state of the Fe in minerals may still be relevant with respect to density, iron partitioning, partial melting, radiative thermal conductivity, and compositional layering. The SMS method provides quadrupole splittings and isomer shifts similarly to traditional Mössbauer spectroscopy but the high brilliance of the synchrotron radiation reduces the data

collection times tremendously, allows easier access for high-pressure studies, and reduces pressure gradients in the observed data. The assignment of a set of parameter values to valence and spin state is usually based on a fingerprinting scheme.

Recently the SMS method has been applied to silicates, oxides, and metals to pressures above 1 Mbar. For a recent review of these studies, the reader is referred to Sturhahn and Jackson (2007).

1.2. MAGNETISM

Magnetic ordering in a material causes a characteristic Zeeman splitting of the nuclear levels of the resonant isotope. The SMS time spectrum carries the signature of such a magnetic splitting. The SMS method has been used to investigate magnetism under high pressure using the ^{57}Fe isotope, the ^{151}Eu isotope, the ^{119}Sn isotope, and the ^{149}Sm isotope.

2. Nuclear Resonant Inelastic X-ray Scattering (NRIXS)

For NRIXS measurements, the energy bandwidth of the incident x-rays determines the resolution of the phonon spectra of the samples. The high-resolution monochromator is tuned around the nuclear transition energy, and the x-rays excite the resonant nuclei in the sample. The incoherently re-emitted radiation is observed with an avalanche photo diode detector that is placed as close as possible to the sample but away from any strong coherent scattering directions. The integrated delayed counting rate is recorded. The NRIXS method directly provides the Fourier-transformed self-intermediate scattering function, $S(k,E)$. The quasi-harmonic model of lattice vibrations is then used to extract the partial (due to information about motions of the resonant nuclei only) and projected (due to a potential angular dependence on the wave-vector, k) phonon DOS from $S(k,E)$. Typical acquisition times for a NRIXS spectrum range between 1 h for iron-rich samples under ambient conditions and days for dilute samples under very high pressures. The evaluation of the measured NRIXS spectra can be performed using the PHOENIX software. The reader is referred to *Sturhahn* (2000, 2004) for a theoretical and technical review on nuclear resonant inelastic scattering of synchrotron radiation. At present, there are three facilities capable of NRIXS measurements: the European Synchrotron Radiation Facility in Grenoble (France), the Advanced Photon Source in the Chicago, IL area (USA), and the Super Photon Ring in Kansai (Japan).

2.1. SOUND VELOCITIES

The starting point for sound velocity measurements is the phonon DOS that is extracted from the NRIXS data. The connection between the phonon DOS and sound velocities may not be immediately obvious. In solids, sound waves and acoustic phonons of wavelengths much larger than inter-atomic distances describe the same physical phenomenon. The "phonon-picture" emphasizes microscopic properties, like inter-atomic force constants, whereas the macroscopic descriptors like elastic moduli and density dominate the understanding of the "sound-wave picture." A quantitative description of the low-energy region of the phonon DOS provides the Debye sound velocity, V_D. For a recent review of such investigations under high-pressure, the reader is referred to Sturhahn and Jackson (2007). For an isotropic solid, the Debye sound velocity is related to the compressional, V_P, and shear, V_S, velocities, using (*Sturhahn* and *Jackson* 2007; *Jackson et al.*, 2009) (Figure 2):

$$(3/V_D^3) = (1/V_P^3) + (2/V_S^3).$$

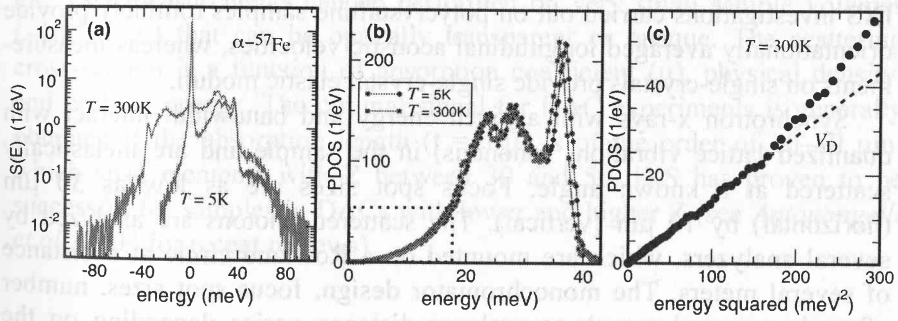

Figure 2. Typical procedure for NRIXS data collection and sound velocity analysis: (**a**) raw NRIXS spectra of polycrystalline α-iron at 300 K and at 5 K, (**b**) extraction of the phonon density of states, and (**c**) the determination of the Debye sound velocity (V_D). The decrease in intensity of the anti-Stokes scattering portion of the spectrum (left side, a) at low temperatures is due to the lower thermal vibrations in the crystal. The data points in (**c**) are taken from the PDOS within the dashed rectangle in (**b**) and are used to determine V_D (dashed straight line, c). Spectra are from *Sturhahn* (2004) and *Angel et al.* (2009).

2.2. TEMPERATURE

The NRIXS raw data has a very fundamental property which is independent of the material under investigation: the spectra follow a detailed balance principle. If the NRIXS data are given by $I(E)$ with $E = 0$ as the exact nuclear transition energy, we can write

$$I(-E) = e^{-\beta E} I(E),$$

where $\beta = 1/(k_B T)$ is the inverse temperature, and k_B is Boltzmann's constant. The above relation permits us to determine the temperature of the sample from the spectral intensity ratios of phonon creation ($E > 0$) and annihilation ($E < 0$) parts (Figure 2a).

3. Momentum Resolved Inelastic X-ray Scattering (IXS)

Notes in this section are taken from portions of Jackson's contribution to *Angel et al.* (2009). The physical processes that underlie momentum resolved inelastic scattering of x-rays (IXS) are similar to those described for inelastic scattering of light (e.g., Brillouin Spectroscopy). The difference between IXS and Brillouin scattering lies in the particle probe. X-rays have shorter wavelengths ($\lambda \sim 0.1$ nm) and therefore provides access to large sections of the dispersion scheme. This is in contrast to inelastic light scattering methods such as Brillouin or Raman scattering that can only determine the acoustic and optic modes, respectively, at very long wavelengths (or small momentum transfers) close to the Brillouin zone center. IXS investigations carried out on polycrystalline samples routinely provide orientationally averaged longitudinal acoustic velocities, whereas measurements on single-crystals provide single-crystal elastic moduli.

Synchrotron x-rays with a given energy and bandwidth interact with quantized lattice vibrations (phonons) in the sample and are inelastically scattered at a known angle. Focus spot sizes are as low as 30 μm (horizontal) by 10 μm (vertical). The scattered photons are analyzed by several analyzers, which are mounted on a Rowland circle at a distance of several meters. The monochromator design, focus spot sizes, number of analyzers, and sample-to-analyzer distance varies depending on the instrument. At present, there are five instruments dedicated to IXS for the study of phonons: ID16 and ID28 at the European Synchrotron Radiation Facility in Gernoble (France), 3ID and 30ID at the Advanced Photon Source in the Chicago, IL area (USA), and BL35XU at the Super Photon Ring in Kansai (Japan). The reader is referred to *Burkel* (2001) and *Krisch et al.* (2007) for details on the theoretical background and recent status of IXS.

3.1. SOUND VELOCITIES AND ELASTIC ANISOTROPY

If the sample is a single crystal, directional dependence of the acoustic modes are obtained and with known density, the C_{ij}'s can be determined. In the cases where the sample is crystalline, the sample must be oriented on a Bragg reflection and selection rules apply. Probing phonon excitations using IXS requires a relative high energy resolution of at least $\Delta E/E = 10^{-7}$.

The acoustic modes are determined by probing their respective phonon dispersion curves close to the Brillouin zone center. In order to obtain accurate sound velocities from the slopes of these phonon dispersion curves, the energy resolution must be high ($\sim 10^{-9}$ eV) at low-energy transfer (near the Brillouin zone center). Therefore, practical use of IXS to determine the sound velocities of materials has only been made possible in the last decade due to advances in x-ray optics and the advent of third generation synchrotron sources.

Together with the extraction of the sound velocities and known density, the single-crystal elastic moduli may be determined with a high degree of accuracy and therefore provide direct information on elastic anisotropy. Aggregate elastic properties can also be obtained from polycrystalline samples, but is generally restricted to the longitudinal acoustic mode due to lower signal to noise ratios (see *Bosak et al.*, 2007). A lower resolution ($>10^{-9}$ eV) could be employed if the studies are not aimed at obtaining sound velocities, but rather the general shape of the dispersion curve.

In general, the higher the resolution is, the longer the collection times are. IXS measurements can be performed on very small sample volumes ($\sim 10^{-4}$ mm^3) that can be optically transparent or opaque. The scattering cross-section is a function of absorption coefficient (μ), physical density, and probing energy. The optimal signal for DAC experiments is generally obtained if the absorption length ($t = 1/\mu$) is of the order of 10–40 μm, which span elements with Z between 30 and 50. IXS has proven to be successful for samples in DACs with lower and higher Z (see *Antonangelli et al.*, 2004 for recent reviews).

References

Angel R., Jackson, J.M., Speziale, S., and Reichmann, H-J., (2009), Elasticity measurements of minerals: A review. *European Journal of Mineralogy: HP-HT Mineral Physics: Implications for Geosciences*, doi:10.1127/0935-1221/2009/0021-1925.

Antonangeli, D., Occelli, F., Requardt, H., Badro, J., Fiquet, G., and Krisch, M., (2004), Elastic anisotropy in textured hcp-iron to 112 GPa from sound wave propagation measurements. *Earth and Planetary Science Letters*, 225(1–2):243–251.

Bosak, A., Krisch, M., Fischer, I., Huotari, S., and Monaco, G., (2007), Inelastic x-ray scattering from polycrystalline materials at low momentum transfer. *Physical Review B*, 75(064106).

Burkel, E., (2001), Determination of phonon dispersion curves by means of inelastic x-ray scattering. *Journal of Physics: Condensed Matter*, 13:7627–7644.

Jackson, J.M., Hamecher, E.A., and Sturhahn, W., (2009): Nuclear resonant X-ray spectroscopic study on $(Mg,Fe)SiO_3$ orthoenstatites, *European Journal of Mineralogy; HP-HT Mineral Physics: Implications for Geosciences*, doi:10.1127/0935-1221/2009/0021-1932.

Jackson, J.M., Sturhahn, W., Shen, G., Zhao, J., Hu, M., Errondonea, D., Bass, J.D., and Fei, Y., (2005), A synchrotron Mössbauer spectroscopy study of (Mg,Fe)SiO_3 perovskite up to 120 GPa. *American Mineralogist*, 90:199–205.

Krisch, M., and Sette, F., (2007), *Inelastic x-ray scattering from phonons.* In M. Cardona, and R. Merlin, Eds. Light Scattering in Solid IX, 108, pp. 317–370. Springer-Verlag Berlin, Heidelberg.

Sturhahn, W., (2000), CONUSS and PHOENIX: Evaluation of nuclear resonant scattering data. *Hyperfine Interactions*, 125:149–172.

Sturhahn, W., (2004), Nuclear resonant spectroscopy. *Journal of Physics: Condensed Matter*, 16:5497–5530.

Sturhahn, W., and Jackson, J.M., (2007), *Geophysical applications of nuclear resonant spectroscopy.* In E. Ohtani, Ed. Advances in High-Pressure Mineralogy, 421, pp. 157–174. The Geological Society of America, Washington DC.

HIGH-PRESSURE X-RAY ABSORPTION SPECTROSCOPY: APPLICATION TO THE LOCAL ASPECTS OF PHASE TRANSITIONS IN FERROELECTRIC PEROVSKITES

JEAN-PAUL ITIE[1,*], ANNE-MARIE FLANK[1], PIERRE LAGARDE[1], SYLVAIN RAVY[1], ALAIN POLIA

[1]*Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin, BP48, 91192 Gif-sur-Yvette Cedex, France,* [2]*PMD, IMPMC CNRS UMR 7590, Université P. et M. Curie-Paris 6, 140 rue de Lourmel 75015 Paris France*

Abstract X-ray absorption spectroscopy (XAS) provides information the local order around a given atom. Under high pressure, this technique been shown to be very sensitive to phase transitions. The evolution of local structure of ferroelectric titanates under high pressure is obtai using XAS showing that the Ti atom remains out of the center of surrounding oxygen octahedron just above the transition to the cubic struct and goes to the center at higher pressure. For $BaTiO_3$ this effect is direc related to the lost of diffuse lines observed in the x-ray diffraction pattern

Keywords: High pressure, ferroelectrics, x-ray absorption spectroscopy, titanate

1. Introduction

The phase diagram of titanate perovskites in the PT plane is extremely r and is dominated by the competition between the ferroelectric and antiferrodistorsive instabilities. The first one corresponds to the displaceme of the Ti atom from the centre of the oxygen octahedron while the seco one is related to the rotation and/or the tilt of the oxygen octahedra.

From the "long-range point of view", these instabilities induce pha transitions to lower symmetry structures as observed by x-ray or neutron

*E-mail: jean-paul.itie@synchrotron-soleil.fr

E. Boldyreva and P. Dera (eds.), *High-Pressure Crystallography: From Fundamental Phenomena to Technological Applications*, DOI 10.1007/978-90-481-9258-8_5