Geophysical applications of nuclear resonant spectroscopy

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ABSTRACT

We summarize recent developments of nuclear resonant spectroscopy methods, such as nuclear resonant inelastic X-ray scattering and synchrotron Mössbauer spectroscopy, and their uses for the geophysical sciences. The inelastic method provides specific vibrational information, for example, the phonon density of states, and, in combination with compression data, it permits the determination of sound velocities and Grüneisen parameters under high pressure and high temperature. The Mössbauer method provides hyperfine interactions between the resonant nucleus and electronic environment, such as isomer shifts, quadrupole splittings, and magnetic fields, which provide important information on valence, spin state, and magnetic ordering. Both methods use a nuclear resonant isotope as a probe and can be applied under high pressure and high temperature. The physical mechanism of nuclear resonant scattering and the specifics in applications to Earth materials are presented with reference to several high-pressure studies on iron-bearing compounds.

Keywords: phonon density of states, sound velocities, Grüneisen parameter, magnetism, nuclear resonant scattering.

INTRODUCTION

The chemical composition, the elastic and transport properties, and the thermodynamic parameters of materials identified or expected in Earth's deep interior are of general importance to geochemical modeling (Tolstikhin and Hofmann, 2005; Coltice and Ricard, 1999), geodynamic simulation (Nakagawa and Tackley, 2005), and interpretation of seismic-wave observations (Birch, 1952; Kellogg et al., 1999; van der Hilst and Kårsason, 1999; Ishii and Tromp, 1999; Ni et al., 2002; Trampert et al., 2004; Mattern et al., 2005). Inferences about the mineralogy and chemical composition of Earth's deep interior must depend on comparisons of accurate, laboratory-derived properties of candidate phases with geophysical observations because our ability to directly sample deep Earth is severely limited. Typically, models of deep Earth have been made by extrapolating mineral properties to appropriate pressure-temperature (P-T) conditions and comparing them with seismologically determined properties, such as sound velocities and density. Many extrapolations use either low P-T data, infer that the chemically complex minerals behave the same as their Mg end-members, use analogue materials, and/or neglect the behavior of the shear properties (due in part to lack of experimental data). Although useful, these assumptions may not accurately reflect the behavior or chemistries of the actual components deep in Earth. Recent advances in experimental methods and theoretical calculations show that elements such as iron, aluminum,
and calcium have appreciable effects on the shear properties of lower-mantle silicates and oxides (Jacobsen et al., 2002; Kung et al., 2002; Karki and Crain, 1998; Kiefer et al., 2002; Jackson et al., 2004; Jacobsen et al., 2004; Jackson et al., 2005b) and therefore alter our interpretations of geophysical observations. The addition of light elements such as silicon, oxygen, sulfur, and hydrogen to iron also has significant effects on the shear properties (Machova and Kadeckova, 1977; Struzhkin et al., 2001; Lin et al., 2003, 2004a; Mao et al., 2004b; Jacobsen et al., 2004). Several experiments have been performed to understand the crystal chemistry of these complex systems (Irifune, 1994; Kesson et al., 1995; Wood and Rubie, 1996; Hirose et al., 1999; Frost and Langenhorst, 2002), and they have shown that even though most of the iron in mantle materials is divalent (Fe	extsuperscript{2+}), a significant amount of trivalent iron (Fe	extsuperscript{3+}) was determined for aluminum-bearing (Mg,Fe)SiO	extsubscript{3}-perovskite (McCammon, 1997). Related to these effects are the possible occurrences of high-spin to low-spin crossovers in the iron component of lower-mantle phases (Badro et al., 2003, 2004; Li et al., 2004; Jackson et al., 2005a; Lin et al., 2005a). Theoretical predictions indicate that material properties influenced by the spin state of iron change smoothly along the geotherm (Sturhahn et al., 2005), but, owing to the possible significance of these electronic changes to our interpretation of geophysical observations, more experiments need to be done to clarify the nature of these changes at typical P-T conditions. Even less is known about the recently discovered post-perovskite phase (e.g., Murakami et al., 2004). The effect of iron (Mao et al., 2004a) and aluminum (Akber-Knutson et al., 2005; Caracas and Cohen, 2005) on the perovskite to post-perovskite transition pressure has been studied experimentally and theoretically, respectively, but still little is known about the physical and chemical properties of post-perovskite. It is necessary to study the elastic parameters (especially the shear properties) of deep Earth materials, the valence state of iron in these materials, and the elemental partitioning under appropriate P-T conditions to constrain the chemistry and composition of this region. Many of these unknowns could be determined using nuclear resonant scattering methods under simultaneous high-pressure and high-temperature conditions.

The environmental conditions of planetary interiors often require challenging studies of materials under pressures exceeding 100 GPa and high temperatures. The combination of synchrotron radiation techniques with high-pressure studies has been very successful over the last decades to address these challenges. In particular, the brightness of third-generation synchrotron radiation facilities has permitted scientists to reach ever higher pressures with increasingly small samples. Focusing optics have been refined to concentrate a significant portion of the X-ray beam into an area of less than 10 × 10 μm² size, and, in combination with efficient high-resolution monochromators, the application of inelastic X-ray scattering and nuclear resonant scattering methods to high-pressure problems has become feasible (see the overview by Hemley et al., 2005). Among nuclear resonant scattering techniques, practical importance has been achieved by nuclear resonant inelastic X-ray scattering (NRIXS) for the study of lattice dynamics and by synchrotron Mössbauer spectroscopy (SMS) for the study of magnetism and valence states. In brief, SMS includes recoilless scattering processes, i.e., without participation of lattice vibrations, whereas NRIXS uses the possibility of simultaneous excitation of nuclear resonance and lattice vibrations. A comprehensive overview of the field has been given in a collection of review articles (Gerdau and de Waard, 1999), and also in more recent reviews on nuclear resonant spectroscopy (Alp et al., 2001; Sturhahn, 2004; Scheidt and de Waard, 1999), and also in more recent reviews on nuclear resonant scattering methods to high-pressure problems has become feasible (see the overview by Hemley et al., 2005). The NRIXS and SMS methods can be applied to materials that contain a nuclear resonant isotope, such as 

### BASICS ON NUCLEAR RESONANCES

Standard text books on experimental techniques with synchrotron radiation discuss mechanisms that are based on the scattering of X-rays by electronic charge and spin. An argument from classical electrodynamics usually provides the justification to ignore the nuclear charge. The Thomson-scattering cross section for electromagnetic radiation by a point charge q with mass m is given by

$$
\sigma_T = \frac{8\pi}{3} \left( \frac{q^2}{mc^2} \right)^2.
$$

(1)

The scattering strength of the nucleus compared to the electron shell is then reduced by a factor (Z m/M)^2 = 10^7, where m and M are the masses of the electron and nucleus, respectively, and Z is the atomic number. In this long-wavelength limit, which is justified for X-rays, the nuclear charge scattering is reduced by orders of magnitude because of the large nuclear mass, and it seems completely appropriate to ignore scattering contributions from the nucleus. However, this argument fails if the time scale of internal nuclear dynamics matches the energy of the X-ray photon, i.e., the nucleus experiences a resonant excitation. The nuclear resonant cross section is then calculated as

$$
\sigma_N = \frac{\lambda^2}{2\pi} \frac{1}{1 + \alpha} \frac{2I' + 1}{2I + 1}.
$$

(2)

where \(\lambda\) is the wavelength of the resonant X-rays, \(\alpha\) is the internal conversion coefficient, and \(I\) and \(I'\) are the spins of the nuclear ground and excited state, respectively. The probability that an
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excited nucleus directly transfers its excess energy to the electron shell followed by expulsion of an inner electron is given by \( \alpha/(1 + \alpha) \). Values of \( \alpha \) for relevant nuclear transitions range from 1 to 1000. The nuclear resonant cross section can become very large, e.g., using values of \( \lambda = 86 \text{ pm} \) (1 pm = \( 10^{-12} \text{m} \)), \( \alpha = 8.6 \), \( I = 1/2 \), and \( I' = 3/2 \), the 14.4 keV nuclear transition of \(^{57}\text{Fe} \) gives a value of \( \sigma = 2.56 \text{ Mmbarn} \) (1 barn = \( 10^{-28} \text{m}^2 \)) and a ratio \( \sigma_{\text{v}}/\sigma_{\text{p}} = 5700 \). It should be noted that the photoelectric cross section \( \sigma_{\text{v}} \) often exceeds \( \sigma_{\text{p}} \), but we still observe \( \sigma_{\text{v}}/\sigma_{\text{p}} = 450 \). Even though the nuclear resonant cross section is very large, the energy width of such resonances is very narrow. The weakness of the nuclear coupling to its electronic surroundings and to the electromagnetic field results in a weakly damped resonance of high quality, e.g., the energy width of the \(^{57}\text{Fe} \) resonance is only \( \Gamma = 4.66 \text{ neV} \).

Such extraordinarily narrow resonances escape traditional X-ray scattering methods because the best energy resolutions of X-ray optics are in the 100 \( \mu\text{eV} \) (=24 GHz) regime (Toellner et al., 2001; Yabashi et al., 2001). A resonant enhancement over a neV scale remains unresolved and unnoticed because even an experiment with bandwidth \( \delta E = 100 \mu\text{eV} \) would find \( \sigma_{\text{v}}/\sigma_{\text{p}} \ll \sigma_{\text{v}}/\delta E \).

Nuclear resonant scattering techniques are nevertheless possible in light of the inverse relationship between lifetime and level width of the nuclear state, \( \tau = \hbar/\Gamma \). The value of \( \tau \) determines the time scale on which a sample containing resonant nuclei would respond to an excitation by a synchrotron radiation pulse. Whereas values for \( \tau \) are in the nanosecond to microsecond range, the duration of a synchrotron radiation pulse is typically less than 100 ps, and the electronic scattering of X-rays occurs typically on the time scale of femtoseconds, virtually immediately compared to nuclear resonant contributions. Detectors with time resolutions of ns or better can exploit this mismatch with a “time-discrimination trick” as illustrated in Figure 1, and we understand how nuclear resonant signals are cleanly separated from other scattering contributions. In Figure 2, we show the collection of nuclear isotopes that possess resonances below 150 keV. The higher transition energies are less favorable because the intensity of synchrotron radiation sources typically decreases with increasing X-ray energy, and X-ray optics, as well as detectors, become less efficient at higher energies. The time resolution of X-ray detectors (presently around 1 ns) limits the feasibility of short-lived isotopes, whereas very long lifetimes lead to low signal rates and to difficulties with the storage ring operations.

**EXPERIMENTAL METHODS**

The pioneering experimental work on nuclear resonant scattering with synchrotron radiation (Gerdau et al., 1985) strongly suggested the utilization of new time-resolved techniques instead of the energy-resolved measurements of conventional Mössbauer spectroscopy. This novel approach resulted from the particular property of synchrotron radiation, which is emitted as a sequence of very short X-ray pulses of typically less than 100 ps duration. The time-decay pattern of X-rays scattered off or transmitted through samples containing a suitable nuclear-resonant isotope is equivalent to an energy spectroscopy in the \( \mu\text{eV} \) to neV (GHz to MHz) range. The measurement and analysis of such time spectra constitute the main part of the SMS method. During the last decade, we saw the refinement of the SMS technique and its application in the area of high-pressure research (Nasu, 1994, 1998; Zhang et al., 1999; Pleines et al., 1999; Lübbers et

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**Figure 1.** Scattering intensity versus time. At zero time, a synchrotron radiation pulse excites a sample containing a nuclear resonant isotope. Electronic scattering is prompt, whereas the response of the resonant nuclei is delayed. Time discrimination is the key to distinguishing nuclear and electronic scattering.

**Figure 2.** Level widths and lifetimes of nuclear resonances below 150 keV. The symbol size is proportional to the nuclear resonant cross section. Isotopes that have been used in nuclear resonant scattering experiments are identified.
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. The exclusion of phonons from the absorption process leads to the extremely high resolving power of these methods. However, theoretical calculations also predicted the exciting opportunity to observe the phonon density of states (DOS) via nuclear resonant excitation (Visscher, 1960; Singwi and Sjölander, 1960). Demonstration experiments using strong radioactive sources that were tuned by large Doppler shifts (Weiss and Langhoff, 1979; Endres et al., 1981) were limited in practice by the notoriously small inelastic absorption cross section and overwhelmingly large background signals. Only recently was the idea of using nuclear resonances to observe phonon excitations revived in synchrotron radiation experiments (Seto et al., 1995; Sturhahn et al., 1995; Chumakov et al., 1995), and the extraction of the phonon DOS was demonstrated (Sturhahn et al., 1995). The use of pulsed synchrotron radiation and a time-discrimination technique circumvented the background problem, and the new NRIXS method started to produce unique results.

The phonon DOS is an important quantity to describe the low-energy collective states of solids and is used to calculate thermodynamic properties related to lattice vibrations. Experimentally, the phonon DOS is often obtained indirectly, e.g., by calculation from the phonon dispersion relations measured on single crystals using inelastic neutron scattering. The NRIXS technique provides direct access to the partial and projected phonon DOS of the resonant isotope only (Kohn et al., 1998; Sturhahn and Kohn, 1999). The apparent disadvantage of results restricted to vibrational information from a few nuclear resonant isotopes has in turn led to several unique applications. The most suitable nuclear resonant isotope is $^{57}$Fe (Fig. 2), and iron-containing materials, molecules, and proteins are of tremendous interest in geophysics, thin-film research, and biophysics. NRIXS signals originate from particular resonant nuclei only, and this complete isotope selectivity is truly unique among techniques for the study of lattice vibrations. For example, materials surrounding the sample that do not contain resonant nuclei produce no unwanted background, and this feature now permits experiments under extreme pressure-temperature conditions that were impossible before (Lübbers et al., 2000a; Mao et al., 2001, 2004b; Struzhkin et al., 2001; Lin et al., 2003, 2004a, 2004b, 2005b; Shen et al., 2004; Papandrew et al., 2004; Kobayashi et al., 2004; Zhao et al., 2004). Details on the scattering mechanisms and methodology for NRIXS and SMS have been published elsewhere (Chumakov and Sturhahn, 1999; Sturhahn, 2004).

A schematic of the typical setup for nuclear resonant scattering experiments found at third-generation synchrotron radiation facilities is shown in Figure 3. The X-ray source consists of electron bunches that are orbiting in the storage ring and periodically pass through an undulator. The X-rays are monochromatized in two steps using a premonochromator and a high-resolution monochromator to an energy bandwidth of ~1 meV or 0.24 THz (Toellner, 2000).

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 photodiode detector that is placed as close as possible to the sample but away from any strong coherent scattering directions (Fig. 3). The integrated delayed counting rate is recorded. The NRIXS method directly provides the Fourier-transformed self-intermediate scattering function.

![Experimental setup for NRIXS and SMS](image-url)

**Figure 3.** Experimental setup for NRIXS (nuclear resonant inelastic x-ray scattering; incoherent) and SMS (synchrotron Mössbauer spectroscopy; elastic coherent forward-directed scattering). For high-pressure applications, the sample is mounted inside a diamond anvil cell and focusing mirrors are installed after the monochromator.
Sn(k, E) = \frac{1}{2\pi\hbar} \int <e^{i\mathbf{kr}(t)}e^{-i\mathbf{kr}(0)}> e^{i\omega t/\hbar} dt, \quad (3)

where \(2\pi\hbar\) is Planck’s constant, \(k\) is the wave vector of the X-rays incident on the sample, and \(r(t)\) is the displacement operator of the resonant nucleus (Sturhahn and Kohn, 1999; Sturhahn, 2004). 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 \(k\)) phonon DOS from \(S(k, E)\) (Sturhahn et al., 1995; Kohn et al., 1998; Hu et al., 1999; Chumakov and Sturhahn, 1999; Sturhahn, 2000, 2004). Typical acquisition times for a NRIXS spectrum range between one hour 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 (Sturhahn, 2000).

The Quasi-Harmonic Model

The vibrations in a solid are determined by the interatomic potential, which is harmonic in the lowest order of the displacement of the atoms from their equilibrium positions. If higher-order terms in the interatomic potential are neglected, a solid with \(N\) atoms shows \(3N-6\) independent collective vibration modes, also known as phonons. The equations of motion can be solved exactly, and the self-intermediate scattering function can be calculated for the thermalized ensemble (Sturhahn and Kohn, 1999) with the result

\[ S(k, E) = f(k)\delta(E) + \sum_{n=1}^{N} S_n(k, E) \]

\[ S_n(k, E) = f(k) \frac{E_\text{r}}{E(1 - \exp[-\beta E])} g(k, |E|) \]

\[ f(k) = \exp\left[-\int \frac{E_\text{r}}{E} \coth\left(\frac{\beta E}{2}\right) g(k, E) dE\right] \quad (4) \]

In this expression, \(f(k)\) is the probability for recoilless absorption of the X-rays, also known as the Lamb-Mössbauer factor, \(E_\text{r} = E_\text{r}(n\hbar)\) is the recoil energy (with nuclear transition energy \(E_\text{r}\), mass of the nuclear resonant isotope \(n\), and speed of light \(c\)), \(\beta = 1/(k_b T)\) is the inverse temperature (with Boltzmann’s constant \(k_b\)), and \(g(k, E)\) is the partial and projected phonon DOS. The expansion has a clear physical interpretation: the value of \(S_n(k, E)\) gives the probability for the creation/annihilation of \(n\) phonons with a total energy between \(E\) and \(E + dE\). The extraction of the phonon DOS from measured data based on Equation 4 using the Fourier-log inversion method has been described previously (Kohn et al., 1998; Hu et al., 1999; Sturhahn, 2000).

Beyond the very powerful harmonic model, anharmonic interatomic potentials can arise either from very special atomic arrangements (Tse et al., 2005) or from increasing atomic separation caused by temperature (Chumakov et al., 1996). Most often, anharmonic effects are described by perturbations of the harmonic approximation using the concepts of “phonon lifetime” and “phonon scattering length.” In the analysis of the self-intermediate scattering function, we distinguish situations of weak and strong anharmonicity. The former is characterized by renormalization of phonon energies (mode softening) and finite phonon lifetime but still assumes the existence of phonons as such, i.e., the coupling between the renormalized vibrational modes is negligible. So, the use of Equation 4 is still justified and will provide the renormalized phonon DOS. Situations of strong anharmonicity defy the phonon interpretation because the collective excitations are very different from phonons and renormalization is not sufficient, e.g., collective excitations in liquids and fast atomic diffusion in solids fall into this category. The quasi-harmonic model assumes the validity of Equation 4 and gives reliable results for cases of weak anharmonicity, as explained already.

If a NRIXS spectrum has been measured on a solid at certain \(P-T\) conditions, the validity of the weak anharmonicity assumption may be of concern, particularly at temperatures close to melting. Several tests based on the internal consistency of Equation 4 have been suggested (Chumakov and Sturhahn, 1999). The Lamb-Mössbauer factor, the kinetic energy per resonant atom, and the average force constant of the resonant atom can be calculated either as moments of the measured \(S(k, E)\) or from the phonon DOS (Lipkin, 1962; Chumakov and Sturhahn, 1999; Sturhahn and Chumakov, 1999). In addition, proper normalization and the positiveness of the phonon DOS can be tested.

Directional Dependence

The dependence of \(S(k, E)\) on the direction of the incident X-rays is implicitly contained in Equation 3 and is expressed via the directional dependence of the phonon DOS. The potential anisotropy of the phonon DOS must not be confused with the elastic anisotropy; the description of the former is given by a symmetric second-rank tensor (Sturhahn and Kohn, 1999), whereas the latter requires a symmetric fourth-rank tensor. Therefore, in crystals with cubic symmetry, such as ambient body-centered cubic (bcc) iron, the phonon DOS is isotropic, even though the elastic anisotropy is large (\(C_{11} = 230\) GPa, \(C_{12} = 135\) GPa, \(C_{44} = 117\) GPa, anisotropy \(A = (2C_{11} - C_{12})/C_{11}\) of \(\sim 60\%\)). Anisotropic behavior of the phonon DOS has been observed in FeBO\(_3\) (Chumakov et al., 1997; Kohn et al., 1998) and hexagonal close-packed (hcp) iron (Giefers et al., 2000), but the anisotropy of the Lamb-Mössbauer factor was reported to be below the detection limits of 3.5% and 0.1%, respectively. Even single crystals of planar organic molecules show only a variation of \(-\sim 2.5\%\) in the Lamb-Mössbauer factor (Rai et al., 2002). The NRIXS spectrum of polycrystalline materials provides an average value <\(S(k, E)\)>, and we write, neglecting the small variations of the Lamb-Mössbauer factor,
Unfortunately the averaged higher-order terms cannot be derived from the averaged one-phonon term, and the formal inversion of Equation 5 to obtain $g(k,E)$, e.g., with the Fourier-log method, requires further justification. If we use the Fourier-log method nevertheless, we would obtain a result for the averaged one-phonon term that would deviate somewhat from the correct expression. This deviation is approximately given by $-\nu/2\langle S_k(k,E)\rangle \delta S_k(k,E)$ with $\delta S_k(k,E) = S_k(k,E) - \langle S_k(k,E)\rangle$.

We note that this correction is a two-phonon term and of second order in the integrated anisotropy functions $\delta_s$. Reported cases of anisotropy (Chumakov et al., 1997; Giefers et al., 2000) lead to estimates of much less than 1% for this term. Direct inversion of the measured NRIXS spectrum therefore provides a reliable value of the averaged phonon DOS, unless the material exhibits a small Lamb-Mössbauer factor and a large anisotropy (which has yet to be observed).

**SMS**

For SMS measurements, the energy bandwidth 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 excite the resonant nuclei coherently and are observed with an avalanche photodiode 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 photons—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 (Sturhahn, 2004)

$$\delta_n(E) = \frac{\lambda}{4\pi} \rho \sigma \gamma \int \frac{W_{nm}}{z_{nm}(E) - 1} dE,$$

where $\lambda$ is the X-ray wavelength, $\rho$ is the volume density of resonant nuclei, $\sigma$ is the nuclear resonant cross section, and $\gamma$ is the Lamb-Mössbauer factor. The sum is over all sublevels of nuclear ground and excited states. The function $z_{nm} = 2(E_{nm} - E)/\Gamma$ depends on the energy difference between excited and ground states $E_{nm}$ and the nuclear-level width $\Gamma$. The weight of each resonance at $E_{nm}$ is given by the second-rank tensor $W_{nm}$. The weights are normalized by $\sum_{nm} W_{nm} = 1$. The index of refraction has sharp maxima at energies $E = E_{nm}$ corresponding to the positions of the nuclear transitions, which are determined by the electronic environment of the nucleus. The time spectrum is given by

$$\frac{dI}{dt} = \frac{l_0}{(2n\pi)^2} \int \left( \exp \left[ i k D \delta_n - \frac{1}{2} \left| \frac{W_{nm}}{z_{nm}(E) - 1} - 1 \right| \right] e^{i2n\pi dE} \right)^2.$$

where $I_0$ is the incident intensity corrected by electronic absorption, $k = E/(hc)$ is the wave number, and $D$ is the physical thickness of the sample. The effective thickness, $\eta = \rho \sigma \gamma D$, is a useful parameter to describe total intensity and the influence of sample thickness on the shape of the time spectra. An effective thickness between 10 and 50 usually provides a good compromise between a distortion of the time spectra for larger values of $\eta$ and a small total counting rate for smaller values of $\eta$. Typical acquisition times for an SMS time spectrum range between minutes for iron-rich samples under ambient conditions and a few hours for dilute samples under high pressures. Measured time spectra can be evaluated with the CONUSS software (Sturhahn, 2000). It should be noted that the index of refraction cannot be calculated by a simple Fourier transformation of the time spectrum. This situation has been described as the phase problem of SMS (Sturhahn, 2001), and experimental schemes to circumvent this problem have been proposed (Sturhahn et al., 2004). At present, such schemes would lead to a large increase in data collection time and are not routinely applied in high-pressure experiments.

**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 interatomic distances describe the same physical phenomenon. The “phonon-picture” emphasizes microscopic properties, like interatomic force constants, whereas the macroscopic descriptors, such as elastic moduli and density, dominate understanding of the “sound-wave picture.” The energy of an acoustic phonon of mode $s$ with a small wave number $q$ (long wavelength) that propagates in the direction $q$ is given by $E = h\nu v(q)$, where $2n\pi$ is Planck’s constant and $\nu(q)$ is the sound velocity. The number of phonon states in momentum space is then $dN = V\int k^2 dk d\Omega_k$, where $k = E/(h\nu)$. $V$ is a normalization volume, and the integration is performed over all directions $q$. The linear phonon dispersion leads to a Debye-like phonon DOS...
This relationship is exact for small energies (long phonon wave\-lengths) and has been experimentally shown to hold even in the case of a partial phonon DOS of a particular type of atom in a compound (Hu et al., 2003). Here, the previous equation is given in a form suitable for quantitative analysis

\[ D(E) = \sum \frac{dN}{dE} = \frac{Ve^2_s}{h^2} \sum \int \frac{1}{\nu_{I}(q)} d\Omega_{q}, \tag{8} \]

where \( \nu_{I} \) is the Debye sound velocity, \( \rho \) is the density of the material, and \( m \) is the mass of the nuclear resonant isotope.

The derivation of the Debye sound velocity from a NRIXS spectrum relies on the validity of several assumptions that may be violated in practice, leading to systematic errors. In the determination of the phonon DOS, we rely on the quasi-harmonic model (see section titled “The-Quasi-Harmonic Model”) and a weak anisotropy of the phonon DOS (see section “Directional-Dependence”). The extraction of the curvature of the phonon DOS can lead to errors related to the limited energy range in which Equation 9 is valid; this is discussed in detail in the following section (Debye Sound Velocity). In special cases (discussed in Compound Mixtures section), small impurities can affect the low-energy region of the phonon DOS strongly and lead to large systematic errors in the Debye sound velocity of the majority phase. The calculation of compression- and shear-wave velocities requires additional knowledge about the static compression behavior of the material and this is discussed in the Compression- and Shear-Wave Velocities section. Systematic errors from this procedure are very small for the shear-wave velocities but are potentially more important for the compression-wave velocities. Identification of the sources for systematic errors in a particular experimental situation is a complex process, but under appropriate conditions cumulative systematic errors can be less than 1%.

### Debye Sound Velocity

The quantitative description of the low-energy region of the phonon DOS via Equation 9 provides the Debye sound velocity. In Figure 4, the low-energy region of the phonon DOS is shown for iron metal under different pressures and temperatures. Fits to the data provide the curvature of the parabola defined by Equation 9, and with the known density, one can derive Debye sound velocities of \( 3.49(5) \text{ km/s} \) for ambient conditions, \( 4.54(6) \text{ km/s} \) for 50 GPa and 300 K, and \( 3.98(1) \text{ km/s} \) for 55 GPa and 1500 K, where values in parenthesis represent standard errors. In a similar way, Debye sound velocities have been obtained for iron metal (Mao et al., 2001), Fe-Ni and Fe-Si alloys (Lin et al., 2003), Fe\(_{90}\)O (Struzhkin et al., 2001), Fe\(_{90}\)S (Lin et al., 2004a), FeH\(_{3}\) (Mao et al., 2004b), and FeS (Kobayashi et al., 2004) under high pressure. Very recently, the same method was applied to measure the temperature dependence of sound velocities in compressed iron metal (Lin et al., 2005b). In Table 1, we compare Debye sound velocities from NRIXS measurements with calculated Debye sound velocities from reported values for the elastic constants. We numerically determined sound velocities from the Christoffel equation (Musgrave, 1970) for all crystal directions and applied the averaging procedure of Equation 9 to obtain the Debye sound velocity.

The derivation of Debye sound velocities from the phonon DOS relies on a linear phonon dispersion that will only be accurate in a limited energy range as seen from the deviations apparent in Figure 4 for energies above \( \sim 15 \text{ meV} \) (3.6 THz). The energy resolution of the NRIXS method depends on the bandwidth of the X-rays incident on the sample and reaches \( \sim 1 \text{ meV} \) (0.24 THz) with present monochromator technology. In measured data, we therefore expect the energy region below \( \sim 2-3 \text{ meV} \) (0.48-0.72 THz) to be obscured by elastic scattering and to be less reliable for sound velocity determination. Even though this does not seem to be a problem for the analysis of the data on pure iron that is shown in Figure 4, other materials may be more problematic. We will estimate the systematic errors resulting from the use of Equation 9 by an improved, empirical relation for the dispersion of the acoustic phonons. Assuming that the phonon energies reach a maximum value of \( E_{s} \) at the Brillouin-zone boundary and that we can describe the phonon energies by \( E_{s} = E_{s} \sin(\hbar q/\lambda_{s}) \), an approximate relationship used before to extract compressional sound velocities using momentum-resolved inelastic X-ray scattering (Krish et al., 1997; Fiquet et al., 2001; Antonangeli et al., 2005), we obtain a relationship similar to Equation 9 but with an energy-dependent Debye velocity.

\[ E_{s} = E_{s} \sin(\hbar q/\lambda_{s}) \]

Figure 4. Phonon density of states (DOS) versus energy squared. The straight lines are fits to the data for energy below \( \sim 15 \text{ meV} \) (3.6 THz). In this energy region, Debye-like behavior is observed. The data were taken from Sturhahn (2004, ambient) and Lin et al. (2005b, high pressure).
TABLE 1. MEASURED DEBYE SOUND VELOCITIES OF EARTH-RELEVANT MATERIALS FROM NRIXS (NOTED WITH *) COMPARED WITH CALCULATED DEBYE SOUND VELOCITIES FROM AVAILABLE SINGLE-CRYSTAL ELASTICITY INFORMATION

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>v_D (m/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe</td>
<td>7.86³</td>
<td>3521 ± 50*</td>
<td>Sturhahn (2004)</td>
</tr>
<tr>
<td>α-Fe</td>
<td>7.86³</td>
<td>3519 ± 48*</td>
<td>Hu et al. (2003)</td>
</tr>
<tr>
<td>α-Fe</td>
<td>7.874</td>
<td>3538</td>
<td>Hearmon (1984)</td>
</tr>
<tr>
<td>Fe_{38}Si_{15}</td>
<td>7.42 ± 0.01</td>
<td>3281 ± 10*</td>
<td>Lin et al. (2003)</td>
</tr>
<tr>
<td>Fe_{38}Si_{13}</td>
<td>7.601</td>
<td>3541</td>
<td>Machova and Kadeckova (1977)</td>
</tr>
<tr>
<td>Fe_{38}Si_{10}</td>
<td>7.675</td>
<td>3556</td>
<td>Machova and Kadeckova (1977)</td>
</tr>
<tr>
<td>Fe_{38}Ni_{60}</td>
<td>8.40 ± 0.02</td>
<td>3530 ± 6*</td>
<td>P = 7.5 GPa (Lin et al., 2003)</td>
</tr>
<tr>
<td>FeS</td>
<td>7.05</td>
<td>2902 ± 6*</td>
<td>Lin et al. (2004)</td>
</tr>
<tr>
<td>FeS</td>
<td>4.6</td>
<td>2831 ± 10*</td>
<td>P = 1.5 GPa, from Kobayashi et al. (2004)</td>
</tr>
<tr>
<td>Fe_{38}O</td>
<td>5.708</td>
<td>2801*</td>
<td>P = 0.9 GPa, from Struzhin et al. (2001)</td>
</tr>
<tr>
<td>Fe_{38}O</td>
<td>5.708</td>
<td>3210</td>
<td>Jackson and Khanna (1990)</td>
</tr>
<tr>
<td>Fe_{38}O</td>
<td>5.721 ± 0.006</td>
<td>3223 ± 7</td>
<td>Jacobson et al. (2002)</td>
</tr>
<tr>
<td>FeO</td>
<td>5.254</td>
<td>4597 ± 100*</td>
<td>This study</td>
</tr>
<tr>
<td>FeO</td>
<td>5.254</td>
<td>4654 ± 100</td>
<td>Lieberman and Schreiber (1968)²</td>
</tr>
</tbody>
</table>

Note: Errors for values from nuclear resonant inelastic X-ray scattering (NRIXS) include statistical contributions only. All values are for ambient conditions, unless mentioned otherwise.

*Debye sound velocity from NRIXS data and corrected for natural Fe-enrichment using Fe_{75}R_{25} and 
\[ v_{\text{corrected}} = \frac{v_{\text{natural}}}{\left(1 - x\right)^{1/2} + x} \]

where \( x \) represents the fraction of nonenriched portion. Note that all other natural conditions. 

Debye sound velocities were calculated from available single-crystal elasticity data (unless mentioned otherwise) using the Christoffel equation and the averaging method outlined in Equation 9.

2Polycrystalline sample.

\[
\frac{1}{v_\phi(E)} = \frac{1}{3} \sum \frac{\text{arcsin}^2 \eta_i}{\eta_i^2 (1 - \eta_i^2) \int \frac{d\Omega_q}{4\pi} v_\phi(q)^2} \]

where \( \eta_i = E/E_{\phi, i} \). If we use the energy interval \([E_1, E_2]\) for analysis with a parabolic fit as indicated in Figure 4, the derived Debye sound velocity is approximately given by

\[
\bar{v}_\phi = v_\phi(0) \left(1 - \frac{5}{63} \left( \frac{E_2}{E_1} \right)^2 \left(1 - \frac{E_1}{E_2} \right)^{5/2} \right) \]

where \( v_\phi(0) \) is the true Debye sound velocity. The reasonable assumption \( E_2 > 2E_1 \) allows us to neglect the fraction. The correction term in this expression is always negative, and analysis of the measured data by a parabolic fit provides a reduced Debye sound velocity depending on the values of \( E_1, E_2, \) and \( E_\phi \). For the ambient iron data shown in Figure 4, parameters of \( E_1 = 22 \) meV, \( E_2 = 3 \) meV, and \( E_\phi = 12 \) meV lead to ~2.4% reduction, but a value of \( E_2 < 8 \) meV brings this effect below 1%. In Figure 5, the deviation percentage shows the effect of different energy intervals on the Debye sound velocity. The solid lines are guides to the eye.

Figure 5. Systematic error of the Debye sound velocity from a parabolic fit to the phonon density of states (DOS) of iron metal versus pressure. Values of \( E_\phi \) between 22 meV (ambient) and 36 meV (153 GPa) were obtained from previously published data (Mao et al., 2001), and systematic errors were estimated using Equation 11 with \( E_2 = 10 \) meV (circles) and \( E_2 = 15 \) meV (squares). The solid lines are guides to the eye.
we show systematic errors from this deviation versus pressure for iron metal. At higher pressures, the phonon spectrum shifts to higher energies, the parabolic region in the phonon DOS is extended, and the derived Debye sound velocity becomes more accurate. The errors can be reduced further by decreasing $E_g$, even though at present, the statistical quality of high-pressure NRIXS data would probably require $E_g \geq 10$ meV.

Compression- and Shear-Wave Velocities

Seismic data of Earth’s interior distinguish between compressional waves and shear waves corresponding to longitudinally and transversely polarized phonons, respectively. The polarization vectors $\mathbf{e}(\mathbf{q})$ of the phonons can be used to define average compression- and shear-wave velocities, $v_p$ and $v_s$, by

$$\frac{1}{v_p} = \sum \frac{\left| \mathbf{q} \cdot \mathbf{e}(\mathbf{q}) \right|^2}{v(\mathbf{q})} \frac{d\Omega_\mathbf{q}}{4\pi}$$

and

$$\frac{1}{v_s} = \frac{1}{2} \sum \frac{\left| \mathbf{q} \cdot \mathbf{e}(\mathbf{q}) \right|^2}{v^2(\mathbf{q})} \frac{d\Omega_\mathbf{q}}{4\pi}.$$  \hspace{1cm} (12)

The NRIXS method provides the Debye sound velocity, which, according to Equations 9 and 12, can now be expressed as

$$\frac{3}{v_D^3} = \frac{1}{v_p^3} + \frac{2}{v_s^3}. \hspace{1cm} (13)$$

For isotropic media, $v_p$ and $v_s$ are independent of direction and follow the additional relationship

$$\frac{K}{\rho} = v_s^2 = v_p^2 - \frac{4}{3} v_s^2, \hspace{1cm} (14)$$

where $K$ and $\rho$ are the adiabatic bulk modulus and density, respectively. Equations 13 and 14 have widely been used to derive compression- and shear-wave velocities from NRIXS data with additional knowledge of adiabatic bulk modulus and density. These equations have general solutions

$$v_s = 0.952 v_D - 0.041 v_D, \hspace{1cm} (15)$$

$$v_p = 0.908 + 0.297 v_D - 0.243 v_D^2.$$  

which are accurate to better than 0.1%. A variation of $v_s$ has only a minor effect on the shear-wave velocity, i.e., $\delta v_s / \delta v_D = -0.041$, whereas $\delta v_p / \delta v_D = 0.908 - 0.243 v_D^2$ reflects the strong influence of $v_D$ on the value for the compression-wave velocity. These findings are material independent, and the weak effect of $v_s$ on the shear-wave velocity determination of FeH$_4$ has been pointed out previously (Mao et al., 2004b). As a result, the NRIXS method is particularly suitable to provide accurate values for the average shear-wave velocity, where the averaging mechanism is defined by Equation 12. In Figure 6, we show examples of sound velocities of iron and iron alloys at room temperature. The straight lines are fits to the NRIXS results and suggest the validity of Birch’s law (Birch, 1952) for $v_p$ and $v_s$, i.e., $v_p \propto \rho$. The same linear dependence of $v_p$ and $v_s$ was also found independently in inelastic X-ray scattering studies (Antonangeli et al., 2004). In addition, recent NRIXS experiments on iron under high pressure and high temperature have demonstrated an explicit temperature dependence of the sound velocities at constant density (Lin et al., 2005b).

It is important to realize that Equation 14 only holds approximately for elastically anisotropic materials. For example, a calculation using elastic constants of iron metal at ambient conditions ($C_{11} = 230$ GPa, $C_{12} = 135$ GPa, $C_{44} = 117$ GPa, anisotropy $A = [2(C_{11} + C_{12} - C_{44})/C_{11}]$ of ~60%) shows that the right side of Equation 14 will fall short of its correct value by ~4% when using the average velocities according to Equation 12, and potentially more for materials with larger elastic anisotropy. Nevertheless average shear-wave velocities can be determined by NRIXS with great precision and high accuracy. Consider solutions $(v_p, v_s)$ of Equations 13 and 14 where $v_p$ and $v_s$ serve as input parameters. A variation of $v_p$ can then simulate the effects of elastic anisotropy.

![Figure 6. Compression-wave and shear-wave velocities versus density. Results from NRIXS (nuclear resonant inelastic X-ray scattering) data: diamonds—Fe (Mao et al., 2001); circles—Fe$_{92}$Si$_{15}$; rectangles—Fe$_{99}$Si$_{15}$ (Lin et al., 2003); left triangles—Fe$_3$S$_2$ (Lin et al., 2004a). Other results: triangles up—Fe, IXS (Fiquet et al., 2001); triangles down—Fe, shock-wave (Brown and McQueen, 1986); crosses—PREM (preliminary reference Earth model) (Dziewonski and Anderson, 1981). The straight lines are fits to the NRIXS results and suggest the validity of Birch’s law.](image)
and uncertainty in the bulk modulus. According to Equation 15, uncertainty about the elastic anisotropy will then mainly influence \( v_\mu \) whereas \( v_\nu \) remains almost unchanged.

### Compound Mixtures

The previous discussion implicitly assumed that the material under investigation was homogeneous. Even though most experiments may try to prepare and study pure samples, the effect of a mixture of compounds with different elastic properties on the sound velocity determination is important. For simplicity, we will assume a mixture of only two compounds with concentrations \( \alpha_1 \) and \( \alpha_2 = 1 - \alpha_1 \). The NRIXS spectrum will then be given by \( S(E) = \alpha_1 S_1(E) + \alpha_2 S_2(E) \), where \( S_i(E) \) are the self-intermediate scattering functions according to Equation 3 for each compound. The extracted phonon DOS is nonlinearly related to \( S(E) \) and is in general not the linear superposition of the phonon DOS of the two compounds (see the discussion in Sturhahn and Chumakov, 1999). If we still assume that the extracted phonon DOS is a linear superposition, we will make an error of the order \( f^2 - 1 - f \ln f \), which can be approximated by \( 3(1 - f)^2/2 \) for Lamb-Mössbauer factors close to unity. For example, hcp-iron at 300 K gives \( f > 0.83 \), and the error would be only a few percent. Under these conditions, it is justified to assume a linear superposition of the phonon DOS, which leads to the following addition rule for the Debye sound velocities:

\[
\rho_1 v_{D1}^3 = f_1 \rho_1 v_{m1}^3 + f_2 \rho_2 v_{m2}^3 \tag{16}
\]

where \( f_1 \rho_1 \) and \( v_{m1} \) are the Lamb-Mössbauer factors, densities, and Debye sound velocities of the two compounds, respectively, and \( f = f_1 / \alpha_1 + f_2 / \alpha_2 \). The value on the left side of Equation 16 is obtained from the measured NRIXS spectrum, but the individual values for the two compounds are not known. An important application of Equation 16 is the assessment of effects caused by a contamination of the compound to be studied. In this case, we may (erroneously) assume that \( \rho = \rho_1 \) and rewrite Equation 16 as follows

\[
\rho_1 v_{D1}^3 = \left( \frac{\alpha_1 + \alpha_2 \xi}{\alpha_1 + \alpha_2 \eta} \right)^3 \tag{17}
\]

where \( \xi = f_1 / f_2 \) and \( \eta = (\rho_1 v_{m1}^3)/(\rho_2 v_{m2}^3) \). In Figure 7, we show the ratio of measured and actual Debye sound velocities \( v_{D1}/v_{D2} \) for various values of \( \eta \). The influence of \( \xi \) on the results is small, and we chose \( \xi = 1 \), which is reasonable for most iron-bearing materials under high pressure. The approximation of Equation 17 for small \( \alpha_2 \) reads \( v_{D1}/v_{m1} = 1 + \alpha_2 \xi (1 - \eta)/3 \), which suggests a strong effect for large \( \eta \). Even small amounts of a dense contaminant with small Debye sound velocity added to a light material with high Debye sound velocity (large values of \( \eta \)) can lead to very different results for the measured value of \( v_{D1} \). For example, a mixture of 0.5% FeO (\( \rho_2 = 5.721 \text{ g/cm}^3, v_{D2} = 3.221 \text{ km/s} \)) and 99.5% perovskite Mg_9Fe_2SiO_3 (\( \rho_1 = 4.106 \text{ g/cm}^3, v_{m1} = 7.21 \text{ km/s} \)) from Sinogeikin et al. [2004] for iron-free MgSiO_3 gives \( \eta = 15.6 \) and \( \alpha_2 = 0.16 \), which would lead to a measured Debye sound velocity of only \( v_{D1} = 4.24 \text{ km/s} \), a 41% reduction. The method is much more robust in the opposite scenario with small values of \( \eta \). For example, a mixture of 10% FeO (\( \rho_2 = 5.721 \text{ g/cm}^3, v_{D2} = 3.221 \text{ km/s} \)) and 90% iron metal (\( \rho_1 = 7.86 \text{ g/cm}^3, v_{D1} = 3.52 \text{ km/s} \)) gives \( \eta = 0.95 \) and \( \alpha_2 = 0.06 \), which leads to a change in the measured Debye sound velocity of only 0.1%.

### Grüneisen Parameters

The volume and temperature dependence of vibrational modes contains important information about the thermodynamic behavior of condensed matter. A microscopic picture was developed by Grüneisen (Grüneisen, 1926) that introduced the isothermal change of the energy \( \omega_i \) of the vibrational mode / with volume as a characteristic parameter. These mode-specific isothermal Grüneisen parameters are defined by the equation

\[
\gamma_i = -\frac{\nu_i}{\omega_i} \left( \frac{\partial \omega_i}{\partial V} \right)_T \tag{18}
\]

In principle, there are \( 3N \) possible different values for \( \gamma_i \) if \( N \) is the number of atoms in the material, and the independent determination of all these parameters is experimentally not feasible. However, the volume dependence of the phonon DOS can be determined by NRIXS.
Several types of Grüneisen parameters have been introduced and are used in the literature (see, e.g., Poirier, 2000). In particular, the Debye-Grüneisen parameter, given by

\[ \gamma_D = \frac{1}{3} \frac{\rho}{\nu_D} \left( \frac{\partial \nu_D}{\partial \rho} \right)_T, \]  

(19)

can be extracted from the measured Debye sound velocities \( \nu_D \). An ansatz of the type \( \gamma_D = \gamma_D^0 (\rho/\rho_0)^q \) (Anderson, 1979) permits us to integrate the previous equation and leads to the following functional description:

\[ \nu_D = \nu_D^0 \frac{R^{1/3}}{q} \exp \left( -\frac{\gamma_D^0}{q} \left( \frac{\rho}{\rho_0} - 1 \right) \right), \]  

(20)

where \( \xi = \rho/\rho_0 \). We used Equation 20 to derive values for \( \gamma_D^0 \) and \( q \) with density-dependent Debye sound velocities obtained from published NRIXS data on bcc-Fe and hcp-Fe (Mao et al., 2001) as well as \( \text{Fe}_{92.7}\text{Ni}_{6.8} \) and \( \text{Fe}_{85}\text{Si}_{15} \) (Lin et al., 2003). The best agreement was achieved with \( \gamma_D^0 = 2.36 \) and \( q = 1.67 \) for hcp-iron, \( \gamma_D^0 = 1.67 \) and \( q = 1.1 \) for \( \text{Fe}_{92.7}\text{Ni}_{6.8} \), and \( \gamma_D^0 = 2.01 \) and \( q = 1.13 \) for \( \text{Fe}_{85}\text{Si}_{15} \). These Debye-Grüneisen parameters and previously published experimental values on hcp-Fe versus the reduced density \( \rho/\rho_0 \) are displayed in Figure 8. Previous NRIXS studies provided \( \gamma_D^0 = 2.0 \) (bcc-Fe) and \( \gamma_D^0 = 1.8 \) (hcp-Fe in the pressure range below 40 GPa) but assumed \( q = 0 \) (Giefers et al., 2000).

**TEMPERATURE**

The NRIXS raw data have a very fundamental property that is independent of the material under investigation: the spectra follow a detailed balance principle (Sturhahn and Kohn, 1999). If the NRIXS data are given by \( I(E) \) with \( E = 0 \) as the exact nuclear transition energy, we can write

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

(21)

where \( \beta = 1/(k_B T) \) is the inverse temperature, and \( k_B \) is Boltzmann's constant. This 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. Recently, this method has been applied to determine the temperature of heated samples of iron under pressures up to 29 GPa (Shen et al., 2004). A comparison of the temperature from the NRIXS data with a temperature obtained by a fit of the thermal radiation spectra to the Planck radiation function up to 1700 K and 58 GPa confirmed independently the validity of temperatures determined from the spectroradiometric method in laser-heated diamond cell experiments (Lin et al., 2004b). In Figure 9, we illustrate the effect of temperature on NRIXS data by introducing a thermal asymmetry function defined by

\[ A = \frac{I(E) - I(-E)}{I(E) + I(-E)}. \]  

(22)

The detailed balance principle predicts the thermal asymmetry to behave as \( A = \tanh (\beta E/2) \). This function was fitted to the data in the region between 5 meV and 50 meV with only temperature as an adjustable parameter. The central part was excluded to avoid the influence of the elastic peak. At large energies, the statistical accuracy of the data points decreases rapidly. A detailed analysis of error sources related to temperature determination using this method has been published previously (Shen et al., 2004). In Figure 10, we show temperatures determined with the spectroradiometric method and from NRIXS spectra on iron in a diamond anvil cell (Lin et al., 2004b). The spectroradiometric temperatures have been averaged over the collection time of the corresponding NRIXS spectra of typically 8 h.

**MAGNETISM**

Magnetic ordering in a material causes a characteristic Zeeman splitting of the nuclear levels of the resonant isotope. According to Equations 6 and 7, 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...
Valence and Spin State

Most of the minerals and polymorphs expected in Earth’s interior are believed to incorporate low concentrations of Fe\textsuperscript{2+} and/or Fe\textsuperscript{3+} of \(-10\) atom\% 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 iron in minerals may still be relevant with respect to density, iron partitioning, partial melting, radiative thermal conductivity, and compositional layering (Shannon and Prewitt, 1969; Gaflhey and Anderson, 1973; Sherman, 1988, 1991; Sherman and Jansen, 1995; Badro et al., 2003, 2004; Li et al., 2004).

The SMS method provides quadrupole splittings and isomer shifts similar 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 (Sturhahn et al., 1998; Lubbers et al., 1999b; Sturhahn, 2004). The assignment of a set of parameter values to valence and spin state is usually based on a fingerprinting scheme (Bancroft et al., 1967).

Traditional Mössbauer spectroscopy had been used previously to study ferro-magnesium silicate perovskite (hereafter referred to as Pv) and Al-bearing Pv under ambient pressure (McCammon, 1997). Recently, the SMS method was applied to Pv using compositions Mg\textsubscript{0.9}Fe\textsubscript{0.1}SiO\textsubscript{3} with \(y = 0.05\) and \(y = 0.1\) up to 120 GPa at room temperature (Jackson et al., 2005a). In
Figure 11. Magnetic hyperfine fields and normalized sound velocities of Fe$_3$S with increasing pressure and time spectra recorded at 6 GPa and at 45 GPa. Below ~20 GPa, the low-pressure magnetic phase displays two magnetic field sites. The higher magnetic field (triangles) decreases with increasing pressure, whereas the lower magnetic field (squares) remains almost constant. A magnetic collapse occurs at ~21 GPa. The dashed lines are guides to the eye. The magnetic collapse is accompanied by a change in the pressure dependence of the normalized compressional- (diamonds) and shear-wave (circles) velocities as shown in the lower panel. At low pressure, the fast oscillations in the time spectrum clearly indicate the magnetic nuclear level splitting. At high pressure, the oscillations are significantly slower and result from the remaining quadrupole splitting and the rather large thickness of the sample. The time spectra were evaluated with the CONUSS programs (Sturhahn, 2000). Black circles—experimental time spectra; solid lines—best calculated time spectra. The data were taken from Lin et al. (2004a).
Figure 12. Quadrupole splittings (Δ) of the three Fe sites in Mg$_{99.5}$Fe$_{0.5}$SiO$_3$ versus pressure, isomer shifts (δ) between Fe$^{2+}$ and Fe$^{3+}$ sites, and time spectra recorded at ambient pressure and at 120 GPa. The solid lines were calculated using an isomorphic volume reduction of the unit cell (Jackson et al., 2005a). In the top panel, triangles and rectangles—sites associated with Fe$^{2+}$; diamonds—Fe$^{3+}$. The symbol size is proportional to the weight of the corresponding Fe site. In the lower panel, triangles—Mg$_{99.5}$Fe$_{0.5}$SiO$_3$; diamonds—Mg$_{99.5}$Fe$_{0.5}$SiO$_3$. Above ~70 GPa, the isomer shift between Fe$^{2+}$ and Fe$^{3+}$ sites changes little. At low pressure, the slower oscillations in the time spectrum clearly indicate smaller nuclear level splittings for all sites. The time spectra were evaluated with the CONUSS program to provide quadrupole splittings, weights, and isomer shifts of each Fe site (Sturhahn, 2000). Circles—experimental time spectra; solid lines—best calculated time spectra. The data were taken from Jackson et al. (2005a).
Figure 12, we show the pressure dependence of the quadrupole splittings of the three Fe sites in Pn. The increase in the splitting was explained by the compression of the perovskite lattice. A change in the pressure dependence of the isomer shift between Fe\textsuperscript{2+} and Fe\textsuperscript{3+} around 70 GPa possibly indicates a change in the Fe\textsuperscript{3+} spin state (Jackson et al., 2005a). X-ray emission spectroscopy has also been applied to probe the spin state of Fe in Pn (Badro et al., 2004; Li et al., 2004), Al-bearing Pn (Li et al., 2004), and (Mg,Fe)O ferropericlase (Badro et al., 2003; Lin et al., 2005a). In contrast to X-ray emission spectroscopy, SMS can distinguish valences in addition to the spin states of Fe. Specifically, SMS data provide us with different Fe sites characterized by isomer shift and quadrupole splitting.

CONCLUSION

We introduced two particular nuclear resonant scattering techniques that are applied to a variety of problems in condensed-matter physics, material science, geophysics, biophysics, and chemistry. In this contribution, we focused on the geophysical applications. The NRIXS and SMS methods have prospered with the commissioning of third-generation synchrotron radiation sources. We expect even greater potential when the brilliance of these sources is further increased by optimization of undulator technology or operating parameters of the storage ring. If fourth-generation sources (X-ray lasers) become a reality at sub-Angström wavelengths, orders of magnitude increases in spectral flux density could lead to tremendous opportunities for the “flux-hungry” nuclear resonant and inelastic X-ray scattering techniques.

The study of planetary interiors encompasses a wide area of research activity. At present, the amount of available facts is far too limited to arrive at definite conclusions about the status quo and the evolutionary history of our planet. Experimental tools that provide information about candidate materials under high-pressure and high-temperature conditions are invaluable in progressing with this task. In this chapter, we have demonstrated how nuclear resonant scattering methods can contribute to the study of Earth materials like iron and iron-bearing compounds. The assembly of a database of sound velocities, Gruneisen parameters, and electronic properties related to valence and spin state of Fe has just begun. Over the next decade, we anticipate a further increase in available X-ray intensity, which will permit more accurate measurements. In addition, the synergy of nuclear resonant scattering methods with other X-ray techniques, e.g., X-ray diffraction for in situ density determination, will be another crucial step toward improved data reliability in the high-pressure, high-temperature sector.

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REFERENCES CITED


Barla, A., Sanchez, J.P., Aksungur, A., Lengsdorf, R., Plessel, J., Doyle, B.P., Rüffer, R., and Abd-Elmeguid, M.M., 2005a, Delocalization of the U\textsuperscript{5f} magnetic moments in UI\textsubscript{1-x}S\textsubscript{x}N\textsubscript{2} and UN\textsubscript{1-x}S\textsubscript{x}N\textsubscript{2} under high pressure: Journal of Physics: Condensed Matter, v. 17, p. S859–S870, doi: 10.1088/0953-8984/17/11/015.


Crack, R., and Cohen, R.E., 2005, Effect of chemistry on the stability and elasticity of the perovskite and post-perovskite phases in the MgSiO\textsubscript{3}-FeSiO\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} system and implications for the lowermost mantle: Geophysical Research Letters, v. 32, L16310, doi: 10.1029/2005GL023164.


Lin, J.-F., Sturhahn, W., Zhao, J., Shen, G., Mao, H.-K., and Hemley, R.J., 2005b, Sound velocities of hot dense iron: Birch’s law revisited: Science,


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