Magnetic transition and sound velocities of Fe₃S at high pressure: implications for Earth and planetary cores

Jung-Fu Lin[a,*], Yingwei Fei[a,1], Wolfgang Sturhahn[b,2], Jiyong Zhao[b,3],
Ho-kwang Mao[a,4], Russell J. Hemley[a,5]

[a]*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015, United States*
[b]*Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, United States*

Abstract

Magnetic, elastic, thermodynamic, and vibrational properties of the most iron-rich sulfide, Fe₃S, known to date have been studied with synchrotron Mössbauer spectroscopy (SMS) and nuclear resonant inelastic X-ray scattering (NRIXS) up to 57 GPa at room temperature. The magnetic hyperfine fields derived from the time spectra of the synchrotron Mössbauer spectroscopy show that the low-pressure magnetic phase displays two magnetic hyperfine field sites and that a magnetic collapse occurs at 21 GPa. The magnetic to non-magnetic transition significantly affects the elastic, thermodynamic, and vibrational properties of Fe₃S. The magnetic collapse of Fe₃S may also affect the phase relations in the iron–sulfur system, changing the solubility of sulfur in iron under higher pressures. Determination of the physical properties of the non-magnetic Fe₃S phase is important for the interpretation of the amount and properties of sulfur present in the planetary cores. Sound velocities of Fe₃S obtained from the measured partial phonon density of states (PDOS) for ^{57}Fe incorporated in the alloy show that Fe₃S has higher compressional and shear wave velocity than those of hcp-Fe and hcp-Fe$_{0.92}$Ni$_{0.08}$ alloy under high pressures, making sulfur a potential light element in the Earth's core based on geophysical arguments. The V_P and V_S of the non-magnetic Fe₃S follow a Birch's law trend whereas the slopes decrease in the magnetic phase, indicating that the decrease of the magnetic moment significantly affects the sound velocities. If the Martian core is in the solid state containing 14.2 wt.% sulfur, it is likely that the non-magnetic Fe₃S phase is a dominant component and that our

measured sound velocities of Fe_3S can be used to construct the corresponding velocity profile of the Martian core. It is also conceivable that Fe_3P and Fe_3C undergo similar magnetic phase transitions under high pressures.

1. Introduction

Iron is the most abundant constituent of the Earth's core [1]. Geophysical and cosmochemical studies suggest that the Earth's outer core also contains certain amount of light element(s) [1–5]. Light element(s) may be present in the inner core, because the differences in the density and sound velocity between solid Fe and the inner core may be as much as 5% [4]. Since the bulk sound velocity of the outer core is 3% higher than that of liquid iron [4], the presence of a major light element in the outer core should reduce the density yet increase the bulk sound velocity of liquid iron [2,4,5]. Sulfur is believed to be an alloying light element in iron-rich planetary cores such as those of the Earth and Mars [2,5–14]. Based on cosmochemical and geophysical arguments, it has been proposed that the Martian core contains 14.2 wt.% sulfur [6,7]. Although it is still not clear if Mars has a solid or liquid core, recent studies have suggested that Mars could have a liquid metallic iron–sulfur outer core together with a solid inner core [11–14].

High-pressure and high-temperature experiments up to 25 GPa and 1500 K in the iron–sulfur binary system have shown that a small amount of sulfur can be dissolved into solid iron. Although the solubility of sulfur in solid iron is only about 1 at.% at 25 GPa, it has been suggested that a substantial amount of sulfur may be incorporated in the Earth's inner core [8]. On the other hand, iron-rich iron–sulfur compounds, such as Fe_3S and Fe_2S, have been synthesized at subsolidus temperatures and high pressures [9,10]. The formation of those intermediate iron–sulfur compounds significantly changes the binary phase diagram that melts incongruently. If sulfur is a major light element in the iron-bearing planetary cores, Fe_3S could be a stable phase together with iron in the solid cores [10]. Therefore, it is important to understand the physical properties of Fe_3S under high pressures.

Fe_3S with 16.1 wt.% sulfur is the most iron-rich iron sulfide known to date in the iron–sulfur system. Fe_3S forms at 21 GPa and 1300 K and has a tetragonal cell (space group $I\bar{4}$) [10]. In situ X-ray diffraction study showed that Fe_3S is stable in the tetragonal structure up to 42.5 GPa [10], whereas theoretical calculations predicted that Fe_3S in cubic $AuCu_3$-type structure is stable at high pressure [15]. Recently, a high-spin to low-spin electronic transition in Fe_3S has also been observed at pressures around 20–25 GPa using X-ray emission spectroscopy [16].

In this study, we used synchrotron Mössbauer spectroscopy (SMS) and nuclear resonant inelastic X-ray scattering (NRIXS) to study the magnetic, elastic, thermodynamic, and vibrational properties of Fe_3S in a diamond anvil cell (DAC) up to 57 GPa [17–24]. Magnetic hyperfine parameters of Fe_3S are derived from analyses of the SMS time spectra whereas the compressional (V_P) and shear wave velocities (V_S) and shear modulus (G) of Fe_3S are obtained from the measured partial phonon density of states (PDOS) for ^{57}Fe incorporated in the alloy [21–24].

2. Experiments

The sample, ^{57}Fe-enriched Fe_3S (approximately 65% enrichment) in the tetragonal structure, was synthesized in a multianvil apparatus at the Geophysical Laboratory, Carnegie Institution of Washington. ^{57}Fe-enriched iron (Fe) and troilite (FeS) were mixed as the starting materials, using the stoichiometric composition of Fe_3S. The mixture was loaded into a MgO capsule and heated with a rhenium heater at 22 GPa and 1300 K for 24 h [9,10]. Electron microprobe and X-ray diffraction analyses showed that the quenched sample had the stoichiometric composition of Fe_3S and was in tetragonal structure (space group $I\bar{4}$).

The sample was loaded into the sample chamber of a DAC with flat diamonds with the culet size of 300 μm. A beryllium gasket was pre-indented to a thickness of 30 μm and a hole of 250 μm was drilled in it. Subsequently, an amorphous boron–epoxy mixture (4:1 by weight) was inserted into the drilled hole and a smaller hole of 80 μm in diameter was drilled and used as the sample chamber [25]. A few ruby chips were placed on top of the sample for pressure measurement according to the R_1 ruby luminescence peak with a non-hydrostatic pressure scale [26]. The pressure uncertainly (1σ) was estimated from multiple pressure measurements.

SMS and NRIXS experiments were carried out at the undulator beamline 3-ID of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A high-resolution monochromator with 1 meV resolution was used to scan the energy range of ± 80 meV around the nuclear resonant energy of 14.4125 keV of ^{57}Fe in steps of 0.25 meV. The focused X-ray beam was less than 10 μm in diameter. The Fe-$K_{\alpha,\beta}$ fluorescence radiation, emitted with time delay relative to the incident X-ray pulses, was collected by three avalanche photodiode detectors, and the fourth detector at the end of the forward direction was used to record synchrotron Mössbauer spectra. The counting time for each NRIXS spectrum was approximately 1 h, and 10 to 15 spectra were collected at the same pressure and added. The high-energy resolution of 1 meV is essential for deriving accurate Debye sound velocities (V_D) from the PDOS (the Debye parabola is best constrained at the lower energy limit) [21–24]. The collection time of the SMS for each time spectrum was approximately 30 min. In the SMS experiments, the time spectrum is a collection of events which reveal the time span between arrival of the synchrotron radiation pulses and arrival of a scattered photon. The time spectra were recorded by an avalanche photodiode detector in the forward direction. Time spectra of Fe₃S were evaluated with the COherent NUclear resonant Scattering by Single crystals (CONUSS) programs to permit derivation of magnetic hyperfine parameters [22,23]. Elastic, thermodynamic, and vibrational properties of Fe₃S under high pressures were derived by evaluating the energy spectra using the PHOnon Excitation by Nuclear Inelastic scattering of X-rays (PHOENIX) programs [22,23].

3. Results and discussions

The SMS time spectra and the PDOS of Fe₃S were measured up to 57 GPa at 300 K (Figs. 1–3; Table 1). The time spectra reveal that Fe₃S undergoes a magnetic to non-magnetic transition at approximately 21 GPa from a low-pressure magnetically ordered state to a high-pressure magnetically disordered state (Figs. 1 and 2). The magnetic transition is found to be reversible with pressure. The magnetic hyperfine fields derived from the time spectra using the CONUSS programs [22,23] show that the low-pressure magnetic phase displays two magnetic hyperfine field sites and that a magnetic collapse occurs at 21 GPa (Fig. 2), consistent with a high-spin to low-spin electronic transition in Fe₃S observed at pressures around 20–25 GPa using X-ray
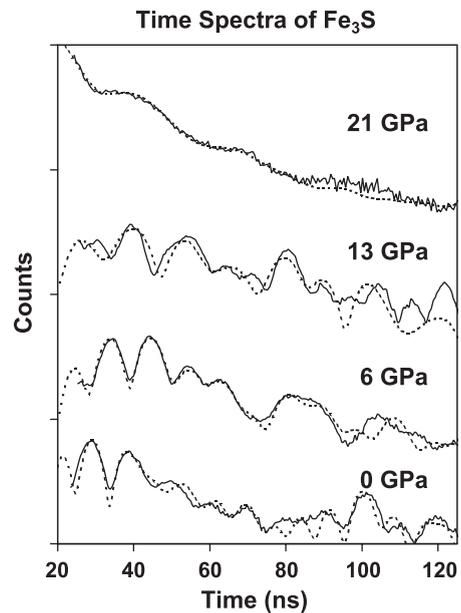
Fig. 1. Representative time spectra of the SMS of Fe₃S under high pressures. Fe₃S undergoes a magnetic to non-magnetic transition at approximately 21 GPa. The alloy was in the magnetically ordered state at 0, 6, 13, and 16 GPa and in magnetically disordered state at 21, 28, 38, 45, and 57 GPa. The decay time is dictated by the nuclear lifetime of the ^{57}Fe nuclei. Observed oscillations in the time spectra originate from the nuclear level splitting [21–23]. The time spectra of Fe₃S were evaluated with the CONUSS programs to derive magnetic hyperfine parameters [22,23] (see Fig. 2). Solid curves: experimental time spectra; dashed curves: time spectra calculated from the CONUSS programs.

Magnetic hyperfine fields of Fe₃S
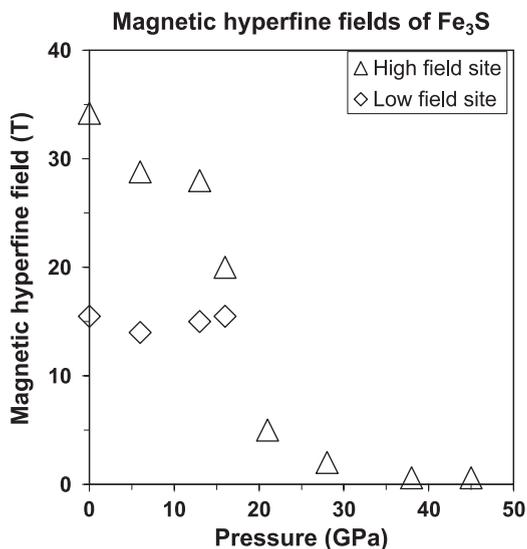
Fig. 2. Magnetic hyperfine fields of Fe₃S under high pressures. The low-pressure magnetic phase displays two magnetic field sites: high and low magnetic field sites. The high magnetic field (open triangles) decreases with increasing pressure whereas the low magnetic field (open diamonds) remains almost constant. A magnetic collapse occurs at approximately 21 GPa. The large thickness leads to line broadening and thus diminished resolving power. Our samples were optimized for the NRIXS experiments which require large thickness and enrichment for improved counting rates. Future experiments with thinner samples may be able to better resolve the different sites in Fe₃S under pressure.

emission spectroscopy [16]. This transition may also be associated with a structural transition [15,16], although it is not observed in the X-ray diffraction study up to 42.5 GPa by Fei et al. [10]. The magnetic collapse has been found to contribute to a substantial volume reduction due to the shortening of ionic distances as revealed in studies of the high-pressure magnetic transition of hematite (Fe_2O_3) [27,28]; however, the compression curve of Fe_3S to 42.5 GPa did not show any discontinuity at the magnetic phase transition pressure of 21 GPa [10].

A quasi-harmonic model was used to derive the PDOS [21–24]. The V_D of Fe_3S was derived from parabolic fitting of the low-energy slope of the PDOS in the range of 3.5 to 14 meV after applying a correction factor, the cube root of the ratio of the mass of the nuclear resonant isotope (^{57}Fe) to the average atomic mass of the sample [24]. While the obtained PDOS gives only part of the lattice dynamics of the

material, the low-energy portion of the PDOS provides the bulk V_D. The method of extracting the V_D from PDOS, based on the quasi-harmonic approximation, has been tested for different ^{57}Fe-bearing materials with Debye-like low-frequency dynamics [24] and used to derive the sound velocities of Fe–Ni and Fe–Si alloys under high pressures [18]. The vibrational kinetic energy (E_k), zero point energy (E_z), vibrational heat capacity (C_{vib}), vibrational entropy (S_{vib}), and other thermodynamic and vibrational parameters were also calculated by integrating the

PDOS of Fe₃S at high pressure
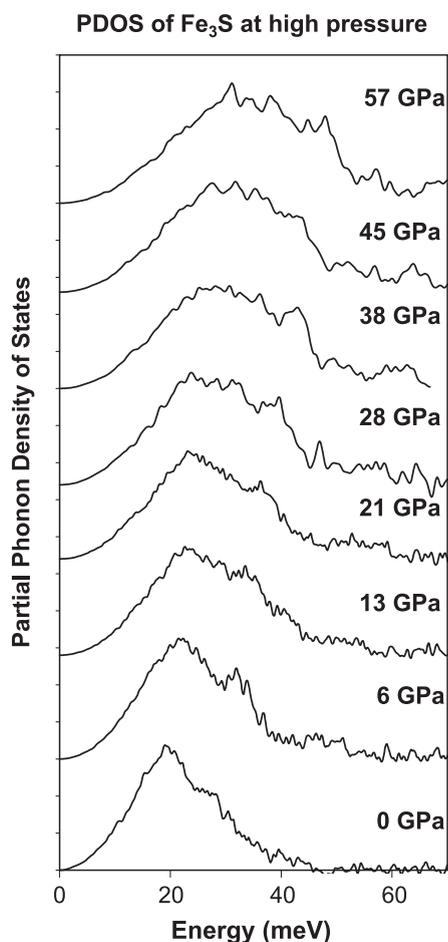
Fig. 3. PDOS of Fe₃S under high pressures. The spectral features of PDOS are shifted to higher energies with increasing pressure, whereas the energy shift is not very significant across the magnetic transition from 13 to 21 GPa. The low-energy slope of the PDOS in the range of 3.5 to 14 meV is used to derive the bulk Debye sound velocity.

Table 1
Elastic, vibrational, and thermodynamic parameters of Fe_3S under high pressures obtained from NRIXS study in a DAC

P (GPa)	0	6.1 (0.4)	13.1 (0.6)	21.3 (0.7)	28.0 (2.1)	37.7 (1.9)	45.2 (2.3)	57.1 (2.9)
V_P (km/s)	5.482 (0.083)	5.976 (0.085)	6.358 (0.089)	6.562 (0.095)	6.811 (0.101)	7.142 (0.104)	7.371 (0.107)	7.797 (0.113)
V_S (km/s)	2.558 (0.006)	2.987 (0.010)	3.237 (0.011)	3.212 (0.009)	3.346 (0.033)	3.519 (0.022)	3.646 (0.024)	3.883 (0.032)
G (GPa)	46.0 (0.2)	65.2 (0.4)	79.4 (0.4)	81.2 (0.3)	90.6 (1.6)	103.9 (1.0)	114.3 (1.1)	135.5 (1.8)
V_D (km/s)	2.880 (0.006)	3.351 (0.009)	3.627 (0.009)	3.607 (0.007)	3.757 (0.032)	3.951 (0.019)	4.092 (0.019)	4.357 (0.027)
E_k (meV/atom)	13.91 (0.17)	14.30 (0.15)	14.49 (0.13)	14.55 (0.12)	14.70 (0.30)	14.75 (0.15)	14.78 (0.15)	15.22 (0.20)
D_{av} (N/m)	119.7 (6.6)	175.9 (6.0)	198.9 (5.0)	213.1 (4.9)	237.0 (12.0)	258.2 (5.0)	291.3 (6.2)	323.2 (7.8)
f_{LM}	0.6153 (0.0012)	0.7079 (0.0012)	0.7473 (0.0011)	0.7581 (0.0009)	0.7760 (0.0019)	0.7992 (0.0012)	0.8143 (0.0011)	0.8336 (0.0013)
$f_{TM,T=0}$	0.8960 (0.0005)	0.9116 (0.0004)	0.9183 (0.0004)	0.9200 (0.0003)	0.9244 (0.0008)	0.9282 (0.0004)	0.9311 (0.0004)	0.9360 (0.0005)
E_Z (meV/atom)	5.45 (0.13)	6.52 (0.11)	7.01 (0.09)	7.22 (0.09)	7.67 (0.23)	8.01 (0.11)	8.45 (0.12)	8.98 (0.15)
C_{vib} (k_B/atom)	2.811 (0.023)	2.733 (0.020)	2.699 (0.017)	2.680 (0.016)	2.641 (0.039)	2.611 (0.021)	2.559 (0.020)	2.529 (0.026)
S_{vib} (k_B/atom)	3.898 (0.021)	3.427 (0.018)	3.208 (0.016)	3.142 (0.014)	2.971 (0.032)	2.821 (0.019)	2.658 (0.017)	2.526 (0.021)

Lamb–Mössbauer factor, f_{LM}; kinetic energy, E_k; mean force constant, D_{av}; Lamb–Mössbauer factor at $T=0$, $f_{TM,T=0}$; kinetic energy at $T=0$, E_Z; vibrational specific heat, C_{vib}; vibrational entropy, S_{vib}; Boltzmann constant, k_B. We note that these values only represent the contribution of the Fe sublattice.

PDOS which represent the contribution of the Fe sublattice [20,21].

The procedure of deriving V_P, V_S, and G from the V_D and equation of state (EOS) parameters, namely, the adiabatic bulk modulus (K_S) and density (ρ), has been described previously by Mao et al. [17] and Lin et al. [18]. The EOS of Fe_3S determined by Fei et al. [10] is used in the calculations. We note that V_S is relatively insensitive to the differences in the EOS data. Therefore, the NRIXS technique is particular good at constraining V_S with a precise measurement of V_D. Since a magnetic transition has been observed in this study, an EOS for the high-pressure non-magnetic phase may be needed in the future to derive the sound velocities more accurately if the magnetic transition is related to a structural transition that contributes significantly to the volume change.

The K_S, ρ, and V_D of the Fe_3S are used to solve for the aggregate V_P, V_S, and G [10,16,18,24]. The V_P and V_S of the non-magnetic Fe_3S follow a Birch's law trend [1], whereas the slopes decrease in the magnetic phase, indicating that the decrease of the magnetic moment significantly affects the sound velocities. Fe_3S has higher V_P and V_S than those of hcp-Fe and hcp-$Fe_{0.92}Ni_{0.08}$ alloy under high pressures, whereas the V_P and V_S of Fe_3S are very similar to those of an hcp-$Fe_{0.85}Si_{0.15}$ alloy [17,18] (Fig. 4). Extrapolation of the V_P and V_S of the non-magnetic Fe_3S to inner core densities indicates that the V_P and V_S are higher than that of the inner core;

however, a temperature dependence on the V_P and V_S has to be further considered. Our results indicate that sulfur alloyed with iron increases the V_P and V_S
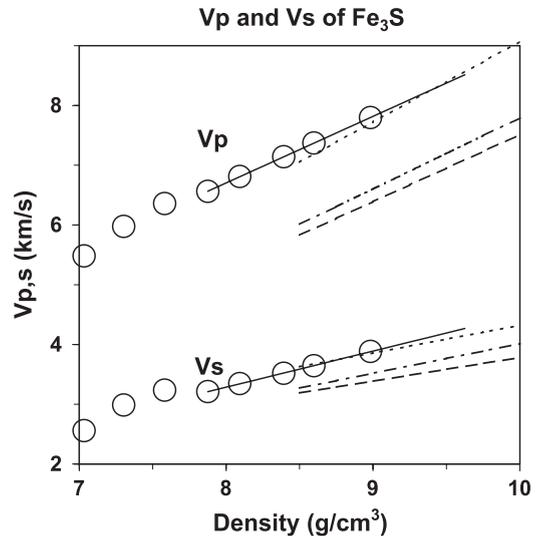
Fig. 4. Comparison of aggregate compressional (V_P) and shear wave (V_S) velocities of Fe_3S, hcp-Fe, hcp-$Fe_{0.92}Ni_{0.08}$, and hcp-$Fe_{0.85}Si_{0.15}$ at high pressures measured from the same NRIXS technique under high pressures [17,18] (see Table 1 for details). The sound velocities of Fe_3S change significantly across the magnetic to non-magnetic phase transition at approximately 21 GPa. Solid lines: linear fits to the V_P and V_S of the non-magnetic phase; dashed lines with dots: extrapolation of hcp-Fe [17]; long dashed lines: extrapolation of hcp-$Fe_{0.92}Ni_{0.08}$ [18]; short dashed line: extrapolation of hcp-$Fe_{0.85}Si_{0.15}$ [18].

of iron under high pressures, making it an eligible light element in the Earth's core based on geophysical arguments [2,4,5]. We note that the increase in the V_P and V_S of Fe_3S is mainly caused by the density decrease of adding sulfur to iron, because the differences in the V_P and V_S of hcp-Fe and Fe_3S are small when plotted against pressure. This is similar to the effect observed on an hcp-$Fe_{0.85}Si_{0.15}$ alloy (sulfur and silicon have similar atomic mass) [18]. In situ X-ray absorption and diffraction experiments on liquid Fe and Fe–S alloys revealed that the addition of sulfur to liquid iron significantly affected the local structure and the incompressibility of iron, making liquid Fe–S alloy of a lower density and bulk sound velocity ($V_\phi = \sqrt{K_S/\rho}$) than pure liquid iron [7,29,30]. Since the pressure and temperature range of the study is very limited [7,29,30], it is not clear whether or not such an effect persists to Earth's core conditions. It has been shown that high temperature has a strong effect on the sound velocities of hcp-Fe; the V_P and V_S of hcp-Fe decrease significantly with increasing temperature under high pressures [20]. Such strong temperature dependence on the V_P and V_S must be further considered in understanding the V_P and V_S of the Fe–S alloys.

The observed magnetic transition also changes the elastic, thermodynamic, and vibrational properties of Fe_3S; across the magnetic transition, the slopes of the Debye sound velocity, Lamb–Mössbauer factor, Lamb–Mössbauer factor at $T=0$ K, kinetic energy, kinetic energy at $T=0$ K, mean force constant, vibrational specific heat, and vibrational entropy changed significantly as a function of pressure. These thermodynamic and vibrational parameters can be applied to test lattice dynamic calculations on iron alloys [17,19]. The observed change in physical properties of Fe_3S would affect the interpretation of the amount and properties of sulfur present in the planetary cores. Since Fe_3S is in the non-magnetic state at which it was synthesized at about 21 GPa and 1300 K [10], studies of the non-magnetic phase of Fe_3S are more relevant than those of the magnetic phase for understanding the properties of the alloying materials under the conditions of planetary cores where the high-pressure and high-temperature conditions ensure the presence of the non-magnetic ordering state. Recent studies have shown that the pressure of the

Martian core is above 20 GPa [7,11,12] and thus above the pressure of the magnetic transition in Fe_3S. If the Martian core is in the solid state containing 14.2 wt.% sulfur [6,7], it is likely that the non-magnetic Fe_3S phase is a dominant component, and that our measured sound velocities of Fe_3S can be used to construct the velocity profile of the Martian core. It is conceivable that the magnetic collapse of Fe_3S and other iron–sulfur compounds (Fe_2S, Fe_3S_2) would affect the binary phase diagram of the iron–sulfur system, changing the solubility of sulfur in iron and the melting curve of the Fe–S system under higher pressures [8]. Theoretical calculations on the electronic structures of iron–sulfur compounds have predicted that sulfur undergoes an electronic transition with increasing compression, leading to a solid solution behavior between Fe and FeS [31,32]. Further in situ study of the binary phase diagram, the crystal structures, and elastic properties of the Fe–S system will provide vital information on the physical properties and stability of the iron–sulfur phases under high pressures and temperatures.

Iron–nickel phosphide [$(Fe,Ni)_3P$] has been found in many iron and stony-iron meteorites [33,34]. Because Fe_3S, Fe_3P, and Ni_3P are all isostructural (space group $I\bar{4}$) under ambient conditions [10,35], it is conceivable that Fe_3P and Ni_3P may undergo similar phase transitions under high pressures, making phosphorus easy to incorporate into Fe_3S at high pressures. Furthermore, carbon is proposed to be a potential light element in the Earth's core [36]. Fe_3C in the orthorhombic structure (space group $Pnma$) is predicted to undergo a similar magnetic phase transition from a low-pressure magnetically ordered state to a high-pressure magnetically disordered state [35]. The thermal expansion coefficients and compressibilities are expected to be very different in the magnetic and non-magnetic states of Fe_3C, affecting the interpretation of carbon in the Earth's core [36–38]. However, in situ X-ray diffraction experiments showed that Fe_3C was stable in the orthorhombic structure up to 70 GPa [38,39]. Further study of the magnetic and elastic properties across the predicted magnetic transition of Fe_3C under high pressures is desirable for improved prediction of the amount of carbon in the Earth's core.

4. Conclusions

We have studied the magnetic, elastic, thermodynamic, and vibrational properties of the most iron-rich iron–sulfur compound, Fe_3S, with synchrotron Mössbauer spectroscopy and nuclear resonant inelastic X-ray scattering up to 57 GPa at room temperature. The time spectra of the synchrotron Mössbauer spectroscopy revealed that Fe_3S undergoes a magnetic collapse at approximately 21 GPa from a low-pressure magnetically ordered state to a high-pressure magnetically disordered state. The magnetic transition significantly affects the elastic, thermodynamic, and vibrational properties of Fe_3S and may also be associated with a structural transition. The observed magnetic transition would affect the interpretation of the amount and properties of sulfur present in the planetary cores. Compressional and shear wave velocities of Fe_3S are higher than those of hcp-Fe and hcp-$Fe_{0.92}Ni_{0.08}$ alloy under high pressures, making sulfur a potential light element in the Earth's core based on geophysical constrains. If the Martian core is in the solid state, the non-magnetic Fe_3S phase is likely a dominant constitute and that the sound velocities of Fe_3S determined in this study can be used to constrain the velocity profile of the Martian core. Other iron-light element compounds, such as Fe_3P, Fe_3C, and Ni_3S, may also undergo a structural and/or magnetic transition under high pressures, affecting our understanding of these potential light elements in planetary cores.

Acknowledgments

References

[1] F. Birch, Elasticity and constitution of the Earth's interior, J. Geophys. Res. 57 (1952) 227–286.

[2] J.P. Poirier, Light elements in the Earth's core: a critical review, Phys. Earth Planet. Inter. 85 (1994) 319–337.

[3] W.F. McDonough, S.S. Sun, The composition of the Earth, Chem. Geol. 120 (1995) 223–253.

[4] W.W. Anderson, T.J. Ahrens, An equation of state for liquid iron and implications for the Earth's core, J. Geophys. Res. 99 (1994) 4273–4284.

[5] J. Li, Y. Fei, Experimental constraints on core composition, Treatise Geochem. 2 (2003) 521–546.

[6] G. Dreibus, H. Wänke, Mars, a volatile-rich planet, Meteoritics 20 (1985) 367–381.

[7] P.S. Balog, R.A. Secco, D.C. Rubie, D.J. Frost, Equation of state of liquid Fe-10wt.%S: implications for the metallic cores of planetary bodies, J. Geophys. Res. 108 (2003) 2124.

[8] J. Li, Y. Fei, H.K. Mao, K. Hirose, S.R. Shieh, Sulfur in the Earth's inner core, Earth Planet. Sci. Lett. 193 (2001) 509–514.

[9] Y. Fei, C.M. Bertka, L.W. Finger, High-pressure iron–sulfur compound, Fe_3S_2, and melting relations in the Fe–FeS system, Science 275 (1997) 1621–1623.

[10] Y. Fei, J. Li, C.M. Bertka, C.T. Prewitt, Structure type and bulk modulus of Fe_3S, a new iron–sulfur compound, Am. Mineral. 85 (2000) 1830–1833.

[11] C.M. Bertka, Y. Fei, Implications of mars pathfinder data for the accretion history of the terrestrial planets, Science 281 (1998) 1838–1840.

[12] F. Sohl, T. Spohn, The interior structure of Mars: implications from SNC meteorites, J. Geophys. Res. 102 (1997) 1613–1635.

[13] D.J. Stevenson, Mars' core and magnetism, Nature 412 (2001) 214–219.

[14] C.F. Yoder, et al., Fluid core size of Mars from detection of the solar tide, Science 300 (2003) 299–303.

[15] D.M. Sherman, Stability of possible Fe–FeS and Fe–FeO alloy phases at high pressure and the composition of the Earth's core, Earth Planet. Sci. Lett. 132 (1995) 87–98.

[16] G. Shen, J.F. Lin, Y. Fei, H.K. Mao, M. Hu, P. Chow, Magnetic and structural transition in Fe_3S at high pressures, Eos. Trans. AGU 84 (46) (2003) F1548–F1549 (Fall Meet. Suppl., Abstract V31E-0961).

[17] H.K. Mao, J. Xu, V.V. Struzhkin, J. Shu, R.J. Hemley, W. Sturhahn, M.Y. Hu, E.E. Alp, L. Vocadlo, D. Alfe, G.D. Price, M.J. Gillan, M. Schwoerer-Böhning, D. Häusermann, P. Eng, G. Shen, H. Giefers, R. Lübbers, G. Wortmann, Phonon density of states of iron up to 153 gigapascals, Science 292 (2001) 914–916.

[18] J.F. Lin, V.V. Struzhkin, W. Sturhahn, E. Huang, J. Zhao, M.Y. Hu, E.E. Alp, H.K. Mao, N. Boctor, R.J. Hemley, Sound velocities of iron–nickel and iron–silicon alloys in the Earth's core, Geophys. Res. Lett. 30 (2003) 2112.

[19] G. Shen, W. Sturhahn, E.E. Alp, J. Zhao, T.S. Toellner, V.B. Prakapenka, Y. Meng, H.K. Mao, Phonon density of states in iron at high pressures and high temperatures, Phys. Chem. Minerals 31 (2004) 353–359.

[20] J.F. Lin, W. Sturhahn, J. Zhao, G. Shen, H.K. Mao, R.J. Hemley, Absolute temperature measurement in a laser-heated diamond anvil cell, Geophys. Res. Lett. 31 (2004) DOI:10.1029/2004GLO20599.

[21] W. Sturhahn, T.S. Toellner, E.E. Alp, X. Zhang, M. Ando, Y. Yoda, S. Kikuta, M. Seto, C.W. Kimball, B. Dabrowski, Phonon density of states measured by inelastic nuclear resonant scattering, Phys. Rev. Lett. 74 (1995) 3832–3835.

[22] W. Sturhahn, Conuss and phoenix: evaluation of nuclear resonant scattering data, Hyperfine Interact. 125 (2000) 149–172.

[23] W. Sturhahn, Nuclear resonant spectroscopy, J. Phys., Condens. Matter 16 (2004) S497–S530.

[24] M. Hu, W. Sturhahn, T.S. Toellner, P.D. Mannheim, D.E. Brown, J. Zhao, E.E. Alp, Measuring velocity of sound with nuclear resonant inelastic X-ray scattering, Phys. Rev., B 67 (2003) 094304.

[25] J.F. Lin, J. Shu, H.K. Mao, R.J. Hemley, G. Shen, Amorphous boron gasket in diamond anvil cell research, Rev. Sci. Instrum. 74 (2003) 4732–4736.

[26] H.K. Mao, P.M. Bell, J.W. Shaner, D.J. Steinberg, Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R_1 fluorescence pressure gauge from 0.06 to 1 Mbar, J. Appl. Phys. 49 (1978) 3276–3283.

[27] G.kh. Rozenberg, L.S. Dubrovinsky, M.P. Pasternak, O. Naaman, T. Le Bihan, R. Ahuja, High-pressure structural studies of hematite Fe_2O_3, Phys. Rev., B 65 (2002) 064112.

[28] J. Badro, G. Fiquet, V.V. Struzhkin, M. Somayazulu, H.K. Mao, G. Shen, T. Le Bihan, Nature of the high-pressure transition in Fe_2O_3 hematite, Phys. Rev. Lett. 89 (2002) 205504.

[29] C. Sanloup, F. Guyot, P. Gillet, Y. Fei, Physical properties of liquid Fe alloys at high pressure and their bearings on the nature of metallic planetary cores, J. Geophys. Res. 107 (2002) 2272.

[30] C. Sanloup, F. Guyot, P. Gillet, G. Fiquet, R.J. Hemley, M. Mezouar, I. Martinez, Structural changes in liquid Fe at high pressures and high temperatures from synchrotron X-ray diffraction, Europhys. Lett. 52 (2000) 151–157.

[31] D.A. Boness, The electronic band structures of iron, sulfur, and oxygen at high pressures and the Earth's core, J. Geophys. Res. 95 (1990) 21721–21730.

[32] D.M. Sherman, Chemical bonding in the outer core: high-pressure electronic structures of oxygen and sulfur in metallic iron, J. Geophys. Res. 96 (1991) 18029–18036.

[33] P.R. Buseck, Phosphide from meteorites; barringerite, a new iron–nickel mineral, Science 165 (1969) 169–171.

[34] R. Skala, M. Drabek, Nickelphosphide from the vicenice octahedrite: Rietveld crystal structure refinement of synthetic analogue, Mineral. Mag. 67 (2003) 783–792.

[35] Yu.N. Vorobyev, Ye.P. Yelsukov, On the hyperfine interaction parameters in Fe3P 25 years later, Phys. Status Solidi, B Basic Res. 205 (1998) R13–R14.

[36] B. Wood, Carbon in the core, Earth Planet. Sci. Lett. 117 (1993) 593–607.

[37] L. Vocadlo, J. Brodholt, D.P. Dobson, K.S. Knight, W.G. Marshall, G.D. Price, I.G. Wood, The effect of ferromagnetism on the equation of state of Fe_3C studied by first-principles calculations, Earth Planet. Sci. Lett. 203 (2002) 567–575.

[38] H.P. Scott, Q. Williams, E. Knittle, Stability and equation of state of Fe_3C to 73 GPa: implications for carbon in the Earth's core, Geophys. Res. Lett. 28 (2001) 1875–1878.

[39] J. Li, H.K. Mao, Y. Fei, E. Gregoryanz, M. Eremets, C.S. Zha, Compression of Fe_3C to 30 GPa at room temperature, Phys. Chem. Miner. 29 (2002) 166–169.