Revision 1

A cotunnite-type new high-pressure phase of Fe$_2$S

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ABSTRACT

We examined pressure-induced phase transitions in Fe$_2$S based on high-pressure and -temperature X-ray diffraction measurements in a laser-heated diamond-anvil cell. Fe$_2$S is not stable at ambient pressure but is known to form above 21 GPa with the Fe$_2$P-type (C22) structure. The
present experiments demonstrate a novel phase transition in Fe$_2$S from the C22 to C23 phase with the Co$_2$P-type cotunnite structure above ~30 GPa. Our experiments also show the transformation from the C23 to C37 (Co$_2$Si-type) phase above ~130 GPa. While these C23 and C37 structures exhibit the same crystallographic symmetry (orthorhombic Pnma), the coordination number of sulfur increases from nine in C23 to ten in C37. Such a sequence of pressure-induced phase transitions in Fe$_2$S, C22 $\rightarrow$ C23 $\rightarrow$ C37, are similar to those of Fe$_2$P, while they are not known in oxides and halogens that often adopt the C23 cotunnite-type structure. The newly found cotunnite-type Fe$_2$S phase could be present in solid iron cores of planets including Mars.

**Keywords:** iron sulfide, high pressure, core, phase transition, cotunnite-type structure, Mars

**INTRODUCTION**

Sulfur is frequently observed in iron meteorites and could be a common impurity element in planetary iron cores in our solar system and beyond. Solid iron sulfide can be an important constituent in such metallic cores, although it is not dense enough for the Earth’s inner core. Phase relations in Fe-S alloy are of great importance to understand metallic cores of terrestrial planets. While Fe–FeS is a simple binary eutectic system at ambient pressure, intermediate compounds of Fe$_3$S, Fe$_2$S, and Fe$_3$S$_2$ form above 14–21 GPa (Fei et al. 2000). The phase relations and elastic property of Fe$_3$S have been relatively well studied (e.g. Kamada et al. 2014; Thompson et al. 2020); it does not undergo a structural phase change but decomposes into Fe + Fe$_2$S above ~250 GPa (Ozawa et al. 2013; Mori et al. 2017; Bazhanova et al. 2017). In contrast, those of Fe$_2$S and Fe$_3$S$_2$ have been little investigated so far (Tateno et al. 2019).
It is known that Fe$_2$S adopts hexagonal $P-62m$ Fe$_2$P-type (C22) structure at 22 GPa (Koch-Müller et al. 2002). The recent experiments performed by Tateno et al. (2019) observed orthorhombic $Pnma$ Co$_2$Si-type (C37) structure in a pressure range from ~190 to 306 GPa. Phase relations in Fe$_2$S remains unexplored by experiments between 22 and ~190 GPa, while theoretical calculations showed that C37 Fe$_2$S is stable between 50 and 400 GPa (Bazhanova et al. 2017). Tateno et al. (2019) reported the equation of state (EoS) of C37-type Fe$_2$S on the basis of experimental data collected at 180 to 294 GPa, demonstrating that it is elastically anisotropic with $a$-axis three times more compressible than $b$- and $c$-axes.

Iron sulfides are known to have affinities with iron phosphides (Stewart and Schmidt 2007; Gu et al. 2014). A sequence of structural phase transitions have been already examined in Fe$_2$P; hexagonal C22-type Fe$_2$P undergoes transformation to the orthorhombic Co$_2$P-type (cotunnite-structured, C23) phase above 8 GPa and further to the Co$_2$Si-type (C37) phase above 42 GPa (Nakajima et al. 2020). C23 and C37 Fe$_2$P are orthorhombic with the identical crystallographic symmetry (space group: $Pnma$) but differ in the coordination number of phosphorus, leading to 2% volume change across the phase transition. Similar isosymmetric phase transition is known in PbF$_2$ that occurs at ~10 GPa (Haines et al. 1998).

In order to reveal a sequence of phase transitions in Fe$_2$S, we carried out synchrotron X-ray diffraction (XRD) measurements in-situ at high-pressure and -temperature ($P$-$T$) to 164 GPa and 2400 K in this study. The results demonstrate a stability of cotunnite-type (C23) Fe$_2$S between ~30 and ~130 GPa at high temperatures, indicating the sequence of pressure-induced structural phase transitions (C22 $\rightarrow$ C23 $\rightarrow$ C37) which is similar to those in Fe$_2$P. The EoS of the new C23-type
Fe₂S phase is also reported. We discuss the possible presence of cotunnite-type Fe₂S in solid metallic iron cores of planets including Mars and Mercury.

**METHODS**

XRD measurements were performed at high \( P-T \) in a laser-heated diamond-anvil cell (DAC) at beamline BL10XU, SPring-8 (Hirao et al. 2020). We used diamond anvils with flat 300 \( \mu \)m or beveled 120 \( \mu \)m culet size. Two different Fe₂S samples were used for starting materials; they were synthesized by melting a mixture of Fe and FeS powder at 28 GPa and \( \sim \) 22 GPa in a multi-anvil apparatus. The former is the same as that previously used in Tateno et al. (2019) and was employed in runs #1–4. It consisted of a mixture of bcc Fe and FeS according to micro-focus X-ray diffractometer measurements using a Cu \( K\alpha \) radiation source with 30 and 100 \( \mu \)m collimators. Such observation is similar but different from that reported by Koch-Müller et al. (2002); they observed that a majority of Fe₂S grains decomposed into Fe₃S + FeS when observed under a transmission electron microscope.

In the first four runs, the sample assembly was MgO/SiO₂/Fe₂S/SiO₂, in which MgO was not in contact with Fe₂S in order to avoid possible chemical reaction at high temperature. After loading, a whole DAC was dried in a vacuum oven at 423 K for at least 1 hr to eliminate moisture in a sample chamber, and then the sample was squeezed in an argon atmosphere. In run #5, Al₂O₃ was used as a pressure medium and a pressure marker. After compression to a target pressure at room temperature, we performed heating from both sides with single-mode fiber lasers. Heating spot size was \( \sim \) 20 \( \mu \)m. Sample temperature was measured by a spectro-radiometric method. Pressure was determined at 300 K from the volume of MgO (Wu et al. 2008) or Al₂O₃ (Dewaele and Torrent...
We corrected for thermal pressure of 5% pressure increase for each temperature increase of 1000 K following previous DAC experiments on silicate (Fiquet et al. 2010) and metals (Mori et al. 2017). Such thermal pressure correction has been shown to be consistent with that considering nearly isochoric heating in the Fe-C-H (Hirose et al. 2019) and Fe-FeO systems (Oka et al. 2019). The overall pressure uncertainty was ±5% (Mori et al. 2017). Angle-dispersive XRD patterns were collected on a flat panel detector (PerkinElmer XRD0822) (runs #1–4) and a CCD detector (Bruker APEX) (run #5) (Fig. 1). A monochromatic X-ray beam energy was ~30 keV, and the incident X-ray beam size was ~6 µm in full-width at half maximum. The variations in temperature within such 6 µm area at the hot spot were less than ±10%. Collected XRD patterns were analyzed using the IPAnalyzer and PDIndexer programs (Seto et al. 2010).

We additionally performed first principles calculations by adopting the Perdew-Burke-Ernzerhof (PBE) form of generalized-gradient approximation (GGA) for the exchange-correlation functional (Perdew et al. 1996). We used Vanderbilt-type pseudopotentials (Vanderbilt 1990). The valence electron configurations and cutoff radii for pseudopotential generations are 3s²3p⁶3d⁶.5⁴s¹⁴p⁰ and 1.8 a.u. for Fe and 3s²3p⁴ and 1.7 a.u. for S (1 a.u. = 0.529177 Å). The cutoff energy for the planewave expansion is 40 Ry, and the k-point mesh was 4×8×4. A smearing technique (Methfessel and Paxton 1989) was used for integration up to the Fermi surface with a smearing parameter of 0.005 Ry. We used the variable-cell-shape damped molecular dynamics for structural optimization. The simulations were made for a unit cell including 12 (8Fe + 4S) atoms (Z = 4). Dynamical matrices were calculated on the 2×2×2 q-point mesh using density-functional perturbation theory (Giannozzi et al. 1991; Baroni et al. 2001). The vibrational contribution was
taken into account within the quasi-harmonic approximation (Wallace 1972). All calculations were performed using the Quantum-ESPRESSO package (Giannozzi et al. 2009)

RESULTS

New cotunnite-type Fe$_2$S phase

We examined the phase relations in Fe$_2$S in four separate sets of high $P$-$T$ experiments between 37 and 166 GPa (Fig. 2). In run #1, weak diffraction signal was observed from the sample when it was compressed to 56 GPa at room temperature (Fig. 1a). When it was heated to 1800 K, we observed new peaks in less than 3 min, all of which are assigned to the orthorhombic C23 structure that has not been reported in Fe$_2$S (Figs. 1b, c). Similarly, the formation and the stability of the new C23 Fe$_2$S phase were confirmed up to 115 GPa and 2300 K in run #2. In run #5, three different spots in a sample were heated with increasing load pressure. The C23 phase was formed at pressures as low as 37 GPa and 1650 K (Fig. 2).

In run #3, on the other hand, we observed broad diffraction peaks from the sample, whose structure could not be identified, before heating at 300 K and ~150 GPa (Fig. 1d). Upon heating to 1500 K at 159 GPa, the C37 phase appeared in 2 min. The diffraction peaks from C37 Fe$_2$S grew with increasing temperature to 2000 K at 163 GPa and further to 2400 K at 166 GPa. The overall XRD pattern was assigned with C37-type Fe$_2$S and MgO (Figs. 1e, f).

These observations indicate that Fe$_2$S undergoes phase transitions from the C22 (Fe$_2$P-type) to C23 (Co$_2$P-, cotunnite-type) structure above ~30 GPa and further to the C37 (Co$_2$Si-type) structure above ~130 GPa (Fig. 2).
Equation of state for C23 Fe$_2$S

These C23- and C37-type Fe$_2$S exhibited the identical crystal symmetry, but their atomic arrangements and lattice parameters are distinct (Table 1) (Tateno et al. 2019). Sulfur atom is coordinated to nine and ten iron atoms in the C23 and C37 structures, respectively (Rundqvist 1960). Upon the phase transformation from the C23 to C37 structure, the orthorhombic unit cell is shortened along $a$-axis but elongated along $b$- and $c$-axes as previously observed in Fe$_2$P (Nakajima et al. 2020).

Figure 3 shows the pressure-volume ($P$-$V$) data at 300 K for the new C23 Fe$_2$S phase. The revised compression curve for C37 Fe$_2$S is also given (Tateno et al. 2019). The unit-cell volume was experimentally collected between 25 and 106 GPa after heating (or thermal annealing at less than 1400 K) at each pressure. When collecting the $P$-$V$ data, temperature was not quenched but gradually decreased to room temperature to avoid nonhydrostatic stress in the sample. We also obtained $V_0 = 134.24$ Å$^3$ at 1 bar and 300 K by first principles calculations. Such $P$-$V$ data were fitted by the Birch-Murnaghan EoS, giving bulk modulus $K_0 = 219(4)$ GPa at zero pressure and its pressure derivative $K_0' = 4.1(2)$. We also obtained the revised EoS parameters of the C37 Fe$_2$S phase by including the present new data at 153 GPa; $K_0 = 223(6)$ GPa with $K' = 4$ (fixed), and $V_0 = 133.4(8)$ Å$^3$. The volume reduction upon C23 to C37 transition is calculated to be 0.8% at a transition pressure of 130 GPa from their EoSs (Fig. 3). Since the transition occurs in Fe$_2$S at much higher pressure, the volume change is smaller than those at similar isosymmetric phase transitions in Fe$_2$P and PbF$_2$ which involve 2.3% and 2% volume reduction at 40 and 10 GPa, respectively (Nakajima et al. 2020; Haines et al. 1998).
DISCUSSION

These results indicate that Fe$_2$S undergoes a series of structural phase transitions, C22 $\rightarrow$ C23 $\rightarrow$ C37, similar to Fe$_2$P (Dera et al. 2008; Nakajima et al. 2020). C23 is the AX$_2$ cotunnite-type structure, widely observed in oxides and halogens. Nevertheless, the C22 to C23 and the C23 to C37 transitions are hardly found in such oxides and halogens except for C22-type TiO$_2$ (note however that C23 transforms into C22 with increasing pressure in TiO$_2$ according to Dekura et al. 2011) and C37-type PbF$_2$ (Haines et al. 1998), suggesting that they do not often form in ionic materials. Alternatively, the C22 $\rightarrow$ C23 $\rightarrow$ C37 transitions may be common in M$_2$Y compounds (M, 3$d$ transition-metals such as Fe, Ni, and Co; Y, 3$p$-block elements such as Si, P, and S). Ni$_2$P and Co$_2$P form in the C22 structure at 1 bar (Dera et al. 2009; Ellner and Mittemeijer 2001). Theoretical calculations showed that C22 Ni$_2$P transforms into C23 at 77–88 GPa and 0–2000 K (Inerbaev et al. 2020). C22 Co$_2$P changes into the C23 phase at low temperatures. Ni$_2$Si and Co$_2$Si have the C37 structure at 1 bar (Errandonea et al. 2008; Geller and Wolontis 1955). The stability of C37 Ni$_2$Si was confirmed experimentally to 75 GPa and theoretically to 400 GPa (Errandonea et al. 2008).

These M$_2$Y phases exhibit coordination numbers (CN) of 4 and 5 for the M1 and M2 sites, respectively, and 8 for Y for both the C22 and C23 phases. The volume difference between the two structures are quite small (< 0.2%) (Ellner and Mittemeijer 2001; Dera et al. 2008). On the other hand, while both the C22 and C23 phases of Co$_2$P and Fe$_2$P are ferromagnetic at ambient conditions, the magnetic moments of C22 have been calculated to be much higher than those of C23 (Zhang et al. 2011; Wu et al. 2010). The transition from the C22 to C23 structure in M$_2$Y including Fe$_2$S
could be caused by the decrease in magnetic moments of transition-metals and resulting volume reduction.

The CN of Y in $M_2Y$ increases from 9 to 10 upon C23 to C37 transition, which results in a volume decrease much larger than that associated with C22 to C23 transition. As described above, the C23 to C37 transition leads to 0.8% volume decrease in Fe$_2$S at 130 GPa (Fig. 3) and 2–2.3% in Fe$_2$P and PbF$_2$ at 10–40 GPa (Nakajima et al. 2020; Haines et al. 1998). These C23 to C37 phase changes could be also related to the depression of magnetic moments (or spin moments) of 3$d$ transition-metals. It is supported by the facts that earlier calculations assuming the absence of spin moments for Fe tend to overestimate the stability of C37 with respect to C23 in Fe$_2$P (Zhao et al. 2017) and Fe$_2$S (Bazhanova et al. 2017) when compared to experimental studies (Dera et al. 2008; Nakajima et al. 2020).

**IMPLICATIONS**

The stability of cotunnite-type Fe$_2$S, first reported in the present experiments, ranges from ~30 to ~130 GPa, which overlaps with the pressure ranges of the cores of Mars (~20–45 GPa) and Mercury (~7–40 GPa) (Tsujino et al. 2013 and references therein; Helffrich 2017) (Fig. 2). While the Fe-FeS is a simple eutectic system at 1 bar, intermediate compounds of Fe$_{3+}X$S$_2$ (Fe + ~27 wt% S, ≥14 GPa), Fe$_2$S (Fe + 22 wt% S, ≥ 21 GPa), and Fe$_3$S (Fe + 16 wt% S, ≥ 21 GPa) are formed under high pressures (Fei et al. 1997, 2000; Koch-Müller et al. 2002). Fe$_2$S appears coexisting with Fe$_{3+}X$S$_2$ or Fe$_3$S when 16 to ~27 wt% S is included in the Fe-S system at 21 GPa (Fei et al. 2000).

The SNC-meteorites that are believed to be derived from Mars are significantly depleted in all chalcophile (sulfur-loving) elements, suggesting that the Martian core is enriched in sulfur much
more than the Earth’s core that likely contains 1.7 wt% S from cosmo-/geochemical estimates (Dreibus and Palme 1996). While a pioneer work by Dreibus and Wänke (1985) proposed 14.2 wt% S, more recent studies suggested higher sulfur concentrations (16–36 wt% S) (e.g. Zharkov and Gudkova 2005; Khan and Connolly 2008; Rivoldini et al. 2011; Terasaki et al. 2018). Constraining the chemical composition of the Mercury’s core is more difficult, but the presence of planetary magnetic field suggests that the core is molten at least partially, calling for the incorporation of impurity element(s) such as sulfur that suppresses the melting temperature of iron to a large extent (Fei et al. 2000; Stewart et al. 2007). Previous studies proposed the sulfur-rich Mercury’s core containing up to 36.5 wt% S (Harder and Schubert 2001; Chabot et al. 2014), although the presence of silicon is also supported from reducing conditions at planetary surface.

Recent geodesy data, the moment of inertia and the Love number $k_2$, indicate that at least the outer part of the Mars’ core is molten (Yoder et al. 2003; Rivoldini et al. 2011). Also, Mercury’s global magnetic field will require the liquid state of the core, and thermal evolution models suggest the presence of a solid inner core (Dumberry and Rivoldini, 2015). Both Mars and Mercury may thus have liquid outer core and solid inner core.

The detailed phase relations in the Fe-FeS system are known only to 21 GPa (Fei et al. 2000). Fe$_2$S appears only in a narrow temperature range at this pressure, but the C22 to C23 phase transition should expand the stability field of Fe$_2$S above ~30 GPa. Indeed, it may be supported by the coexistence of Fe + Fe$_2$S (22 wt% S) rather than Fe + Fe$_3$S (16 wt% S) observed by Stewart et al. (2007) at 40 GPa. It is also noted that Fe$_2$P exhibits a large liquidus field in the Fe-FeP system even at 1 bar. The stability of Fe$_2$S was confirmed in the present study to 1650 K at 37 GPa in the Martian core pressure range (Fig. 2). It agrees with the Mars’ core temperatures that have been
recently estimated considering the presence of its inner core (Helffrich 2017). It is therefore possible that \( \text{C23 cotunnite-type Fe}_2\text{S} \) is present in the solid inner core of Mars. It might appear in the Mercurian core as well if \( \text{Fe}_2\text{S} \) is stable to higher temperatures or Mercury’s core temperatures are lower than currently estimated (Fig. 2).

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**REFERENCES CITED**


FIGURE 1. XRD patterns in runs #1 (a, b) and #3 (d, e) collected at ~64 GPa and ~164 GPa, showing the formations of the C23 cotunnite-type and C37 Fe₂S phases upon heating, respectively. The calculated XRD patterns are given for the C23 (c) and C37 structures (f). sm; starting material.

FIGURE 2. Phase diagram of Fe₂S. The stabilities of the C22, C23, and C37 phases are shown by green, blue, and red symbols, respectively. Reverse triangle, Fei et al. (2000); pentagon, Koch-Müller et al. (2002); diamond, run #1; triangles, run #2; squares, run #3; cross, run #4; circles, run #5. P-T conditions for the Martian (brown) and Mercurian cores (blue) are from Tsujino et al. (2013) and Helffrich (2017).

FIGURE 3. Compression curves of C23 (blue) and C37 Fe₂S (magenta) at 300 K. Filled and open symbols were data by experiments and calculations, respectively. Circles, data from this study (Table 1); triangles, Tateno et al. (2019). See text for elastic parameters.
Calc. C23 Fe$_2$S

quenched from 64 GPa and 1800 K

before heating

Calc. C37 Fe$_2$S

on heating 164 GPa and 2400 K

before heating
<table>
<thead>
<tr>
<th>Structure</th>
<th>Pressure (GPa)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
</tr>
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<td>C23</td>
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<td>5.863</td>
<td>3.586</td>
<td>6.384</td>
<td>134.24</td>
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<td>3.452(2)</td>
<td>6.352(5)</td>
<td>122.16(39)</td>
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<tr>
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<td>5.563(8)</td>
<td>3.452(3)</td>
<td>6.353(6)</td>
<td>121.98(48)</td>
</tr>
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<td>3.413(3)</td>
<td>6.304(6)</td>
<td>118.29(43)</td>
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<td>116.27(13)</td>
</tr>
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<td>3.381(1)</td>
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<td>4.679(3)</td>
<td>3.283(2)</td>
<td>6.165(5)</td>
<td>94.73(27)</td>
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*Theoretically calculated at 0 GPa*