An *ab initio* study of the relative stabilities and equations of state of Fe$_3$S polymorphs

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**Abstract**

An investigation of the relative stabilities and equations of state of possible Fe$_3$S polymorphs was conducted using first-principles pseudopotential calculations. These calculations were based on density functional theory and performed using ultrasoft Vanderbilt pseudopotentials within the generalized gradient approximation. In accord with experiment, we found that the tetragonal Fe$_3$P-type polymorph is the only stable phase along the 0 K isotherm as a function of pressure. Fe$_3$S exhibits permanent magnetism at ambient conditions (Fei *et al.*, 2000), but magnetism is suppressed by pressure and temperature, and therefore non-magnetic data are appropriate ones to use for modelling planetary interiors. For this reason, and because the Fe$_3$P-type polymorph of Fe$_3$S contains 32 atoms per unit cell it was impractical to incorporate magnetic properties into the simulations of this phase, we studied the behaviour of the non-magnetic phase. We obtained values of 250 GPa for the bulk modulus, $K_0$, and 4.61 for its first derivative with respect to pressure, $K_0'$, by fitting a 3rd order Birch-Murnaghan equation of state to the calculated internal energy as a function of volume for the non-magnetic Fe$_3$P-type Fe$_3$S. This suggests that a pressure far greater than that expected in the Martian interior would be needed to achieve a density comparable to that of the Martian core. We therefore conclude that it is unlikely that the core of Mars contains significant amounts of solid Fe$_3$S.

**Keywords:** equation of state, Fe$_3$S polymorph, Mars, non-magnetic data.

**Introduction**

Planetary dynamics data and cosmochemical models for Mars suggest that the core is composed of iron plus some light alloying component. The light element component is widely believed to be sulphur, based on the presence of sulphur in meteorites and its ability to dissolve in molten iron at the pressure and temperature ranges expected to be encountered in an accreting planet (Kieffer *et al.*, 1992), and the recent identification of sulphur-rich phases on the surface of Mars (e.g. Brückner *et al.*, 2003). Therefore, an understanding of the properties of iron alloys, particularly iron sulphides, at high pressure will allow models of the Martian core to be constrained.

Previous studies (e.g. Usselman, 1975) have shown that at pressures up to 14 GPa, metallic iron and iron sulphide (FeS) form a simple binary eutectic system. An intermediate compound (Fe$_2$S$_2$) forms at higher pressures (14–18 GPa), changing the melting relations in the Fe-S system from the simple binary eutectic to a binary system in which the intermediate compound (Fe$_2$S$_2$) melts incongruently (Fei *et al.*, 1997). More recent experiments (Fei *et al.*, 2000) identified two further intermediate compounds (Fe$_2$S and Fe$_3$S) at higher pressure, significantly increasing our understanding of melting relations in the Fe-S system under conditions relevant to the Martian core. Fe$_3$S is the least sulphur-rich solid iron sulphide known to exist. Fei *et al.* (2000) found...
that Fe$_3$S forms at pressures between 18 and 21 GPa and that the Fe + Fe$_3$S assemblage is stable up to pressures of at least 23.5 GPa. Using powder X-ray diffraction techniques they found Fe$_3$S to be isostructural with Fe$_3$P ($\bar{4}$) and other transition metal phosphides (e.g. Ni$_3$P, Cr$_3$P), having a 32-atom tetragonal unit cell (Fig. 1). They report that there is a eutectic between Fe and Fe$_3$S with eutectic temperature of 1075°C and eutectic composition of Fe $\approx$ 15.4 wt.% S, and that the Fe$_3$S compound melts incongruently: Fe$_3$S $\rightarrow$ Fe$_2$S$_2$ + liquid. They report that the Fe$_2$S phase is only stable over a narrow temperature range at 21 GPa.

The pressure range of the Martian core is estimated to be $\sim$23.5–50 GPa (Folkner et al., 1997). The Fe-$S$ phase diagram at 21GPa reported by Fei et al. (2000) may therefore be taken to be the lowest pressure representation of the Fe-$S$ system under the conditions of the Martian core. Both FeS and Fe$_3$S have large regions of stability at this pressure and their properties are likely to be important in the development of models of the Martian interior. Our investigation of the relative stabilities and equations of state of FeS polymorphs has been previously reported (Martin et al., 2001). In this work Fe$_3$S has been studied in detail using ab initio simulations. Fe$_3$S has been simulated previously (Sherman, 1995), but only as a simple face-centred cubic (AuCu$_3$-type) structure, whereas in this study we have considered several other hypothetical Fe$_3$S polymorphs, ranging from the relatively simple AuCu$_3$-type to the relatively complex Fe$_3$P-type.

In order to determine the relative stabilities and equations of state of Fe$_3$S polymorphs as a function of pressure, ab initio calculations have been carried out to determine the internal energy as a function of volume. The calculation methodology is described in the next section. The results of this study are presented in the third section, and in the final section we offer our conclusions.

Calculation methodology

The ab initio computer simulations used in this study were based on density functional theory, using ultrasoft Vanderbilt pseudopotentials within the generalized gradient approximation, implemented in the computer program VASP (Kresse and Furthmüller, 1996), and performed on the Cray T3E at the Manchester CSAR facility. All of the pseudopotentials used have been constructed using non-linear partial core corrections (Louie et al., 1982). In the Fe pseudopotential, all electron states up to 3$p$ are treated as core states, i.e. with an [Ne]3$s^2$ frozen core, while for the S pseudopotential all electron states up to 2$p$ are treated as core states, i.e. with an [Ne] frozen core. The accuracies of these Fe and S pseudopotentials have previously been reported (e.g. Vočadlo et al., 1997; Alfè and Gillan, 1998).

Seven polymorphs were considered in the preliminary investigation of Fe$_3$S: the Fe$_3$P-type that has been observed experimentally (Fei et al., 2000), the AuCu$_3$-type that had previously been studied using computer simulations (Sherman, 1995), and five other common structures of $R_3X$ compounds (BiF$_3$, LaF$_3$, ReO$_3$, UO$_3$, and YF$_3$) (Wyckoff, 1951). For the AuCu$_3$-type structure, in which all atoms sit on crystallographic special points, the energy of the system was simply found for a range of volumes with fixed atomic positions and unit-cell geometry. For the other structures, the energy of the system was found for a range of volumes, whilst allowing the atoms and cell geometry to relax into their lowest energy configuration for each given volume. The calculations were performed with the number of symmetry unrelated k-points used ranging from 9 to 56, derived using Monkhorst-Pack sampling grids (Monhorst and Pack, 1976) ranging from $3 \times 3 \times 5$ to $11 \times 11 \times 11$, with a cutoff energy of $\sim$300 eV. All the total energies were converged to within 0.01 eV per formula unit. Although Fei et al. (2000) reported that the Fe$_3$S phase exhibits permanent magnetism, the large system size of the Fe$_3$P-type polymorph made the computational cost of incorporating magnetic properties into the simulations of this phase prohibitively large, and so spin-polarized calculations were not performed in this study.

![Fig. 1. Fe$_3$P-type Fe$_3$S structure.](image-url)
Results and discussion

This study found that the tetragonal Fe₃P-type polymorph is the only stable phase along the 0 K isotherm as a function of pressure (Fig. 2). Although mechanically stable, all the other hypothetical Fe₃S polymorphs studied were energetically less favourable for all volumes considered.

Role of magnetism

Fei et al. (2000) reported that the Fe₃S phase exhibits magnetism. In previous studies it has been found that the difference in volume between a magnetically ordered phase (spin unrestricted simulation) and non-magnetically ordered phase (spin restricted simulation) at ambient conditions is of the order of 10%. So, for example, Vočadlo et al. (2002) show that the difference in volume between spin unrestricted and spin restricted simulations of Fe₃C is ~7% (Table 1). Hence, we expect that the absence of magnetic components in the simulations would cause the cell parameters, and \( V_0 \) obtained from them, to be significantly smaller than those observed experimentally. The cell parameters and, as described below, \( V_0 \) obtained from the simulations of Fe₃S were indeed smaller than those found experimentally. However, it is known that ferro- and antiferro-magnetism is suppressed at both the high pressures and temperatures found in planetary interiors. Thus, Fe₃C loses its magnetic properties at temperatures greater than 483 K (Häglund et al., 1991) and pressures greater than ~60 GPa (Vočadlo et al., 2002). Therefore, we expect that the magnetism in Fe₃S would be lost at the high pressures and temperatures found in the Martian core, and consequently it is more appropriate to apply the results of our non-magnetic simulations of Fe₃S to models of such extreme environments, rather than to extrapolate the lower-pressure, magnetic experimental data.

![Fig. 2. Energy-volume curves for Fe₃S polymorphs produced by fitting a 3rd order Birch-Murnaghan equation of state to energy-volume data.](image)

**Table 1.** 3rd order Birch-Murnaghan equation of state and structural data for Fe₃P-type Fe₃S, and, for comparison, 3rd order Birch-Murnaghan equation of state data for non-magnetic and magnetic Fe₃C.

<table>
<thead>
<tr>
<th></th>
<th>This study Fe₃S (simulation)</th>
<th>Fei et al. (2000) Fe₃S (experiment)</th>
<th>Vočadlo et al. (2002) Fe₃C (simulation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-magnetic</td>
<td>Magnetic</td>
<td>Non-magnetic Magnetic</td>
</tr>
<tr>
<td>( V_0 (\text{Å}^3) )</td>
<td>338±3</td>
<td>377</td>
<td>8.968±0.007</td>
</tr>
<tr>
<td>( K_0 ) (GPa)</td>
<td>250±3</td>
<td>170±8</td>
<td>316.62±0.02</td>
</tr>
<tr>
<td>( K'_0 )</td>
<td>4.61±0.04</td>
<td>2.6±5</td>
<td>4.30±0.02</td>
</tr>
<tr>
<td>( A (\text{Å}) )</td>
<td>8.824</td>
<td>9.144±0.002</td>
<td>5.79±0.41</td>
</tr>
<tr>
<td>( C (\text{Å}) )</td>
<td>4.315</td>
<td>4.509±0.002</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fractional atomic co-ordinates</th>
<th>Tetragonal ( (\text{Å}) )</th>
<th>Tetragonal ( (\text{Å}) )</th>
</tr>
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<tr>
<td>Fe</td>
<td>0.17369 0.22029 0.75214</td>
<td>0.17170 0.21950 0.75480</td>
</tr>
<tr>
<td></td>
<td>0.36152 0.03193 0.96852</td>
<td>0.36050 0.03100 0.98600</td>
</tr>
<tr>
<td></td>
<td>0.08271 0.10164 0.23546</td>
<td>0.07930 0.10590 0.23380</td>
</tr>
<tr>
<td>S</td>
<td>0.28826 0.04240 0.48603</td>
<td>0.29210 0.04540 0.49030</td>
</tr>
</tbody>
</table>
Structural properties

In agreement with experiment, our simulations find a tetragonal unit cell that is isostructural with Fe₃P (Fei et al., 2000). Our unit-cell parameters are ~4% smaller than those found experimentally, as expected due to the lack of magnetic components in the simulation. Although the cell parameters obtained from the simulations are significantly smaller than those observed experimentally, the \( c/a \) ratio is maintained at ~0.49 (Table 1). The positions of the atoms within the unit cell are within ±0.5% (of the associated cell parameter) of those reported for Fe₃P (Wyckoff, 1951).

Equations of state

Values for \( V_0, K_0 \) and \( K'_0 \) were obtained for the non-magnetic Fe₃P-type Fe₃S by fitting a 3rd order Birch-Murnaghan equation of state to the data produced via the simulations. Naturally, the \( K_0 \) obtained from the calculations performed in this study is not directly comparable with that obtained by experiments on the magnetic phase. However, it is recognized that GGA calculations usually give a good description of the bulk modulus as a function of density (e.g. Price et al., 2004). Thus, a plot of bulk modulus as a function of density (Fig. 3) shows that our calculated value of the bulk modulus is in good agreement with the measured value of \( K \) at \( \rho = 4.2355 \text{ g cm}^{-3} \) (Fei et al., 2000). Within the quasi-harmonic approximation, this figure can also be used to infer the bulk modulus, and hence the seismic parameter, at conditions relevant to the Martian core, where \( \rho \approx 6 \text{ g cm}^{-3} \) (Kieffer et al., 1992). However, we note that the pressure needed to achieve such density is predicted to be >100 GPa, far greater than that expected in the Martian interior (~50 GPa), even without considering the effect of thermal pressure. We therefore conclude that it is unlikely that the core of Mars contains significant amounts of solid Fe₃S.

Conclusions

Fe₃S is the most Fe-rich iron sulphide currently known, and so has been suggested to be a possible component in planetary interiors and specifically the Martian core. This work includes the first simulations of the experimentally observed polymorph of Fe₃S, and is the first to consider a variety of other hypothetical polymorphs. We found that the tetragonal Fe₃P-type polymorph is the only stable phase along the 0 K isotherm as a function of pressure. Our non-magnetic simulations of Fe₃S are the most appropriate to apply the results to models of extreme environments such as the Martian core, as the magnetic moment is lost at high pressures and temperatures. For Fe₃S, we predict that pressures over 100 GPa would be required to achieve a density comparable to that expected in the Martian core, and so we conclude that it is unlikely that the core of Mars contains significant amounts of solid Fe₃S.

Acknowledgements

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References


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