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An *ab initio* study of the relative stabilities and equations of state of Fe_3S polymorphs

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ABSTRACT

An investigation of the relative stabilities and equations of state of possible Fe_3S 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_3P-type polymorph is the only stable phase along the 0 K isotherm as a function of pressure. Fe_3S 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_3P-type polymorph of Fe_3S 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_3P-type Fe_3S. 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_3S.

Keywords: equation of state, Fe_3S 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_3S_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_3S_2) melts incongruently (Fei *et al.*, 1997). More recent experiments (Fei *et al.*, 2000) identified two further intermediate compounds (Fe_2S and Fe_3S) at higher pressure, significantly increasing our understanding of melting relations in the Fe-S system under conditions relevant to the Martian core. Fe_3S is the least sulphur-rich solid iron sulphide known to exist. Fei *et al.* (2000) found

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that Fe_3S forms at pressures between 18 and 21 GPa and that the Fe + Fe_3S assemblage is stable up to pressures of at least 23.5 GPa. Using powder X-ray diffraction techniques they found Fe_3S to be isostructural with Fe_3P ($I\bar{4}$) and other transition metal phosphides (e.g. Ni_3P, Cr_3P), having a 32-atom tetragonal unit cell (Fig. 1). They report that there is a eutectic between Fe and Fe_3S with eutectic temperature of 1075ºC and eutectic composition of Fe $\approx$ 15.4 wt.% S, and that the Fe_3S compound melts incongruently: $Fe_3S \rightarrow Fe_3S_2$ + liquid. They report that the Fe_2S phase is only stable over a narrow temperature range at 21 GPa.

The pressure range of the Martian core is estimated to be ~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_3S 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_3S has been studied in detail using *ab initio* simulations. Fe_3S 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_3S polymorphs, ranging from the relatively simple $AuCu_3$-type to the relatively complex Fe_3P-type.

In order to determine the relative stabilities and equations of state of Fe_3S 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.

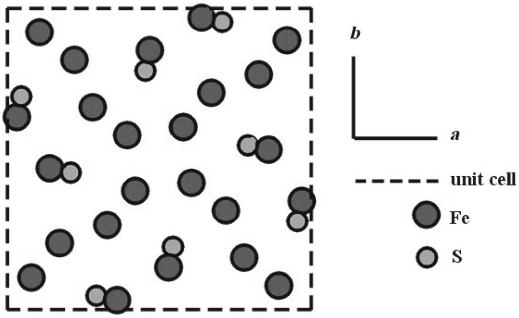

FIG. 1. Fe_3P-type Fe_3S structure.

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 $3p$ are treated as core states, i.e. with an $[Ne]3s^2$ frozen core, while for the S pseudopotential all electron states up to $2p$ 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_3S: the Fe_3P-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 ~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_3S phase exhibits permanent magnetism, the large system size of the Fe_3P-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.

Results and discussion

This study found that the tetragonal Fe_3P-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 Fe_3S polymorphs studied were energetically less favourable for all volumes considered.

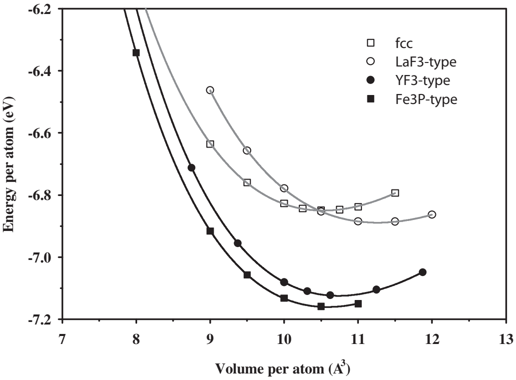

FIG. 2. Energy-volume curves for Fe_3S polymorphs produced by fitting a 3rd order Birch-Murnaghan equation of state to energy-volume data.

Role of magnetism

Fei *et al.* (2000) reported that the Fe_3S 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 Fe_3C 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 Fe_3S 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, Fe_3C 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 Fe_3S 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 Fe_3S to models of such extreme environments, rather than to extrapolate the lower-pressure, magnetic experimental data.

TABLE 1. 3rd order Birch-Murnaghan equation of state and structural data for Fe_3P-type Fe_3S, and, for comparison, 3rd order Birch-Murnaghan equation of state data for non-magnetic and magnetic Fe_3C.

	This study Fe_3S (simulation) Non-magnetic	Fei *et al.* (2000) Fe_3S (experiment) Magnetic		Vočadlo *et al.* (2002) Fe_3C (simulation) Non-magnetic	Magnetic
V_0 (Å^3)	338±3	377	377	8.968±0.007	9.578±0.037
K_0 (GPa)	250±3	170±8	150±2	316.62±0.02	173.02±0.08
K_0'	4.61±0.04	2.6±5	4	4.30±0.02	5.79±0.41
A (Å)	8.824	9.144±0.002			
C (Å)	4.315	4.509±0.002			

Fractional atomic co-ordinates

	Tetragonal ($I\bar{4}$)			Tetragonal ($I\bar{4}$)		
Fe	0.17369	0.22029	0.75214	0.17170	0.21950	0.75480
	0.36152	0.03193	0.96852	0.36050	0.03100	0.98600
	0.08271	0.10164	0.23546	0.07930	0.10590	0.23380
S	0.28826	0.04240	0.48603	0.29210	0.04540	0.49030

Structural properties

In agreement with experiment, our simulations find a tetragonal unit cell that is isostructural with Fe_3P (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 Fe_3P (Wyckoff, 1951).

Equations of state

Values for V_0, K_0 and K_0' were obtained for the non-magnetic Fe_3P-type Fe_3S 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 Fe_3S.

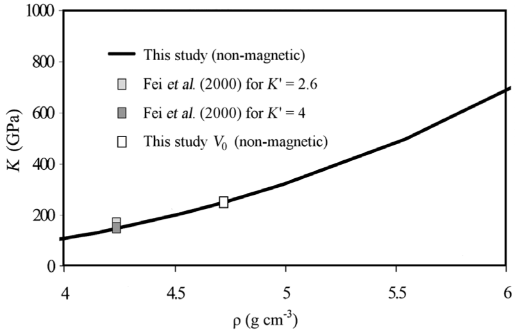

FIG. 3. Bulk modulus as a function of density for Fe_3P-type Fe_3S from simulation (this study) and experiment (Fei *et al.*, 2000).

Conclusions

Fe_3S 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 Fe_3S, and is the first to consider a variety of other hypothetical polymorphs. We found that the tetragonal Fe_3P-type polymorph is the only stable phase along the 0 K isotherm as a function of pressure. Our non-magnetic simulations of Fe_3S 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 Fe_3S, 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 Fe_3S.

Acknowledgements

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