

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

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## ABSTRACT

An investigation into the relative stabilities and equations of state of stoichiometric FeS 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. We have identified four stable polymorphs of FeS along the 0 K isotherm as a function of pressure: troilite, an orthorhombic MnP-type structure, a monoclinic structure, and a CsCl-type structure. The calculated internal energy as a function of volume for each polymorph was fitted to 4<sup>th</sup> order logarithmic and 3<sup>rd</sup> order Birch-Murnaghan equations of state, yielding values for the bulk modulus,  $K$ , and its first and second derivatives with respect to pressure,  $K'$  and  $K''$ . These equations of state may be used to characterize models of planetary cores.

**KEYWORDS:** iron sulphide, *ab initio* simulations, equations of state, Mars.

## 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). Therefore an understanding of the properties of iron alloys, including iron sulphides, at high pressure will allow models of the Martian core to be constrained.

Stoichiometric iron sulphide (FeS) is of particular interest as an end-member composition. Experimental investigations of FeS have found the anti-ferromagnetic mineral troilite to be the stable phase of FeS at ambient pressure and temperature (King and Prewitt, 1982). Two structural phase transitions have been observed experimentally with increasing pressure at

ambient temperature (King and Prewitt, 1982; Fei *et al.*, 1995; Kusaba *et al.*, 1997; Nelmes *et al.*, 1999; Marshall *et al.*, 2000). The first is at 3.4 GPa to an MnP-type structure and the second is at 6.7 GPa to a monoclinic structure (King and Prewitt, 1982). The structural transition at 6.7 GPa is accompanied by an abrupt shortening of the  $c$  axis corresponding to an ~10% increase in density, and the disappearance of the magnetic moment (Rueff *et al.*, 1999). It has been suggested by Kobayashi *et al.* (1997) that a distinct change of the  $3d$  electron configuration of Fe takes place at this pressure, and that the electron delocalization produces the collapse of the magnetic moment in the Fe atom. Kobayashi *et al.* (1997) also suggest that the large increase in the bulk modulus that they find at this transition is due to the transition from the magnetic semi-metallic state to the non-magnetic metallic state, rather than a simple structural transition. Takele and Hearne (1999) confirm that the troilite and MnP structures have a high-spin magnetic-electronic configuration, whereas the monoclinic phase adopts a magnetically quenched low-spin state.

The troilite structure ( $P\bar{6}2c$ ) is believed to be unique to FeS (King and Prewitt, 1982). It has a 24 atom unit cell that may be indexed as a

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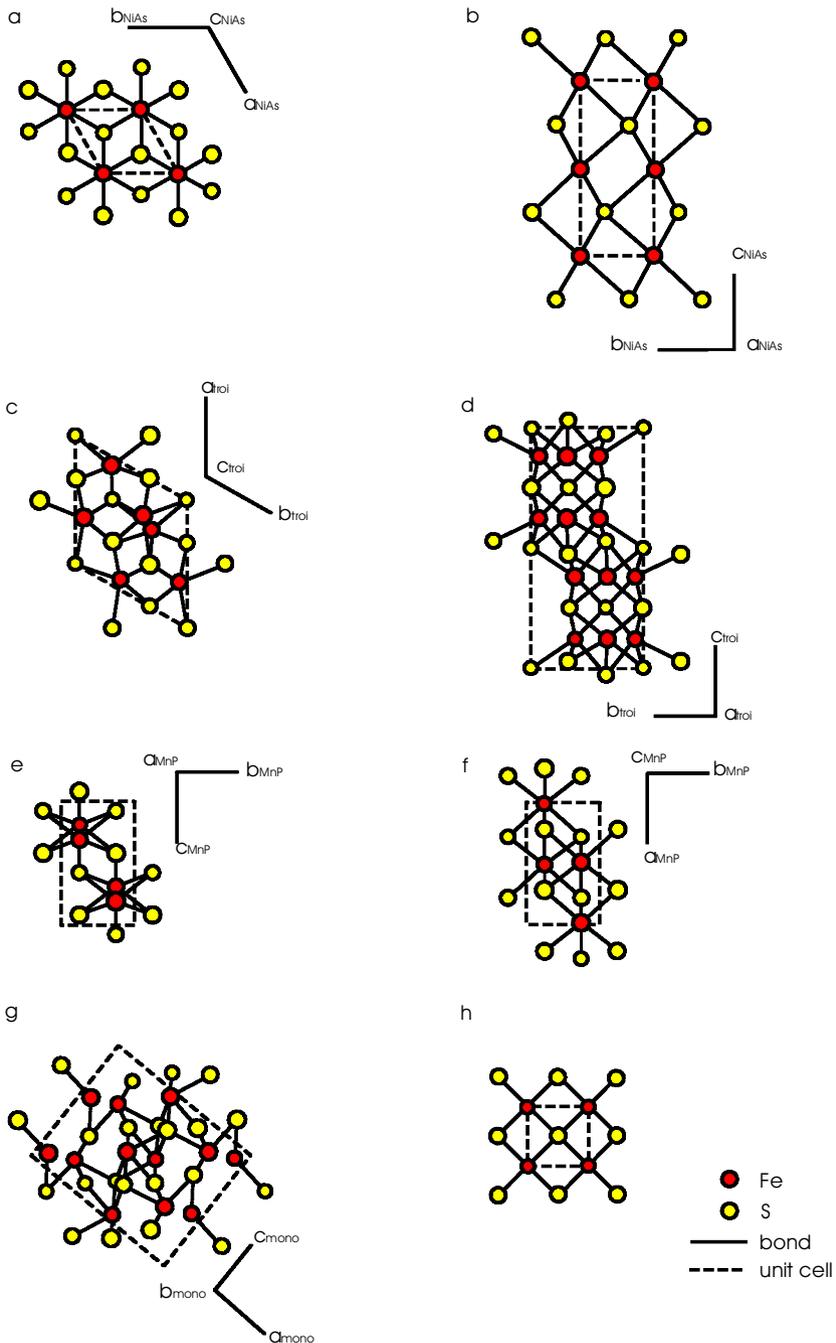


FIG. 1. FeS polymorphs: (a) ideal NiAs-type structure viewed down  $c_{NiAs}$  axis; (b) ideal NiAs-type structure viewed down  $a_{NiAs}$  axis; (c) troilite structure viewed down  $c_{troi}$  axis; (d) troilite structure viewed down  $a_{troi}$  axis; (e) MnP-type structure viewed down  $a_{MnP}$  axis; (f) MnP-type structure viewed down  $c_{MnP}$  axis; (g) monoclinic structure viewed down  $b_{mono}$  axis, rotated 50 degrees anti-clockwise in the  $a_{mono}$ - $c_{mono}$  plane; and (h) CsCl-type structure, viewed down  $c_{CsCl}$  axis.

distorted NiAs-type structure (Fig. 1c,d). Based on the  $a_{NiAs}$  and  $c_{NiAs}$  axes of the NiAs structure, (Fig. 1a,b) the troilite axes may be given as  $a_{troi} \approx \sqrt{3}a_{NiAs}$  and  $c_{troi} \approx 2c_{NiAs}$ . In this phase the magnetic spins are aligned parallel to the  $c_{troi}$  axis. The MnP-type phase ( $Pmna$ ) has only 8 atoms per unit cell (Fig. 1e,f). In this phase the magnetic spin direction is perpendicular to the  $c_{MnP}$  axis. The MnP-type cell axes may be given as  $a_{MnP} \approx c_{NiAs}$ ,  $b_{MnP} \approx a_{NiAs}$  and  $c_{MnP} \approx \sqrt{3}b_{MnP}$ . The third phase has only recently been confirmed as monoclinic, with a 24 atom unit cell (Fig. 1g) (Nelmes *et al.*, 1999). The  $b_{mono}$  axis has equivalent direction to both  $a_{troi}$  and  $c_{MnP}$ . The properties of this phase are still the subject of intense investigation. The cubic CsCl-type phase (Fig. 1h) has not been found experimentally, as its stable field lies beyond the range currently accessible by experiment. However, previous simulations (Sherman, 1995) have suggested this phase to be stable at very high pressures.

In order to determine the relative stabilities and equations of state of FeS as a function of pressure, *ab initio* calculations have been carried out to determine the internal energy as a function of volume. In the next section the calculation methodology will be described. In the third section we present and discuss the results of this study, 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 and performed using ultrasoft Vanderbilt pseudopotentials within the generalized gradient approximation, implemented in the computer program VASP (Kresse and Furthmüller, 1996), performed on the Cray T3E at the Manchester CSAR facility. All of the pseudopotentials used were 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<sup>2</sup> frozen core, while for the S pseudopotential all electron states up to 2p are treated as core states, i.e. with a [Ne] frozen core. The accuracy of the Fe and S pseudopotentials were reported previously (e.g. Vočadlo *et al.*, 1997; Alfè and Gillan, 1998). Nine polymorphs were considered in the preliminary investigation, three of which were observed experimentally (troilite, MnP, and monoclinic), five being

standard structures of RX compounds (CsCl, NaCl, sphalerite, NiAs, anti-NiAs) (Navrotsky, 1994; Wyckoff, 1951), and a hexagonally close-packed (hcp) structure. For structures in which all atoms sit on crystallographic special points (CsCl, NaCl and sphalerite), the energy of the system was 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 k-points used ranging from 10–125, along with a cutoff energy of ~300 eV, such that all the total energies were converged to within 0.01 eV per atom.

## Results and discussion

The preliminary investigation found four stable polymorphs of FeS along the 0 K isotherm as a function of increasing pressure to be troilite, an orthorhombic MnP-type structure, a monoclinic structure, and a CsCl-type structure respectively (Fig. 2). The large system sizes of some of these polymorphs prevents us from obtaining accurate estimates of the transition pressures involved, although the convergence was sufficient that we are confident of the elastic properties and equations of state reported here. Although mechanically stable, the other hypothetical FeS polymorphs studied were energetically highly unfavourable under all volumes considered.

### Magnetic properties

The influence of magnetic properties on each of the four stable structures was investigated by performing spin-polarized and non-spin-polarized calculations. For the troilite structure, consideration of spin polarization resulted in a decrease in internal energy of more than 0.1 eV per atom. For the MnP-type phase, spin polarization resulted in a decrease in internal energy of more than 0.05 eV per atom at  $V_0$ . The stability of these phases is therefore clearly dependent on their magnetic properties as the magnetic structures have a significantly lower internal energy than their non-magnetic equivalents. A variety of spin configurations was investigated. Within the troilite structure the spins were distributed as reported by J. Parise (pers. comm.) from experiment (Fig. 3a,b). The

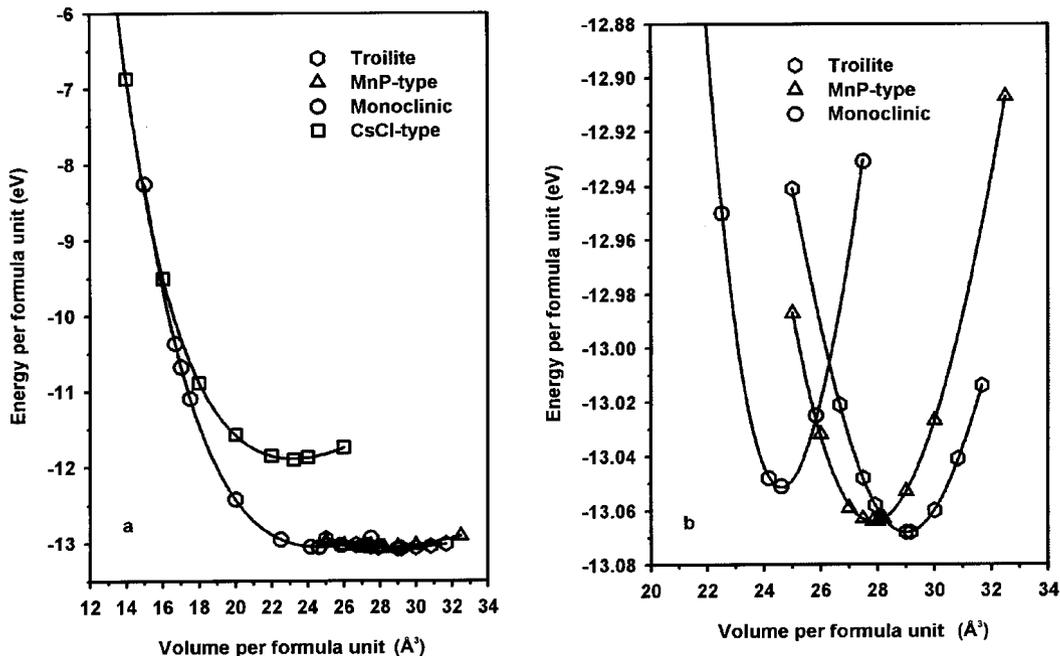


Fig. 2. Energy-volume curves for stable FeS polymorphs produced by fitting 4<sup>th</sup> order logarithmic equation of state to energy volume data. The curve with the lowest energy at a given volume indicates the structure that is stable at the equivalent pressure.

three possible distributions of spins within the MnP-type structure were investigated (Fig. 3*c,d,e,f,g,h*) and it was found that the configuration corresponding to Fig. 3*c,d* had the lowest free energy at 0 K. The incorporation of spin polarization into simulations of the monoclinic and CsCl-type phases did not affect the free energy at 0 K, indicating that these phases are non-magnetic. This is in clear agreement with experimental observations, which also indicate that the structural transition to the monoclinic phase is accompanied by the disappearance of the magnetic moment (Kobayashi *et al.*, 1997; Rueff *et al.*, 1999; Marshall *et al.*, 2000).

The computed magnetic moments decrease as a function of increasing pressure (Fig. 4) in close agreement with Marshall *et al.* (2000) who obtain 3.21–3.05  $\mu_B$  for troilite between 0 and 3 GPa and 2.96–2.79  $\mu_B$  for the MnP-type structure between 4.0 and 6.2 GPa. Over the pressure range 0–11 GPa we calculate the magnetic moment of troilite to be 2.8–2.1  $\mu_B$  and that of the MnP-type structure to be 2.7–1.6  $\mu_B$ .

### Structural properties

The structural properties of the four phases are generally similar to those reported previously (Fig. 5). Our calculated cell parameters for the troilite structure were found to be very close to those observed experimentally (King and Prewitt, 1982) (Table 1). Many of the positions of the atoms within the unit cell are identical to those reported from experiments. Those that are slightly different are within  $\pm 0.02$  Å of those suggested by experiment. In this structure the Fe atoms form triangular clusters perpendicular to the  $c_{troi}$  axis, separated by layers of S atoms (Fig. 1*c,d*).

Cell parameters, similar to those observed experimentally, were obtained for the MnP-type structure (King and Prewitt, 1982) (Table 2). The positions of the atoms within the unit cell are within  $\pm 0.06$  Å of those suggested by experiment. In this phase the Fe and S atoms form layers perpendicular to the  $a_{MnP}$  axis (Fig. 1*e,f*). The layering system is therefore maintained across the first pressure-induced phase boundary as the  $c_{troi}$  and  $a_{MnP}$  axes have equivalent direction (Fig. 1*c,d,e,f*).

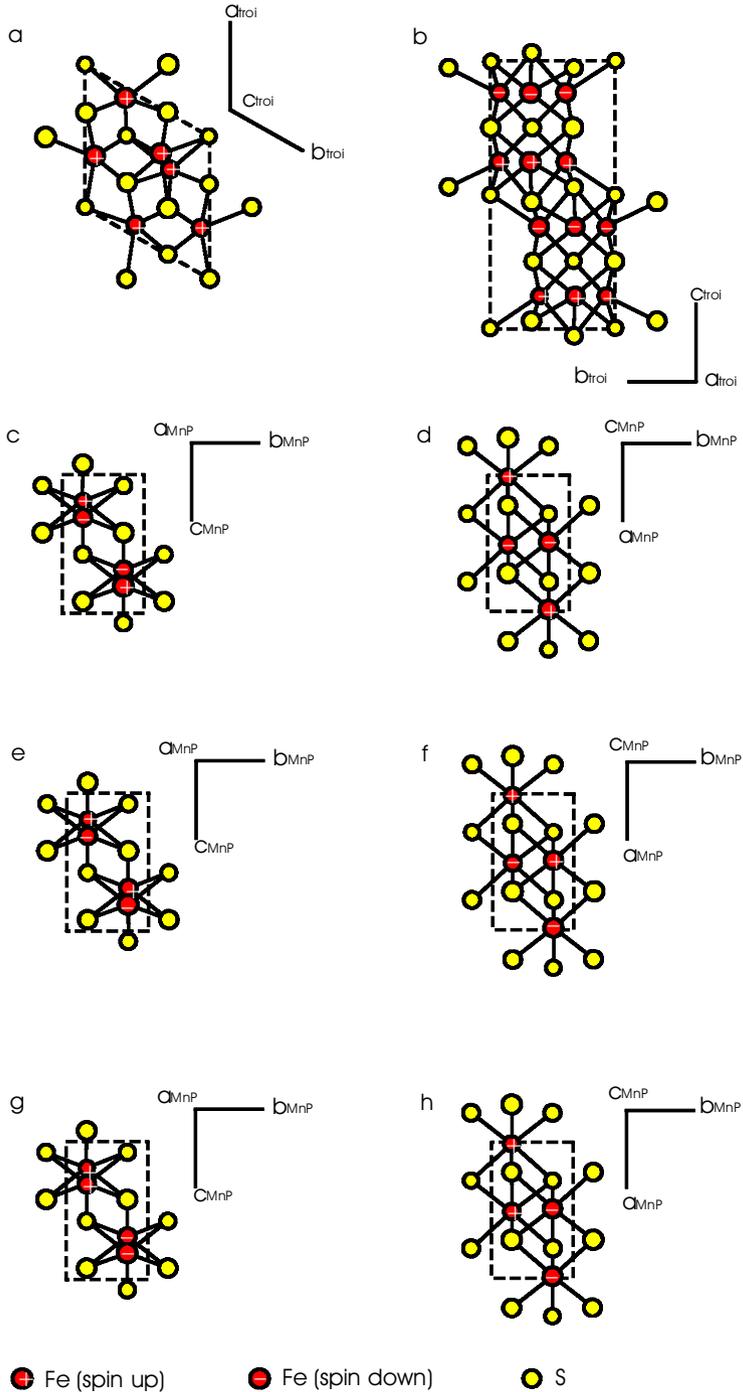


FIG. 3. Magnetic configurations. (a, b) troilite structure; (c, d, e, f, g, h) MnP-type structure. The (c, d) configuration has the lowest free energy at any given volume for the MnP-type structure.

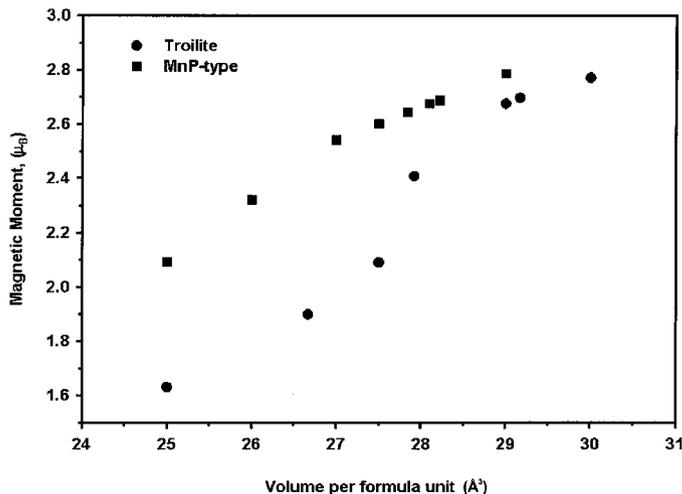


FIG. 4. Magnetic moment as a function of volume (pressure) for the troilite and MnP-type structures.

The lattice parameters and the positions of the atoms within the unit cell obtained for the monoclinic structure also compare well with those found experimentally (Nelmes *et al.*, 1999) (Table 3). The Fe and S atoms also form layers in this structure parallel to the  $b_{mono}$  axis (Fig. 1g), illustrating that each of these structures may be viewed as a slight distortion of either of the other two. This distortion trend does not continue across the transition to CsCl-type structure. The cell parameters of the cubic CsCl-

type structure are similar to those reported previously by Alfè and Gillan (1998) (Table 4).

#### Density of states (DOS)

The electronic properties of FeS as a function of pressure are uncertain (Marshall *et al.*, 2000). Hence the densities of states (DOS) for each of the four stable structures were calculated. For the troilite structure (Fig. 6a) the total DOS falls to zero at the Fermi energy, forming a small band gap of <0.5 eV,

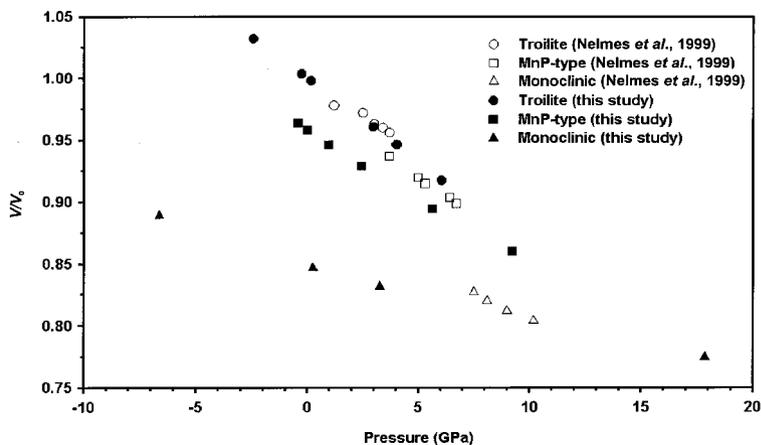


FIG. 5.  $V/V_0$ -pressure plots for stable FeS polymorphs from this study with comparison to experimental results reported by Nelmes *et al.* (1999).

TABLE 1. Equation of state and structural data for troilite.

Troilite	This study (simulation)			King and Prewitt (1982) (expt)			Kusaba <i>et al.</i> (1997) (expt)
	LnEOS*	Magnetic		BMEOS <sup>†</sup>			BMEOS <sup>†</sup>
$V_0$ (Å <sup>3</sup> )	29.002(8)		29.06(2)	30.16(9)			
$K$ (GPa)	80.2(4)		75.6(7)	82(7)			73(3)
$K'$	1.18(7)		-0.9(2)	-5(4)			
$K''$	-1.13(2)						
$E_0$ (eV)	-13.0681(1)		-13.0677(4)				
A (Å)	5.981			5.963(1)			5.966(1)
B (Å)	5.981			5.963(1)			5.966(1)
C (Å)	11.232			11.754(1)			11.76(1)
Fractional atomic co-ordinates		Hexagonal $P\bar{6}2c$		Hexagonal $P\bar{6}2c$			Hexagonal
Fe	0.3943	0.0727	0.12044	0.3787(2)	0.0553(2)	0.12300(9)	
S	0.000	0.000	0.000	0.000	0.000	0.000	
	0.333	0.667	0.0278	0.333	0.667	0.0208(2)	
	0.6641	0.0066	0.25	0.6648(6)	-0.0041(4)	0.25	

\* 4<sup>th</sup> order logarithmic equation of state (Poirier and Tarantola, 1998)

† 3<sup>rd</sup> order Burch-Murnaghan equation of state

indicating that this structure is a semi-conductor. For the MnP-type phase (Fig. 6b) there is no band gap in the total DOS, indicating that this phase should be metallic. The structural transition from the troilite

phase to the MnP-type phase therefore should be accompanied by an electronic transition from a semi-conductor to a metallic state. The metallic state is maintained across the following two high-

TABLE 2. Equation of state and structural data for MnP-type FeS.

MnP	This study (simulation)			King and Prewitt (1982) (expt)			Kusaba <i>et al.</i> (1997) (expt)
	LnEOS	Magnetic		BMEOS			BMEOS
$V_0$ (Å <sup>3</sup> )	27.84(2)		27.84(1)	28.2(3)			26.89
$K$ (GPa)	78(1)		76.8(3)	35(4)			44(3)
$K'$	2.0(1)		2.20(9)	5(2)			
$K''$	-0.18(4)						
$E_0$ (eV)	-13.0642(2)		-13.0641(2)				
A (Å)	5.685		5.736				
B (Å)	3.389		3.371				
C (Å)	5.780		5.838				
Fractional atomic co-ordinates		Orthorhombic $Pnma$		Orthorhombic $Pnma$			Hexagonal
Fe	0.014	0.25	0.192	0.008(2)	0.25	0.206(1)	
S	0.218	0.25	0.577	0.222(2)	0.25	0.577(2)	

TABLE 3. Equation of state and structural data for monoclinic FeS.

Monoclinic	This study (simulation)			Kusaba <i>et al</i> (1997) (expt)	Nelmes <i>et al.</i> (1999) (expt)	Kobayashi <i>et al.</i> (1997) (expt)
	Non-magnetic					
	LnEOS	BMEOS		BMEOS	BMEOS	BMEOS
$V_0$ ( $\text{\AA}^3$ )	24.615(8)	24.65(3)		24.17		
$K$ (GPa)	148.8(6)	157.7(8)		96(3)		127
$K'$	5.83(1)	4.72(3)				
$K''$	-0.105(2)					
$E_0$ (eV)	-13.0514(7)	-13.056(3)				
A ( $\text{\AA}$ )	7.9775			8.044(3)	8.1103(3)	
B ( $\text{\AA}$ )	5.6655			5.611(2)	5.6666(2)	
C ( $\text{\AA}$ )	6.5350			6.433(4)	6.4832(2)	
$\beta^\circ$	92.8			93.11	93.0	
Fractional atomic co-ordinates		Monoclinic $P2_1/a$		Monoclinic $P2_1$ or $P2_1/m$	Monoclinic $P2_1/a$	
Fe		0.061	0.803	0.090	0.065(2)	0.800(4) 0.082(2)
		0.210	0.208	0.174	0.211(2)	0.212(3) 0.178(3)
		0.422	0.774	0.458	0.423(1)	0.763(2) 0.450(2)
S		0.191	0.067	0.869	0.188(4)	0.076(4) 0.865(3)
		0.524	0.914	0.758	0.519(3)	0.911(2) 0.756(6)
		0.340	0.426	0.593	0.335(3)	0.420(3) 0.591(1)

pressure phase transitions (Fig. 6c,d). The DOS near the Fermi energy for the troilite and MnP-type structures are dominated by contributions from the Fe 3d electrons (Fig. 7a,b). For all four polymorphs the contributions from the Fe 3d and the S 3p

electrons overlap one another, indicating a significant degree of covalent bonding (Fig. 7). A small band gap at ~2 eV below the Fermi energy indicates splitting of the crystalline field into high and low spins of the Fe 3d electrons.

TABLE 4. Equation of state and structural data for CsCl-type FeS.

CsCl	This study (simulation)			Sherman (1995) (simulation)	Alfè and Gillan (1998) (simulation)	
	LnEOS	Non-magnetic BMEOS			Non-magnetic	Magnetic
$V_0$ ( $\text{\AA}^3$ )	23.21(3)	23.18(3)			22.99	24.33
$K$ (GPa)	172(3)	173.7(7)		190	191	143
$K'$	4.30(4)	4.55(2)		4.06	4.11	4.09
$K''$	0.000(3)					
$E_0$ (eV)	-11.889(4)	-11.890(3)				
A ( $\text{\AA}$ )	2.8529				2.8434	2.8977
B ( $\text{\AA}$ )	2.8529				2.8434	2.8977
C ( $\text{\AA}$ )	2.8529				2.8434	2.8977
Fractional atomic co-ordinates		Cubic		Cubic	Cubic	
Fe		0.000	0.000	0.000		
S		0.500	0.500	0.500		

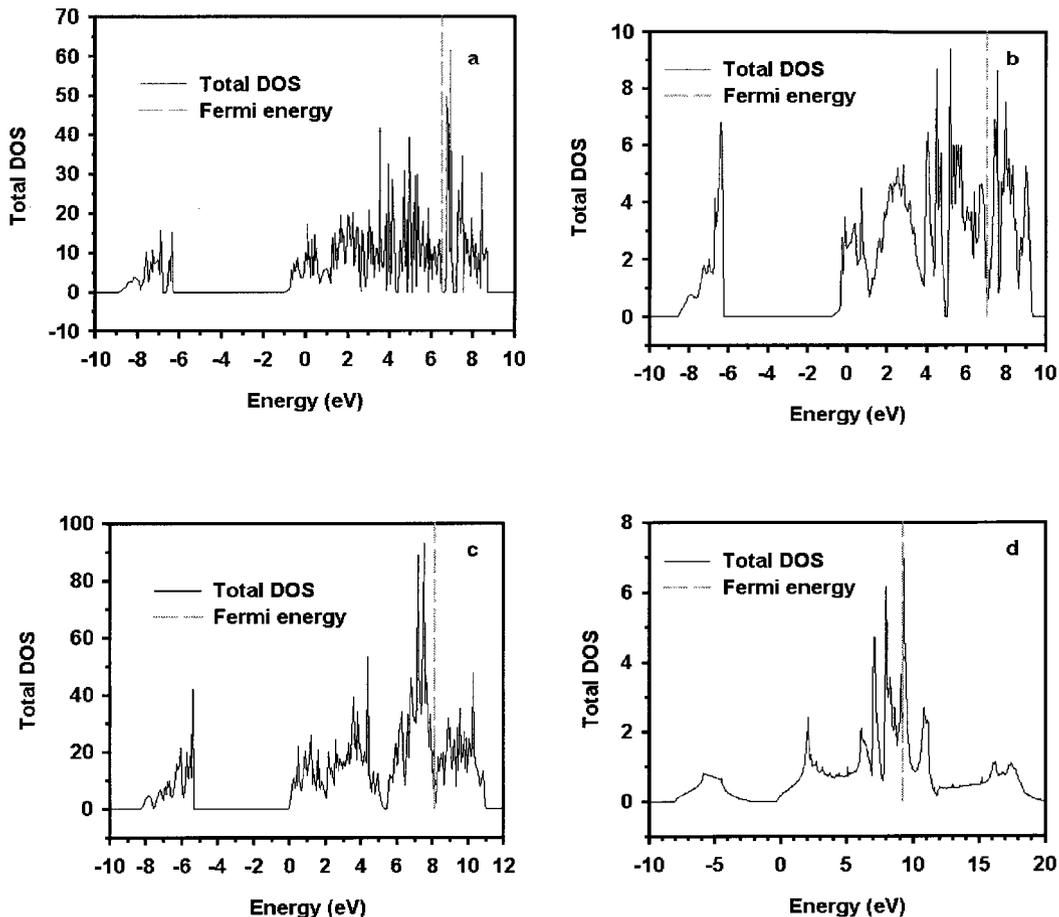


FIG. 6. Total DOS: (a) troilite; (b) MnP-type phase; (c) monoclinic phase; (d) CsCl-type phase.

### Equations of state

Values for  $V_0$ ,  $K$ ,  $K'$ ,  $K''$  and  $E_0$  were obtained for each of these structures by fitting a 4<sup>th</sup> order logarithmic equation of state (Poirier and Tarantola, 1998) and a 3<sup>rd</sup> order Birch-Murnaghan equation of state to the data produced via the simulations.

Fitting of the 3<sup>rd</sup> order Birch-Murnaghan equation of state to the troilite data gave values of  $K$  and  $K'$  consistent with those obtained by King and Prewitt (1982). The choice of equation of state is very important (e.g. Vočadlo *et al.*, 2000; Cohen *et al.*, 2000). Use of the 3<sup>rd</sup> order Birch-Murnaghan equation of state may have resulted in the surprisingly negative value of  $K'$  reported by King and Prewitt for this phase as

fitting of the more rigorous 4<sup>th</sup> order logarithmic equation of state (Poirier and Tarantola, 1998) yielded a positive value of  $K'$ . It is noted that the  $K'$  values from both the present work and from King and Prewitt (1982), for this phase are very close to zero. The unusually small values of  $K'$  could be due to the particularly shallow nature of the energy minimum for this phase.

Fitting of the equations of state to the energy-volume data for the MnP-type and the monoclinic phases produced similar values for  $V_0$  to those found experimentally (King and Prewitt, 1982; Kusaba *et al.*, 1997; Nelmes *et al.*, 1999). For the MnP-type phase we found significantly larger values of  $K$  than that previously reported (King and Prewitt, 1982; Kusaba *et al.*, 1997) and

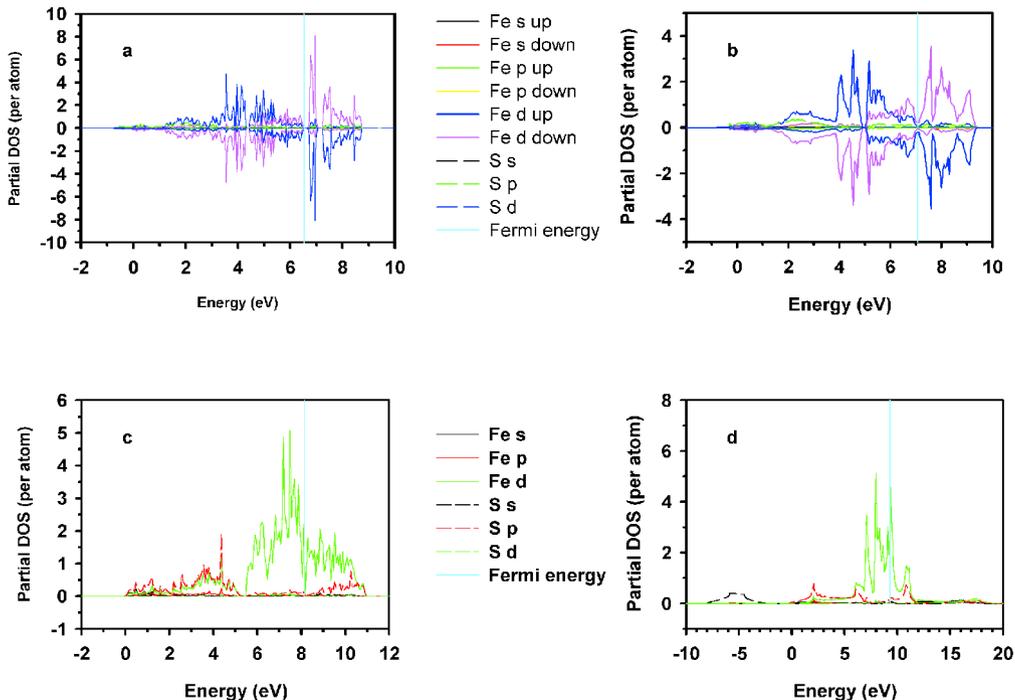


FIG. 7. Partial DOS: (a) troilite; (b) MnP-type phase; (c) monoclinic phase; (d) CsCl-type phase.

reasonably small values for  $K'$  (Table 2). The values of  $K$  previously reported for the monoclinic phase (Kusaba *et al.*, 1997; Kobayashi *et al.*, 1997) are remarkably different from one another, and yet are both significantly smaller than those we report here (Table 3). The origin of the discrepancies between the values of  $K$  and  $K'$  resulting from other experiments and those reported here are unclear.

Values of  $V_0$ ,  $K$  and  $K'$  for the CsCl-type phase compare well to those reported from previous simulations (Sherman, 1995; Alfè and Gillan, 1998) (Table 4). The discrepancies between our values and those reported by Alfè and Gillan (1998) are due to variations in the fitting procedure used to determine the equations of state.

We provide the first reported value of  $K'$  for the monoclinic phase and the first reported value of  $K''$  for each of the phases. The negative values of  $K''$  obtained for the troilite, MnP-type and monoclinic phases are most likely to be a reflection of the particularly shallow nature of their energy minima.

## Conclusions

Investigation of the relative stabilities of FeS using *ab initio* simulations has found four stable polymorphs of FeS along the 0 K isotherm with increasing pressure: troilite, an MnP-type structure, a monoclinic structure and a CsCl-type structure. Our simulations of the magnetic behaviour of FeS at a range of pressures are in agreement with the experimentally-observed behaviour.

The DOS simulations indicate that the first pressure-induced structural phase transition is accompanied by an electronic transition from a semi-conducting to a metallic state. This metallic state is then maintained across each of the following high-pressure induced structural transitions. The experimentally determined electronic properties of FeS as a function of pressure remain uncertain as experiments indicate that the monoclinic phase is non-metallic (Marshall *et al.*, 2000). Further work on this issue is required.

The results obtained from the *ab initio* energy-volume calculations compare well with experi-

mental results in most instances. The reasons for the discrepancies between some values remain uncertain, but may reflect the experimental problems associated with studying stoichiometric FeS.

The results of this preliminary investigation of FeS polymorphs indicate that the monoclinic phase is stable under the pressure range of the Martian core (23–50 GPa) and the CsCl phase is most likely to be stable at Earth's inner core pressures (>330 GPa). These calculations therefore provide details of the properties of FeS at high pressures that have yet to be investigated experimentally. In order for the results of future Mars missions such as those which will deploy a seismic network to be interpreted, detailed models of the Martian interior must be developed. The application of computational mineral physics to the understanding of the Martian interior will allow such models to be constrained.

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