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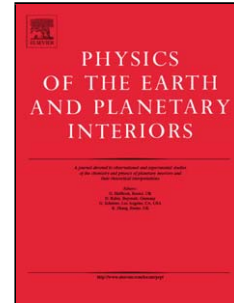
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Equation of state (EOS) and collapse of magnetism in Iron-rich meteorites at high pressure by first-principles calculations

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Abstract

We have calculated electronic and structure properties, equation of state (EOS) and collapse of magnetism of different meteoritic materials at high pressure using density functional theory (DFT). The fully optimization structures are obtained by minimization of the total energy and atomic forces of iron rich materials, which are in good agreement with the experiment. Phase transition of Fe₂P (C22 type structure) barringerite into Fe₂P (C23 type structure) allabogdanite is calculated to be 26 GPa. Collapse of magnetism (high spin-low spin) of some iron rich materials are described at various pressures. It has been observed that the optimized equilibrium volume has been changed due to transition of non-magnetic to magnetic material at high pressure, so EOS parameters have also been changed. EOS parameters such as bulk modulus (B_0) and derivative of bulk modulus with respect to pressure (B'_0) for magnetic and non-magnetic configurations have been calculated by fitting E-V curves with Birch-Murnaghan equation, which confirm the experimental results.

1. Introduction

High pressure study of materials has great importance for the understanding of phase transition mechanism, mechanical stability and the internal structure of Earth core and other planets. The Bulk modulus of material determines mechanical properties of the material and the amount of energy stored in solid material in the Earth's core. The equation of state (EOS) is an important parameter for characteristic of a material. One of the most abundant constituent of the Earth core is iron. The Earth's outer core also contains certain amount of light elements because the difference in the density between solid iron and the inner core may be as much as 5%. (McDonough et al., 1995; Anderson et al., 1994; Sohl et al., 1997). Phosphorous, carbon and sulphur are believed to be alloying light elements in iron-rich planetary cores, such as, those of the Earth and Mars (Li et al., 2003; Poirier., 1994).

Determination of the physical properties of the magnetic and non-magnetic phase is important for the interpretation of existence of light elements in Earth and planetary cores. The study of density difference between pure iron and light element contained compounds such as Fe_2P , Fe_3P , Fe_3S and Fe_3C is very important for the estimation of light elements in Earth's core. Physical properties of meteoritic materials under core conditions can be significantly affected by the state of magnetization. High pressure magnetism in transition metal oxides had been investigated with in density function theory (DFT) (Cohen et al., 1997). Fe_2P is a very common material which is found in two structures as meteoritic samples. Hexagonal Fe_2P barringerite with space group $P\bar{6}2m$ (C22 structure type) is found in ambient pressure and orthorhombic polymorph of Fe_2P allabogdanite with space group Pnma (C23 type structure) are also known as stable or metastable at ambient conditions (Britvin et al., 2002).

In this present work, the lattice parameters of expected Earth core materials are measured. We have used first principle calculation to determine EOS parameters and volume in both the magnetically ordered and non-magnetic configurations of Fe_2P (barringerite), Fe_2P (allabogdanite), Fe_3P , Fe_3S , Fe_3C , Fe (bcc), and Fe (hcp). The magnetic transition (high spin to low spin) pressures of iron rich materials have been calculated. Magnetic transition in the material can occur due to the widening of bands (Ohnishi, 1978). Phase transition of Fe_2P (barringerite) in Fe_2P (allabogdanite) has also been investigated in this paper.

2. Computational Details

We have studied the high-pressure-induced electronic structure, EOS, magnetic transition in iron-rich materials by performing first-principles calculations based on the DFT (Kohn et al., 1965). *Ab initio* simulations were performed using the projector-augmented wave (PAW) method (Blochl., 1994) as implemented in Vienna *ab initio* simulation package (VASP) code (Kresse et al., 1999). Generalized gradient approximation (GGA) (Perdew et al., 1992) was used to describe the electronic exchange-correlation effects. Fe_3P and Fe_3S have tetragonal structure with space group $I\bar{4}$, and Fe_3C has orthorhombic structure with space group Pnma. We used denser K-point grid for total energy calculations. The calculations were carried out using $7\times 7\times 11$, $9\times 9\times 9$, $8\times 6\times 8$, $16\times 16\times 16$, $9\times 9\times 7$, $3\times 3\times 7$ and $3\times 3\times 7$ k-points meshes for Fe_2P (C22), Fe_2P (C23), Fe_3C , Fe(bcc), Fe(hcp), Fe_3P and Fe_3S , respectively. All Brillouin zone integrations were performed with a Monkhorst-Pack generated k-points mesh (Monkhorst et al., 1976). The PAW potentials have been used with 4s, 3d electrons in valence for iron, 3s, 3p electrons for phosphorous and sulfur and 2s, 2p electrons in valence for carbon. A kinetic energy cutoff of 400 eV was used for the plane wave basis set for all materials. The atomic geometries were fully optimized until the Hellmann-Feynman forces on each atom were less than the threshold value of 10^{-4} eV/Å. For the

Brillouin zone integrations, the Gaussian smearing method with a 0.02 eV smearing width has been used for the geometry optimization.

In DFT, the interaction between valence and core electrons are described by pseudo potentials and valence orbital which are expressed as plane waves. All calculations have been performed at 0 K and vibrational contributions are not included. The EOS is calculated by using the internal energy of the crystal at different chosen volume. The resulting energy versus volume data have been fitted to an integrated third-order Birch-Murnaghan (BM) equation (Birch., 1978), which is given in equation 1.

$$E(V) = -\frac{9}{16} B_o \left[(4 - B'_o) \frac{V_o^3}{V^2} - (14 - 3B'_o) \frac{V_o^{7/3}}{V^{4/3}} + (16 - 3B'_o) \frac{V_o^{5/3}}{V^{2/3}} \right] + E_o \quad (1)$$

The pressure is obtained by taking volume derivative of the total energy. The bulk modulus $B_o = -V_o dP/dV$ is also calculated from P-V relation where V_o is the equilibrium volume obtained from full structural relaxation and B'_o is the first derivative of bulk modulus with respect of pressure. Both magnetic (spin polarized with ferromagnetic ordering) and non-magnetic (non-spin polarized) treatment have been considered. The total energy has been obtained by fully self-consistent ab initio electronic structure calculations for each configuration.

3. Results and Discussion

In table 1, the structure parameters of some meteoritic materials and the equilibrium unit cell volume for each structure obtained by geometrical optimization procedure using first-principles method, which are very close to the experimental results. Deviation between experimental and theoretical values of unit cell volume is varied from 2 to 3.6 % (Fe_2P (C22), Fe_2P (C23), Fe_3P , Fe_3C , Fe_3S , Fe (bcc) and Fe (hcp)).

Sulphur, phosphorous and silicon are the main candidates for the light element core constituent. Fe_2P is ferromagnetic in both crystal structure and structural phase transformation, which occur from hexagonal barringerite with the C22 type structure to orthorhombic allabogdanite with the C23 type structure under high pressure (Senateur et al., 1976). Our calculations describe that hexagonal Fe_2P undergoes structure phase transformation into orthorhombic Fe_2P at 26 GPa. We have compared the total density of states (TDOS) of orthorhombic Fe_2P and hexagonal Fe_2P in Fig. 1, which also indicates that Fe_2P (orthorhombic) is more stable at 26 GPa. Both structures are ferromagnetically stable but magnetic moment per Fe atom of Fe_2P (C22) is higher than Fe_2P (C23). The calculated phase transition pressure of Fe_2P is somewhat higher than the experimental value (Dera et al., 2008). Main reason of this theoretical overestimation is the temperature, because experimental phase transformation is observed at 8 GPa and 1400 K.

Both magnetic and non-magnetic calculations were performed for some iron rich alloys. The total energy and the volume curves of different materials were fitted by third order BM equation (Anderson., 1995) to obtain the bulk modulus (B_0), its first derivative with respect to pressure (B'_0) and equilibrium volume for each structure. The results are presented in Table 2 together with the results from other theoretical prediction and available experimental data. The non-magnetic phase of materials has higher incompressibility and density than the magnetic phase. We find that there is a significant difference in the EOS parameters of the magnetic and nonmagnetic phase of materials. Studies of the non-magnetic phase of iron rich materials are more relevant than the magnetic phase for understanding the properties of materials under the conditions of planetary cores because of high pressure and temperature. Bulk modulus (B_0) and its first derivative (B'_0) of Fe_3C for non-magnetic calculations are 297.3 GPa and 4.9 respectively

which are in good agreement with previous results, $B_0 = 316.6$ and $B'_0 = 4.3$ (Vocadle et al., 2002). Magnetic (spin polarized) calculation of EOS parameter such as bulk modulus of some meteoritic materials are slightly overestimated as compared with the experimental results.

The magnetic collapse (high spin-low spin) of materials have been found due to the contribution of substantial volume reduction and shortening of ionic distances as described in the study of high pressure magnetic transition of hermatite (Fe_2O_3) (Rozenberg et al., 2002; Badro et al., 2002). Fig. 2 shows the calculated variation of magnetic moment with pressure of some meteoritic materials. It is clear from the figure that magnetic moment of meteoritic materials decrease with the increase of pressure, which is due to band widening. The magnetic to non-magnetic phase transition affects the elastic, thermodynamics, compressibility and mechanical properties of materials. We have observed that pressure induced magnetic transition (high spin to low spin) of Fe_3C and Fe_3S at pressures of 32-38 and 24-30 GPa respectively, which are slightly larger than the experimental values 25 GPa , 21 GPa respectively (Lin et al., 2004, Lin et al., EPSL 2004). It is well known that magnetic moment of material reduces or become low at higher temperature. Our DFT calculations are performed at 0 K but all experiments are done at 300 K. This could be one of the reasons that our results are always overestimated. Collapse of magnetism of Fe_2P (C23) occurs at 56 GPa approximately. Magnetic transitions of iron rich materials affect the description of the amount and properties of light elements in the Earth's core. Volume differences between magnetic and non-magnetic calculation of iron-rich compounds are between 2.8 to 7.42 % (see in table 2). Physical properties such as compressibility and thermal expansion of the iron rich materials are changed due to volume reduction at magnetic transition pressures.

In this work, Ferromagnetism of iron rich materials has also been investigated. Ferromagnetic stability has been determined by the total energy difference ($\Delta E = E_{AFM} - E_{FM}$) per unit cell between the anti ferromagnetic (AFM) configuration and ferromagnetic (FM) configuration. If ΔE is negative, the AFM configuration is more stable than FM and vice versa. At ambient pressure, materials such as Fe₂P (C22), Fe₂P (C23), Fe₃P, Fe₃S, Fe₃C and Fe (bcc) are ferromagnetic stable with average magnetic moment 1.4, 0.7, 1.8, 1.9, 1.7 and 2.2 μ_B per iron atom, respectively. Our results agree with previous experimental and theoretical results (Vocadlo et al., 2002, Caspersen et al., 2004).

4. Conclusions

To summarize the complete analysis of the structure, electronic and magnetic properties of some meteoritic materials have been presented using first-principles technique. EOS parameters of some Earth core materials (Fe₂P (C22), Fe₂P (C23), Fe₃P, Fe₃S, Fe₃C and Fe (bcc)) are calculated for both magnetic and nonmagnetic calculations, which are in good agreement with experimental results but some of them are slightly overestimated. The first-principles calculations also show that the non-magnetic phase has a high bulk modulus than magnetic phase. It is also observed that phase transition of Fe₂P (barringerite) into Fe₂P (allabogdanite) is at 26 GPa. Collapse of magnetism of these meteoritic materials is described at different pressures. The observed magnetic transition would affect the interpretation of the amount and properties of the light elements present in the planetary cores. All above mention meteoritic materials are ferromagnetic stable at ambient pressure except Fe (hcp), which is anti-ferromagnetically stable. We hope our work will prompt more experimental studies about magnetism under high pressure for these materials.

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Table 1. Optimized Lattice parameters (a, b and c, Å) and cell volumes (V, Å³) of iron-rich materials

Materials	This work (GGA)				Experimental			
	a	b	c	V	a	b	c	V
Fe₂P (C22)	5.794	-	3.440	100.01	5.876 ^a	-	3.449	103.15
Fe₂P (C23)	5.543	3.559	6.503	128.32	5.381 ^a	3.447	6.422	119.12
Fe₃P	9.027	-	4.369	355.96	9.107 ^b	-	4.46	369.9
Fe₃S	9.08	-	4.348	359.32	9.144 ^c	-	4.509	377.0
Fe₃C	4.995	6.759	4.432	149.67	5.058 ^d	6.703	4.506	152.77
Fe (bcc)	2.83	-	-	22.63	2.866 ^d	-	-	23.54
Fe(hcp)	2.445	-	3.886	20.1	2.523 ^d	-	4.037	22.25

^a Dera et al., (2008)^b Rundqvist., (1962)^c Fei et al., (2000)^d Mao et al., (1967)

Table 2. Equation of state (EOS) parameters for different light element containing components of Earth core (Bulk modulus, B_0 , in GPa and its first derivative with respect to pressure, B'_0) and equilibrium volume, V_0 , \AA^3)

Material	Non-spin Polarized Calculation			Spin Polarized Calculation			Previous data	
	B_0	B'_0	V_0	B_0	B'_0	V_0	B_0	B'_0
Fe₂P (C22 type)	241.1	4.9	10.77	183.9	5.8	11.05	174 ^a	4.0
Fe₂P (C23 type)	209.6	4.6	10.68	219.0	2.6	10.99	177 ^a	4.0
Fe₃P	248.5	5.0	10.58	179.9	4.0	11.18	159 ^b	4.0
Fe₃S	195.4	4.0	10.72	158.9	4.0	11.27	156 ^c	3.8
Fe₃C	297.3	4.9	8.93	183.9	4.8	9.42	175 ^d 316 ^e	5.2 4.3
Fe (bcc)	268.2	4.6	10.47	194.4	4.6	-	187 ^f 201 ^g	-
Fe (hcp)	288.9	4.6	10.18	-	-	11.31	293 ^f	-

^a Dera et al., (2008)

^b Scott et al., (2007)

^c Seagle et al., (2006)

^d Scott et al., (2001)

^e Vocadle et al., (2002)

^f Caspersen et al., (2004)

^g Sha et al., (2006)

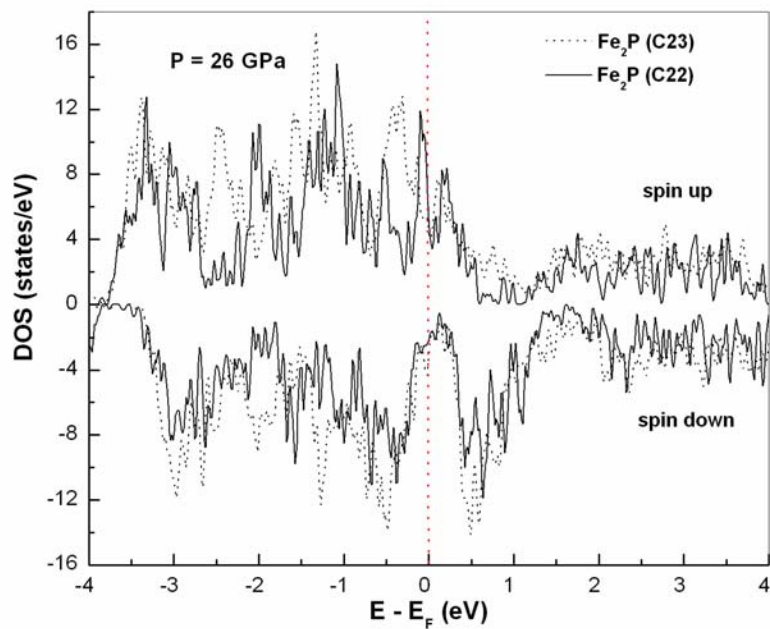


Fig. 1. Comparison of total density of state (TDOS) of Fe_2P (C22) and Fe_2P (C23) at 26 GPa, the vertical red dot line indicate Fermi level ($E_F = 0$ eV)

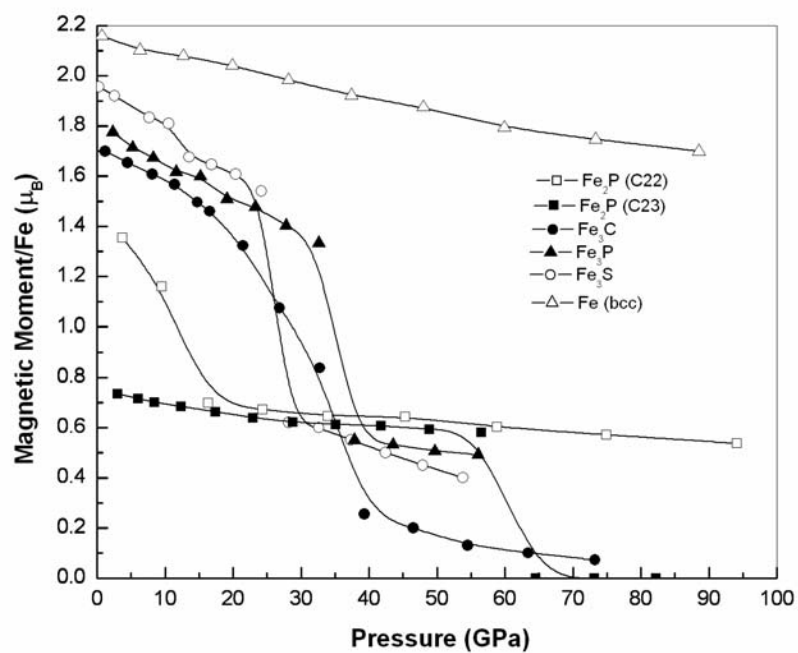


Fig. 2. Magnetic moment (μ_B) per Fe atom for different materials as a function of pressure