

MAGNETIC AND STRUCTURAL TRANSITIONS OF Fe_3P AND IMPLICATIONS FOR PHOSPHORUS IN PLANETARY CORES. T. Gu^{1,2}, X. Wu², S. Qin², Y. Fei¹, ¹Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., N.W., Washington DC 20015, USA (e-mail: gtt.pku@gmail.com), ²School of Earth and Space Sciences, Peking University, Beijing 100871, P.R. China.

Introduction: By analogy with Earth, terrestrial planets, such as Mars, Mercury and Venus, also contain light elements in their metallic cores through core-mantle differentiation process. Different differentiation conditions of the terrestrial planets will lead to different core compositions depending on the high-pressure behaviors of the metallic alloys containing iron and the light elements. Sulfur is likely to be one of the major light elements in the cores of the terrestrial planets such as Mars and Mercury. Recent observations from the MESSENGER spacecraft have indicated high sulfur content on the surface of Mercury [1]. Phosphorus is also unambiguously a candidate light element in planetary cores due to the abundance of iron phosphides minerals in meteorites, such as schreibersite (Fe_3P) [2], allabogdanite ($(\text{Fe,Ni})_2\text{P}$) [3], and perryite ($(\text{Ni,Fe})_8(\text{Si,P})_3$) [4]. Since many Fe-P minerals are isostructural with Fe-S minerals, phosphorus is found to dissolve in crystalline iron at 23 GPa in Fe-S-P system up to 4 wt% and are likely to form extensive solid solutions with sulfur, such as $\text{Fe}(\text{S,P})$, $\text{Fe}_2(\text{S,P})$, and $\text{Fe}_3(\text{S,P})$ [5]. Compared with FeS, FeP is likely to have a stabilization effect on FeS within planetary cores due to the lack of phase transformation and electronic transition [6]. In the iron-rich side, Fe_3S are more likely to be a dominant component of planetary cores. Fe_3P is isostructural with Fe_3S , and its high-pressure behavior will provide valuable insights into the structural evolution of Fe_3S and implications for phosphorus storage in planetary cores. In previous studies [7, 8], a phase transition of Fe_3P was reported above 17 GPa after laser heating. Although the high pressure phase is unidentified, the closest matched structure is from the orthorhombic system. In order to understand the structure type of the high-pressure phase of Fe_3P and its implications for planetary cores, we carried out *ab initio* calculations to explore the stabilities of Fe_3P in several structures. We further checked our calculations by Mössbauer spectroscopy studies and compared our results with X-ray diffraction data.

Calculations and Experimental Data: The *ab initio* computer simulations are based on density functional theory, with highly accurate projector augmented wave method (PAW) as implemented in Vienna *ab-initio* simulation package (VASP) and the generalized gradient approximation (PBE-GGA) is applied. Several structures were calculated and discussed, including structures close to the original $I\bar{4}2m$

structure, i.e., $I\bar{4}2m$, $P4_2/n$, and $P4_2/nbc$, and other possible high pressure structures like $Pnma$ (cementite structure), $P4/mnc$, $Pm\bar{3}m$ and $Fm\bar{3}m$. ⁵⁷Fe Mössbauer spectra were also measured to determine the magnetic properties of Fe_3P .

Magnetic collapse of Fe_3P . Magnetic moments are calculated as $2.24\mu_B$, $2.04\mu_B$, and $1.62\mu_B$ for Fe I Fe II and Fe III at 0 GPa by GGA method, agree with experimental values ($2.12\mu_B$, $1.83\mu_B$ and $1.25\mu_B$ [9]). A drastic drop of the magnetic moment around 65 GPa demonstrates the magnetic collapse. Measured Mössbauer spectra also show the order-to-disorder magnetic crossover, but the transition pressure is much lower. At ambient condition, Fe_3P is ferromagnetic with six-line patterns. Above 25 GPa, the sextets merge into doublets, indicating a magnetic collapse. The asymmetry of the doublets can be attributed to two nonequivalent iron sites. Therefore, a new structure of Fe_3P with two non-equivalent sites appears to develop along with the magnetic collapse.

Predicted phase transformation of Fe_3P . A fit of our simulation results to the third-order Birch-Murnaghan finite strain equation of state (BM-EoS) [10] yields $K_0 = 172$ GPa, $V_0 = 359.04 \text{ \AA}^3$ and $K' = 3.9$, compared with the experimental values, $K_0 = 159$ GPa, $V_0 = 369.28 \text{ \AA}^3$, with $K' = 4$ [7]. The enthalpy differences as a function of pressure, demonstrate all the Fe_3P -type related structures ($I\bar{4}2m$, $P4_2/n$, $P4_2/nbc$) are unstable at least before the magnetic collapse pressure. While a transition to a distorted cementite $Pnma$ or tetragonal $P4/mnc$ structure appears to occur around 65 GPa (Figure 1), the same pressure as the magnetic collapse.

Calculated a and c parameters of cementite $Pnma$ structure become close to each other at elevated pressures, meaning that the structure distorted from typical orthorhombic cementite formwork to a pseudo-tetragonal structure. While the $P4/mnc$ structure shows an obvious anisotropy of a and c axis under high pressure. Both structures have two non-equivalent iron sites which would be consistent with the Mössbauer spectrum data.

XRD patterns of the predicted $Pnma$ and $P4/mnc$ structures at about 25 GPa were calculated. By indexing the observed new peaks in the high-pressure XRD experiments [8], we found that almost all the new peaks can be indexed by the $Pnma$ structure, while the $P4/mnc$ structure could not explain all the new peaks. Therefore, the likely high-pressure

polymorph of Fe_3P is in a distorted cementite $Pnma$ structure.

Discussions and implications: Phosphorus could be an important light element candidate in planetary cores because of the abundance of iron phosphides in meteorites and of its solubility in iron sulfides and melts in the Fe-S-P system. During core formation, droplets of Fe-FeS liquid with dissolved phosphorus would separate from the silicate liquid and sink rapidly to the planetary cores [11, 12].

Martian soils and rocks, especially ancient (ca. 3-4 Ga) sulfate-rich rocks, have high phosphorus content [13]. Phosphorus concentration in Martian mantle is believed to be ten times more than that in the Earth's mantle [14]. Depending on the phosphorus partitioning coefficient between silicate and metal, a significant amount of phosphorus could be incorporated into Martian core. Because Martian core pressures range from 19 GPa to 47 GPa at the center, phosphorus would be either dissolved in the metallic melt or crystallized as the $\text{Fe}_3(\text{S,P})$ high-pressure phase in Martian core.

For Mercury, the high sulfur and low iron on the surface indicates highly reducing conditions when it formed [1], which is in favor of phosphorus that has two oxidation states existing at a wide redox conditions [15]. With a core radius approximately 75% of the planetary radius [16], the pressure in Mercury's core has a wide range, from 8 GPa to 40 GPa. Mercury is likely to have a large solid inner core and thin liquid outer core. The mineralogy of the solid inner core strongly depends on the concentrations of sulfur and

phosphorus in the core. Under the central pressure of 40 GPa, the likely stable phase in the Fe-S-P system is $\text{Fe}_3(\text{S,P})$. The structure, magnetic properties, and equations of state of both end-members (Fe_3S and Fe_3P) have been investigated. Magnetic collapse of both Fe_3S and Fe_3P phases was observed at pressures within the range of Mercury's core [17, this study]. The effect of magnetic transition on core property needs to be further explored. Further study of the high-pressure behavior of $\text{Fe}_3(\text{S,P})$ solid solution will also provide data needed for comprehensive compositional models of the the core.

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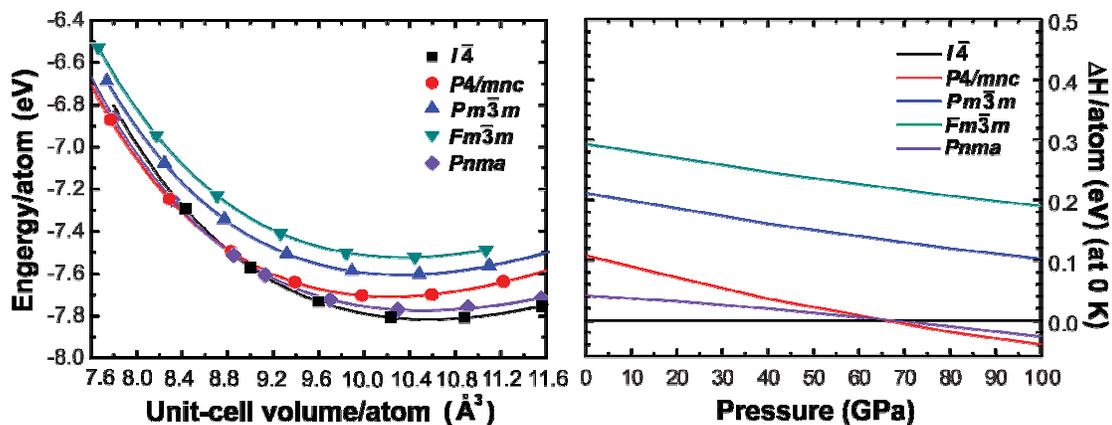


Figure 1. The total energy and enthalpy differences for the predicted structures with non-spin-restricted calculations.