Elasticity and anisotropy of Fe$_3$C at high pressures

MAINAK MOOKHERJEE*

Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth D95440, Germany

ABSTRACT

Using static electronic structure calculations, we determine the equation of state, the full elastic constant tensor and the sound wave velocities of cementite (Fe$_3$C) at pressures up to 410 GPa. Fe$_3$C is ferromagnetic (fm) at ambient pressures. Upon compression, the magnetic moment of the Fe atoms are gradually lost and, at around ~62 GPa, Fe$_3$C becomes non-magnetic (nm). We find that the pressure-volume results for the Fe$_3$C (fm) phase are well represented by a Vinet equation of state with $K_0^{in} = 183$ GPa, $K_0 = 5.9$, and $V_0 = 151.6$ Å$^3$ and that of the Fe$_3$C (nm) phase are well represented by a Vinet equation of state with $K_0^{in} = 297$ GPa, $K_0 = 4.9$, and $V_0 = 143.2$ Å$^3$. A third-order Birch-Murnaghan equation of state formulation for the Fe$_3$C (nm) phase yields similar parameters with $K_0^{in} = 304$ GPa, $K_0 = 4.5$, and $V_0 = 143.3$ Å$^3$. At pressures relevant to the Earth’s inner core, the full elastic constant tensor of Fe$_3$C (nm) reveals significant P-wave anisotropy (~10%). A crystal preferred orientation with the [110] directions of Fe$_3$C aligned along the pole axis would be required to explain the inner core anisotropy. Comparing, pure hcp Fe and iron carbides with varying stoichiometry, we find that the shear wave velocity decreases linearly with the increasing C content.

Keywords: Fe$_3$C, magnetic collapse, elasticity, anisotropy, Earth’s inner core

INTRODUCTION

Iron carbides such as cementite (Fe$_3$C) phase have been reported from naturally occurring basaltic rocks (Goodrich and Bird 1985), inclusion in diamond (Sharp 1966) and from iron meteorites (Brett 1966). Occurrence of iron carbide in natural samples provides insights into the oxidation state within the mantle (Rohrbach et al. 2007; Dasgupta and Hirschmann 2010). Based on thermodynamic extrapolations to conditions pertaining to the Earth’s core, and for most likely S to C ratios, Fe$_3$C has been proposed as an ideal inner core candidate, which could also account for the density deficit of the core (Wood 1993). The extrapolations were based on the predicted equation of state parameters ($K_0^{in} = 174$ GPa and $K_0 = 5.1$) from the systematics of compressibility for various inter-metallic phases. Subsequent high-pressure studies (Scott et al. 2001; Li et al. 2002) on ferromagnetic (fm) Fe$_3$C phase were in good agreement with the prediction. However, first-principle simulations revealed a ferromagnetic (fm) to non-magnetic (nm) transition at ~60 GPa (Vočadlo et al. 2002). From the first-principle simulations it was revealed that the high-pressure nm phase also has a substantially stiffer bulk modulus ($K_0^{nm} = 316$ GPa). Based on the experimental investigation of the high-pressure magnetic collapse (Lin et al. 2004) and re-analysis of the high-pressure X-ray data, the bulk modulus of nm phase has been found to be stiffer ($K_0^{nm} = 288 ± 42$ GPa) as predicted by simulations. Recent high-pressure results (Sata et al. 2010) on the nm phase reveal similar bulk modulus ($K_0^{nm} = 290$ GPa). This renders the thermodynamic extrapolations based on the $K_0^{in}$, erroneous and eventually ruled out Fe$_3$C as a possible inner core candidate (Vočadlo et al. 2002). More recently, with a renewed interest, the Fe-C-(S) system has been explored at higher pressures and temperatures (Nakajima et al. 2009; Dasgupta et al. 2009; Lord et al. 2009). It has been observed that Fe$_3$C iron carbide is the likely solid phase coexisting with the iron carbide melt (i.e., liquidus phase) at higher pressures relevant for the Earth’s core. In addition to the pressure and temperature, the relative stability of Fe$_3$C and Fe$_3$C is also strongly dependent on the composition i.e., bulk C content. Although, recent experimental studies indicate that at high pressures, solid Fe$_3$C coexists with the iron carbide melts, Fe$_3$C could still be an important candidate phase at higher pressures at relatively lower bulk C contents of around 0.2 wt%, which is more likely geochemical estimates in the Earth’s core (McDonough 2003). Experiments (Rouquette et al. 2008) and first-principle (Huang et al. 2005) studies have demonstrated that at lower bulk C contents, Fe$_3$C is energetically more stable than C dissolved in interstitial sites within the iron metal. Recent first-principle study indicates that Fe$_3$C is likely to be energetically stable with respect to hcp Fe and Fe$_3$C, with at a bulk C content of 6.67 wt%, whereas at slightly higher bulk C content of 8.4 wt%, Fe$_3$C is likely to be energetically stable with respect to Fe$_3$C and diamond (Mookherjee et al. 2011). Hence, it is extremely important to examine the physical properties of Fe$_3$C at higher pressure relevant to planetary cores. Sound velocity at inner core conditions would be crucial to evaluate its role in addressing the density deficit of core. So far, sound velocities measurements have been limited to ~70 GPa (Gao et al. 2008; Figuet et al. 2009). To address this, in this study we determine the full elastic constant tensor for the Fe$_3$C (nm) iron carbide up to 410 GPa, using first-principle simulations.

METHODS

Static density functional theory calculations were performed with highly accurate projector augmented wave method (PAW) (Kresse and Joubert 1999) as...