Phase relations of the iron carbides Fe_2C, Fe_3C, Fe_7C_3 at the Earth's core conditions

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The Fe-C is one of the important systems in the study of the composition and structure of the Earth's core [1, 2]. A number of intermediate compounds were considered as a possible carbon-bearing phase in the core: Fe_3C, Fe_3C_2, Fe_5C_2, Fe_7C_3 и Fe_2C [3-6]. It was assumed that among these carbides Fe_2C is most stable under the Earth's inner core conditions [6–7], however this conclusion is based on calculations at 0 K.

In the present work we investigated the stability of various iron carbides at pressures and temperatures of the Earth's core based on the calculations within the density functional theory, quasiharmonic approximation and structure prediction methods.

The crystal structure predictions performed for Fe_2C, Fe_3C, and Fe_7C_3 revealed two new phases: Fe_3C-*C*2/*m* and Fe_7C_3-*C*2/*m* which are thermodynamically stable above 300 GPa at 0 K.

The energy relationships between the predicted crystal structures are shown in Fig. 1. According to the calculated convex hull, Fe_7C_3-*C*2/*m* is not stable and decomposes into a mixture of Fe_3C+$2Fe_2C$ at 0 K. Fe_3C-*C*2/m is stable relative to a mixture of Fe_2C+Fe at 0 K.

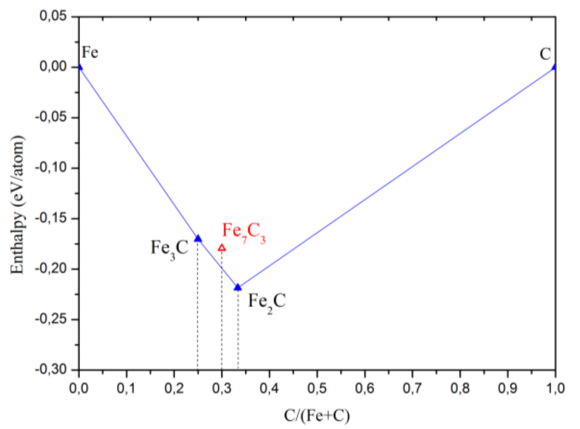

Figure 1. Convex hulls of the Fe–C system at 400 GPa

Using the quasiharmonic approximation, we investigated the effect of temperature on the stability of iron carbides (Fig. 2). According to the results, at P-T parameters of the Earth's inner core, Fe_3C is thermodynamically stable in the form of *I*-4, Fe_7C_3 – in the form of a newly predicted *C*2/*m* phase, and Fe_2C – in the form of *Pnma*-II, predicted by Bazhanova et al. [6]. Iron carbide Fe_7C_3 is unstable relative to a mixture of Fe_3C+$2Fe_2C$ at high temperatures (Fig. 2). In this case, the stabilization of the reaction products is achieved due to the transition from cementite to *I*-4 phase. This transition also stabilizes Fe_3C relative to a mixture of Fe+Fe_2C over the entire range of pressures and temperatures. At 329 GPa, corresponding to the boundary between the inner and outer core, and 0 K, the difference in the Gibbs free energies of Fe+Fe_2C and Fe_3C is 53.7 meV/f.u. and this value increases with increasing temperature.

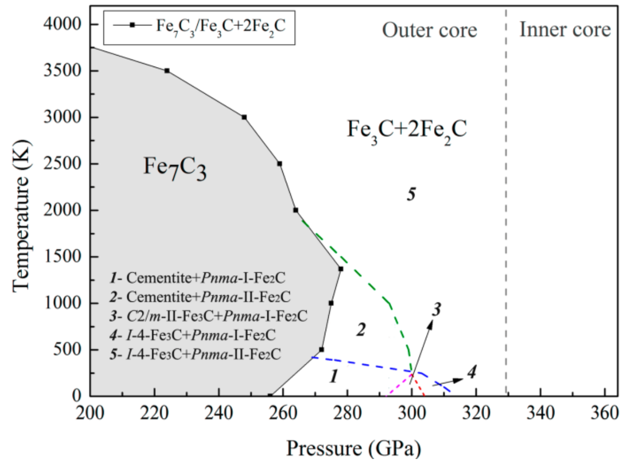

Figure 2. The boundary of the reaction $Fe_7C_3 \rightarrow Fe_3C + 2Fe_2C$ in P-T coordinates. The numbers indicate the stability fields of the mixture Fe_3C + $2Fe_2C$ with different combinations of the structures Fe_3C and Fe_2C.

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