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Unit cell angles  $\alpha$ ,  $\beta$ , and  $\gamma$ , not fixed by symmetry, give an additional degree of freedom on the stage of crystal formation. For this reason, monoclinic crystals are the most numerous ones at ambient conditions. The oblique angles play the same role in thermal expansion; in particular they permit to demonstrate sharply anisotropic thermal expansion up to contraction along some directions. In 1982 great jump of the appearance of frequency of crystals, showing negative linear thermal expansion, was discovered between orthorhombic and monoclinic crystals [1]. It occurred that at least one third of monoclinic and triclinic crystals contracts along certain directions on heating due to so-called shears [1, 2]. This fact correlates with the existence of oblique cell angles in monoclinic and triclinic crystals only. Last quarter of a century was test and development period of the thermal contraction concept. Many types of the phenomenon were considered [2, 3 etc.]: shears, hinges, rocking polyhedra and symmetry related types etc. And now we can say that both among chemical compounds and in the earth's crust, shears are the most fruitful case of linear thermal contraction of crystals. Taking into consideration anti-similarity of thermal and pressure deformations of crystals, the same situation should be expected in connection with linear elongation under pressure.

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Keywords: negative thermal expansion, high-temperature x-ray diffraction, inorganic compounds

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### The structure of type I semiconducting clathrates under pressure

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Semiconductor clathrates are compounds consisting of an open framework lattice of mainly, Si, Ge and Ga, containing a second large cation (alkali or alkali-earth) trapped in its cages. In this work, *in-situ* high pressure powder diffraction was performed on two Ge clathrates:  $\text{Ae}_8\text{Ga}_{16}\text{Ge}_{30}$ , where Ae = Sr, Ba. The pressure was applied to the samples by means of a diamond anvil cell (DAC) to 25 GPa and powder diffraction data were collected with high energy (100 KeV) x-rays at the APS Sector 1 at Argonne National Lab. This technique allows data collection over a wide  $q$  range [ $0.2 \text{ \AA}^{-1}$ - $50 \text{ \AA}^{-1}$ ]. The structure of both samples was analyzed as a function of pressure, particularly with respect to the guest atom electron density and host lattice bonding. Both clathrates show amorphization of the host lattice for pressures in excess of 20 GPa, the structural characteristics of the structure factor functions  $S(Q)$  and radial distribution functions  $G(r)$  will be presented, elucidating both the local environment of the guest atoms and their short range ordering. This result suggests a promising route for obtaining periodic arrangement of guest atoms embedded in an amorphous semiconductor matrix. Oak Ridge National Laboratory is supported by the Division of Materials Sciences, U.S. D.O.E. (contract DE-AC05-00OR22725 with UT-Battelle, LLC).

Keywords: semiconducting clathrates, *in-situ* high pressure diffraction, pair distribution function

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### Magnetic transition and equation of state of iron carbide to 400 GPa

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It is known that the Earth's inner core is different from pure iron because the physical properties of pure iron can not explain those of the Earth's inner core estimated by seismological observations. Cosmochemical arguments imply that minor lighter elements should be present to account for the discrepancies of physical properties between pure iron and the seismological observations. C, O, S, Si, and H are considered to be the most probable candidates. Wood (1993) proposed that iron carbide might be the major phase in the inner core based on extrapolations of thermodynamic calculations and an equation of state of iron carbide. Recently, significant advances have been achieved in static high-pressure experiments. Although the P-T range of high-pressure experiments has been extended, it is difficult to achieve extreme conditions corresponding to the Earth's inner core. In contrast, recent developments of the first-principle calculations can provide independent data from high-pressure experiments. In this study, the magnetic properties and the equation of state of Fe<sub>3</sub>C were investigated by the first-principle calculations. We performed DFT method using VASP package to calculate magnetic states and equilibrium volumes and pressures. A method of *ab initio* molecular dynamics calculation was also used at high temperatures. The magnetic phase transition was observed at a pressure of ~55 GPa. This indicates that the stable Fe<sub>3</sub>C is a paramagnetic phase at pressures corresponding to the Earth's core. The density of Fe<sub>3</sub>C estimated by *ab initio* molecular dynamics calculations was sufficient different from seismological data. Our results precluded Fe<sub>3</sub>C as the major inner core-forming phase.

Keywords: *ab-initio* calculations, iron compounds, molecular dynamics

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### Crystallography of intermetallic CaLi<sub>2</sub> at high pressure

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Lithium and calcium are usually considered as simple metals because of the simple electronic structures with one and two conduction electrons, respectively. Recent studies have indicated that both lithium and calcium have anomalous properties at high pressure. Thus, the high-pressure properties of the Laves-phase CaLi<sub>2</sub>, the only intermetallic compound between Li and Ca at ambient conditions, would be very interesting. Recently, Feng *et al* [1] have studied the electronic structure of CaLi<sub>2</sub> under pressure and found the bandwidths of the valence states decrease rapidly under compression just as in Li and Ca. Moreover, they predicted CaLi<sub>2</sub> could be a potential