Comment on "New Metallic Carbon Crystal"

In this Comment, we show that the investigation of Itoh *et al.* [1] on the electronic properties of a new cubic structure of carbon, the K_4 crystal, is incomplete. This K_4 structure was derived originally from the enumeration of 3D connected nets of atoms, and subsequently rediscovered from graph theory (see Ref. [2] and references cited therein). From first-principles calculations, Itoh *et al.* showed that K_4 carbon is metallic and metastable with respect to graphite and diamond. A possible conversion pathway from graphite was also proposed [1]. However, the investigation reported in Ref. [1] failed to establish the stability unequivocally and, therefore, the possible existence of this material.

The K_4 crystal consists of locally planar (sp^2) C atoms (C_3 unit with a C-C-C bond angle of 120°). The dihedral angle between two nearest neighbor C_3 units is ca. 70°. Unlike graphite, this conformation is not ideal for π conjugation. Therefore, no π bonding to stabilize the C-C bonds is expected. Inspection of the crystal structure shows that the twisted arrangement of the sp^2 C_3 is highly strained and may be unstable. This observation is consistent with the very small cohesive energy as compared to diamond or graphite. Since energetic calculations alone cannot establish the stability of a crystal, a thorough analysis of the elastic and dynamical stability is required.

To investigate the structural stability, phonon dispersions at ambient pressure were calculated with first-principles methods [3] (Fig. 1). The phonon band structure confirms that the K_4 carbon is unstable with a very large imaginary frequency. It is highly unlikely that K_4 carbon will be entropically stable. Two significant points emerged from the calculations. First, the predicted highest vibrational frequency of 1100 cm^{-1} is significantly lower than the single sp^3 bonded diamond structure of 1400 cm^{-1} [4] and the π-conjugated sp^2 bonding in graphite of 1500 cm^{-1} [5]. Thus, the bond order in K_4 carbon is less than 1. The absence of π bonding is also revealed from the topological analysis of the charge density [6] and electron localization functions [7]. Second, the largest imaginary frequency is at ca. $500i$ cm^{-1} at the P symmetry point. Examination of the eigenvectors of the imaginary modes at this point indicates that the lattice distortion is close to that for in-plane and out-of-plane bending vibrations.

In summary, K_4 carbon is structurally unstable and will not exist. Twisting of neighboring C_3 units prohibits efficient π interactions. C atoms are constrained to sp^2 hybridization and singly occupying electrons in the p orbital perpendicular to the sp^2 hybrids are pointed into the interstitial space which is responsible for the metallic character. The structure is also unlikely to be stable at high pressure. This is confirmed by additional phonon calculations showing that the frequency at the P symmetry point remains imaginary to at least 50 GPa. Apart from the unfavorable bonding, displacement of the C atoms into the void space is needed to compensate for the very large crystal volume, and, therefore, the crystal symmetry cannot be retained.

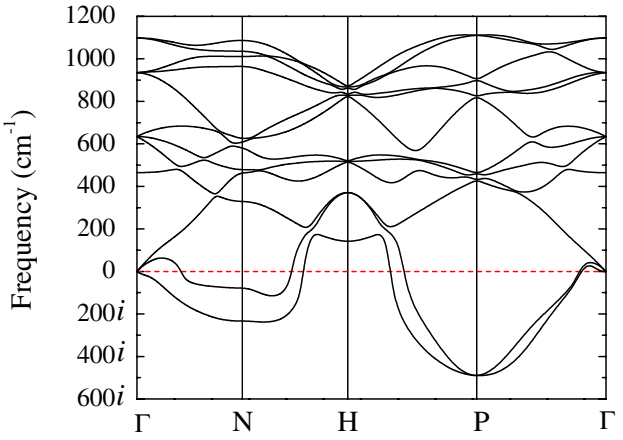

FIG. 1 (color online). Calculated phonon band structure for K_4 carbon at ambient pressure.

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