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Brief Reports

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Electronic structure of γ-C

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Due to the suggestion of interesting properties of the γ-carbon, including high-T_c superconductivity, Hartree-Fock and full-potential linear augmented-plane-wave local-density-approximation electronic-structure studies were carried out. The binding-energy result shows, however, that this phase may well be unstable, with all corrections considered. Discussions and comparisons with the electronic structures of other metals and diamond were made.

The synthesis of γ-carbon was reported by Palatnik in 1984.[1] This new phase has a face-centered cubic (fcc) structure with monoatomic unit cell, and is metallic. Upon the detection of such a structure, it was believed that it might exhibit a wide variety of very interesting and useful properties, including superconductivity. After the discovery of high-T_c superconductors (HTSC's),[2] especially after doped C_{60} was found to be HTSC,[3] it was reconsidered and thought to be likely as a candidate for a HTSC parent material.[4]

For the cuprate HTSC's, many experimental and theoretical studies have been carried out. Their electronic structures have been reviewed by Pickett.[5] For C_{60}, there have been a large number of experimental studies and some theoretical works.[6] However, an electronic-structure study for γ-C is still lacking, although it is essential for the full understanding of all properties of the material. Therefore, an electronic structure study was carried out for this phase of carbon.

In Ref. 1, it was reported that γ-C has the same lattice constant as diamond, i.e., 3.57Å. However, it has only one atom per unit cell, which reduces the lattice structure accordingly from diamond structure to fcc. This structure has the space group O_h^5 ($Fm3m$) (No. 225).[7]

For the present study, both all-electron Hartree-Fock (HF) computation[8] and a full-potential linear augmented-plane-wave local-density approximation (FP LAPW LDA) calculation[9] were carried out. For the HF study, a basis set by Huzinaga *et al.*[10] was used with the contracted Gaussian basis being split, and polarization, the d basis function (exponent 0.65), included to allow more flexibility and/or polarizability.

Surprisingly, the HF binding energy E_b^{SCF} for γ-C with the reported lattice constant $a=3.57$ Å indicates that it is unstable, with

$$E_b^{\mathrm{SCF}} = -1.65\pm0.35 \text{ eV/u.c.}$$
$$= -1.65\pm0.35 \text{ eV/atom},$$

where u.c. = unit cell. Stollhoff *et al.* studied the correlated electronic structure for diamond very extensively.[11] It was found there that the finite basis correction to the binding energy can be 1.52 eV/u.c. ~ 0.76 eV/atom. Moreover, the correlation contribution to the binding energy is significant, about 3.8 eV/u.c. ~ 1.9 eV/atom. This may also be the case in γ-C. However, even though a correlation and basis contribution of 2.66 eV/atom to E_b^{total} is estimated, the stability will still be very marginal, with a E_b^{total} not much more than 1 eV/u.c. Compared with that for carbon dimer, ~6.5 eV,[12] and for diamond, ~14.8 eV/u.c.,[11] this marginal stability may influence the potential application of this material.

The computed HF band structure and the total density of states (DOS) for γ-C are shown in Fig. 1. The DOS of fcc lithium, a typical metal, and the DOS of $SrCuO_2$, the typical parent material of HTSC's,[13] are given as insets in the figure. For comparison, the bands computed with the FP LAPW LDA method are given as an inset, and the HF bands and DOS of diamond are given in Fig. 2 as well.[11]

One of the most important consequences of this structural transition is that the sp^3 band which is fully occupied in diamond becomes only partially filled. As a result, the Fermi energy ϵ_F falls in the middle of the band which makes the material metallic, according to traditional band theory. By comparing the band structure of γ-C with that of diamond just below ϵ_F, and the γ-C DOS with the shaded part of the diamond DOS, a clear correspondence is seen.

By comparing the γ-C DOS with the lithium DOS and

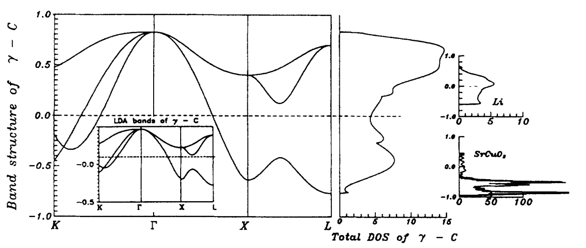

FIG. 1. The HF band structure and total DOS of γ-C (low-lying bands omitted). The LDA bands are given as an inset. The total HF DOS's for Li and $SrCuO_2$ are given as insets, too. Notice the scale difference among figures. The energy unit is Ry, and the DOS unit states/(Ry* u.c.). ϵ_F is marked with a dashed line; otherwise $\epsilon_F = 0.0$.

$SrCuO_2$ DOS, it can be seen that there is a clear similarity between γ-C and lithium. It is difficult to find much in common between γ-C and $SrCuO_2$. The LDA band structure shows a perfect consistency, with the expected squeezed dispersion compared with the HF result.

According to the BCS theory,[14] once there is an attractive potential V between two electrons (in BCS due to phonons) around ϵ_F, electrons may pair together, and the superconducting state will build up. The superconducting temperature T_c can be expressed as

$$T_c = 1.14\Theta_D \exp\left[-\frac{1}{N(\epsilon_F)V}\right], \tag{1}$$

where $\Theta_D = \hbar\omega/k_B$ is the average phonon energy scaled in the temperature units, and $N(\epsilon_F)$ is the total DOS at the Fermi energy (ϵ_F). So T_c increases with the increasing $N(\epsilon_F)$.

The BCS theory may not be fully applicable for the γ-C superconductivity. But if Θ_D is simply considered as an average energy scaled in temperature units, and V is of the corresponding origin, (1) should still give the right trend.

It can be clearly seen from the DOS's displayed in Fig. 1 that the γ-C DOS and lithium DOS around ϵ_F are only about half that of $SrCuO_2$ A smaller DOS means roughly a larger electronic mobility and better metallicity. A good metal will usually not become a superconductor.

From Eq. (1), this point is also clear. The quantities in (1) are of the orders of magnitude

$$T_c \sim 10^1 , \quad \Theta_D \sim 10^3 ,$$

and

$$\exp\left[-\frac{1}{N(\epsilon_F)V}\right] \sim 10^{-2} ,$$

so that one-half of the DOS at ϵ_F will roughly result in a T_c two orders of magnitude smaller according to the BCS theory, which means almost a complete elimination of superconductivity. So even if γ-C becomes superconducting, the electronic structure shown above predicts that it may not be a HTSC. But if doping or any other technique can change the electronic structure significantly from that given above, the situation can be, of course, different. *sp* (valence) electrons are usually very delocalized, form wide bands, and do not give as high a DOS as *d* electrons do.

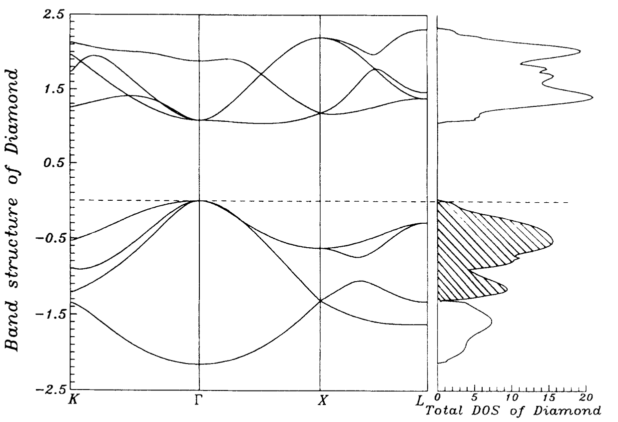

FIG. 2. The HF band structure and total DOS of diamonds. The shaded part of the diamond DOS corresponds to the region of the valence-band DOS of γ-C.

To investigate the stability question, computations with smaller lattice constants were performed. However, from the reported $a = 3.57$ Å up to $a = 2.19$ Å, which corresponds to a nearest-neighbor distance equal to that in diamond, there is no sign that the system becomes more stable. For comparison, a computation for a bcc structure with $a = 3.57$ Å was performed. Its HF binding energy, $E_b^{\mathrm{SCF}} = -3.85 \pm 0.25$ eV, indicates that it is more unstable than γ-C. A computation for a three-layer γ-C slab (simulating a thin film) with $a = 3.57$ Å was done. But it has a similar binding energy to the bulk case.

From the studies discussed above, it seems that the γ-phase C is likely to be unstable. The comparison of its electronic structure with that of a typical metal and a typical HTSC parent material indicates that it does not look like a promising candidate for a HTSC parent material. It is possible, though, that doping may change the electronic structure significantly to produce HTSC.

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