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Optical properties of superconducting K_3C_{60} and insulating K_6C_{60}

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The electronic structures and the linear optical properties of superconducting fcc K_3C_{60} and insulating bcc K_6C_{60} are calculated by means of a first-principles method within the local-density approximation. The calculated optical properties for these two crystals as well as those of fcc C_{60} are in very good agreement with recent electron-energy-loss spectra measurements.

The recent discovery of superconductivity in the M_3C_{60} system [where M=K, Rb, and Cs (Refs. 1-4)] with a critical temperature T_c as high as 33 K in the $Cs_xRb_yC_{60}$ system[4] calls for a systematic study of their electronic structures in order to gain some insight into the mechanisms involved. We have already reported band-structure, density-of-states (DOS), and Fermi-surface (FS) studies for the crystalline K_xC_{60} system with $x=1$, 2, 3, and 6 (Ref. 5) in the face-centered cubic (fcc) and the body-centered cubic (bcc) structures. In an earlier paper, the electronic structure and the optical properties of fcc C_{60} were reported.[6] In this paper, we present the results of optical properties calculations for K_3C_{60} and K_6C_{60} crystals, and compare them with that of fcc C_{60} and some of the very recent experimental data on K-doped C_{60} films.

We have used the first-principles orthogonalized linear combination of atomic orbitals (OLCAO) method in the local-density approximation (LDA) to study the electronic structures of C_{60} and K_xC_{60}. Since the computational method has been adequately described in the literature,[5-7] it will not be repeated here. Our basis function includes the $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic functions of C and $1s$, $2s$, $3s$, $4s$, $2p_x$, $2p_y$, $2p_z$, $3p_x$, $3p_y$, $3p_z$, $4p_x$, $4p_y$, $4p_z$, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$, and $3d_{3r^2-z^2}$ atomic orbitals of K. Each of the C (K) atomic functions are expanded in terms of 16 Gaussian-type orbitals (GTO) with exponents ranging from 50000 to 0.15. The final fitting error in the charge-density representation by a sum of atom-centered Gaussian functionals is less than 0.002 electron per valence electron. For the fcc (bcc) lattice of K_3C_{60} (K_6C_{60}), 2 (2) special **k** points were used in the self-consistent iterations, while in the DOS calculation using the linear analytic tetrahedron method, 89 (91) regularly spaced **k** points in the irreducible portion of the fcc (bcc) Brillouin zone (BZ) were employed. In addition, secular equations were solved at a large number of sampling **k** points for plotting the band structure along the symmetry axes and for the mapping of FS cross sections. The lattice constants used in our calculation are 14.20 Å for the fcc K_3C_{60} and 11.39 Å for the bcc K_6C_{60}, respectively. The atomic positions for K are those determined by Stephens *et al.*[8] for K_3C_{60} and by Zhou *et al.*[9] for K_6C_{60}.

The band structures for fcc C_{60}, fcc K_3C_{60}, and bcc K_6C_{60} are shown in Figs. 1(a)-1(c), respectively. fcc C_{60} and bcc K_6C_{60} are insulators, while K_3C_{60} is found to be metallic. The occupied portion of the half-filled band has a width of only 0.18 eV. The highest occupied band for K_6C_{60} has a width of 0.46 eV. These band structures are similar to those obtained by other LDA calculations.[10-12] Still, subtle variations exist between all these calculations and we expect these differences to diminish as each group further refines and increases the accuracy of their calculations. The numerical numbers for bandwidth, gap sizes, DOS at Fermi level $N(E_F)$, etc., had been summarized in Table I of Ref. 5. An important point is that we have obtained an $N(E_F)$ value of 17 states/eV cell for K_3C_{60}. This is in excellent agreement with the value of 20

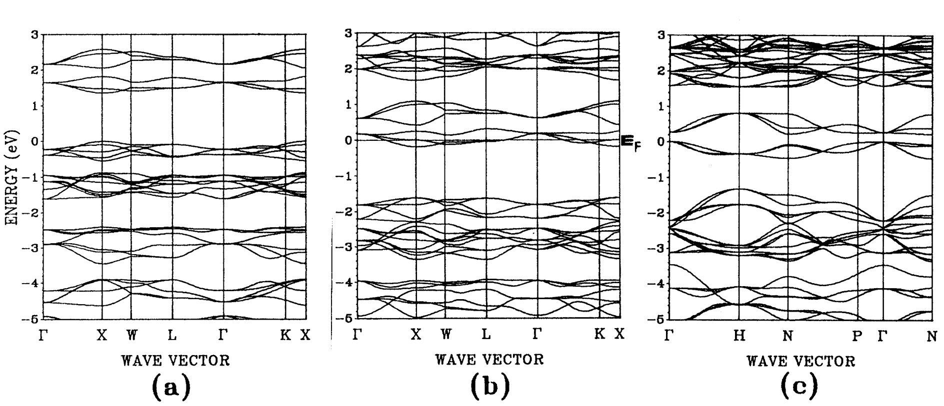

FIG. 1. Band structure of (a) fcc C_{60}, (b) fcc K_3C_{60}, and (c) bcc K_6C_{60}. The zero energy is either at the top of the valence band or at the Fermi level.

states/eV cell deduced from the ^{13}C NMR spectroscopy of Tychko *et al.*[13] In arriving at this experimental value, they have estimated the Fermi contact density $|\Psi(0)|^2$ to be of the order of 4×10^{23} cm^{-3}. Calculation of the pressure dependence of the electronic structure in K_3C_{60} (Ref. 14) show a drastic reduction in $N(E_F)$ as pressure is applied, consistent with the experimental observation of decreasing T_c with an increased pressure.[15] The good agreement between the calculated DOS spectra[5,6] with the photoemission data,[4,16] and now a more quantitative agreement in $N(E_F)$ value in K_3C_{60} lend great credence to the calculated electronic structure.

The FS of K_xC_{60} with $x=1,2,3$ were investigated in Ref. 5. In Fig. 2, we display the calculated FS cross sections in two perpendicular planes of the fcc BZ for K_3C_{60}. The most conspicuous feature is the existence of a large hole pocket centered at Γ. In the $K_z=0$ plane [see Fig. 2(a)], the cross section of this hole pocket is close to being circular with a radius of $0.48(2\pi/a)$. However, in the perpendicular plane [Fig. 2(b)], the vertical FS line is parallel to the K_z axis such that the three-dimensional FS of the hole pocket resembles that of a Chinese palace lantern. We have estimated the volume of this hole pocket and the corresponding FS area to be 0.051 Å^{-3} and 0.90 Å^{-2}, respectively.

We now turn to our main result for this paper, namely, the optical properties of the superconducting fcc K_3C_{60} and the insulating bcc K_6C_{60}. We shall compare them with that of the pure fcc C_{60} which has shown to be a semiconductor with a direct gap of about 1.39 eV at the point X (Ref. 6). The procedure for the optical calculation has been described before.[6,7] We only emphasize that in the present calculation, the momentum matrix elements associated with the optical transition were fully taken into account using the wave functions obtained at the 22 (30) **k** points in the irreducible portion of the BZ for the fcc K_3C_{60} (bcc K_6C_{60}) lattice. Figure 3 shows the calculated imaginary part of the dielectric functions $\epsilon_2(\omega)$ for fcc C_{60}, K_3C_{60}, and K_6C_{60}. For the fcc C_{60}, $\epsilon_2(\omega)$ shows five disconnected absorption bands in the 1.4–7.0 eV range. Within each band, there are sharp structures that may be attributed to critical-point transitions.[6] As K ions are added, the disconnected absorption band starts to merge, indicating an overall change in the electronic structure. Hence, the electronic structures of K_3C_{60} cannot be simply interpreted as the filling of extra electrons in the lowest unoccupied conduction bands in the context of a rigid-band model.

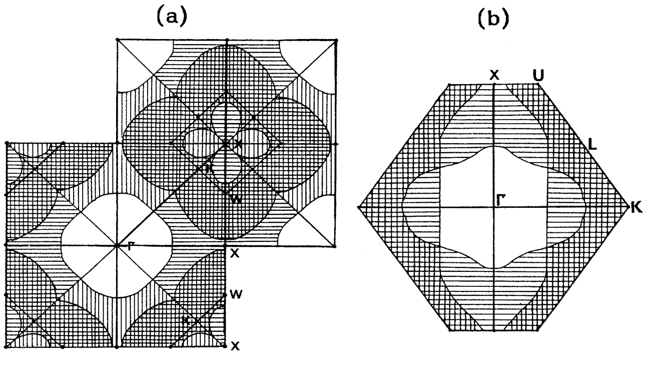

FIG. 2. Calculated Fermi surfaces of K_3C_{60} in the (a) $K_z=0$ plane, and (b) $K_y=0$ plane of the fcc BZ.

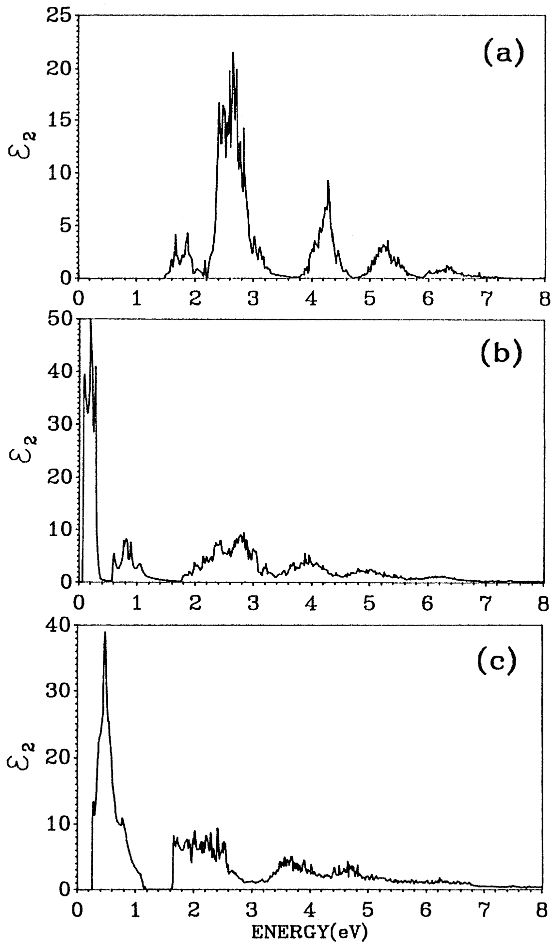

FIG. 3. Calculated imaginary part of the dielectric function of (a) fcc C_{60}, (b) K_3C_{60}, and (c) K_6C_{60}.

Figure 4 shows the real part of the dielectric function $\epsilon_1(\omega)$ for the three crystals obtained from $\epsilon_2(\omega)$ of Fig. 3 by a Kramers-Kronig transformation. The static dielectric constant ϵ_0, for fcc C_{60}, K_3C_{60}, and K_6C_{60} are 4.4, 42.2, and 19.2, respectively. Since K_3C_{60} has a metallic band structure, it is not surprising to see it has the highest ϵ_0 among the three crystals. However, in a metallic system, intraband transitions may be involved which were neglected in our calculation. So the ϵ_0 value of 42.2 for K_3C_{60} may be somewhat uncertain. For K_6C_{60}, the ϵ_0 of 19.2 is comparable to those of narrow gap semiconductors such as InSb ($\epsilon_0=17.9$) and GaSb ($\epsilon_0=15.7$).[17] The static dielectric constant is an important physical quantity which may play a major role in formulating plausible models for superconductivity.[18]

The electron-energy-loss functions (calculated as $-\mathrm{Im}[1/\epsilon(\omega)]$) for the C_{60}, K_3C_{60}, and K_6C_{60} crystals are shown in Fig. 5. For fcc C_{60}, the calculated energy-loss function has three sharp peaks at 3.5, 4.8, and 5.8 eV, and

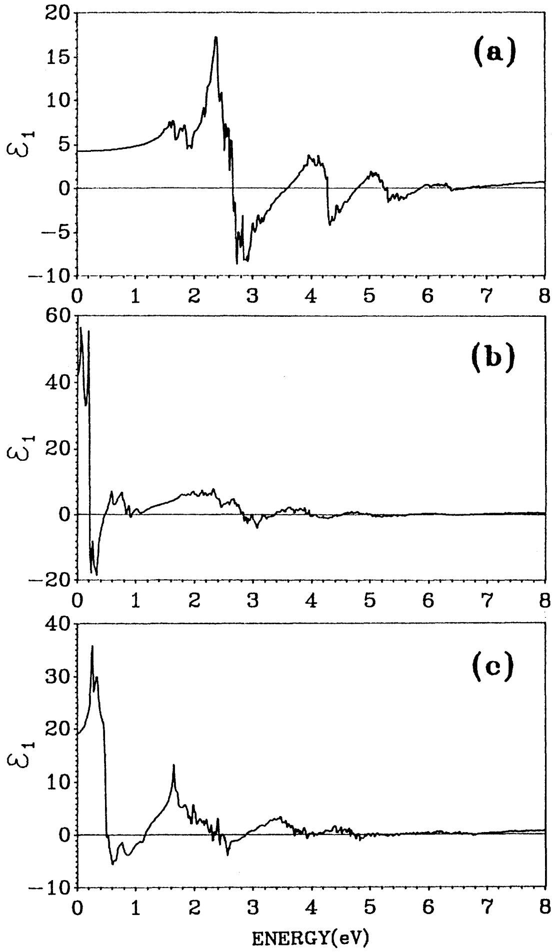

FIG. 4. Calculated real part of the dielectric function of (a) fcc C_{60}, (b) K_3C_{60}, and (c) K_6C_{60}.

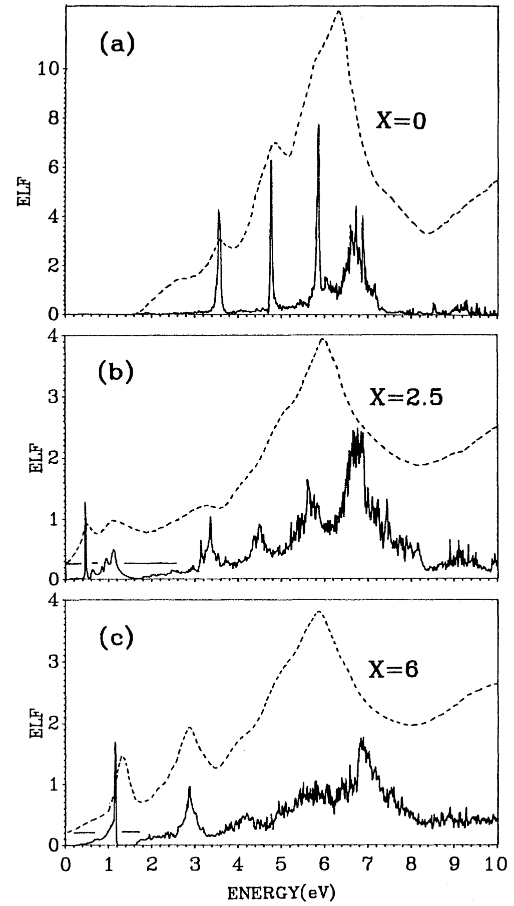

FIG. 5. Calculated electron-energy-loss function of (a) fcc C_{60}, (b) K_3C_{60}, and (c) K_6C_{60}. The dashed lines are the experimental data from Ref. 19 for K_xC_{60} with $x=0$, 2.5, and 6, as indicated.

a broader peak at 6.7 eV which was interpreted as a bulk plasmon excitation.[6] We are fortunate to have experimental data from Sohmen, Fink, and Kratschmer (SFK) for comparison.[19] SFK have measured the energy-loss function for K_xC_{60} thin films with different K content using high-energy electron-loss spectroscopy with an energy resolution of 0.14 eV. The measured spectra corresponding to a momentum transfer of $|q|=0.2$ Å^{-1} for $x=0$, 2.5, and 6.0 are reproduced in Fig. 5 as dashed lines. For $x=2.5$, it is conceivable that the samples used in the experiment may consist of mixed phases with K_3C_{60} as the major component. Therefore, the comparison in Fig. 5(b) is not for the same stoichiometric composition. The agreement between the theory and the experiment shown in Fig. 5 is amazingly impressive. Almost all the major structures in the measured data are reproduced by our calculation, including some of the weak shoulderlike structures. Of particular significance is the reproduction of the two prominent peaks at 1.3 and 2.9 eV in K_6C_{60} which are clear evidence for K_6C_{60} being an insulator with a well-defined band gap. The only deficiency seems to be that the calculated major plasmon peaks at 6.7, 6.8, and 6.9 eV in fcc C_{60}, K_3C_{60}, and K_6C_{60} are at a higher energy than the corresponding peaks from the measurement. This could be due to the minimal basis set used in our calculation. If the basis set is further extended, the higher conduction-band states will be shifted downward slightly due to the increased variational freedom of the state wave function. This will result in a downward shift of the major plasmon peaks in closer agreement with the experiment. Since the work of SFK is the only set of experimental data on the optical properties of K_xC_{60} that we are aware of, and since the sample used by SFK may contain a small amount of C_{70}, it is premature to make too definitive a conclusion at this time. The fact that the calculated optical properties of all three crystals, C_{60}, K_3C_{60}, and K_6C_{60}, with well-determined crystal structures are in good agreement with measurement implies that the calculated electronic structures for these systems are essentially correct. We are currently in the process of studying the change in the electronic structure with pressure in K_3C_{60} and with intercalating elements in C_{60} other than K so as to obtain a more complete picture on the electronic and linear optic properties of this fascinating family of compounds.

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