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Effect of van Hove Singularity on T_c in Rb doped C_{60}

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In the present study we investigate the role of van Hove singularity on the optimization of T_c in Rb doped fullerenes $C_{60}Rb_3$. A first principles self-consistent full potential linear muffin-tin orbital method using density functional theory in local density approximation was employed. The doped Rb atoms are of two types occupying the tetrahedral and interstitial positions in the fcc lattice. The added Rb atoms fill the t_{1u} band of the undoped fullerenes C_{60} up to half which makes $C_{60}Rb_3$ conducting. Saddle points leading to van Hove singularities are observed in the neighbourhood of the symmetry point L. The shifting of the van Hove singularity with the volume of the lattice is investigated. We observe a saddle point just at the Fermi level for a lattice constant of 14.435 Å. The highest value of T_c should thus be observed at the above lattice constant. This result is in excellent agreement with the observed high value of T_c measured in $C_{60}Rb_3$ for a lattice constant of 14.435 Å.

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1. Introduction

It is now more or less accepted that in alkali doped fullerenes the mechanism of superconductivity is of BCS type i.e., electron–phonon interaction alone is responsible for the superconducting behaviour. In the optimization of the transition temperature, the density of states (DOS) at the Fermi level (E_F) plays a crucial role. Saddle points may appear at the symmetry points of the Brillouin zone and may lead to van Hove singularities (vHs) which incur a high density of electron states at E_F in case the vHs lies at E_F. The study of fullerenes is interesting because it does not contain any CuO_2 planes observed in oxide superconductors and the superconductivity arises from the 3-dimensional behaviour of C_{60} solid.

In the present article, we have investigated the crucial role of vHs in the optimization of T_c. In an earlier publication [1] we have reported the results of our first principles calculation obtained for $C_{60}K_3$. We predicted that an expanded solid of $C_{60}K_3$ having a lattice constant of 14.51 Å will reveal maximum value of T_c.

Here, we discuss the role of vHs in achieving high value of T_c in the case of $C_{60}Rb_3$. The interstitial Rb^{3+} ions possess large sizes and will expand the lattice.

2. Results and discussions

Above 249 K, pure solid C_{60} exists in a orientally disordered face centered cubic structure. However, at 249 K, C_{60} makes a first-order phase transition to an orientally ordered simple cubic structure with four C_{60} molecules per unit cell. We confine our study to the ordered fcc unit cell containing one molecule to cope with the available computation facility. The point-group symmetry of this structure is T_h, which is the highest one. The fullerene molecule contains 20 hexagonal and 12 pentagonal faces. In the structure, there are three non-equivalent carbon atoms, namely C(1), C(2), and C(3) and their numbers are 12, 24, and 24, respectively. In a full potential linear muffin-tin orbital (LMTO) calculation one needs to consider the empty space lying within the C_{60} molecule and also the interstitial space between the various C_{60} molecules. The empty space has been filled by a number of 48 empty spheres of various sizes. The chosen muffin-tin sphere for each C atom has a radius of 1.3 a.u.

Three Hankel functions with decay energies −0.01, −1.0, and −2.3 Ry were chosen for the carbon atom and two Hankel functions with decay energies −1.0 and −2.3 Ry for empty spheres were needed to fill the interstitial empty space. For carbon atoms, the linear muffin-tin orbitals having angular momentum up to $l = 4$ and for the empty spheres up to $l = 2$ were included in the calculation. In order to achieve high accuracy throughout the whole energy region of electron states, the self-consistent calculation was performed for the linearized wave functions expanded at three different energies −0.01, −1.0, and −2.3 Ry. The exchange correlation potential of Hedin–Lundqvist [2] was chosen. The core electrons are relaxed and the core electron density is evaluated in each iteration. C ($2s$, $2p$) and Rb ($5s$, $5p$, $4d$) valence states are considered. The electronic structure for the undoped C_{60} solid at the various symmetric points of the Brillouin zone, i.e. Γ $(0,0,0)$, X $(1,0,0)$, W $(1,0.5,0)$, L $(0.5,0.5,0.5)$ is reproduced in Fig. 1. The chosen lattice constant is 14.10 Å. The highest occupied states i.e., the valence band maximum (VBM) which appears at the X-symmetry point is chosen as origin of the energy. The next empty conduction band state arises from t_{1u}-type states. The solid is semiconducting with a direct band gap of 0.7 eV at the X-point, which

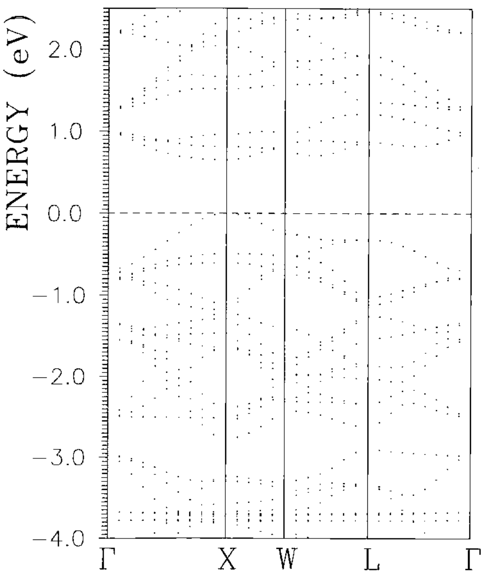

Fig. 1. Electronic band structure for the undoped C_{60} solid at the various symmetric points of the Brillouin zone.

is a bit lower than the experimental value of 1.0 eV. This underestimation of energy gap is typical of a local density approximation, where the on-site many-body effects of the exchange and correlation energies have been ignored. Appreciable dispersion is shown by the states lying in the neighbourhood of the gap because of the C_{60}—C_{60} interaction.

3. $C_{60}Rb_3$

As the incorporation of large sized rubidium ion will expand the C_{60} lattice, a lattice constant of 14.43 Å was chosen for calculating the energy and the electronic structure. Rb atoms are located in the two types of vacant sites lying between the C_{60} molecules possessing tetrahedral and octahedral point-group symmetries. One rubidium atom Rb [1] occupies the octahedral site and two Rb atoms the tetrahedral site. The radius for each Rb muffin-tin sphere is chosen as 2.34 a.u. The three electrons donated by the three Rb atoms fill the conduction band up to half making the $C_{60}Rb_3$ solid metallic. The electronic structure for $C_{60}Rb_3$ is shown in Fig. 2a. The dispersion of the other states is reduced because of the expanded lattice. The conduction band arises from the hybridization of C ($2p$) and sp^3 orbitals of Rb. The saddle point appears in the neighbourhood of the L-symmetry point near E_F as can be seen in Fig. 2b, where a blown up electronic structure is shown. The shifting of saddle point was studied by varying the volume of the crystal. For a lattice constant 14.435 Å, the vHs peak appears just at E_F.

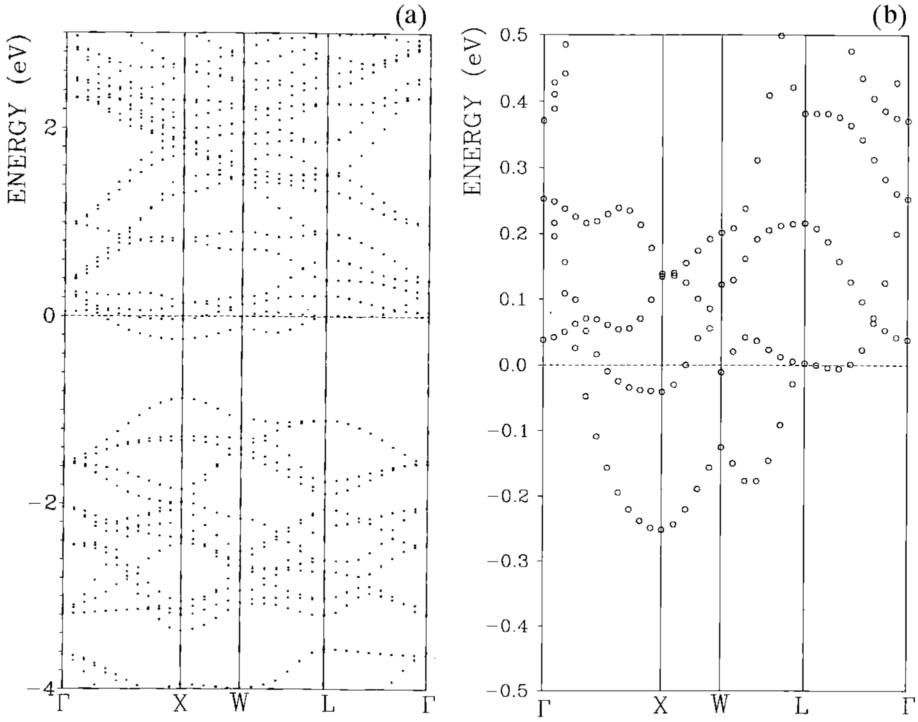

Fig. 2. (a) Electronic band structure (dispersion curves) and (b) blown up structure in the neighbourhood of Fermi level for $C_{60}Rb_3$.

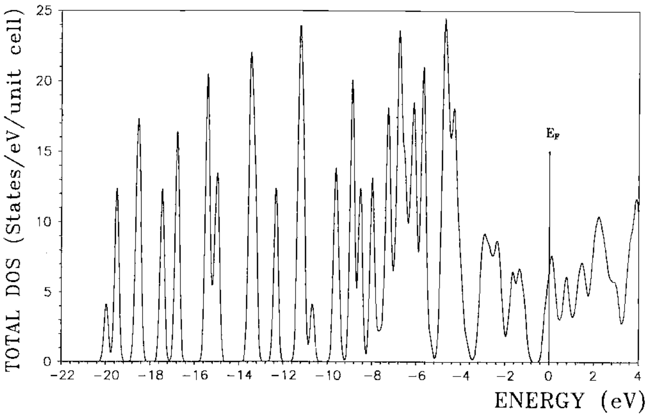

Fig. 3. Total electronic density of states for $C_{60}Rb_3$.

The electronic density of states and the projected density of states (PDOS) per unit cell on the various non-equivalent C and Rb atoms are shown in Figs. 3 and 4, respectively. The DOS was calculated for a selected number of 12 k-points with a broadening of 0.01 Ry.

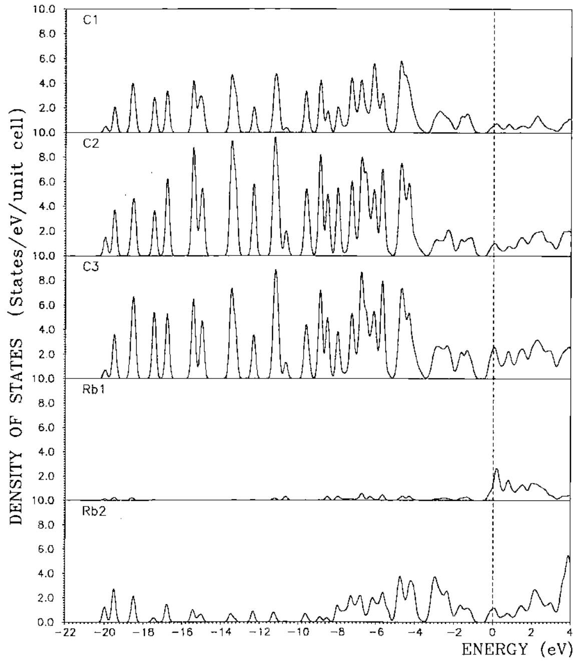

Fig. 4. Projected density of states at various atoms of $C_{60}Rb_3$.

The PDOS shown in Fig. 4 at carbon atoms is quite similar to that of undoped C_{60}. The valence charges inside the Rb (1) and Rb (2) muffin-tin spheres are 0.016 and 0.044, respectively, which reveal almost complete ionization of Rb atoms. The PDOS at all the three different species of the host carbon atoms near E_F are comparable with the PDOS at the Rb atoms. The electron states in the neighbourhood of E_F are quite delocalized and are extended throughout the unit cell. The strong attractive interaction of these electrons mainly with the tangential vibrations of the carbon atoms results in the occurrence of the superconductivity. The overall DOS is comparatively high at the Fermi level which will give rise to maximum value of T_c for the predicted lattice constant of 14.435 Å. This is in excellent agreement with the high value of 29.5 K of T_c measured by Schilling et al. [3] for a lattice constant of 14.43 Å.

4. Conclusion

We predict the occurrence of highest value of T_c in rubidium doped C_{60} at a lattice parameter of 14.435 Å which is in excellent agreement with the experimental data reported for $C_{60}Rb_3$.

Acknowledgments

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