Electronic band structure, electron-phonon interaction, and superconductivity of (5,5), (10,10), and (5,0) carbon nanotubes

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The electronic band structure, electron-phonon interaction, and superconducting transition are investigated for the (5,5), (10,10) armchair and (5,0) zigzag single walled carbon nanotubes (SWCNT). While the electron-phonon interaction and superconducting transition temperature are very small in (5,5) and negligibly small in (10,10) armchair tubes, they are considerable in the (5,0) zigzag tube. The (5,0) tube, which is a semiconductor with π-bands alone contributing to the band structure, exhibits metallic character with π-σ bands hybridization. As a result the van Hove like singularity in the density of states moves towards the top of the valance band enhancing the effective density of states near the Fermi energy. Consequently the electron-phonon interaction increases and the (5,0) tube turns out to be a superconductor with appreciable transition temperature and found to be the most probable member of the family of 4 Å diameter carbon nanotubes for which the superconducting transition temperature is experimentally measured.

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The successful fabrication and functionalization of carbon nanotubes have opened a new chapter in modern physics as well as lead to important technological applications.[1–5] There is a steep rise in the interest in studying the various properties of these systems. The discovery of superconductivity in 4 Å diameter nanotubes in zeolite matrix[6] and in nanotube ropes[7] has initiated theoretical investigation of electron-phonon interaction and superconductivity.[8–16] In this paper we report our investigation of the electronic band structure, electron-phonon interaction, and superconductivity in (5,5), (10,10), and (5,0) single walled carbon nanotubes. While the (5,5) and (10,10) tubes are chosen to study the effect of curvature on the electron-phonon interaction the (5,0) tube is chosen because it has the diameter (3.96 Å) which is very close to the experimentally measured diameter of the well separated carbon nanotubes for which superconductivity has been observed.[6] Also theoretical predictions regarding the electron-phonon interaction and superconductivity for the (5,0) tube are contradictory.[9,12,13,15] For (5,5) and (10,10) tubes the superconducting fluctuations as a function of doping level have been estimated.[21] Barnett *et al.*[14] have analyzed in detail the band structure, phonon dispersion, electron-phonon interaction, superconductivity, and charge-density wave (CDW) instabilities in (5,0) and (5,5) carbon nanotubes. They have used zone folding and tight binding methods to get the band structures.

In the work reported in this manuscript the band structures are obtained using a variant of the zone folding method (ZFM) and the Vienna *ab initio* simulation package, VASP.[17] In the zone folding method we have chosen a unit cell which *spirals* along the length of the tube. Also we have used average density of states near the Fermi energy rather than density states at the Fermi energy to take into account the role of van Hove like singularities[18,19] which are unique for the carbon nanotubes. The electron-phonon interaction is treated using McMillan's theory[20] in conjunction with the prescription by Gaspari and Gyorffy.[21] Even for simple systems like Li[22] treating electron-phonon and electron-electron interactions on the same footing using *ab initio* methods has been impossible. In most of the previous calculations[14,22] the electron-phonon interaction is treated using McMillan's theory[20] and the effect of electron-electron interaction (μ^*) on pairing is taken into account assigning most probable values (0.1–0.2) to it. Therefore it is obvious that for systems like carbon nanotube we have followed the same treatment.

We have used a unit cell which *spirals* up (like a helix) along the length of the tube. The allowed components of the **k** vectors due to confinement are obtained by projecting the **k** vectors along the circumferential direction. This choice of the unit cell, we hope, gives a better representation for the carbon nanotube, which was initially called as "helical microtubules"[1] and described in a manner similar to helical chain polymer with translational symmetry.[23] With this unit cell the band structures are obtained, using the above mentioned ZFM, for (5,5), (10,10), and (5,0) tubes along the Γ-X direction which is parallel to the tube axis. As pointed out in the introduction the band structures are also obtained using the VASP.[17] Ultrasoft pseudopotentials are used with 41 K points distributed uniformly along the Γ-X. The band structures for the (5,5), (10,10), and (5,0) tubes obtained using ZFM and VASP are given in Figs. 1–6. The band structure of the (5,0) tube (Figs. 3 and 6) with π-σ bands hybridization exhibits metallic character.[14,24]

Tersoff's bond-order potential,[25] which is parametrized for carbon and capable of describing both sp^2 and sp^3 c bonding, is used to describe the covalent bonds between the carbon atoms[26] for the purpose of the phonon band structure calculations. Since from the point of view of superconductivity we are interested in the averaged phonon frequency square, $\langle\omega^2\rangle$, the use of above classical potential for getting the phonon spectrum should be sufficient. The phonon dispersion relations are obtained for (5,5) and (10,10)

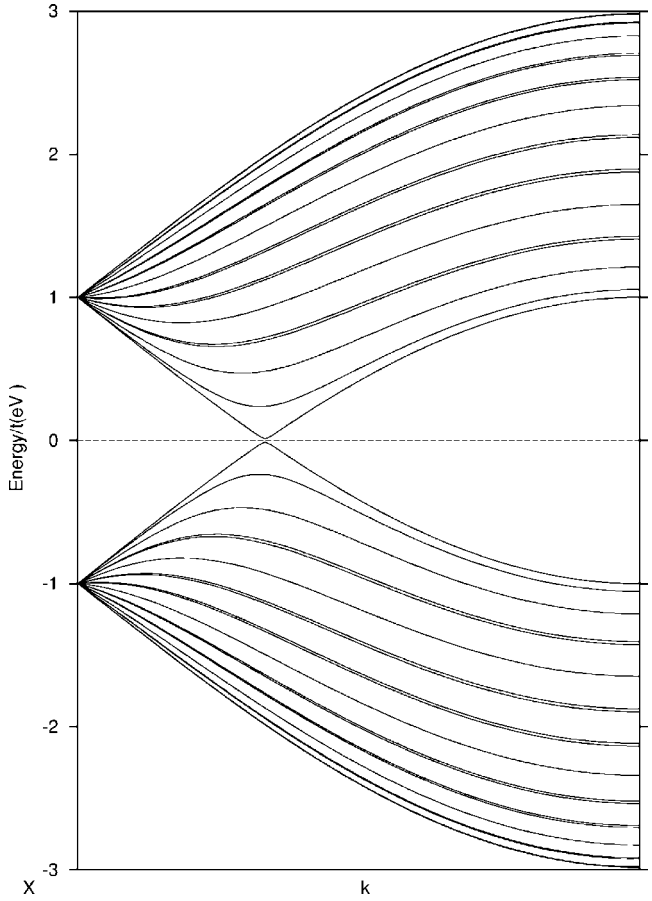

FIG. 1. Band structure of (5,5) CNT (ZFM).

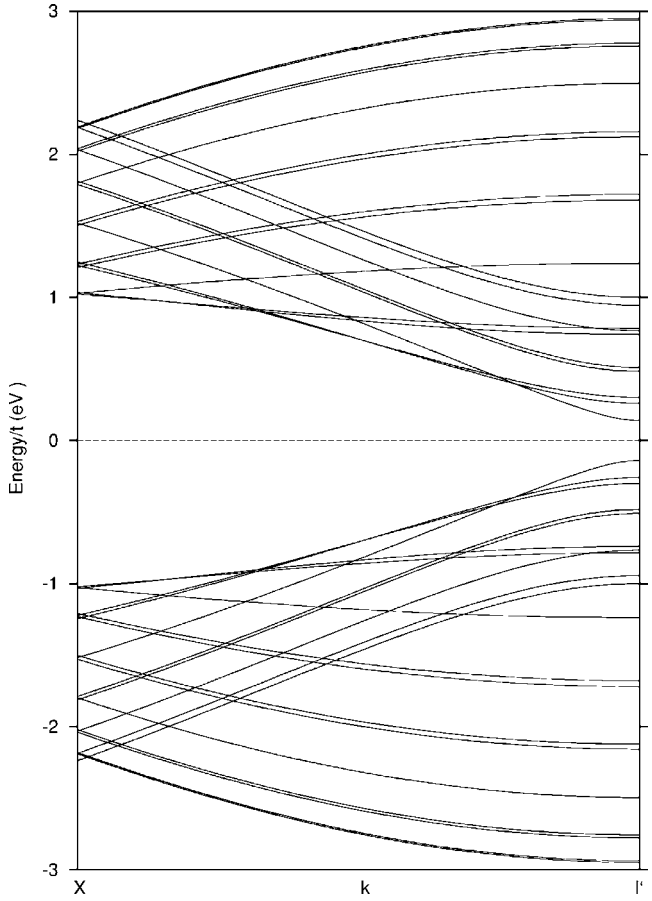

FIG. 2. Band structure of (5,0) CNT (ZFM).

SWCNTS. The general features are similar to the spectra reported previously.[3,4,26] ω_{max} decreases with the increase of the curvature of the tube. Since the phonon spectra of (5,5) and (5,0) tubes have similar features,[14] we have used the (5,5) tube phonon spectrum in estimating $\langle\omega^2\rangle$ for the (5,0) tube taking into account the effect of curvature.

The electron-phonon interaction plays an important role in imparting superconductivity in the material. The factors, which determine superconducting behavior, are electron-phonon interaction, λ, the effect of electron-electron (Coulomb) interaction on pairing, μ^*, averaged phonon frequency square, $\langle\omega^2\rangle$, and Debye temperature θ_D. According to McMillan's[20] definition the electron-phonon interaction factor is

$$\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle}, \tag{1}$$

where M is the atomic mass, $\langle\omega^2\rangle$ is an average of the phonon frequency square and $\langle I^2\rangle$ is an average (over the Fermi energy) of the reduced electron-phonon matrix element square. This relation has been well tested[20,22] for a variety of systems including carbon nanotube.[11]

The density of states at the Fermi energy, $N(E_F)$, which is playing a vital role here, needs a special treatment. The situation one faces here in the carbon nanotube, a pseudogap in the density of state curve, is similar to the one encountered in a BCS superconductors.[18] In a BCS superconductor the normal state and the superconducting state are separated by a gap, ϵ, at the Fermi energy E_F, and the new density of states has an energy gap of magnitude 2ϵ centered around the Fermi energy. The modified density of states is, then given by,[18]

$$N(E) = N(E_F)^* \int EdE/(E^2 - \epsilon^2)^{1/2}$$

or

$$N(E) = N(E_F)^* \Sigma_i [E_i/(E_i^2 - \epsilon^2)^{1/2}], \tag{2}$$

which has van Hove type singularity at the edges of the gap, $E = \epsilon$.

Normally when the density of states at the Fermi energy, $N(E_F)$, is large and phonon frequency is not high, then $\mathbf{k}$ is restricted to $\mathbf{k}_F$ and the bands crossing the Fermi level are taken into consideration. But for the 1D system like carbon nanotube where we have a very small density of states at the Fermi energy (pseudogap) and large phonon frequency, one has to use, like in a BCS superconductor,[18] a modified density of states in calculating the electron-phonon interaction parameter λ. The modified or effective density of states is obtained by averaging the density of states $[N_{ave}(E)]$ near the Fermi energy over an energy window.[18,27] We have computed the $\langle\omega^2\rangle$ from the calculated phonon spectra. The $\langle\omega^2\rangle$

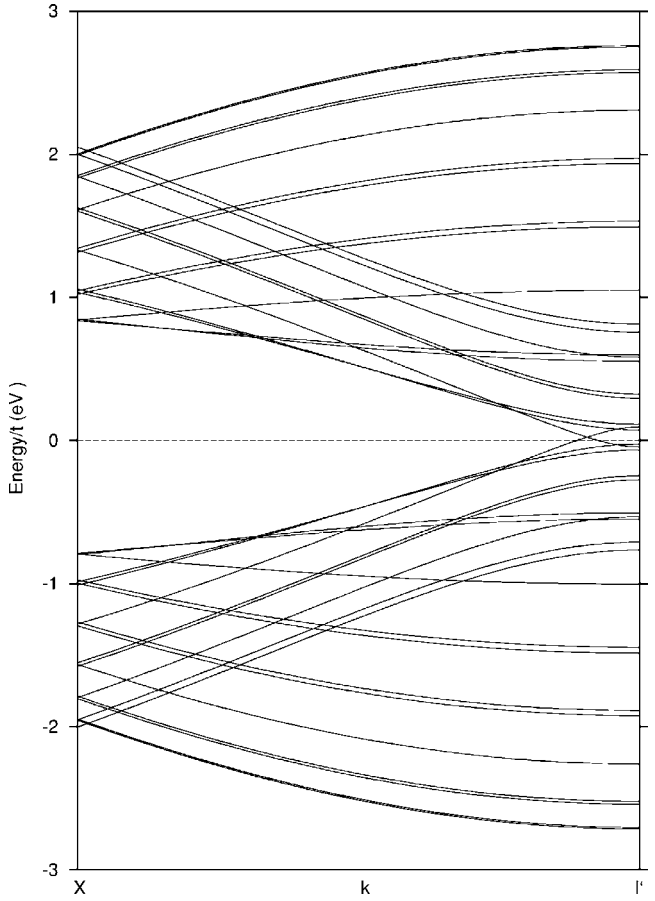

FIG. 3. Band structure of (5,0) CNT (ZFM) with pi-sig hybridization.

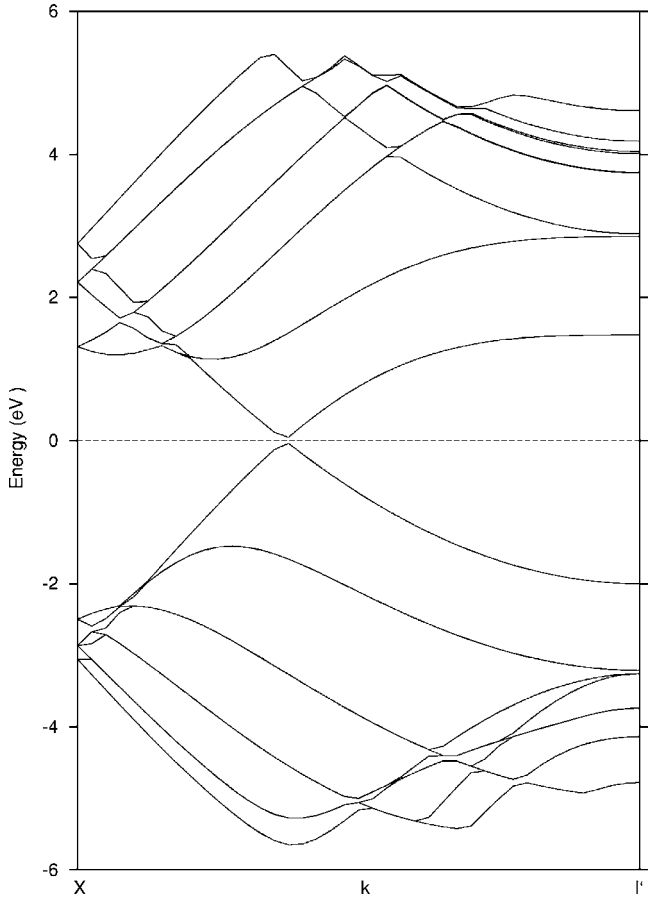

FIG. 4. Band structure of (5,5) CNT (Vasp).

for the (10,10) tube is enhanced compared to the (5,5) tube. As pointed out earlier, for want of data on the (5,0) tube we have used the $\langle\omega^2\rangle$ value of (5,5) to get $\langle\omega^2\rangle$ for (5,0) tube taking into account the curvature effect. The $\langle\omega^2\rangle$ value decreases with increase of curvature.

For all the three tubes the electron-phonon interaction parameters, λ, are computed and the corresponding superconducting transition temperatures T_C are calculated using McMillan's formula:[20]

$$Tc = \frac{\theta_D}{1.45} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right], \tag{3}$$

which gives a good estimate of the Tc value. Here μ^*, the electron-electron interaction parameter, is chosen to be 0.0, 0.1 (most commonly used) and 0.19. θ_D, the Debye temperature of the carbon nanotube, is taken as 1400 K.[8] We have also looked into the variation of $\theta_D$with tube curvature. The relation,[22]

$$\theta_D(R) = (E_F/E_F^i)^{1/2}(R_i/R)^{1/2}\theta_D(R_i), \tag{4}$$

where R is the radius of the carbon nanotube, takes care of this. We got an estimate of $\langle\omega^2\rangle$ for the (5,0) tube by making use of a relation similar to the above one. The relation, taking into account the decreasing nature of $\langle\omega^2\rangle$ with increase of curvature, is:

$$\langle\omega^2\rangle(R) = (E_F/E_F^i)^{1/2}(R_i/R)^{-1/2}\langle\omega^2\rangle(R_i). \tag{5}$$

In the electron-phonon interaction parameter λ and the superconducting transition temperature T_C are computed for (5,5), (10,10), and (5,0) tubes following the above mentioned procedure. The results are summarized in Table I. For the (5,5) tube the values of λ and T_C are very small, for the (10,10) tube the λ and T_C values are negligibly small even though Jiang *et al.*[16] report that in such tubes the electron-phonon coupling strengths for the transverse modes are larger than for the longitudinal modes. For the (5,5) tube the reported[14] λ value is 0.031. In these tubes the van Hove singularities are far away from the Fermi energy, so their contribution to the averaged density of states is not appreciable. Inclusion of Coulomb interaction enhances CDW transition in these tubes. However, T_C values are larger than the CDW transition calculated for (5,5) by Barnett *et al.*[14] They have reported a T_C value of 1.11×10^{-12} K for the (5,5) tube with $\mu^*=0$.

In the (5,0) tube the van Hove type singularity is now closer to the Fermi energy compared to an armchair tube. As a result the computed average density of states over the selected energy window is many times larger than that of (5,5) and (10,10) armchair metallic tubes. With this modified density of states the λ and T_C are estimated (Table I). The λ values computed by us are well within the range (0.2–0.8) predicted by Gonzalez.[12] The λ and T_C values reported for the (5,0) tube by Barnett *et al.*[14] are 0.57 and 64 K with

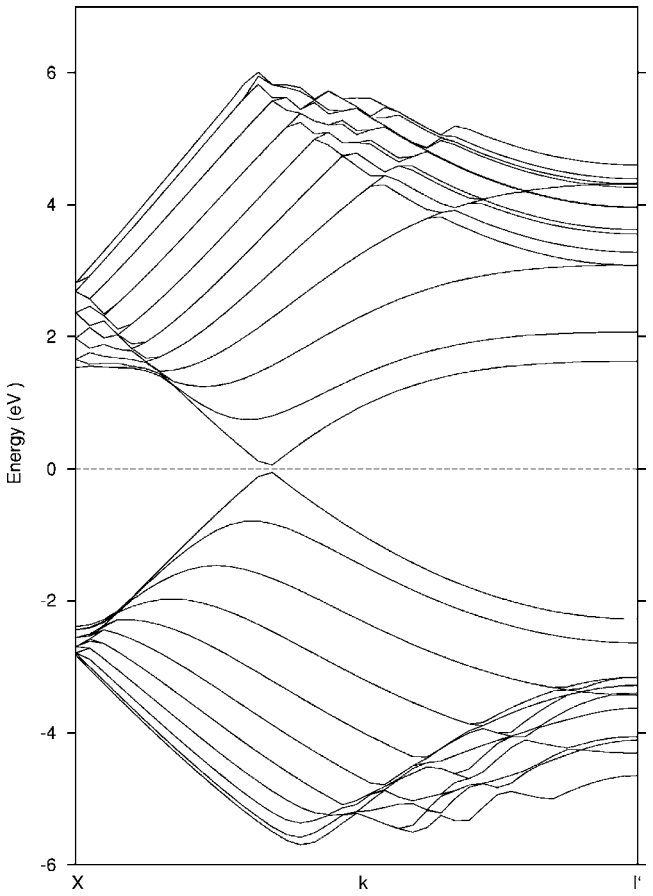

FIG. 5. Band structure of (10,10) CNT (Vasp).

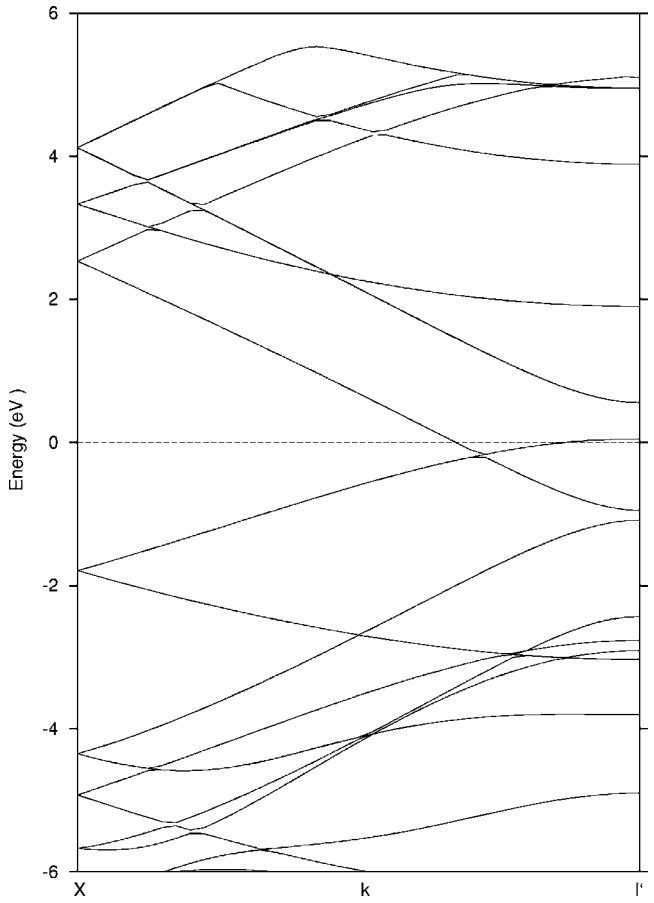

FIG. 6. Band structure of (5,0) CNT (Vasp).

$\mu^*=0$, 13 K with $\mu^*=0.1$ and 1.1 K with $\mu^*=0.19$. The T_C values are larger than CDW transition arising out of Peierls instability and in the (5,0) tube with the increase of Coulomb interaction the CDW transition is suppressed[14] in contrast with the (5,5) tube. For the (5,0) tube the phonon-exchange interaction lying in the range 0.2–0.8 and the Coulomb potential up to 0.2 the superconducting phase is dominant over the CDW phase.[12]

In a recent report Connetable *et al.*[15] have questioned the occurrence of superconductivity in (5,0) tube by arguing that because of the hybridized π-σ bands the (5,0) tube undergoes a metal to semiconductor transition with T_{CDW} larger than room temperature. However, in our case the (5,0) tube, with the π-σ bands hybridization, undergoes a semiconductor to metal transition. For such a case Barnett *et al.*[14] have computed the T_{CDW} with Coulomb interaction and found it to be very small. The carbon nanotube being a 1D electronic system, the quantum fluctuations inevitably reduce all classical transition temperatures. This is applicable to McMillan formulation of superconductivity. Our results set an upper bound[28] to the superconducting temperature and are compatible with the previous theoretical estimates[9,13,14] and the experimental situation.[6] For the (3.3) tube which is another potential candidate in the group of 4 Å carbon nanotubes, Bohnen *et al.*[29] have reported the electron-phonon interaction and the possible T_C value without electron-electron interaction ($\mu^*=0$).

If we look at the experimental situation the CDW state

TABLE I. Electron-phonon interaction parameter λ and superconducting transition temperature T_C.

SWCNT		ZFM $T_C(K)$				VASP $T_C(K)$		
	λ	$\mu^*=0.0$	$\mu^*=0.1$	$\mu^*=0.19$	λ	$\mu^*=0.0$	$\mu^*=0.1$	$\mu^*=0.19$
(5,5)	0.04	3×10^{-9}	—	—	0.028	2×10^{-14}	—	—
(10,10)	0.014	2.6×10^{-30}	—	—	0.0141	3×10^{-30}	—	—
(5,0)	0.58	57.3	24.2	6.0	0.57	55.3	22.7	5.3
with θ_D variation		75.6	31.9	7.9		73.0	30.0	7.0

arising out of Peierl's instability which is characteristic of a 1D metallic system has never been observed in carbon nanotube.[14] Tang *et al.*[6] measured the superconducting transition temperature of well separated carbon nanotubes in a zeolite matrix as 15 K. The diameter of the tubes are around 4 Å. Also they observed Meissner effect. The (5,0) tube, which we have studied, with diameter 3.96 Å may be the tube present in the zeolite matrix. It has appreciable electron-phonon interaction ($\lambda=0.57$) and with Coulomb interaction $\mu^*=0.1$ its T_C value is 22.7 K and with $\mu^*=0.19$ the T_C value is 5.3 K. This T_C value could be further improved to get closer to the experimental value by proper choice of μ^* such that it is large enough to suppress the CDW transition and maintain superconductivity.

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