PHYSICAL REVIEW B VOLUME 52, NUMBER 17 1 NOVEMBER 1995-I

First-principles calculation of the electronic and optical properties of the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

Yong-Nian Xu and W. Y. Ching*
Department of Physics, University of Missouri–Kansas City, Kansas City, Missouri 64110

Y. C. Jean and Y. Lou
Department of Chemistry, University of Missouri–Kansas City, Kansas City, Missouri 64110

(Received 19 June 1995)

The electronic structure and the optical properties of the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ are fully elucidated by means of first-principles self-consistent local-density calculation. The band effective masses on the Fermi surfaces are found to be $m_\alpha^{b*}=1.77$ m and $m_\beta^{b*}=3.50$ m, and the density of state at the Fermi level is 12.8/eV cell. These results are quite different from the existing calculations based on semiempirical methods, and are in much better agreement with experiments. Remarkable similarities in the electronic structure between the organic superconductors and the alkali-doped fullerene superconductors are pointed out and the implications discussed.

Since the discovery of the first organic superconductor (OS) in [TMTSF]PF$_6$ ($T_c=0.9$ K at 12 kbar) more than 15 years ago,[1] there have been many reports on the discoveries and properties of new OS's with increasing values of T_c.[2–4] As of today, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$ Cu[N(CN)$_2$]Br have the highest T_c of 10.4 and 12.0 K, respectively at ambient pressure. BEDT-TTF stands for the electron donor molecule bis(ethylendithio) tetrathiafulvalenel or simply abbreviated as ET. Almost all of the OS's are quasi-two-dimensional charge-transfer salts with complex crystal structures of low symmetry. While superconductivity in organic compounds with chainlike structure was predicted by Little more than 30 years ago,[5] the OS's of today consist mostly of planar aromatic molecules interlaced with other polymeric groups.

The mechanism for organic superconductivity is still not fully understood, although there is ample evidence for a BCS ground state. It has been argued that many features of OS's resemble that of the high-temperature oxide superconductors.[6] Since OS's can be prepared in much purer form free of defects and lattice imperfections compared to the oxides superconductors, there has been a concerted effort in studying their various normal and superconducting properties.[2–4] Understanding the electronic structure is the key step in understanding the normal state properties of any material. Up to now, the band structures of OS's have not been studied in detail by any first-principles methods.[7,8] For κ-(ET)$_2$Cu(NCS)$_2$, semiempirical calculations based on the tight-binding extended Hückel method have been carried out to obtain the band structures near the Fermi level (E_F) (Refs. 9,10) which provided useful information in interpreting some important experimental observations, such as in the Shubnikov–de Haas (SdH) effect.[9,11,12] However, it has been long recognized by the community that although the calculated Fermi surfaces (FS's) have the correct features due to the simplicity of the band near E_F, there are serious problems with other band parameters such as the effective band masses, bandwidths, and the density of states (DOS) at E_F or $N(E_F)$. Ironically, interpretation of the several important experiments[13–17] had to rely on these band parameters implicitly or explicitly, and the use of imprecise values can certainly lead to wrong conclusions. The effective mass m^* from the SdH effect is not a direct measurement; rather, it is obtained by fitting to the amplitude and period of magnetic oscillations which depend on both the FS area and the Dingle temperature. In the conventional BCS theory, $N(E_F)$ in conjunction with vibrational frequencies can be used to estimate T_c. The FS area can be used to estimate the Fermi velocity, mean free path, and scattering time of the charge carries. The magnetic penetration depth $\lambda(T)$ depends on m^*. The width of the band signifies the strength of Coulomb repulsion which may explain the observed small isotope effect in OS's.[16] Recently, photoemission experiments has been carried out on several OS's[18] providing information about the energy distribution in the entire valence-band (VB) region. It is therefore highly desirable to determine the electronic structure of the OS by first-principles methods.

In this paper, we present a detailed calculation of the electronic structure of the κ-(ET)$_2$Cu(NCS)$_2$ crystal using the self-consistent orthogonalized linear combination of atomic orbitals (OLCAO) method.[19] The OLCAO method is based on the local approximation of the density functional theory and has been very effective in providing an accurate electronic structure of complex crystals. We briefly outline the calculation below and refer the details of the method to the published literature.[19] The crystal structure of κ-(ET)$_2$Cu(NCS)$_2$ as reported by Urayama *et al.*[20] was used. The monoclinic cell contains four ET molecules and two Cu(NCS)$_2$ molecules for a total of 118 atoms and 466 valence electrons. The Bloch functions were expanded in terms of atomic orbitals represented by a linear combination of Gaussian type of orbitals (GTO). A minimal basis set for each atom plus the S-$3d$ and S-$4s$ orbitals were included in the basis set for the Bloch function. The crystal charge density and the site-decomposed effective one-electron potential were expressed as sums of Gaussian functionals centered at

0163-1829/95/52(17)/12946(5)/$06.00

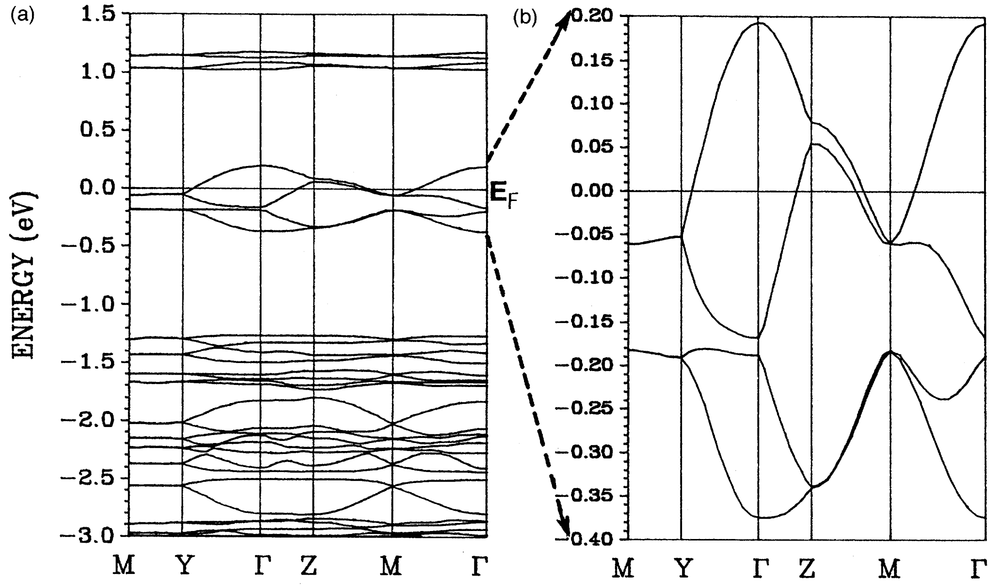

FIG. 1. Calculated band structure of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

each atom. Interaction integrals between any pairs of atoms up to any neighbors were included and the lattice summation carried out to convergence. After orthogonalization to the core orbitals, the secular equation has a dimension of 602×602. The crystal potential was iterated to self-consistency, and convergence was very slow because of the large number of atoms of different types in the system. The criterion for convergence was such that the energy eigenvalues stabilize to within 0.0001 eV. The large degrees of freedom involved in a system like the OS is the most difficult aspect of electronic structure calculation. A judicious choice of the fitting functions for the potential and charge density representation is crucial in obtaining accurate and well-converged result. The energy eigenvalues and wave functions at 160 k points in the 1/4 of the Brillouin zone (BZ) were obtained to calculate the DOS and the interband optical conductivity. A large number of k-point sampling is necessary for the accurate determination of the band parameters.

Figure 1(a) shows the calculated band structure for κ-(ET)$_2$Cu(NCS)$_2$ in the region from -3.0 to $+2.0$ eV where the zero energy is set at E_F. Figure 1(b) focuses on the two sets of ET-derived bands near E_F which accommodate a total of four electrons. The upper band with a width of 0.36 eV is half-occupied (occupied width 0.17 eV), and the lower fully occupied band has a width of 0.20 eV. The general shape of these two sets of band is similar to the semiempirical calculations of Oshima *et al.*[9] and Jung *et al.*[10] with several important differences. (1) Our calculated band width is only half of that reported in Ref. 10 while Ref. 9 did not provide the energy scale. (2) The bottom of the half-occupied band at Γ is lower in our case mainly due to the inclusion of the S-3d orbital in the calculation. This leads to a smaller semiminor axis for the elliptic hole. Had we used a minimal basis without S-3d and S-4s orbitals, the band shape is very close to the semiempirical bands. (3) Our calculated gap between FS's along Z-M where magnetic break down may occur is larger than those obtained by semiempirical calculations because of the greater splitting of the pair of bands along Z-M. (4) The area of the FS's above the β orbit (to be discussed below) is larger in our case. These differences clearly underscore the importance of self-consistency in potential and the *ab initio* aspect of the calculation for the charge-transfer salts. We also notice than the next set of the VB is almost 1.3 eV below E_F and the minimum gap between the top of the partially occupied band and the next set of conduction bands (CB's) is almost 1.0 eV. An effective charge calculation based on the Mulliken scheme shows that on average, each ET molecule donates 0.45 electron to the Cu(NCS)$_2$ molecule which is close to the nominal value of 0.5 electron.

The calculated FS shown in Fig. 2 shows an oval-shaped quasi-two-dimensional hole cylinder centered at Z, and an open quasi-one-dimensional FS along Y-M. The cross-sectional area of the hole is about 12% of the BZ cross-section area. This percentage is to be compared with the experimental ones obtained by SdH experiments ($18\pm3\%$, Ref. 9; 16.3%, Ref. 11) and the two-dimensional angular-correlation-of-annihilation-radiation (2D-ACAR) measurement (13%).[21] Of particular importance is the sizable gap in the Z-M direction which separates the two FS's. At high magnetic field, electrons can tunnel through the gap and magnetic breakdown occurs as indicated by the dotted lines in Fig. 2. In accordance with the convention, we label the two possible orbits in Fig. 2 as α and β, respectively. We have calculated the bare band effective masses for these two orbits to be $m_\alpha^{b*}/m=1.72\pm0.05$ and $m_\beta^{b*}/m=3.05\pm0.10$ (m, mass of electron) by evaluating $m^*=\hbar^2/(2\pi)d(S(0))/dE$, where $S(0)$ is the FS area of the orbit. It should be noted that the change in $S(0)$ with energy is not isotropic as can be seen from the bandslopes at E_F in Fig. 1(b). Hence accurate determination of m_α^{b*} and m_β^{b*} requires precise mapping of the FS's. The generally accepted experimental values for m_α^* and m_β^* are 3.5 and 6.5 m, respectively,[12]

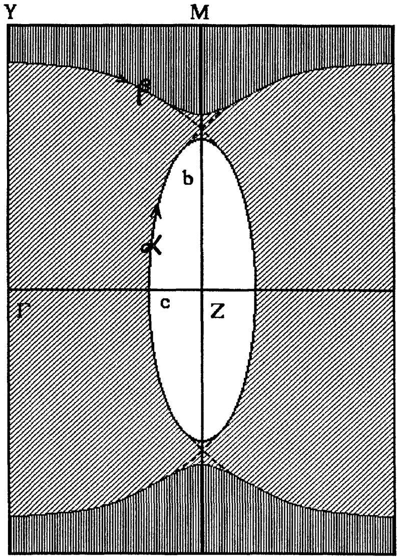

FIG. 2. Calculated Fermi surface of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The two orbits α and β are marked. The dashed lines indicate the path of electron in the magnetic breakdown.

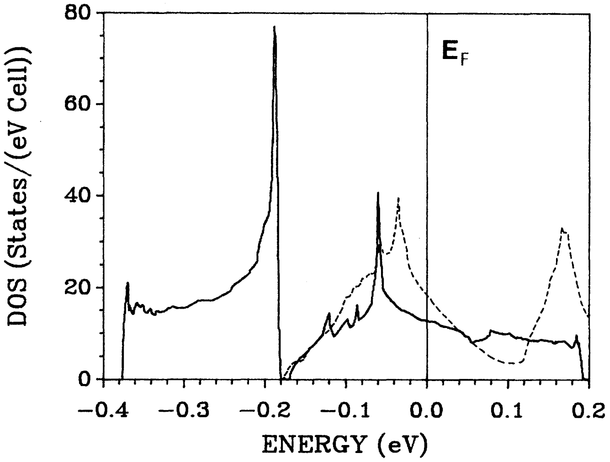

FIG. 3. Calculated density of states of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (solid line); K_3C_{60} (dashed line).

which indicate a mass enhancement factor of about 2 over the bare effective mass. The mass enhancement is the result of electron-phonon and electron-electron interactions which renormalize the electron self-energy. The large enhancement factor is consistent with the narrow metallic band. Semiempirical bands, because of the large bandwidths, predict much smaller bare effective masses and an unrealistically large enhancement factor of greater than 4. Caulfield *et al.*[12] had used an effective dimer model to estimate the bare effective masses to be $m_\alpha^{b*}/m = 0.64$ and $m_\beta^{b*}/m = 1.27$, about half of what we obtained. We also note that the calculated ratio of $m_\beta^{b*}/m_\alpha^{b*} = 1.77$ is quite close to the experimental ratio of $m_\beta^*/m_\alpha^* = 1.86$, indicating that the mass enhancements at the two orbits are fundamentally of the same origin.

The DOS of κ-(ET)$_2$Cu(NCS)$_2$ in the energy range from -0.4 to $+0.2$ eV is shown in Fig. 3. For the purpose of comparison to be discussed below, we display the DOS of a K_3C_{60} superconductor as well. The calculated DOS value at E_F is 3.2 states per ET molecule or, equivalently, 12.8 states per eV cell. We also notice that there is a Van Hove singularity (VHS) peak at about 0.06 eV below E_F which is related to the saddle point of the band at M. By resolving the DOS into atomic and orbital components, we find that the DOS at E_F are exclusively derived from the C and S atoms in the ET molecules, and their orbital components are almost entirely of p character (45% of C-2p, 52% of S-3p, and 3% of S-3d). Recent photoemission experiments[18] failed to detect any evidence of a FS in OS's, in contrast to SdH and other magnetic field related experiments,[9–12] and also the 2D ACAR experiments,[21,22] which clearly establish the existence for a FS. We believe that the difficulty in detecting the Fermi edge in OS's by the photoemission technique is related to the narrow and relatively isolated metallic band at E_F. The calculated VB DOS in the range down to -20 eV, when broadened (not shown), show reasonable agreement with photoemission spectrum of Ref. 18.

The electronic structure of the κ-(ET)$_2$Cu(NCS)$_2$ is remarkably similar to the alkali-doped C_{60} crystal such as K_3C_{60}. These include the width of the half-occupied metallic band, the existence of a hole pocket and its percentage in the BZ, the DOS at E_F, and the presence of the VHS peak and its location below E_F. This comparison is summarized in Table I where the results[23] of the calculation for the fcc K_3C_{60} crystal using the same method are also presented. The similarities in the electronic structure between these two low-dimensional C-related superconductors have profound implications as to the mechanism of organic superconductivity. Newns *et al.*[24] have emphasized the importance of the

TABLE I. Comparison of the calculated band parameters of κ-(ET)$_2$Cu(NCS)$_2$ and K_3C_{60}. VHS stands for Van Hove singularity. $S(0)$ is the Fermi surface area of the hole pocket. A_{BZ} is the area of the section of the BZ.

Crystal	T_c (K)	Bandwidth (eV) Total	(occupied)	$N(E_F)$ (state/eV cell)	VHS peak position (eV)	$S(0)/A_{BZ}$ (%)
κ-(ET)$_2$Cu(NCS)$_2$	10.4	0.36	(0.17)	12.8	-0.06	12.0
K_3C_{60}	18.0	0.48	(0.18)	18.0[a]	-0.04	~16.4[b]

[a] Calculated by ignoring the rotational disorder of the C_{60} molecule in the fcc lattice.

[b] Estimated value for the k_x-k_y plane.

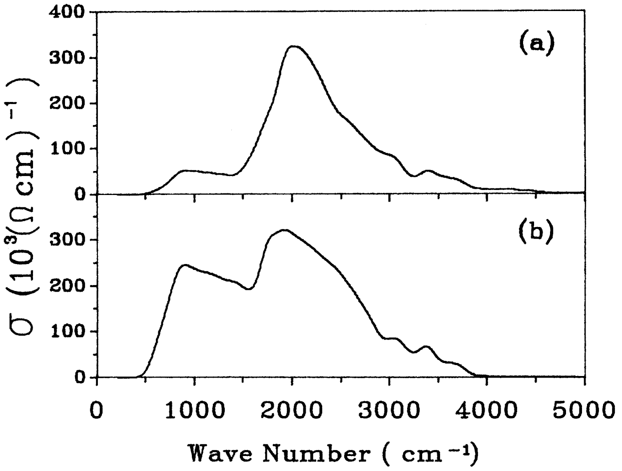

FIG. 4. Calculated optical conductivity of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$: (a) $E\|\mathbf{b}$; (b) $E\|\mathbf{c}$.

VHS immediately below E_F in explaining the linear dependence of resistivity and thermopower in cuprate superconductors. A similar mechansim for carrier transport in OS's and in the alkali-doped C_{60} superconductors cannot be ruled out. There is actually a positive correlation for T_c, $N(E_F)$, and the proximity of the VHS to E_F between the two superconductors. Both crystals have the same pressure dependence of T_c, $N(E_F)$, and m^*.[12,23]

The interband optical conductivity of κ-(ET)$_2$Cu(NCS)$_2$ for photon frequencies up to 5000 cm^{-1} was also investigated. The calculation accurately took into account the dipole transition matrix between each pair of k-conserving transitions evaluated using the calculated Bloch functions at 160 k points in the BZ. Accurate determination of the conductivity must include the summation over the full BZ and cannot be inferred from inspection of the band structure along the symmetry lines because of the strong k dependence of the matrix elements. This is an ambitious calculation since the system is extremely complex. However, it is very important since optical data are the best way to validate the calculated electronic structure and to establish the size of the bandwidth. Our preliminary results for the interband optical conductivity for components parallel to **b** and **c** axes of the crystal are shown in Fig. 4. Within the 5000-cm^{-1} region, all the transitions are within the two sets of bands near E_F shown in Fig. 1(b). As can be seen, the calculated results show interband transitions in the 500–4500 cm^{-1} region with a broad peak near 2000 cm^{-1}. This is in good agreement with the optical measurements of Ugawa *et al.*[25] and Kornelsen *et al.*[26] Our results show very little anisotropy in the interband conductivity except in the 500–1500 cm^{-1} region where the transition strength for the component $E\|\mathbf{c}$ is much stronger than the component $E\|\mathbf{b}$. Ugawa *et al.* also found the optical anisotropy in κ-(ET)$_2$Cu(NCS)$_2$ to be very small and attributed it to the fact that within the unit cell of the OS, there are two kinds of the orientation of the dimer unit which are almost mutually perpendicular. However, the data of Ref. 26 show that the interband peak for $E\|\mathbf{b}$ is at a higher frequency than that of $E\|\mathbf{c}$ by roughly 1000 cm^{-1} and our calculated result is more consistent with the data for $E\|\mathbf{c}$. More work is needed to resolve this controversy. Below 1000 cm^{-1}, the experimental data show a rapid increase in conductivity characteristic of metallic Drude absorption. The Drude type of intraband transition is not included in our calculation. Detailed results on the optical properties of κ-(ET)$_2$Cu(NCS)$_2$ will be reported elsewhere.[27]

In conclusion, we have performed the first detailed first-principles calculation of the electronic structure and the Fermi surfaces of the κ-(ET)$_2$Cu(NCS)$_2$ superconductor. Several important band parameters are firmly established. Our calculated results are in good agreement with a variety of experimental data. Of particular significance is the good agreement with the optical conductivity measurements which ensures the accuracy of the calculated band structure. Our results are quite different from the existing ones obtained by semiempirical methods especially in the size of the bandwidth, although the general shape of the Fermi surface is similar. We also found the inclusion of S-3d orbitals in the calculation to be quite important in getting the accurate band structure and crystal wave functions.

This work was supported by the NSF under the Grant No. DMR9402655.

---

[*] Author to whom all correspondence should be addressed.

[1] D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris) Lett. **41**, L95 (1980).

[2] *Organic Superconductivity,* edited by V. Z. Kresin and W. L. Little (Plenum, New York, 1991).

[3] *Organic Superconductors (Including Fullerenes)*, edited by J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carson, U. Geiser, H. H. Wang, A. M. Kini, and M.-H. Whangbo (Prentice Hall, Englewood Cliffs, NJ, 1991).

[4] J. M. Williams *et al.*, Science **252**, 1501 (1991).

[5] W. A. Little, Phys. Rev. A **134**, 1416 (1964).

[6] See, for example, R. L. Green, in Ref. 2, p. 7.

[7] J. Kübler, M. Weger, and C. B. Sommers, Solid State Commun. **62**, 801 (1987). The authors attempted a first-principles calculation for the β-(ET)$_2$I$_3$ crystal. However, the validity of that result was later disputed (see Ref. 9).

[8] M. Yoshimura, H. Shigekawa, H. Nejoh, G. Saito, Y. Saito, and A. Kawazu, Phys. Rev. B **43**, 13 590 (1991). The authors showed the $|\phi|^2$ for the highest-occupied molecular-orbital (HOMO) state of the BEDT-TTF molecule calculated by an *ab initio* method. No explanation or reference with regards to the calculations were given.

[9] K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, Phys. Rev. B **38**, 938 (1988).

[10] D. Jung, M. Evain, J. J. Novoa, M.-H. Whangbo, M. A. Beno, A. M. Kini, A. J. Schultz, J. M. Williams, and P. J. Nigrey, Inorg. Chem. **28**, 4516 (1988).

[11] T. Sasaki, H. Sato, and N. Toyota, Solid State Commun. **76**, 507 (1990).

[12] J. Caulfield, W. Lubczynski, F. L. Pratt, J. Singleton, D. Y. K. Ko,

W. Hayes, M. Kurmoo, and P. Day, J. Phys. Condens. Matter **6**, 2911 (1994).

[13] O. Klein, K. Holczer, G. Grüner, J. J. Chang, and F. Wudl, Phys. Rev. Lett. **66**, 655 (1991); D. Achkir, M. Poirier, C. Bourbonnais, G. Quirion, C. Lenoir, P. Batail, and D. Jérome, Phys. Rev. B **47**, 11 595 (1993); M. Dressel, O. Klein, G. Grüner, K. D. Carlson, H. H. Wang, and J. M. Williams, *ibid.* **50**, 13 603 (1994).

[14] M. Lang, N. Toyota, T. Sasaki, and H. Sato, Phys. Rev. Lett. **69**, 1443 (1992).

[15] L. P. Le *et al.*, Phys. Rev. Lett. **68**, 1923 (1992); D. R. Harshman, A. T. Fiory, R. C. Haddon, and M. L. Kaplan, T. Pfiz, E. Koster, I. Shinkoda, and D. Li. Williams, Phys. Rev. B **49**, 12 990 (1994).

[16] K. D. Carlson *et al.*, Physica C **215**, 195 (1993).

[17] A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **74**, 3455 (1995).

[18] R. Liu, H. Ding, J. C. Campuzano, H. H. Wang, J. M. Williams, and K. D. Carlson, Phys. Rev. B **51**, 13 000 (1995).

[19] W. Y. Ching, J. Am. Ceram. Soc. **73**, 3135 (1990).

[20] H. Urayama, H. Yamochi, G. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama, and H. Inokuchi, Chem. Lett. **1988**, 463 (1988).

[21] L. P. Chan, K. G. Lynn, D. R. Harshman, and R. C. Haddon, Phys. Rev. B **50**, 10 393 (1994).

[22] Y. C. Jean *et al.*, Physica C **221**, 399 (1994).

[23] Y. N. Xu, M.-Z. Huang, and W. Y. Ching, Phys. Rev. B **44**, 13 171 (1991); **46**, 6572 (1992).

[24] D. M. Newns, C. C. Tsuei, R. P. Huebener, P. J. M. van Bentum, P. C. Pattnaik, and C. C. Chi, Phys. Rev. Lett. **73**, 1695 (1994).

[25] A. Ugawa, G. Ojima, K. Yakushi, and H. Kuroda, Phys. Rev. B **38**, 5122 (1988).

[26] K. Kornelsen, J. E. Eldridge, C. C. Homes, H. H. Wang, and J. M. Williams, Solid State Commun. **72**, 475 (1989); Phys. Rev. B **44**, 5235 (1991).

[27] W. Y. Ching, Y.-N. Xu, Y. C. Jean, and Y. Lou (unpublished).