PHYSICAL REVIEW B VOLUME 58, NUMBER 16 15 OCTOBER 1998-II

Correlation and electron-phonon effects in the valence-band photoemission spectra of single-phase K_3C_{60} films

A. Goldoni
Department of Applied Physics and Center for Material Research, Stanford University, Stanford, California 94305
and Istituto Nazionale per la Fisica della Materia and Sincrotrone Trieste S.C.p.a, S.S. 14 Km 163.5, 34012 Trieste, Italy

S. L. Friedmann and Z.-X. Shen
Department of Applied Physics and Center for Material Research, Stanford University, Stanford, California 94305

F. Parmigiani
Istituto Nazionale per la Fisica della Materia, and Department of Mathematics and Physics, Catholic University,
Via Trieste 17, 25121 Brescia, Italy

(Received 8 April 1998; revised manuscript received 2 June 1998)

Ultraviolet photoemission spectroscopy is used to show that the density of states just below the Fermi edge of a high quality single-phase K_3C_{60} film is significantly affected by temperature. In addition, the possible contribution of electron-phonon and electron-plasmon interactions, as well as of correlation effects to the lowest unoccupied molecular orbital derived photoemission spectrum is addressed by reproducing the experimental data starting from theoretical density of states reported in the literature and by comparison with the photoemission spectrum of a single-ordered layer of C_{60} on Ag(100). [S0163-1829(98)10339-9]

I. INTRODUCTION

Because of the superconductivity at relatively high temperature in the stable A_3C_{60} phase (A is alkali metal or binary composition of alkali metals),[1] the electronic structure near the Fermi level of the alkali-metal fullerides has been widely investigated by means of valence-band photoemission spectroscopy.[1–10] Since high-quality single crystals are not available for photoemission measurements, most experiments have been performed on A_xC_{60} samples obtained by adding the alkali metals to a thick-ordered or -disordered C_{60} film. Unfortunately, this preparation technique leads to sample inhomogeneities and multiphase formation, producing a nonequilibrium distribution of phases and disorder in the film. As a consequence, a reliable comparison of both the experimental results and their interpretations with theoretical predictions is difficult. At this light, a detailed and reliable knowledge of the electronic density of state of A_3C_{60}, is lacking. In particular, the effects of the rapid re-orientation of the C_{60} molecules (i.e., the flipping motion) on the density of states (DOS) near the Fermi level has never been addressed to our knowledge experimentally and the contribution of electron correlations, electron-phonon coupling, and Jahn-Teller (JT) distortion to the electronic properties as well as to the photoemission spectra is still unclear.

One of the most peculiar phenomena is the unusual behavior of these materials as a function of the alkali-metal doping: only A_3C_{60} is metallic while all other stable phases are insulating. This is in contradiction with band-structure calculations[1,11–22] that predict all of them to be metallic (apart A_6C_{60}) due to the threefold degeneracy of the lowest unoccupied molecular orbital (LUMO)-derived conduction band. This experimental evidence points to the existence of strong correlation effects in fullerides and, indeed, the estimated Hubbard energy U (1.6–0.6 eV, depending on the system and on the estimation[10,23–25]) is larger than, or of the same magnitude of the calculated band width W (0.4–0.5 eV).[11–22] Based on this fact, one should expect A_xC_{60} compounds be Mott insulators for any integer $x=1,\ldots,5$. It has therefore been suggested that stoichiometric A_3C_{60} is a Mott insulator and that the observed Fermi edge in photoemission is due to the emission from a nonstoichiometric sample or surface.[23]

To shed light in this situation, photoemission data of well-ordered single-phase A_3C_{60} solids are required. This paper reports on ultraviolet valence-band photoemission data from a well-ordered single-phase film of K_3C_{60} at 300 and 93 K. It is supposed that the temperature dependence of the density of states (DOS) just below the Fermi edge can be ascribed to the slowing down of the flipping motion of the C_{60} molecules as the temperature is decreased. In addition, by simulating the low-temperature experimental data using theoretical density of states reported in the literature,[11–22] the contribution of electron-phonon and electron-plasmon interactions, as well as of correlation effects to the LUMO-derived photoemission spectrum of K_3C_{60} have been discussed.

II. EXPERIMENT

A 200-Å-thick K_3C_{60} single-phase ordered film was grown in ultra high vacuum on a clean Ag(100) surface following the *vacuum distillation technique*.[26,27] Particular care was devoted to ensure cleaning conditions and an homogeneous distribution of the K atoms during the film growth. C_{60} molecules and K atoms were evaporated from outgassed Ta crucible and commercial SAES getter source, respectively. An under stoichiometric $K_xC_{60}\,(x=1.5)$ film was grown ‘‘layer by layer’’ at the top of the well-ordered C_{60}/Ag(100) monolayer (ML) by alternating about 4 ML of C_{60} with an

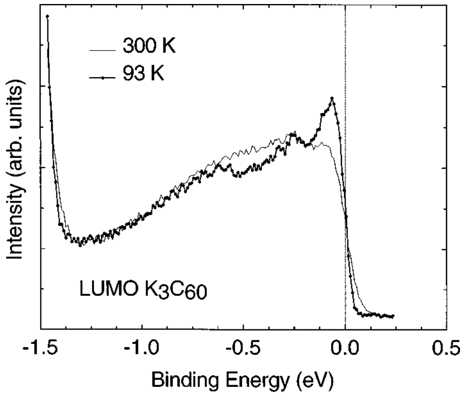

FIG. 1. LUMO-derived photoemission spectra at 93 K and RT of an ordered K_3C_{60} single-phase film.

amount of K atoms necessary to reach the $x=1.5$ stoichiometry. During the growth, the substrate temperature was 400 K. When a thick homogeneous $K_{1.5}C_{60}$ film was obtained, the sample was kept at 600 K for 75 h. In this way, by evaporation of the exceeding C_{60} molecules, it is allowed the formation of an ordered K_3C_{60} single-phase film[26,27] as demonstrated by core level x-ray photoemission,[28] low-energy electron diffraction (LEED), and valence-band ultraviolet photoemission. The sample showed a two-domain exagonal LEED pattern at 100 K. The two domains were related by a 90° rotation. Further annealing at 600 K did not lead to further changes in the photoemission spectra and LEED pattern, demonstrating that the distillation process was carried out to completion.

In the present experiment, photoelectrons were excited by the He-I radiation and collected at an emission angle of 45° with respect to the surface normal by an angle-resolved 50-mm hemispherical analyzer. The overall energy resolution was about 50 meV, while the origin of the binding energy scale was set at the Fermi edge E_F of the Ag(100) substrate.

III. RESULTS AND DISCUSSION

Before discussing the experimental data, it is important to highlight the importance of the sample quality in this experiment. Figure 1 shows the LUMO-derived valence-band photoemission spectrum of the single-phase film at 93 K and room temperature (300 K,RT). As reported in previous studies,[2–10] the width of the LUMO-derived spectral weight is about 1.35 eV, which is significantly larger than that predicted by band-structure calculations in the local-density approximation (LDA).[11–22] This anomalous width has been in turn associated to the presence of phonon and plasmon satellites,[5,7] correlation effects,[6,22,23] band reconstruction due to JT distortion of the molecules,[20] and inequivalence between surface and bulk contributions in the photoemission spectrum.[9] Of course, all these mechanisms can generate peculiar spectral features. Indeed, the spectrum at 93 K is characterized by a first sharp peak at about -0.06 eV followed by a shoulder at -0.1 eV, two clear peaks at -0.26 and -0.32 eV, and a large feature at ≈ -0.65 eV. Although the general shape of this spectrum is similar to the best valence-band photoemission spectra reported in the literature for K_3C_{60} films at 10 and 40 K,[5–7] it is worth noting that, in spite of the worse-energy resolution and higher temperature, all these structures are better resolved here. Very likely this is due to the high quality of the sample used for the present experiment.

Having established the importance of the sample quality, Fig. 1 shows that on going from 93 K to RT the fine structure observed in the spectral region between -0.4 eV up to E_F, is almost completely washed out. In particular, the first peak at -0.06 eV is strongly quenched and the spectral intensity at E_F decreases by about 7%. On the contrary, the emission intensity increases in the region around -0.45 eV. The completely reversible nature of these changes as a function of temperature points to an intrinsic origin. Moreover, the spectral-weight transfer from the region close to E_F to the region around -0.45 eV and the decrease of DOS at E_F suggest that this effect is not solely due to thermal broadening of the Fermi-Dirac distribution.

On the other hand, similar temperature behaviors are reported for photoemission spectra of Rb_3C_{60} (Ref. 5) and K_3C_{60} (Ref. 7) films. In these works it is shown that the LUMO-spectral changes occur continuously with temperature in the range 10–425 K and that K_3C_{60} and Rb_3C_{60} films show essentially the same temperature dependence.[5,7] The authors of these works[5,7] have ruled out that the observed behavior is due to the contemporary presence of many A_xC_{60} phases and to variation in the relative amounts of each composition with temperature. Furthermore, if the sample is stoichiometric as in the present case, from analogy with bulk studies[29] no phase changes would occur across the temperature range used here. Finally, calculations[5] including the A_g and H_g phonon modes (the only intramolecular vibrations of the right energy that can couple with the LUMO electrons[30]) have shown that phonon population changes with temperature cannot account for the present temperature dependence of the photoemission spectra.

Instead the gross changes occurring on going from 93 K to RT can be tentatively explained as a consequence of electron-electron interactions together with a growing up (or a slowing down) of the flipping motion of the C_{60} molecules as the temperature increases (decreases), as discussed in the following.

A. Effects of orientational disorder

In the stable K_3C_{60} solid, the fullerene balls form a fcc lattice, while the potassium atoms are intercalated in the octahedral and tetrahedral interstitial sites.[1,31] An important issue, in describing this structure is the intrinsic orientational disorder of the C_{60} molecules. Two orientations (A and B) for the C_{60} molecules related by a $\pi/2$ rotation about a twofold axes (merohedral disorder) seem to be present in K_3C_{60}. At room temperature these orientations are equally populated and randomly distributed.[31–33] The molecules continuously jump between A and B orientations (the flipping motion). As in the case of pure C_{60} solid in its low-temperature, simple-cubic phase,[34] the flipping motion is slowed down as the temperature decreases and the populations of the two orientations are expected to vary as a function of temperature.

To understand the role that this intrinsic molecular orientational disorder could play in determining the DOS near

E_F, the effects of the molecular orientations on the electronic structure of K_3C_{60} have been studied by means of tight-binding models.[13,16,17,21,22] For a system where all the molecules of the unit cell have the same static orientation (A or B, uniaxial order), the DOS of the LUMO-derived bands presents substantial structures: deep minima, sharp peaks, and shoulders.[11–22] As shown by several works,[16,21,22] these features are almost completely washed out when a randomly distributed merohedral disorder of the molecules is taken into account (maximal or uncorrelated disorder). In particular, the DOS in the uniaxial ordered case has a sharp peak a few tens of meV below E_F, which gradually disappears as the degree of disorder evolves toward the maximal disorder. A similar behavior is observed in our photoemission spectra on going from 93 to 300 K. The sharp peak at −0.06 eV, present in the low-temperature spectrum, is strongly depressed at room temperature. Furthermore, all the calculations provide for the ordered case a density of states $N(E_F)$ at the Fermi level higher than in the disordered one. This is again in agreement with our experimental observation. Therefore, the photoemission spectra of Fig. 1 seems to suggest an increased orientational order on going from RT to low temperature.

On the other hand, the uniaxial ordered structure is almost certainly not the most favorable one. Calculations[35] then confirmed by experimental data[36] have predicted that the lowest-energy structure at $T=O$ is the one where neighboring molecules have opposite orientations as far as possible (i.e., molecules oriented A are surrounded by molecules oriented B). This orientational correlation at low temperature is, however, restricted to neighboring molecules and there is no long-range order:[36] the expected DOS has a quite smeared out shape as in the case of uncorrelated disorder. Given the above arguments, it is very unlikely that the observed changes are related to an ordering of the C_{60} molecules as the temperature decreases.

A possible explanation for the observed changes in the spectral region close to E_F as a function of temperature is instead related to the flipping motion of the C_{60} molecules. It is known that the cubic crystal field splits the C_{60} carbon atoms in three nonequivalent species, namely, C1, C2, and C3 with ratio 1:2:2. Calculations[12,37] suggest that the distribution of the charge donated by K atoms to C_{60} is strongly anisotropic over the three carbon species when the molecules are in a frozen state (low temperature). The fast flipping motion of the molecules at high temperature is expected to partially average this charge anisotropy, as claimed by nuclear magnetic resonance data[32,38] and recent C 1*s* core-level spectroscopy.[28] In particular, Yoshinari *et al.*[32] suggest that this mechanism could modify the DOS near E_F. The width of the occupied part of the LUMO states as provided by LDA or tight-binding calculations is, however, too small (about 0.20–0.25 eV) as compared with the width of the photoemission band (about 1.35 eV), to explain all the features observed experimentally. As pointed out before, other mechanisms should be considered to describe properly the photoemission spectrum.

B. Simulations

To achieve more information on the electronic properties of K_3C_{60} and to understand the role played by electron-phonon interaction and correlation effects, we have performed a crude simulation of the photoemission spectrum at 93 K. Two theoretical tight-binding DOS of the t_{1u} LUMO-derived band,[16] calculated in the case of uncorrelated disorder (DOS1) and uniaxial order (DOS2) are used, guessing that reality is closer to the former case. The chosen DOS are representative of the majority of such a kind of calculations[11–22] and are shown in the inset of Fig. 2.

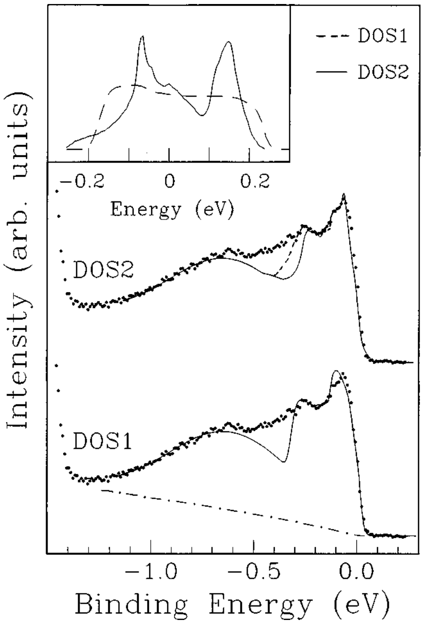

FIG. 2. LUMO-derived photoemission spectrum at 93 K (points) together with the best simulation curves (lines) obtained with the two density of states, DOS1 (uncorrelated disorder) and DOS2 (uniaxial order) (Ref. 16) reported in the inset. For details see text and Table I. The used background is also shown by dotted-dashed line under the bottom curves. The effect of the inclusion of multiphonon excitations (Ref. 40) on the simulation is shown for DOS2 by a dashed line.

Since charged C_{60} is expected to undergo JT distortions, the photoemission spectrum is simulated by adding phonon replica, due to the coupling with the JT-active H_g modes and the $A_g(2)$ phonon,[30,39] to the assumed DOS (convoluted with the Fermi-Dirac distribution at 93 K and with a Gaussian representing the experimental broadening). The large bump at −0.65 eV has been simulated by a Gaussian representing a plasmon excitation as suggested by Knupfer *et al.*,[5] in agreement with the strong plasmon feature observed at about 0.55 eV in the electron-energy loss spectra of K_3C_{60}.[7,27] For each DOS, the phonon-replica intensities as well as the plasmon intensity have been changed until a satisfactory ''fit'' of the photoemission spectrum is obtained. The results[40] are shown in Fig. 2 and the phonon intensities (relative to the intensity of the used DOS) are reported in Table I together with the assumed phonon energies.[41]

From the curves of Fig. 2 the following is clear.

(a) The inclusion of the phonon replica allows us to reproduce the photoemission line shape between −0.25 eV and E_F (or between −0.35 eV and E_F if we assume multiphonon excitations[40]), while the plasmon peak fits the spectrum in the region below −0.55 eV.

(b) There is a quite large region between −0.35 and−0.55 eV that is not reproduced with such simulations.

TABLE I. Energies (Ref. 41) and intensities of the phonon and plasmon replica used in the simulations of Fig. 2. The intensities are relative to the intensity of the DOS used in the simulation.

Mode	Energy (meV)	DOS 1	DOS 2
Hg(1)	33	40.0%	21.0%
Hg(2)	54	25.0%	42.0%
Hg(3)	88	10.0%	17.0%
Hg(4)	96	1.5%	21.0%
Hg(5)	136		13.0%
Hg(6)	155	10.0%	7.0%
Hg(7)	177	24.0%	3.0%
Hg(8)	195	30.0%	26.0%
Ag(2)	180	32.5%	20.0%
Plasmon	550	50.0%	50.0%

Being aware of the simplicity of these simulations, one can, however, recognize that the main contribution to the large width of the LUMO photoemission spectrum comes from plasmon and phonon satellites. The discrepancy in the region between −0.35 and −0.55 eV is clearly a sign of the crudeness of the simulations and it can be probably reduced by more accurate models. More accurate models account for a broadening of the spectral function due to the inclusion of the dynamics of holes and electrons coupled with phonons inside a partially filled band having a finite bandwidth,[42] the inclusion of correlation (electron-electron) effects,[6,22,23] and/or band reconstruction due to the JT distortions[20] disregarded in the model adopted here. Alternatively, the emission from bulk states[9] could enhance the intensity in this binding energy region of the spectrum being the remaining part representative of the surface states or vice versa, as also suggested by Gu *et al.*[43] in the case of Rb_3C_{60}.

This latter hypothesis is difficult to support since it is not clear why a bulk (surface) emission should exhibit temperature dependent features (see Fig. 1). Furthermore, as shown in Fig. 3(a), the photoemission spectra of the LUMO-derived band taken at 45° and at normal emission are very similar. As a matter of fact, if the emission in the region between −0.55 and −0.35 eV was related to bulk (surface) states, on going from 45° to normal emission the spectral weight should increase (decrease) by about a factor of two with respect to the emission from the surface (bulk). Since the spectra of Fig. 3(a) are almost identical, the surface versus bulk effects must be ruled out. In other words, in this sample the surface and bulk electronic structures are comparable.

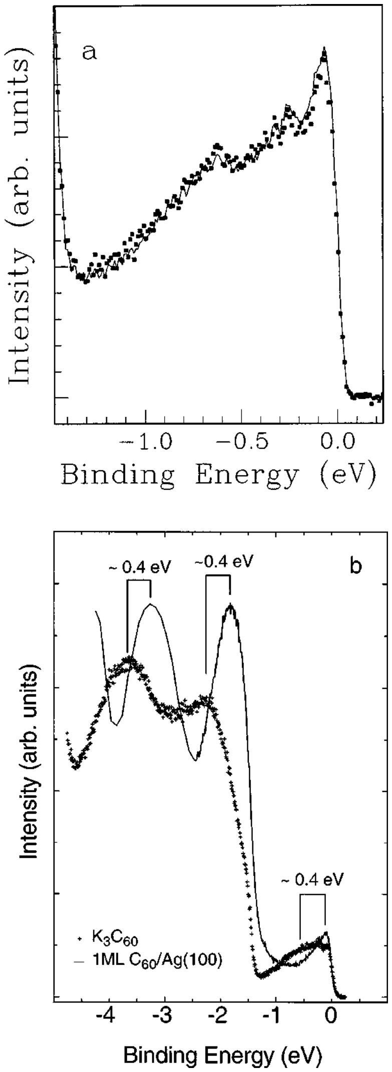

FIG. 3. (a) Comparison between the LUMO-derived photoemission spectra of the ordered K_3C_{60} single-phase film taken at 45° (line) and normal (squares) emission. The temperature was 93 K. (b) Comparison between the valence-band photoemission spectrum of the ordered K_3C_{60} single-phase film and that of 1 ML-C_{60}/Ag(100) at RT.

To verify the presence of correlation effects, it is helpful the comparison with 1 ML-C_{60}/Ag(100), a system where the C_{60} molecules exhibit a charge state close to 3-.[44] Figure 3(b) compares the valence-band photoemission spectra of K_3C_{60} and of 1 ML-C_{60}/Ag(100) taken at RT under the same experimental conditions and normalized to the same intensity at E_F. The HOMO (highest occupied molecular orbital), HOMO-1, and LUMO-photoemission derived bands of the monolayer system are narrower than those of K_3C_{60}. Moreover, HOMO-1 and HOMO are shifted by about 0.40 eV toward the Fermi level (i.e., the HOMO-LUMO gap is reduced by this amount) and the LUMO loses spectral weight around −0.45 eV and gains intensity close to E_F becoming sharper. A similar behavior was already observed by Tjeng *et al.*[45] by comparing the valence-band photoemission spectra of a film of K_3C_{60} and of 1 ML-C_{60}/Ag(111) doped with potassium. Apparently, a strong reduction of the HOMO-LUMO gap and a shrinking of the LUMO- and HOMO-derived bands emission is achieved when the layers underneath the surface are replaced by a metal substrate. As shown by Hesper, Tjeng, and Sawatzky[46] using an image-charge model, this effect is due to proximity of the metal surface and the reduction of the HOMO-LUMO gap in the monolayer system corresponds uniquely to the reduction of the Hubbard energy U. The comparison of Fig. 3(b) clearly indicates that in 1 ML-C_{60}/Ag(100) the energy U is reduced by about 0.40 eV with respect to the K_3C_{60} solid. If part of the photoemission spectral weight of the LUMO-derived band of K_3C_{60} is due to correlation effects, we expect that in 1 ML-C_{60}/Ag(100) the LUMO-derived emission is narrower than in K_3C_{60} because of such a strong decrease of the effective Coulomb interaction due to the metallic screening. Since this corresponds to the behavior shown in Fig. 3(b), it is possible that the spectral weight of the LUMO-derived band of K_3C_{60} around -0.45 eV is due to correlation effects. In this frame, the spectral weight in the region between -0.35 and -0.55 eV should reflect the broad incoherent part of the spectral function (the lower Hubbard band), while the used tight-binding DOS (Ref. 16) should represent the coherent part.

Although there is evidence for the screening of U in the monolayer system, there could be alternative explanations for the shrinking of the LUMO emission with respect to K_3C_{60} related to the electron-plasmon coupling. In a two-dimensional (2D) system, the plasmon energy is expected to depend on the exchanged momentum q as $q^{1/2}$ and therefore it starts at zero at $q=0$. This could explain the narrower spectrum in the monolayer system if the exchanged momentum between the photoelectron and the excited plasmon is $q\rightarrow 0$. However, it is questionable whether one monolayer of C_{60} can be considered a 2D system. In addition, a plasmon peak at 0.7 eV has been observed in the electron-energy loss spectra at $q\rightarrow 0$ of a very similar monolayer system,[47] namely, 1 ML-C_{60}/Cs/Au(110). On the other hand, the LUMO-photoemission spectrum of 1 ML-C_{60}/Cs/Au(110) is comparable to the LUMO emission of 1 ML-C_{60}/Ag(100). All these features rule out the above mechanism as a possible source of the spectral narrowing, whilst suggesting that in the photoemission spectra of monolayer systems the coupling with the plasmon could be reduced with respect to the bulk systems. A fit of the LUMO-photoemission spectrum of 1 ML-C_{60}/Ag(100) at 100 K (Ref. 44) requires a large peak between 0.45–0.55 eV of binding energy, which probably corresponds to the plasmon loss. The relative intensity of this peak with respect to the used DOS is about 25%, i.e., one half of that found for K_3C_{60}. Therefore, also the reduced coupling with the plasmon could account for the narrowing of the LUMO emission in the monolayer systems. However, this phenomenon alone cannot explain the strong decrease of spectral weight in the middle of the LUMO spectrum and the transfer of spectral weight close to E_F [see Fig. 3(b)]. Thus, one can speculate that a combined reduction of the electron-plasmon coupling and of the Hubbard energy U is responsible for the observed narrowing of the LUMO-photoemission spectra in C_{60} monolayer metallic systems.

That electron correlation plays a role has been also claimed on the basis of optical studies[48,49] of K_3C_{60} and Rb_3C_{60} crystals, showing that the normal state properties of these compounds deviate considerably from the simple Drude-like behavior expected for conventional metals. Of particular interest is the presence in the midinfrared frequency range of an absorption component at about 0.5 eV. The presence of this excitation indicates a break down of the simple band picture and has been associated to an incoherent band related to strong electron-phonon and/or electron-electron interactions.[48] Of relevance is also the observation of a low-frequency absorption peak in the optical conductivity at about 0.06 eV,[49] which suggests again the importance of electron-correlation effects in the normal state of A_3C_{60}. Also, the anomalous nonlinear (T^2) temperature dependence of the resistivity of K_3C_{60} and Rb_3C_{60} in their normal states (from 30 K up to about 500 K) (Refs. 50 and 51) has been associated to strong electron-electron interactions dominating the normal state conductivity of these compounds.[51] The T^2 behavior of the resistivity can, however, be reproduced assuming an electron-phonon scattering mechanism as well, with a reasonable distribution of coupling constants to several phonons at different energies. In addition, an experimental work[52] has suggested that the resistivity at constant volume is linear in T, raising new questions for both electron-electron and electron-phonon scattering explanations of the resistivity behavior.

IV. CONCLUSIONS

By means of ultraviolet photoemission applied to a well-ordered single-phase film of K_3C_{60} kept at 93 K and RT, it has been shown that the occupied states near the Fermi edge strongly change as a function of temperature. Moreover, by simulating the experimental data at low temperature, the contribution of electron-phonon and electron-plasmon interaction and correlation effects to the LUMO-derived photoemission spectrum of K_3C_{60} has been discussed. Interestingly, an almost complete description of the photoemission spectrum is achieved when the coupling of t_{1u} electrons with H_g and A_g phonon modes and a plasmon loss are considered, even in the very simple model adopted here. The possible contribution of correlation effects to the LUMO-photoemission spectra of K_3C_{60} has been discussed by comparing these spectra with the photoemission spectra of a single-ordered layer of C_{60} on Ag(100) and on Cs/Au(110).

---

[1] For a general review see *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, New York, 1994), Vol. 48; O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).

[2] C. T. Chen, L. H. Tjeng, P. Rudolf, G. Meigs, J. E. Rowe, J. Chen, J. P. McCauley Jr., A. B. Smith III, A. R. McGhie, W. L. Romanow, and E. W. Plummer, Nature (London) **352**, 603 (1991); P. J. Benning, J. L. Martins, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Science **252**, 1417 (1991); G. Wertheim, J. E. Rowe, D. N. E. Buchanan, E. E. Chaban, A. F. Hebard, A. R. Kortan, A. V. Makhija, and R. C. Haddon, *ibid.* **252**, 1419 (1991).

[3] T. Takahashi, T. Morimoto, and T. Yokoya, Physica C **232**, 227 (1994); H. Katayama-Yoshida and T. Takahashi, J. Phys. Chem. Solids **54**, 1817 (1993); T. Morikawa and T. Takahashi, Solid State Commun. **87**, 1017 (1993); T. Takahashi, T. Morikawa, H. Katayama-Yoshida, S. Hasegawa, and H. Inokuchi, J. Phys. Chem. Solids **53**, 1699 (1992); T. Takahashi, S. Suzuki, T. Morikawa, H. Katayama-Yoshida, S. Hasegawa, H. Inokuchi, K. Seki, K. Kikuchi, K. Ikemoto, and Y. Achiba, Phys. Rev. Lett. **68**, 1232 (1992).

[4] M. Merkel, M. Knupfer, M. S. Golden, J. Fink, R. Seemann, and R. L. Johnson, Phys. Rev. B **47**, 11 470 (1993).

[5] M. Knupfer, M. Merkel, M. S. Golden, J. Fink, O. Gunnarsson, and V. P. Antropov, Phys. Rev. B **47**, 13 944 (1993).

[6] P. J. Benning, F. Stepniak, and J. H. Weaver, Phys. Rev. B **48**, 9086 (1993).

[7] T. R. Cummins, J. F. Armbruster, M. S. Golden, M. Knupfer, H. A. Romberg, M. Sing, and J. Fink, Physica C **235-240**, 2491 (1994).

[8] O. Gunnarsson, H. Handschuh, P. S. Bechthold, B. Kessler, G. Gantefor, and W. Eberhardt, Phys. Rev. Lett. **74**, 1875 (1995).

[9] G. Wertheim, D. N. E. Buchanan, E. E. Chaban, and J. E. Rowe, Solid State Commun. **83**, 785 (1992); G. Wertheim and D. N. E. Buchanan, Phys. Rev. B **47**, 12 912 (1993).

[10] P. A. Bruhwiler, A. J. Maxwell, A. Nilsson, N. Martensson, and O. Gunnarsson, Phys. Rev. B **48**, 18 296 (1993); P. A. Bruhwiler *et al.*, Int. J. Mod. Phys. B **6**, 3923 (1992).

[11] S. C. Ervin and W. E. Pickett, Science **254**, 843 (1991).

[12] D. L. Novikov, V. A. Gubanov, and A. J. Freeman, Physica C **191**, 399 (1992).

[13] S. Satpathy *et al.*, Phys. Rev. B **46**, 1773 (1992).

[14] A. Oshiyama and S. Saito, Phys. Rev. Lett. **66**, 2637 (1991); Solid State Commun. **82**, 41 (1992); A. Oshiyama, S. Saito, Y. Miyamoto, and N. Hamada, J. Phys. Chem. Solids **53**, 1689 (1992).

[15] M.-Z. Huang, Y.-N. Xu, and W. Y. Ching, Phys. Rev. B **46**, 6572 (1992).

[16] M. P. Gelfand and J. P. Lu, Phys. Rev. Lett. **68**, 1050 (1992); M. P. Gelfand and J. P. Lu, Appl. Phys. A: Solids Surf. **56**, 215 (1993).

[17] R. P. Gupta and M. Gupta, Phys. Rev. B **47**, 11 635 (1993).

[18] G. Chen, Y. Guo, N. Karasawa, and W. A. Goddard III, Phys. Rev. B **48**, 13 959 (1993).

[19] M. S. Deshpande, S. C. Erwin, S. Hong, and E. J. Mele, Phys. Rev. Lett. **71**, 2619 (1993).

[20] A. A. Remova, V. P. Shpakov, U-Hyon Paek, and V. R. Belosludov, Phys. Rev. B **52**, 13 715 (1995).

[21] J. Lu, L. Zhang, and Z. Cao, Mod. Phys. Lett. B **10**, 1417 (1996).

[22] A. Ceulemans, L. F. Chibotaru, and F. Cimpoesu, Phys. Rev. Lett. **78**, 3725 (1997).

[23] R. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, Phys. Rev. Lett. **68**, 3924 (1992); M. Meinders, Ph.D. thesis, University of Groningen, The Netherlands, 1993.

[24] V. P. Antropov, O. Gunnarsson, and O. Jepsen, Phys. Rev. B **46**, 13 647 (1992).

[25] S. Krummacher, M. Biermann, M. Neeb, A. Liebsch, and W. Eberhardt, Phys. Rev. B **48**, 8424 (1993).

[26] D. M. Poirier, Appl. Phys. Lett. **64**, 1356 (1994).

[27] M. Knupfer, J. Fink, J. F. Armbruster, and H. A. Romberg, Z. Phys. B **98**, 9 (1995).

[28] A. Goldoni, L. Sangaletti, S. L. Friedmann, Z.-X. Shen, M. Peloi, F. Parmigiani, G. Comelli, and G. Paolucci (unpublished).

[29] O. Zhou and D. E. Cox, J. Phys. Chem. Solids **53**, 1373 (1992).

[30] P. R. Surjan, L. Udvardi, and K. Nemeth, J. Mol. Struct.: THEOCHEM **311**, 55 (1994).

[31] R. C. Haddon *et al.*, Nature (London) **350**, 320 (1991); P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S.-M. Huang, R. Kaner, F. Deiderich, and K. Holczer, *ibid.* **351**, 632 (1991).

[32] Y. Yoshinari, H. Alloul, V. Brouet, G. Kriza, K. Holczer, and L. Forro, Phys. Rev. B **54**, 6155 (1996); Y. Yoshinari, H. Alloul, G. Kriza, and K. Holczer, Phys. Rev. Lett. **71**, 2413 (1993).

[33] R. Tycko, G. Dabbagh, M. J. Rosseinsky, D. W. Murphy, A. P. Ramirez, and R. M. Fleming, Phys. Rev. Lett. **68**, 1912 (1992).

[34] J. D. Axe, S. C. Moss, and D. A. Neumann, Solid State Phys. **48**, 149 (1994).

[35] O. Gunnarsson, S. Satpathy, O. Jepsen, and O. K. Andersen, Phys. Rev. Lett. **67**, 3002 (1991).

[36] S. Teslic, T. Egami, and J. E. Fischer, Phys. Rev. B **51**, 5973 (1995).

[37] W. Andreaoni, P. Giannozzi, and M. Parrinello, Phys. Rev. B **51**, 2087 (1995).

[38] K. Holczer, Int. J. Mod. Phys. B **6**, 3967 (1992).

[39] O. Gunnarsson, H. Handschuh, P. S. Bechthold, B. Kessler, G. Gantefor, and W. Eberhardt, Phys. Rev. Lett. **74**, 1875 (1995).

[40] In these simulations, for simplicity, only single-phonon excitations were considered. The inclusion of multiphonon replica (double and triple losses) improves the simulations, as shown for one case in Fig. 2 (dashed line), but it does not affect the main conclusions. Moreover, although the intensity of the phonon replica is strongly sensitive to the inclusion of multiphonon excitations, the main trend reported in Table I for the phonon intensities does not change.

[41] T. Pichler, M. Matus, and H. Kuzmany, Solid State Commun. **86**, 221 (1993); J. Winter and H. Kuzmany, Phys. Rev. B **53**, 655 (1996).

[42] O. Gunnarsson, V. Meden, and K. Schönhammer, Phys. Rev. B **50**, 10 462 (1994).

[43] C. Gu, B. W. Veal, R. Liu, A. P. Paulikas, P. Kostic, H. Ding, K. Gofron, J. C. Campuzano, J. A. Schluter, H. H. Wang, U. Geiser, and J. M. Williams, Phys. Rev. B **50**, 16 566 (1994).

[44] A. Goldoni, C. Cepek, E. Magnano, A. D. Laine, S. Vandre, and M. Sancrotti, Phys. Rev. B **58**, 2228 (1998).

[45] L. H. Tjeng, R. Hesper, A. C. Heessels, A. Heeres, H. T. Jonkman, and G. A. Sawatzky, Solid State Commun. **103**, 31 (1997).

[46] H. Hesper, L. H. Tjeng, and G. A. Sawatzky, Europhys. Lett. **40**, 177 (1997).

[47] M. R. C. Hunt, P. Rudolf, and S. Modesti, Phys. Rev. B **55**, 7889 (1997).

[48] Y. Iwasa and T. Kaneyasu, Phys. Rev. B **51**, 3678 (1995).

[49] L. Degiorgi, G. Briceno, M. S. Fuhrer, A. Zettl, and P. Wachtler, Nature (London) **369**, 541 (1994); L. Degiorgi, Mod. Phys. Lett. B **9**, 445 (1995).

[50] X. D. Xiang, J. G. Hou, G. Briceno, W. A. Vareka, R. Mostovoy, A. Zettl, V. H. Crespi, and M. L. Cohen, Science **256**, 1190 (1992); X. D. Xiang, J. G. Hou, V. H. Crespi, A. Zettl, and M. L. Cohen, Nature (London) **361**, 54 (1993); O. Klein, G. Gruner, S.-M. Huang, J. B. Wiley, and R. B. Kaner, Phys. Rev. B **46**, 11 247 (1992).

[51] T. T. M. Palstra, A. F. Hebard, R. C. Haddon, and P. B. Littlewood, Phys. Rev. B **50**, 3462 (1994).

[52] W. A. Vareka and A. Zettl, Phys. Rev. Lett. **72**, 4121 (1994).