Band Gap, Excitons, and Coulomb Interaction in Solid C_{60}

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(Received 11 March 1992)

The band gap of solid C_{60} is found to be 2.3 ± 0.1 eV. The on-site molecular C_{60} Coulomb interaction (U) as determined from the *KVV* C_{60} Auger spectrum is found to be 1.6 ± 0.2 eV. This value of U is shown to lead to Frenkel-type molecular excitons in the 1.5–2 eV range. These results lead us to suggest that doped C_{60} should be considered as a highly correlated system with U/W comparable to that in high-T_c cuprates and that stoichiometric K_3C_{60} is a Mott-Hubbard insulator with a gap of about 0.7 eV.

PACS numbers: 79.60.Eq

Since the discovery of C_{60} [1] there has been an ongoing experimental and theoretical effort to understand its electronic and optical properties, especially in connection with the occurrence of high-temperature superconductivity in the alkaline-doped solids [2]. Band-structure calculations in the local density approximation (LDA) [3] predict an electron structure with narrow bands (≈ 0.4 eV), and a direct band gap of 1.5 eV. Experimentally the low-energy electron-energy-loss spectrum (ELS) of C_{60} solids shows a peak at 1.55 eV [4], which has been interpreted as an excitation across the (h_u-t_{1u}) indirect gap. This observation is consistent with the reported optical absorption spectrum in the solid which shows an onset at about 1.5 eV [5]. It is remarkable that the optical absorption spectrum of C_{60} in solution (n-hexane) has an onset at only slightly higher energies [6].

This last observation and the common observation that LDA calculations usually underestimate the gap encouraged us to look more carefully at this system. In retrospect it seems possible that the electronic gap is much larger than the reported 1.5 eV and that the low-energy features in the optical spectrum should in fact be assigned to Frenkel excitons. This is a common feature in molecular crystals like naphthalene and anthracene [7] and in transition metal oxides [8]. Earlier Benning *et al.* [9] and Takahashi *et al.* [10] have reported photoemission–inverse-photoemission experiments with gaps considerably larger than 1.5 eV. It is in that context that we decided to do a precise measurement of the gap and in view of the possible similarity to molecular crystals with Frenkel-type excitons we also report for the first time a study of the on-site Coulomb interactions using high-resolution Auger spectroscopy.

C_{60} was obtained from Syncom BV and had a purity better than 99.9%. Samples were prepared by heating of the material in a Knudsen cell to 425 °C and depositing 3 to 6 monolayers on a clean Si[100] substrate. Figure 1 shows the photoemission (PES) and inverse-photoemission (IPES) spectra of C_{60} which are very similar to those reported by Benning *et al.* [9] and Takahashi *et al.* [10]. The PES spectrum was taken with He I radiation ($\hbar\omega = 21.2$ eV). The inverse-photoemission data were obtained using a normal-incidence grating spectrometer. The incident electron energy was 22.7 eV and the sample current was 2.5 μA. The position of the Fermi level was obtained by measuring a silver reference, which was in good electrical contact with the sample. In both cases the spectra were checked for charging effects. These were absent in PES but for IPES we observed an electron-current-dependent shift of 0.08 eV/μA. The IPES spectrum shown in Fig. 1 has been corrected for a uniform charging of 0.2 eV by extrapolating to zero current. At electron currents higher than 2.5 μA the sample also deteriorated quite rapidly as observed by strong changes in the IPES spectra. The value of the gap obtained from the onsets of the occupied fivefold-degenerate h_u valence band and the threefold-degenerate t_{1u} conduction band is 2.3 ± 0.1 eV. The peak-peak splitting is found to be 3.5 eV. Hereby we took into account the experimental resolution of 100 and 300 meV for PES and IPES, respectively. The PES and IPES onsets used for the gap determination are indicated by the vertical lines in Fig. 1.

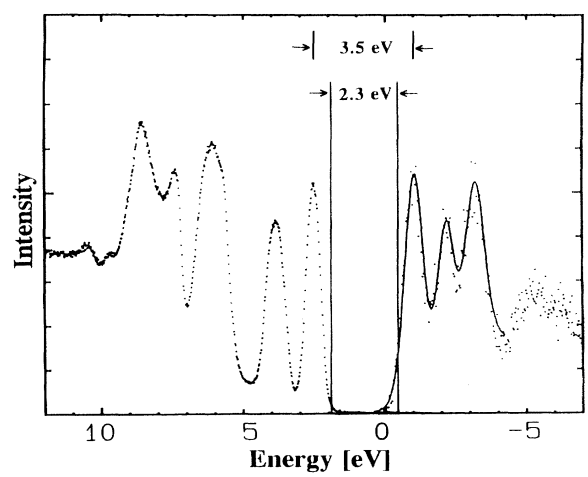

FIG. 1. Photoelectron (left) and inverse-photoelectron (right) spectra of solid C_{60}. The zero of energy is at the Fermi level of an Ag reference sample. The vertical lines indicate the onsets for the gap determination. The solid line in the IPES spectrum is meant as a guide to the eye.

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From the above we conclude that the 1.5-eV optical onset must be of excitonic origin. Such exciton states can occur in systems with strong local attractive electron-hole or repulsive electron-electron or hole-hole interactions. We can get a measure of the hole-hole interactions from Auger spectroscopy. Using 1486.6-eV photons we obtained a high-resolution Auger spectrum. Figure 2 displays the *KVV* Auger spectrum of C_{60}, which shows extensive structure. To get an estimate of the on-site molecular Coulomb interactions, we compare the Auger spectrum with the self-convolution of the valence-band photoelectron spectrum.

To emphasize the structure, Fig. 2 also shows the Auger spectrum after subtracting a smooth average curve and comparing it to the self-convoluted photoelectron spectrum of Fig. 1 treated in the same way. This procedure is nearly the same as comparing derivatives. It is clear that the spectra are very similar if we shift the self-convolution to higher binding energies by about 1.6 eV as done in Fig. 2 which then is a direct measure of the Coulomb repulsion (U) of two holes on the same site in solid C_{60}. This also indicates that the molecular orbitals remain intact for the two-hole states and that the hole-hole interaction is only weakly dependent on the molecular orbital of the hole. A somewhat better fit can be obtained by assigning a separate U to each peak, with a minimum of 1.4 eV for the highest occupied orbital and a maximum of 1.8 eV. This nearly constant interaction suggests that interactions also involving the lowest unoccupied molecular orbital will be close to these. In comparing the Auger spectra to the self-convoluted valence-band spectra one should keep in mind that relative intensities can be different because of different transition matrix elements. In this case this problem is not very severe because all of the orbitals in the energy range shown originate from predominantly C $2p_\pi$-like atomic orbitals. In addition, the Auger spectra can show splittings not present in the self-convolution because of multiplet interactions leading to splittings of several tenths of an eV [11]. This multiplet structure will be discussed in more detail elsewhere [12].

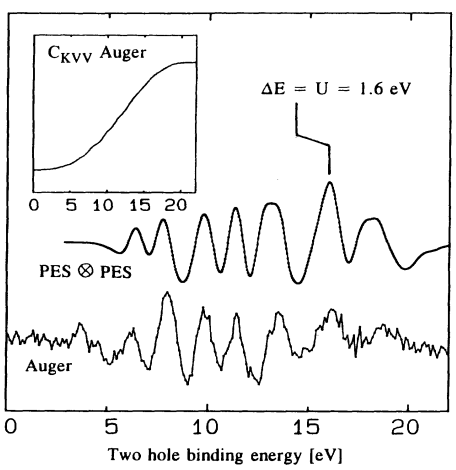

FIG. 2. Comparison of the C_{KVV} Auger spectrum of solid C_{60} with the self-convolution of the PES spectrum. Inset: The original Auger spectrum. The bottom curve emphasizes the structure as obtained from the original Auger spectrum by subtracting a smooth curve. The central curve (dots) is obtained from the self-convolution of the photoelectron spectrum after also subtracting a smooth curve and shifting the whole spectrum to higher energies by 1.6 eV as indicated.

This value of U is in excellent agreement with estimates based on a screened gas-phase value. U is in general defined as $U=E_I-E_A-\Delta$, with E_I the ionization potential, E_A the electron affinity, and Δ the highest-occupied–lowest-unoccupied molecular-orbital splitting. Note that within the same band $\Delta=0$ and U has its usual definition. Gas-phase measurements yield $E_I=7.6$ eV [13–15] and $E_A=2.65$ eV [16]. This together with a molecular-orbital splitting $\Delta\approx 1.6$ eV yields an "atomic" U of 3.4 eV. Calculation of U for molecular ${C_{60}}^{n^-}$ yields values slightly higher than 3 eV [17]. Placing C_{60} into a polarizable surrounding as in a solid results in a reduction of E_I and an increase of E_A each by $E_p=ze^2\alpha/2R^4$ [18], where α is the C_{60} polarizability (~ 80 Å^3 [19]), R is the inter-C_{60}-molecule distance, and z is the coordination number ($z=12$ for fcc). U for the solid is then estimated to be 1.6 eV [17,20].

We now show that these results are consistent with an identification of the lowest optical excitations as molecular Frenkel excitons. To do this we describe the system with a two-band-like Hubbard Hamiltonian of the form

$$\mathcal{H}=\sum_{k\sigma}\epsilon_k c_{k\sigma}^\dagger c_{k\sigma}+\sum_k \eta_k d_{k\sigma}^\dagger d_{k\sigma} + U\sum_{i\sigma}(n_{i\sigma}n_{i-\sigma}+m_{i\sigma}m_{i-\sigma}) \quad (1)$$

($n_{i\sigma}=c_{i\sigma}^\dagger c_{i\sigma}$, $m_{i\sigma}=d_{i\sigma}^\dagger d_{i\sigma}$), with ϵ_k the dispersion of the h_u-based band, η_k that of the t_{1u}-based band, and U the interaction between two electrons on one C_{60} site which for simplicity we assume to be independent of the molecular orbital. Also we neglect for now the orbital degeneracy of the h_u and t_{1u} orbitals. The Auger spectrum corresponding to two holes in the h_u-based band, and again neglecting degeneracy, is given by the imaginary part of the two-particle Green's function [21],

$$G(\omega)=\frac{1}{2\pi N}\sum_k\left[\frac{I(\omega,k)}{1-UI(\omega,k)}\right], \quad (2)$$

$$I(\omega,k)=\sum_l[\omega-\epsilon_l-\epsilon_{l-k}]^{-1}, \quad (3)$$

and ϵ_l are the one-*hole* band energies. For $U=0$, $\mathrm{Im}G(\omega)$ equals the self-convolution of the one-particle density of states. For $U\gg W$ (the one-hole bandwidth) as is the case here, almost all of the Auger weight is in the so-called quasiatomic bound state [21] at an energy (as measured from the center of the self-convoluted one-

particle density of states)

$$\omega_{\text{Auger}}(k) \simeq U + \frac{A^2(k)}{U} \tag{4}$$

as described in Ref. [22]. For a fcc tight-binding band,

$$A^2(k) = \tfrac{1}{24} W^2 + \tfrac{1}{72} W^2[\cos k_x a \cos k_y a + \cdots]. \tag{5}$$

For $W=0.4$ eV and $U=1.6$ eV the dispersional width of the two-hole bound states amounts to about 0.02 eV and the energy position of the bound state is a direct measure of U as assumed above.

The same procedure can now be used to describe the excitons. To do this we rewrite $\mathcal{H}$ in terms of an electron-hole notation with an electron in t_{1u} and a hole in the h_u band and limit ourselves to describing the motions of a single electron-hole pair. In the atomic limit ($W=0$) there are two kinds of electron-hole pairs: interatomic at an energy of $\Delta+U$ and intra-atomic at an energy Δ. Here Δ is equal to the C_{60} molecular $h_u \rightarrow t_{1u}$ excitation energy. In this zero-bandwidth limit the band gap would also be $\Delta+U$ and the Frenkel type of exciton energy would be U lower than the energy of a dissociated electron-hole pair. In exciton notation therefore $-U$ is the on-site electron-hole attraction. The description of the electron-hole spectrum is now identical to that of the Auger spectrum except that two bands are involved. de Boer, Haas, and Sawatzky [18] have described this in some detail and find a spectral distribution as in Eq. (1) but with

$$I(k,\omega) = \sum_l (\omega - \epsilon_l - n_{l-k})^{-1}, \tag{6}$$

where n_{l-k} is the electron addition energy in the t_{1u} band and ϵ_l is the electron removal energy from the h_{1u} band. In this theory the band gap is given by

$$E_{\text{gap}} \simeq \Delta + U - W \text{ for } W_{h_u} \approx W_{t_{1u}} \tag{7}$$

and the local exciton states exist for $U > W$ (the h_u or t_{1u} bandwidth).

For large U the exciton energy is close to Δ with a small downward shift given approximately by $W^2/24U$ [22] and an exciton dispersional width given by $W_{\text{exciton}} \simeq W^2/12U$ for an fcc lattice. So for $U \simeq 1.6$ eV, $\Delta+U = 3.5$ eV from Fig. 1, and $W=0.4$ eV from LDA, we predict strongly bound Frenkel excitons at an energy of 1.9 eV and with a dispersional width of about 0.02 eV. These excitons should therefore exhibit local vibronic structure and are expected to be similar to optical excitations of C_{60} in solution or in an Ar matrix [23]. We note that the exciton can be either singlet or triplet with the triplet as the lowest-energy state. Optical as well as ELS data suggest a triplet-singlet splitting of about 0.24 eV [24]. In ELS the triplet exciton can be reached via exchange processes which are expected to be important at low incident energies. The energy-dependent intensity of the 1.55-eV structure in ELS [4] is therefore support for a triplet character of this exciton.

Before we can compare this to optical-ELS exciton energies which are at 1.55 eV for the triplet and 1.79 eV for the singlet, we must take into account the exchange interaction as well as the fact that the optical values quoted are for vibrational 0-0 transitions whereas the peak positions used from PES-IPES data refer to the "vertical" transition energies. It is not our purpose here to discuss this in detail but to show that a value of $U=1.6\pm0.2$ leads to strongly bound excitons in the energy range observed. Auger spectroscopy for a system with only one type of atomic orbital C $2p_\pi$ of importance reaches only the two-hole singlet states. The value of 1.9 eV found above for the exciton energy (possibly corrected downward by probably a few tenths of an eV for the vibronic correction) should therefore be compared to the singlet exciton energy at 1.79 eV [25]. A detailed discussion of this will be published elsewhere [12].

In conclusion, we have demonstrated that the gap in solid C_{60} is 2.3 ± 0.1 eV. The on-site molecular Coulomb interaction is nearly molecular-orbital independent with $U=1.6\pm0.2$ eV. The local exchange interaction (singlet-triplet splitting) as obtained from optical data is $J \simeq 0.2\pm0.1$ eV. With bandwidths of the h_u and t_{1u} bands of 0.4 eV as obtained from band theory we predict the existence of strongly bound Frenkel-like excitons in the range 1.5–2 eV corresponding to h_u-t_{1u} intramolecular excitation which correspond to the lowest-energy-observed optical transitions of electronic origin. Since $U \gg W$, C_{60} should be considered as a strongly correlated system. We suggest that this is also the case for K_3C_{60}. This latter system should therefore be described by a Hamiltonian of the form

$$\mathcal{H} = \sum_k \sum_m \epsilon_k c^\dagger_{km} c_{km} + \sum_i \sum_{m_1 m_1' m_2 m_2'} U_{m_1 m_1' m_2 m_2'} c^\dagger_{im_1} c_{im_1'} c^\dagger_{im_2} c_{im_2'}, \tag{8}$$

where m labels the spatial as well as the spin degrees of freedom of the threefold-degenerate t_{1u} molecular orbit and i is a molecular site label. The band energy ϵ_k is defined relative to the molecular t_{1u} configuration. All the $U_{m_1 m_1' m_2 m_2'}$ can be written in terms of two Slater-like integrals; a screened monopole Coulomb integral $U_0 \simeq 1.6\pm0.2$ eV and a dipolar integral of $U_2 \simeq 50$ meV [17]. We note that the exchange splitting will hardly be screened as it requires ineffective multipolar screening mechanisms [26]. The multiplet structure is completely determined by U_2. Locally two electrons in t_{1u} split into $^3T_{1g}$, ^1H_g, and ^1A_g states at energies $U_0 - \frac{5}{3}U_2$, $U_0 + \frac{1}{3}U_2$, and $U_0 + \frac{10}{3}U_2$. These correspond to ^3P, ^1D, and ^1S states of an atom with two electrons in a p orbital. Three electrons in a t_{1u} state split locally into multiplets ^4A_u, ^2H_u, and $^2T_{1u}$ with energies at $3U_0 - 5U_2$, $3U_0 - 2U_2$, and $3U_0$. We note that $U > W$ but also the multiplet splitting ($\sim 5U_2$) is of the order of W suggesting

strongly correlated systems with a significant tendency for local spin and orbital polarizations.

Provided the values of the parameters found here are transferrable to K_3C_{60} which we have provided some evidence for, we would predict that stoichiometric and ordered K_3C_{60} is a half-filled-shell Mott-Hubbard insulator with a gap of about 0.7 eV. The gap is obtained from $E_{gap}(K_3C_{60}) \simeq E_{gap}(C_{60}) - \Delta$ with Δ the h_u-t_{1u} splitting in C_{60}. The "pseudo" gap observed by Takahashi *et al.* [27] supports this conclusion. It is in our opinion very likely that the actual superconductor has an off-stoichiometric composition and is very similar in many regards to the high-T_c cuprates.

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) and the Netherlands Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for the Advancement of Pure Research (NWO) and the Committee for the European Development of Science and Technology (CODEST) program.

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