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Band Gap, Excitons and coulomb interactions of solid C_{60}

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The onsite molecular Coulomb interaction (U) of solid C_{60} is determined by means of a comparison of the selfconvolution and the KVV Auger spectrum and found to be 1.6 ± 0.2 eV and nearly independent of the molecular orbitals. This value of U leads to Frenkel type molecular excitons in the 1.5 - 2 eV range.

1. Introduction

Recently C_{60} had been considered as a semiconductor with a band gap of about 1.5 eV. This band gap could be measured from the onsets of low energy electron-energy loss spectra [1] and optical absorption spectra [2]. These onsets were interpreted as an excitation across the gap, where the top of the valence band was derived from the h_u molecular orbital and the bottom of the conduction band from the t_{1u} . This was in excellent agreement with the LDA calculations [3]. However Benning et al. [4] and Takahashi et al. [5] reported photo-emission / inverse photo-emission experiments with gaps considerably larger than 1.5 eV. Also the molecular optical absorption spectra of C_{60} in solution was remarkably similar to that of the solid [6]. This reminded us of the case of naphthalene, anthracene which form molecular crystals. Here as well as in the case of transition metal oxides [7] the low energy features in the optical spectra are assigned to Frenkel excitons and indeed LDA always underestimates the real band gap in these cases. We have therefore investigated solid C_{60} with photo-emission (PES) and inverse photo-emission (IPES) and Auger spectroscopy.

2. The experiments

C_{60} was obtained from Syncom BV and had

a purity better than 99.99 percent. Samples were prepared by depositing a few monolayers on clean Si[100] substrates in a UHV chamber with a base pressure of 10^{-9} mBar. We have done the PES and IPES on the same sample. For more details see ref.[8]. The result is given in figure 1. The most important conclusion from this measurement is the value of the band gap that is 2.3 eV. This is in agreement with the values reported by Takahashi and Benning and is a clear demonstration that for C_{60} the conductivity gap is not identifiable with the optical gap.

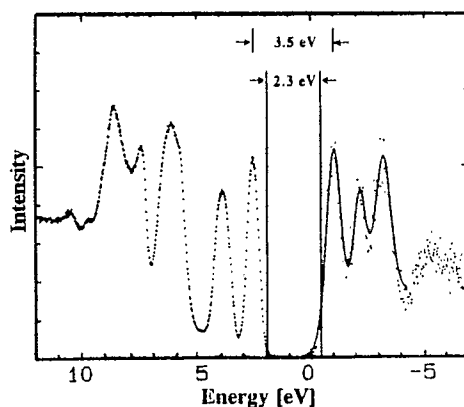


figure 1. Photoelectron (left) and inverse photoelectron (right) spectra of solid C_{60} . The vertical lines indicate the onsets for the gap determination.

A charge conserving local excitation, forming a electron-hole pair on one buckyball can lower the energy by the attraction of the electron and the

hole. In retrospect of this we have tried to measure in a direct way the electron-electron repulsion on a buckyball in the solid. We have done this by comparison of a selfconvolution of the valence band and the KVV Auger spectrum. The Auger spectrum in figure 2 was obtained using 1486.6-eV photons.

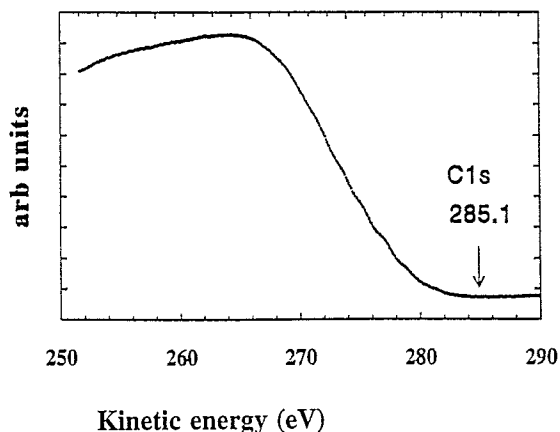


figure 2. C_{KVV} Auger spectrum of solid C_{60} .

The fermi energy of gold is taken as the zero. The spectrum consist of a large broad peak (50 eV wide) on which only tiny wiggles are seen. These small features however can be identified in a 1 to 1 relation with peaks in a selfconvolution of the valence band. In order to see the correspondence of the individual peaks in the spectra we passed the data through a filter which effectively subtracts the wide structures and keeps the wiggles. We also corrected for the difference in cross-section in both processes (in the PES spectrum the features at lower binding energies have relatively large cross sections). The resulting spectra a plotted in figure 3. The Auger spectrum is mapped onto a two hole binding energy spectrum by subtracting the C1s binding energy of 285.1 eV. Special care has been taken to reference all the energies to the fermi energy of gold in the case of XPS and Auger or silver in the case of PES and IPES. Also the valence band features of C_{60} in the XPS data could be used as a reference once the position where known from PES. The accuracy of this reference is estimated to be better than 0.1 eV. The result is given in figure 3a. and in figure 3b we have shifted the selfconvolution

by 1.6 eV.

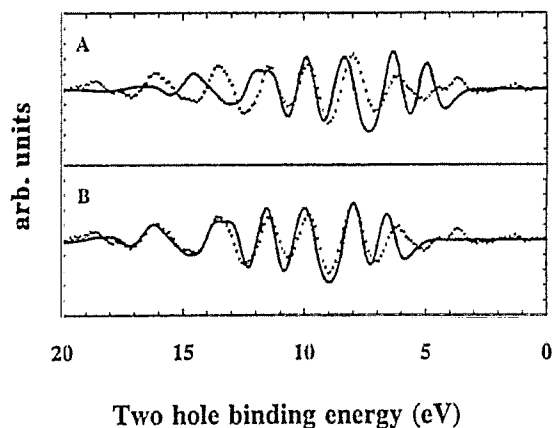


figure 3. (a) The C_{KVV} Auger spectrum (dots) and the valence band selfconvolution (solid line) after filtering as a two hole binding energy spectrum. (b) The valence band selfconvolution is shifted 1.6 eV towards higher binding energy.

The correspondence of nearly all the features is clear. The fact that we can shift the spectrum rigidly means that any pair of holes (and therefore also the electrons) in the valence band of C_{60} feels on the average a coulomb repulsion (U) of 1.6 eV. The value of U is in excellent agreement with theoretical estimates [9]. Only the peak at 6 eV corresponding with two holes in the h_u orbital has a considerably smaller shift of 1.2 eV. The first small peak in the Auger spectrum has no corresponding peak in the valence band selfconvolution. This peak is due to a shakeup excitation with the creation of the core hole. This is the singlet h_u-t_{1u} transition $\Delta_s = 1.8$ eV that is seen as a satellite in the C1s XPS spectrum[10]. Before the Auger decay can take place the core hole can be screened by an electron of the nearest neighbour molecule (called a spectator) [11]. A rough estimate of the energy of this spectator Auger spectrum resulting from an intermediate state $\underline{c}_A h_u^{10} t_{1uA} h_u^9 B$ (where we have molecule A with a core hole and an extra electron in the LUMO and nearest neighbour molecule B with a hole in the HOMO) can be made as follows. The energy gained by forming this state starting from $\underline{c}_A h_u^{10} h_u^{10} B$ is $\Delta_s + U - V - (U_c - V_c)$, where V is the nearest neighbour coulomb interaction of valence electrons, U_c is the coulomb interaction of

a valence band electron with a core electron on the same molecule and V_c on nearest neighbour molecules. The final state is described by $\underline{c}_A h_u^9_A h_u^9_B$ (where we have a hole in the HOMO for both A and B) and has an energy $U - V$ lower than the final state without the spectator: $\underline{c}_A h_u^8_A h_u^{10}_B$. So the peak will shift with $\Delta E = \Delta_s + 2*(U - V) - (U_c - V_c)$ with respect to the first peak without the shakeup. For $U=1.2$, $V=0.5$, $U_c=2.2$ [11] and $V_c = 0.7$ eV (we estimated V_c slightly larger than V because of the localization of the core electron) we get $\Delta E = 1.7$ eV. If in the final state the holes are driven apart by their repulsion the final state energy is lowered only by U . Then we get $\Delta E = 2.2$ eV. This is reasonably close to the measured value of 2.5 eV.

3. Discussion

There are 3 important aspects of these results which we would like to discuss further. These are:

- The significance of the fact that the two hole states are, aside from an overall shift, very similar to the self-convolution of the one hole states.
- The importance of a value of U considerably larger than the one electron band width.
- The importance of the band width or one electron hopping integrals in describing the exciton dispersion.

Concerning point a) we look again at fig. 3b to emphasize the similarity of the two hole states to the self-convolution of the one hole states. This is remarkable since C_{60} itself is composed of atoms and we may have expected the influence of an atomic on site U_c to strongly distort the C_{60} molecular Auger spectrum from a simple self convolution. The fact that this does not happen is a strong indication that the Coulomb interaction between two holes on a bucky ball is uniform i.e. long range and cannot be described by a Hubbard like model in which only the on site atomic interaction is considered to be important. To understand why this could happen we must realize that a C_{60} molecule is a finite size system. In a solid of infinite size the long range part of the Coulomb interaction is efficiently screened because of the polarizable medium surrounding

the particles and at short range the interaction will be less screened. A C_{60} molecule on the other hand is a spherical shell. Consider for example a shell of polarizable atoms as in Fig. 4 with a negative test charge on the shell to the left. The atoms will polarize due to the field of the test charge approximately as drawn. The total potential due to the induced dipoles at a position on the shell at an angle of 180° is exactly zero because of the 90° angle between the polarization vectors and the vectors towards the point where the potential is measured. Short range ($\theta < 180^\circ$) interactions will however be screened in this model. As θ increases the screening will decrease until for a largest distance i.e. $\theta = 180^\circ$ the screening will be zero.

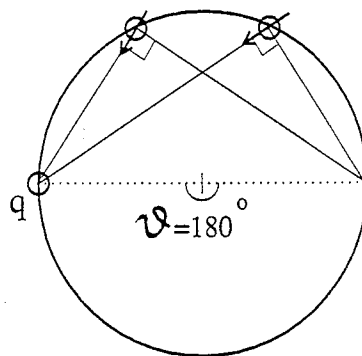


figure 4. A model for the screening on a C_{60} molecule (see text).

A realistic calculation by Gunnarsson [12] shows that the long range potential is in fact larger than the bare potential, i.e. anti-screened! This leaves the interaction nearly independent of the distance between the charges on the ball. This explains our result and also shows why a Hubbard model should not be used for a C_{60} molecule itself. The Coulomb energy of placing two holes on a buckyball is therefore a constant (i.e. our measured U) and is nearly independent of the distance between the charge on the ball.

We now turn to point b. We find a U value of 1.6 eV or perhaps it is better to use the value of 1.2 eV for the h_u holes. From the PES/IPES experiment we can also derive a value for U concerning the h_u and t_{1u} orbitals. In these experiments the U can be derived from the onsets

of both spectra above and below the band gap. The coulomb interaction is given by: $U = E_I - E_A - \Delta + W$, where E_I is the ionization potential, E_A the electron affinity, Δ the molecular orbital splitting of the HOMO and the LUMO and W the bandwidth. $E_I - E_A = 2.3$ as seen in figure 1. We can take $\Delta \approx 1.6$ eV from PES on C_{60}^- [13] or the $h_u - t_{1u}$ difference in the PES spectra of K_6C_{60} [14]. The bandwidth W is 0.4 eV. In this way we get a U of 1.1 eV, which is a conservative estimate and we feel a lower limit. This is still considerably larger than the one electron band width! If we take the peak-peak distance as a measure for $E_{h_u} - E_{t_{1u}}$ than we arrive with $U = E_{h_u} - E_{t_{1u}} - \Delta = 1.9$ eV. It is clear that the width of the h_u and the t_{1u} levels in the PES and IPES spectra do not really reflect the bandwidth but is determined largely by phonons and vibrons. This means that U is overestimated in this way. If we can use the value of 1.1 eV for also the doped C_{60} compounds, then we would expect all of the stoichiometric integer doped systems to be Mott-Hubbard insulators. This could explain why K_4C_{60} , Rb_4C_{60} , K_3C_{60} and all Cs_xC_{60} compounds [15,16,17] etc. are not metallic whereas one electron band theory would predict all of them to be metals. Nearest neighbour interactions will not influence this conclusion. Although a nearest neighbour interaction V acts to lower the energy of the excitation of an electron to a nearest neighbour site it does not act to lower the effective value of U in determining the conductivity gap. This because the conductivity gap is determined by excitations where an electron is moved far away from its parent molecule so the hole left behind and excited electron no longer interact. This rather important point is described in more detail in J. v.d. Brink et al. [18] and M. Meinders [19]. The question why then the $x=3$ systems are metals is still open. One explanation could be that they are not stoichiometric.

Now to point c. Although we have stressed the point that solid C_{60} should be considered as a molecular crystal we should now back off a bit because there are important differences with the extreme cases of anthracene, naphthalene etc. C_{60} has a relatively small band gap and has a relatively large band width when comparing to extreme cores of molecular crystals. This means

that the influence of the intermolecular hopping integrals in the exciton dispersion relation cannot be neglected. In fact we find that it dominates over the usual dipole-dipole mechanisms proposed for the extreme Frenkel exciton cases. As we discussed in a previous paper [8] a second order perturbation calculation yields an exciton band width given roughly by $W_{\text{exciton}} \approx W^2/12U$ for an FCC lattice where W is the one electron band width. For W between 0.4 and 0.6 and $1 < U < 1.6$ we get a band width ranging between 8 and 30 meV. In any case at least an order of magnitude larger than found in ordinary molecular crystals. It is also important to note that both the singlets and triplets will have these large band widths again quite different from ordinary molecular crystals. We are in the process of calculating the dispersion relations for the various symmetries of excitons states more precisely including also the Davydov splitting.

4. Conclusion

We have measured the C_{KVV} Auger spectrum of C_{60} and found a detailed structure of peaks which could very well be compared with the structures arising from a selfconvolution of a UPS spectrum of the valence band. We have pointed out that the confinement of the electrons leads to a nearly spatial independent potential on a buckyball. This leads to a rigid shift of two hole states and therefore a nearly orbital independent molecular U . We have determined this U to be 1.6 eV. Only the state with two holes in the h_u orbital shows a smaller shift of 1.2 eV. Also the U for a hole in the h_u and an electron in the t_{1u} derived from PES and IPES measurements seems to be smaller, about 1.1 eV. The extra feature in the Auger spectrum could be identified as due to a shake up process in combination with screening of the core hole by charge transfer from the nearest neighbour. U/W being larger than one leads to bound states as well for the two hole final state in the Auger process and for optical processes. These optical bound states behave like Frenkel excitons and have energies smaller than the band gap. We have also discussed the significance of such a large U value in describing

the electronic structure of the doped systems. We can explain why a majority of C_{60} compounds are non-metallic and suggest that A_3C_{60} is not stoichiometric. We also argued that solid C_{60} is different from the extreme molecular crystals with a much larger exciton dispersion for both singlets and the triplets.

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