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Band-gap and correlation effects in the organic semiconductor Alq_3

M. Knupfer, H. Peisert, and T. Schwieger
Institut für Festkörper und Werkstofforschung Dresden, D-01171 Dresden, Germany

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We present a spectroscopic study of the electronic properties of a molecular organic semiconductor Alq_3, and its potassium intercalation compound $KAlq_3$. It is argued that both compounds are strongly correlated materials with a band gap that is to a large extent determined by electron correlation effects. In particular, the Coulomb repulsion energy for two electrons on an Alq_3 molecule in the solids is about 1.4 eV that renders $KAlq_3$ a Mott-Hubbard insulator and causes a large exciton binding energy in solid Alq_3. The implications of these results for organic devices are discussed.

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The class of organic semiconductors offers a wide range of potential applications in novel electronic or optoelectronic devices (e.g., Refs. 1–5). In addition, field-effect devices on the basis of molecular organic semiconductors such as pentacene, anthracene, or C_{60} have been used to demonstrate the occurrence of the fractional quantum Hall effect[6] and of superconductivity[7,8] with transition temperatures up to 52 K (the latter in hole-doped C_{60}) in such systems. The materials used in organic devices are based upon various π-conjugated polymers and oligomers. A microscopic understanding of any device and its optimization requires a knowledge of the fundamental electronic properties of the system in question. The performance of most devices is directly related to the transport properties, i.e., the nature, size, and dynamics of the charge carriers in the individual device components. A central parameter to model the transport behavior of materials is the energy gap, which is the energy difference between a free electron in the conduction band and a free hole in the valence band. Directly connected to the transport relevant energy gap is the question of the binding energy (BE) of the lowest lying optical excitation, which is defined as the energy difference between the excitation energy as measured in optical experiments (optical gap) and the transport gap. Despite more than a decade of intense research in the field of organic semiconductors there is still no consensus about the relative size of these two gaps. For instance, exciton binding energies ranging from 0.1 to 1.4 eV have been discussed previously for various systems.[9–20] This—at least to some extent—arises from the fact that the obvious presence of various effects like electron-phonon coupling and electronic correlations and their interplay are often not considered appropriately that makes the analysis and discussion of various results less conclusive or ambiguous (see Refs. 15, 21 for an instructive discussion). The situation becomes even more unclear comparing the results of actually equivalent experiments on one particular organic semiconductor, copper phtalocyanine, where the reported transport relevant energy gaps differ by more than 1 eV.[20,22]

In order to shed light on these important issues, we have studied the electronic structure of solid Alq_3 (8-tris-hydroxyquinoline aluminum) and its potassium intercalated compound $KAlq_3$ using photoemission spectroscopy. Taking into account complementary results from the literature we demonstrate that the experimental observations are consistently rationalized within the framework of strong electron correlations in solid Alq_3. In particular, the Coulomb interaction between two electrons on one Alq_3 molecule in the solid is at least 1.4 eV. The large Coulomb repulsion causes a large exciton binding energy in solid Alq_3 of also about 1.4 eV and renders the intercalated compound $KAlq_3$ insulating. The latter compound thus has a Mott-Hubbard ground state.

The photoemission experiments have been carried out in an ultrahigh vacuum (UHV) chamber (base pressure 10^{-10} mbar) using a He discharge lamp providing photons with 21.2 eV [ultraviolet photoemission spectroscopy (UPS)] and a commercial PHI 5600 analyzer. The UPS spectra have been corrected for the contributions from HeIβ and HeIγ radiation. The total-energy resolution was 100 meV. Thin Alq_3 films were prepared by evaporation under UHV conditions onto a sputter-cleaned gold foil. To intercalate Alq_3, potassium was evaporated from standard, commercial SAES getter sources and the degree of intercalation has been determined using core-level photoemission spectroscopy (for further details see Ref. 23).

In Fig. 1 we show representative UPS spectra of solid Alq_3 and $KAlq_3$ down to a BE of 11 eV. The data are consistent with those from previous studies.[23–27] The spectra reveal several sharp features with a half-width of about 1 eV or smaller which arise from excitations of electrons that occupy different molecular orbitals of Alq_3. Typically, the bandwidth in solids with delocalized electronic states is much larger than 1 eV. For instance, the width of the occupied part of the π band in graphite is larger than 5 eV.[28] In comparison, the well structured features in the spectra up to a binding energy of 10 eV in the spectra of Alq_3 show that solid-state broadening due to band formation is much smaller in Alq_3 in agreement with other molecular, van der Waals-type solids (e.g., the fullerene C_{60}[29]) where one finds a bandwidth of 0.5 eV or smaller of the bands related to the molecular levels. The feature that represents emission from the highest occupied molecular orbital (HOMO) of Alq_3 is labeled H. The HOMO and the lowest unoccupied molecular orbital (LUMO) of Alq_3 consist of three almost degenerate molecular levels that are not resolved in Fig. 1 and which represent the three ligands of the Alq_3 molecule[30] (see Fig. 1).

Going from Alq_3 to $KAlq_3$ the valence-band features show a constant shift to higher binding energy that is related to a shift of the chemical potential upon intercalation. The

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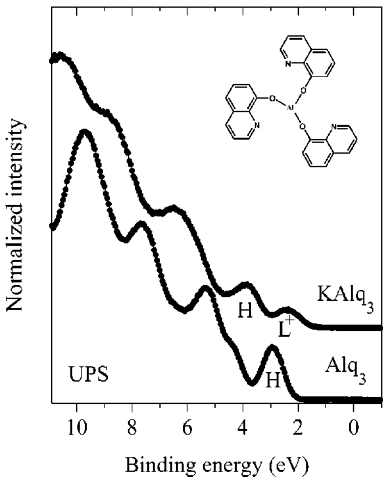

FIG. 1. Photoemission (UPS) profiles of solid Alq_3 and its potassium intercalation compound KAlq_3. The low binding-energy spectral features that are derived from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Alq_3 are labeled H and L^+, respectively. For comparison, the spectrum of KAlq_3 is offset in *y* direction. Also shown is a schematical representation of the molecular structure of Alq_3.

constant energy shift is indicated by the same spectral shape of the two curves shown in Fig. 1 except the lowest binding-energy feature in the case of KAlq_3. Moreover, also all core levels show the same energy shift[23] that can only be understood in terms of a shift of the chemical potential upon intercalation. The new structure in the spectrum of KAlq_3, labeled L^+, is observed at about 2.4 eV BE (onset at 1.5 eV BE) which arises from emission from the LUMO of Alq_3, which is filled as a result of the charge transfer of the potassium 4*s* electrons to the Alq_3 molecule upon intercalation. From Fig. 1 it is obvious that both compounds do not show emission from the Fermi energy (=0 eV BE); i.e., both compounds are insulating. While this is expected for pristine Alq_3 with a closed-shell electronic structure, the insulating ground state of solid KAlq_3 contradicts expectations within an independent electron consideration where a charge transfer of one electron to the LUMO-derived conduction band would result in a partially filled band, i.e., in a metallic behavior.

In the following, we will address the different mechanisms, that could render intercalated KAlq_3 films insulating, and discuss their consequences for charge transport through Alq_3 thin films as used in organic devices.

(i) It has been argued that the introduced counterions in intercalated films of organic semiconductors might impact the electronic structure of the individual molecules. This could, in principle, lead to a localization of the charge carriers to a part of the molecule and thus to a reduced spectral weight at the Fermi level as a function of a reduced transfer integral between the molecules. However, it is very unlikely that the counterions push the electronic states more than 1.5 eV away from the Fermi energy and *simultaneously* split the LUMO-derived features into an occupied and an unoccupied part. Indeed, theoretical considerations of alkali-metal interactions in Li-Alq_3 or K-Alq_3 complexes predict a stabilization of the LUMO of the order of half an eV but no splitting is reported.[26,31] Moreover, related systems such as $\mathrm{K}_3\mathrm{C}_{60}$[29] or Li intercalated poly(9,9-dioctyl-fluorene)[32] also contain counterions but do show emission from the Fermi level. Consequently, we rule out that the potassium counterions play a major role in the determination of the ground state and the energy gap of KAlq_3.

(ii) It is well established that the introduction of charges into molecules like Alq_3 results in a relaxation of the molecular structure, i.e., there is considerable electron-phonon coupling in these organic semiconductors. This alone, of course, cannot lead to a metal-insulator transition for KAlq_3 but only renormalizes the charge-carrier properties, like the effective mass, and thus results in the formation of polarons. If, however, the formation of a bipolaron state, i.e., a bound pair of polarons, was energetically more favorable, one could imagine a redistribution of the electronic density of states such that an energy gap at the Fermi level shows up. This would then correspond to a charge-density wave insulator. While bipolarons have been predicted to be stabilized on small molecules[33,34] the virtual threefold degeneracy of the LUMO level in Alq_3 contradicts the formation of bipolarons. Instead, as a function of electron transfer to Alq_3, the three ligands are negatively charged successively with a very small interaction between them.[26] In addition, the energy gap of more than 1.5 eV as observed in Fig. 1 is far too large to be explained by a bipolaron formation.[16,35]

(iii) So far, we have not considered that Alq_3 forms a molecular solid with relatively small interactions between the molecules. In other words, the wave function of the charge carriers are rather localized to the molecular units. This situation is reminiscent of other molecular solids based upon small π-conjugated molecules such as anthracene or C_{60}. In these cases it is well established that the electronic properties cannot be described on the basis of an independent electron approach but that strong electron correlation effects have to be taken into account in order to rationalize the electronic behaviors. Here, strong electron correlation effects means that the Coulomb repulsion of two electrons (or holes) on the same molecule in the solid is significantly larger than the bandwidth of the corresponding one-particle bands. This suppresses charge fluctuations, i.e., transport, thus enhancing the band gap of the pristine materials and rendering doped materials insulating. For instance, the transport relevant band gap of anthracene is about 4.15 eV (Ref. 36) while the energy of the lowest lying singlet exciton is only about 3.13 eV, i.e., the exciton binding energy is 1 eV.[21] Within a simple Mott-Hubbard approach this exciton binding energy now is a direct measure of the difference of the Coulomb repulsion energy U, and the bandwidth W: $\tilde{U}=U-W$. The equivalent situation is found in C_{60}, where $\tilde{U}$ is about 0.5 eV.[29,37] In addition, $\tilde{U}$ in C_{60} intercalation compounds is large enough to drive $\mathrm{K}_4\mathrm{C}_{60}$, which has a partially filled conduction band, insulating.[38] Consequently, since the size of the Alq_3 molecule and the interaction in the solid is very similar to those of anthracene and C_{60} we conclude that solid Alq_3 and its intercalation compound KAlq_3 as well are strongly correlated materials. The correlations lead to a splitting of the partially filled conduction band in KAlq_3. The insulating

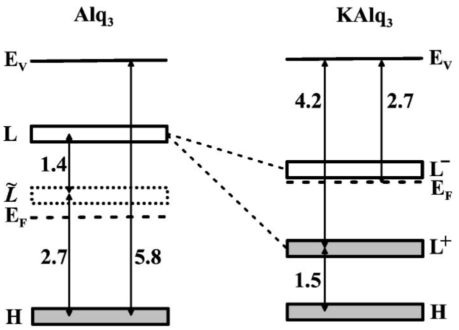

FIG. 2. Schematic energy level diagram for solid Alq_3 and its potassium intercalation compound KAlq_3. The energy levels are labeled H for the HOMO-derived bands, and L (Alq_3) or L^+ and L^- (KAlq_3). $\tilde{L}$ denotes the ground state position of the LUMO in Alq_3, which has no relevance as regards transport properties. E_v and E_F denote the vacuum level and the Fermi energy, respectively.

ground state of KAlq_3 is thus best described as a Mott-Hubbard insulator and the onset of the lowest BE feature in Fig. 1 gives an estimate of the size of the effective Coulomb energy $\tilde{U}$, which is about 1.5 eV or even larger.

This conclusion now has important consequences for pristine Alq_3. The transport relevant energy gap of Alq_3 should exceed the energy gap as measured by optical experiments by as much as $\tilde{U}\sim 1.5\,\mathrm{eV}$. Indeed, while the onset of the optical absorption is at about 2.7 eV,[23] the transport gap as measured by a combination of photoemission and inverse photoemission spectroscopy is about 1.4 eV larger[20] in almost perfect agreement with the inference above. A schematic summary of the energy levels that are relevant for transport through Alq_3 or KAlq_3 solids is presented in Fig. 2. The HOMO- and LUMO-derived bands are denoted as H and L, respectively. We note that the bandwidth in molecular solids is small that allows one to discuss the energy-level diagram on the basis of the molecular states. In pristine Alq_3 the ground-state energy difference of the HOMO and the LUMO (denoted $\tilde{L}$ in Fig. 2) is about 2.7 eV as seen in transient photoemission studies[39] or as the onset in optical absorption[23,40] where the latter measures the lowest singlet exciton in Alq_3. The binding energy of this lowest singlet exciton is about 1.4 eV (Ref. 20) and one thus arives at a transport relevant energy gap of about $2.7\,\mathrm{eV}+1.4\,\mathrm{eV}=4.1\,\mathrm{eV}$. The ionization potential of solid Alq_3 is 5.8 eV. Adding one electron to the Alq_3 molecules via potassium intercalation reduces the ionization potential to 4.2 eV and results in a splitting of the LUMO-derived bands into an occupied (L^+) and unoccupied (L^-) lower and upper Hubbard band, respectively. In addition, the introduction of charges and counter ions leads to a work function of 2.7 eV and causes an energy relaxation of the energy levels with a resulting difference of H and L^+ of 1.5 eV.

The numbers given in Fig. 2 underline that the use of optical methods to access the energy position of the LUMO-derived conduction band in molecular organic semiconductors—as has been often carried out in the past—inherently leads to a large error and renders the conclusions on, for instance, injection barriers or other interface properties, that are relevant for organic devices, questionable. Furthermore, the presence of strong electron correlations and as a consequence strongly bound excitons should be taken into account when choosing the appropriate material for organic devices, e.g., light emitting diodes or solar cells. While in the latter a large exciton binding energy is very unfavorable for the device performance as one has to separate the charges, it can help to optimize the quantum yield efficiency in the former.

The very large exciton binding energy in solid Alq_3 contrasts with reports of exciton binding energies in various polymers of only about 0.3–0.4 eV (e.g., Refs. 15 and 19). Most probably the size of the molecules harbors the explanation for this difference. The larger the molecules become, the smaller is the Coulomb repulsion U, as the two charges can better delocalize and thus avoid each other.

Lastly, the situation schematically drawn in Fig. 2 raises the question on the spin order in solid KAlq_3. Usually, Mott-Hubbard insulators exhibit an antiferromagnetic ground state that is a direct consequence of the electronic correlations. This, however, can be altered by other mechanisms like electron-phonon coupling or a particular crystal symmetry leading to frustration and further studies are necessary to decide this question.

To summarize, we have shown that a consistent rationalization of the experimental results on the electronic properties of solid Alq_3 requires the consideration of strong electron correlation effects. In particular, the Coulomb repulsion of two charges on an Alq_3 molecule in the solid is larger than or equal to 1.4 eV, which also defines the exciton binding energy of the lowest lying singlet exciton. The electronic correlations are responsible for the insulating ground state of KAlq_3.

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