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Investigation of the absorption edge of C_{60} fullerite

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Absorption measurements on single crystals of C_{60} fullerite have been performed as a function of temperature, hydrostatic pressure, and magnetic field in the optical visible range. Various structures observed in the fundamental absorption edge are assigned to excitonic transitions based on comparison with calculations, including many-electron and electron-hole interaction effects. The strength of the electron-phonon interaction is discussed in view of these results.

The electronic structure of the fullerites has attracted much interest from both the theoretical as well as the experimental point of view.[1] Theoretically, different approaches have been employed to study this material, including the local-density approximation[2] (LDA) and the *ab initio* quasiparticle method.[3] These methods provide the same band ordering for C_{60} crystals in the $Fm3$ structure, which consists of highest occupied molecular orbitals (HOMO's) of H_u symmetry and lowest unoccupied molecular orbitals (LUMO's) of T_{1u} symmetry, but the respective band gap changes from 1.04 eV (in the LDA calculation) to 2.15 eV (in the GW quasiparticle picture[4]). Experimentally, direct and inverse photoemission experiments[5–8] gave values for the gap closer to the GW approach prediction than to the LDA one. This has to be compared to results of microwave conductivity experiments[9] providing excitation energies of about 1.85 eV whereas luminescence experiments[10] reported an emission band at around 1.7 eV. The discrepancy with the optical gap could be due to excitonic effects, but this remains to be demonstrated. In order to investigate the fundamental properties of the absorption edge of this semiconductor, we have performed systematic transmission measurements on fullerite single crystals as a function of temperature, hydrostatic pressure, and magnetic field. Calculations including electron-hole interactions have also been made, and comparison between experimental and theoretical data leads to the conclusion that the absorption edge is essentially made of states of a Frenkel excitonic nature, strongly coupled to vibrational modes.[7,11]

Performing reliable absorption measurements on C_{60} single crystals is difficult, due to their mechanical and chemical fragility. Any type of polishing results in damaging irreversibly the sample. Because fullerites are easily polluted by water vapor or any solvent,[12] samples have been heated up to 130 °C for at least 12 h before starting the experiments. The single crystal platelets, characterized by x-ray analysis, were grown by a vapor-transport technique, in an open-ended quartz tube subjected to a temperature gradient. C_{60} powder of very high purity was sublimated at one end at 600 °C, and driven by a purified (O_2-free) argon flow to the growth area at a temperature ranging between 500 and 550 °C. Such platelets with thicknesses ranging from a few μm to about 400 μm were selected and investigated with accurate spectrometry equipment. The temperature was monitored with a helium-flow cryostat, also allowing low-temperature investigations under magnetic fields up to 15 T and under hydrostatic pressure using the diamond-anvil cell technique.

The natural platelets developed interferences in the transparent region, allowing a relatively good accuracy of the determination of the thickness when knowing the refractive index.[9] Figure 1(a) displays the absorption coefficient α measured at different temperatures. The compound is known to undergo a phase transition[13] with decreasing temperature at around 260 K from a high-temperature orientational disordered structure (fcc) to a low-temperature ordered one ($Pa3$). While the absorption edge remains structured below 260 K, it gets smeared above the phase transition. The values of α are quite weak compared to standard values reported for direct-gap and electric-dipole-allowed transitions in semiconductors. This is not surprising since the HOMO-LUMO electric-dipole transitions are forbidden by parity. The reason why they appear weakly allowed is likely due to a Herzberg-Teller and/or a Jahn-Teller vibronic effect. It is indeed surprising that the measured spectra are very close to those obtained in C_{60} fullerenes dissolved in solution.[14] This already favors the idea that the fundamental absorption-edge transitions are very localized and thus probably strongly coupled to vibrations. Hence, one expects the transitions to be either phonon-assisted with low-energy phonons or phonon replica of these ones. However, while all transitions above 1.75 eV have a reproducible oscillator strength, the band around 1.7 eV is very likely of extrinsic origin because its shape is not conventional and its relative strength is significantly decreased following a heating process under vacuum. Luminescence features are commonly observed at 1.7 eV in our samples as well as in others,[10] and this explains why it has been assigned, probably incorrectly, to the lower-energy transition of the compound. The intrinsic transitions can be grouped in three pairs around 1.86 eV (A), 1.94 eV (B),

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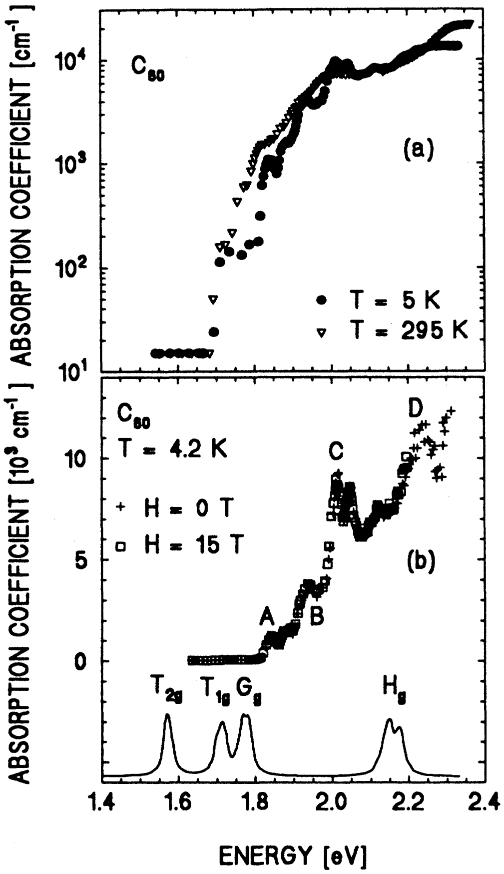

FIG. 1. (a) Absorption coefficients of the fundamental absorption edge of fullerite at 5 and 295 K and (b) comparison between absorption curves without magnetic field and with a magnetic field of 15 T. The calculated density of states for excitonic transitions is displayed in the lower part of the figure.

and 2.03 eV (C), and a broad structure at 2.3 eV (D). In order to obtain more insight into the nature of the intrinsic transitions, a magnetic-field investigation has been performed. The results are reported in Fig. 1(b), where spectra at 0 and 15 T are compared. A closer look at these results shows that within the experimental uncertainty (≈ 0.5 meV) both spectra are identical. This result agrees with the picture of very localized transitions: if one assumes that the transition takes place on a single molecule with an exciton Bohr radius of about 0.5 nm, the expected diamagnetic shift at 15 T would be less than 10^{-3} meV, which is not measurable.

High-pressure experiments at low temperatures (30 K) have also been performed using the diamond-anvil cell technique with Xe as a pressure medium. Results are presented in Fig. 2 and require much care when being interpreted. The absorption measurements in diamond-anvil cells are not absolute measurements, and important corrections have to be made to take into account the stray light. In addition, the structures are smeared out under increasing pressure, reflecting the influence of the pressure medium despite its chemical inertness. This requires a deconvolution procedure with Gaussian-like bands for each structure to interpret the data. The resulting precision for α is quite poor and for that reason reliable results have only been obtained for the three lower-energy structures. One finds, for the three excitonic structures, the pressure coefficients: -45 ± 5 meV/GPa (peak A), -60 ± 8 meV/GPa (peak B), and -80 ± 10 meV/GPa (peak C). These values are deduced from a linear interpolation of four measurements made between 0 and 1.5 GPa. The resulting error for the coefficients is quite important.

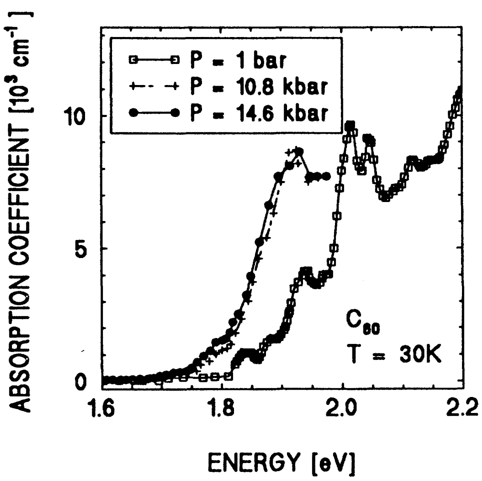

FIG. 2. Low-temperature absorption spectra of C_{60} crystals for different values of the hydrostatic pressure.

We now compare the experimental results with theoretical realistic predictions which include electron-hole interaction in *ab initio* calculations, treating accurately both many-electron and molecular orientational effects. To treat excitons, we solve a Hamiltonian of the form $H = H_e + H_h + H_{e\text{-}h}$. Here H_e and H_h describe an electron or a hole in the solid, within a proper quasiparticle picture.[3] $H_{e\text{-}h}$ describes the screened Coulomb electron-hole interaction. There are three parts: the long-range, unscreened part $(-e^2/r)$, the attraction on the same C_{60} molecule, and modification of the first two parts by screening effects in the crystal. Attractions on the C_{60} molecule are treated in the Parr-Pariser-Pople scheme.[15] We use tabulated values for the π-π Coulomb integrals, scaled to match attraction inferred from vapor-phase experiments.[16] Screening effects are evaluated with a self-consistent, point-dipole model: each C_{60} can acquire an induced dipole, due to electric fields of the electron, hole, and other molecules' polarization. We use the theoretical polarizability, giving a screened interaction in agreement with other work.[17] The calculation gives the correct singlet-triplet splitting (0.28 eV). The lowest photon energy needed to create a singlet exciton was found theoretically to be 1.57 eV, in reasonable agreement with the experimental 1.83 eV value. The theoretical excitonic density of states is given in Fig. 1(b) and compared to the experiment. A complete report of our calculations will be given elsewhere.[18] The low-lying exciton wave functions are found to be Frenkel-like, i.e., the electron and hole are tightly bound mostly to one single C_{60} molecule, while higher-lying states (above 2.2 eV) have significant charge-transfer character,[18] in agreement with previous calculations.[9,20] It is then natural to use the symmetry labelings of the icosahedral group to describe the four lowest exciton bands. The excitons have the approximate symmetry of $T_{1u}\otimes H_u=T_{1g}+T_{2g}+G_g+H_g$, where T, G, and H indicate threefold, fourfold, and fivefold degeneracy for exciton levels of isolated molecules. Our calculations find effectively four structures to be compared to the experimental ones. A careful analysis of the calculated wave functions shows that the lowest-lying complex for both the singlet and triplet excitons are of T_{2g} symmetry. This is consistent with configuration-interaction calculations[15,21] for the isolated molecule. In an effort to address this issue, several groups have performed experiments to resolve the symmetry of the lowest-lying excitonic states.[11,22–24] These authors argue that the lowest-energy singlet exciton has T_{1g} symmetry, in contrast to the above results. At the absorption edge, the theoretical density of exciton states gives four excitonic structures (artifically broadened by a Lorentzian with a full width at half maximum of 0.02 eV). Neither the absorption strength nor the phonon replica are reproduced since the electron-phonon interaction is not included in our calculations. Note that the bandwidth of electronic excitations is now reduced from 0.9 eV (GW quasiparticle picture) to exciton bands with dispersion about 0.05 eV or less in the presence of electron-hole interactions. Pressure coefficients for the three lowest-energy excitonic structures have also been calculated in the $Pa3$ structure using the low-temperature experimental bulk modulus of 10.3 GPa.[25] We found that the energy of the levels changes at a rate of -44 meV/GPa for both T_{2g} and T_{1g} excitons and -54 meV/GPa for the G_g exciton, in good agreement with the experiment given the large uncertainty on the reported values for the bulk modulus.[25–28] The theoretical and experimental results support the excitonic nature of the absorption edge and give strong support to the proposed assignment because the different excitons are sufficiently distinct. Thus, we arrive at a picture with four excitonic vibronic lines A, B, C, and D of different symmetry and with phonon replica, at least for the first three. These even-parity excitons have a forbidden electric-dipole activity, and the very weak measured oscillator strength is presumably due to the interaction with odd-parity phonons. The variation of the absorption coefficient for these structures reflects the relative electron-phonon coupling strength because simple considerations of excitonic density of states [Fig. 1(b)] do not explain the differences. The electron-phonon interaction is clearly needed to explain the experimental findings.

This interaction is also evident in the temperature variation of the optical transitions. One can always write for any transition energy E_0:

$$\left.\frac{\partial E_0}{\partial T}\right|_P=\left.\frac{1}{\Omega}\frac{\partial \Omega}{\partial T}\right|_P\,\Omega\left.\frac{\partial E_0}{\partial \Omega}\right|_T+\left.\frac{\partial E_0}{\partial T}\right|_\Omega, \tag{1}$$

where the temperature coefficient is decomposed into an extrinsic part [the first term on the right-hand side of Eq. (1)] due to the thermal expansion of the lattice, and an intrinsic part due to the electron-phonon interaction. The evaluation of the extrinsic part is easy to perform when the temperature-dependent thermal expansion coefficient,[13] the bulk modulus[25] for the different phases, and the related pressure coefficient of the transition energies are all known. These coefficients are not determined with a good accuracy and are temperature dependent, especially across the phase transition. In the present case we have assumed a constant value for them and checked that our conclusions were not dependent on this crude choice. The integral

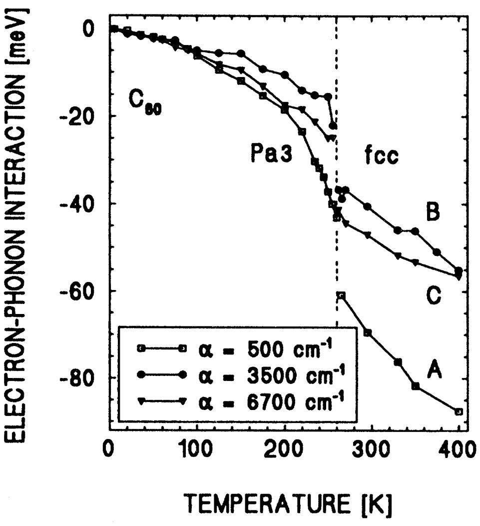

FIG. 3. Intrinsic contribution of the electron-phonon interaction to the transition energy vs temperature for constant values of the absorption coefficient α.

$$I_{\text{el-ph}}=\int_0^T\left(\frac{\partial E_0}{\partial T}\right)_\Omega dT$$

can then be evaluated for different values of α specific to the structures A, B, and C. The results are displayed in Fig. 3. It is clear that the intrinsic part of $I_{\text{el-ph}}$ is a monotonic increasing function of temperature that undergoes an abrupt increase at the orientational order-disorder phase transition. This interaction is also specific to the symmetry of the excitonic state and appears to be significantly more important for the exciton A. The increase of $I_{\text{el-ph}}$ with temperature can be understood from the theories of Fan, and Brooks and Yu,[29] as applied to excitonic states. In this description, electronic states, renormalized by phonons, are shifted to lower energy. As temperature increases, the phonon occupation number increases, leading to a larger shift in the exciton energies. The discontinuity in the energy shifts at the structural phase transition is most likely a result of the discontinuous change in the low-energy phonon spectrum, as calculated in Ref. 30. They argue that the libron modes are softened in the fcc phase. This would increase the phonon occupation numbers at a given temperature, resulting in an abrupt increase in the energy shifts of electronic states. Our measurements show that the overall magnitude of the electron-phonon interaction is quite large. This is consistent with the view that an electron-phonon mechanism is important for superconductivity in the alkali-doped C_{60} compounds.

In conclusion, the absorption edge of the fullerite single crystals has been investigated as a function of temperature, magnetic field, and hydrostatic pressure. The comparison between these results and predictions obtained from *ab initio* calculations including the electron-hole interaction strongly support the assignment of structures to even-parity excitonic transitions strongly localized on the molecules. The weak but finite oscillator strengths, the existence of strong phonon replica, and the large intrinsic temperature variation of the absorption edge demonstrate the important role of the electron-phonon interaction in the physical properties of these compounds.

Note added in proof. The theoretical exciton levels in this work were calculated using Lowdin's parameters for the π-π Coulomb integrals,[15] whereas different sets of parameters can reduce or change the sign of the T_{2g}-T_{1g} splitting. Therefore, it is difficult at present to establish from theory alone whether the lowest singlet excitons have T_{2g} or T_{1g} symmetry. This will be discussed further in Ref. 18.

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