Crystal-field induced mixing of electron states in C₆₀ crystals at high pressure

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Optical absorption spectra of thin fullerene (C_{60}) crystals in the range 1.7 to 3.8 eV have been measured at T = 300 K and at pressures up to 2.5 GPa. The spectrum shifts toward the red with pressure, and the electron absorption intensity is redistributed among its bands. The intensity of the band associated with the lowest direct electron interband transition monotonically increases with pressure, whereas the intensity of the upper interband feature decreases. Bands related to weak edge absorption in the range between 1.7 and 2.2 eV gradually merge with the band associated with the lowest interband transition, whose intensity rises with pressure. A similar redistribution of intensity among electron transition bands has been observed when comparing the spectrum of an isolated C_{60} molecule and that of a C_{60} crystal. The results indicate that the crystal-field induced mixing of electron states is present in solid C_{60} , and they can be discussed in terms of the Craig–McClure model, which was suggested to describe crystal-field induced mixing of electron states in anthracene and naphthalene molecular crystals. © 1998 American Institute of Physics. [S1063-7761(98)02101-5]

1. INTRODUCTION

Electronic spectra of C₆₀ molecules and C₆₀ crystals have been discussed in numerous theoretical and experimental works. The first calculations of C₆₀ molecule electron spectra were reported soon after the discovery of stable large all-carbon molecules in products of graphite laser ablation.¹⁻³ Then followed more accurate quantum mechanical models of the C60 molecular structure, electron and phonon spectra.^{4–8} Experimental study of the C₆₀ electron spectrum became a real possibility after the efficient technique for synthesizing fullerenes in a graphite arc had come into being.⁹⁻¹² Detailed measurements of C₆₀ molecular absorption spectra and their vibrational analysis were performed for solid solutions of C₆₀ in argon and hexane matrices by means of high-resolution Fourier-transform spectroscopy.^{13,14} This research indicated that the range of weak edge absorption in the C_{60} molecular spectrum, 1.78 to 3.04 eV, is due to electron-phonon replicas of dipole-forbidden electron transitions. These transitions, assisted by non-totally-symmetric, phonons are due to the Hertzberg-Teller and Jahn-Teller effects, and also show up in absorption spectra of C₆₀ films and C₆₀ thin crystals.^{15,16} Dipole-allowed electron transitions have been detected above 3 eV, and the most intense of them generate spectral features at 4.84 and 5.88 eV.14

The recorded absorption spectrum of the C_{60} molecule is in very good agreement with theoretical calculations of its electron spectrum, although certain differences in numerical parameters are present.^{8,14} Optical absorption spectra of C_{60} crystals are similar to the C_{60} molecule absorption spectrum, overall, which is quite common in molecular crystals. Essentially all features of the C_{60} crystal absorption spectrum can be also seen in the molecule spectrum, but shifted to the low-energy side. This shift in molecular crystal spectra is called a crystalline shift, and its value, which is proportional to the transition intensity, can be up to hundreds of millielectronvolts. Meanwhile, intensities of absorption bands in spectra of C_{60} crystals and C_{60} molecules in both gas-phase and solid solutions are notably different.¹⁷ The major difference is a broad absorption band between 2.2 and 3.1 eV in the crystal spectrum. Its intensity is notably higher than those of weak edge features, but, it is weaker than the dipole-allowed absorption features on the high-energy side.

Attention has been focused on the origin of this band in several studies, and the most common view is that the band is due to direct transitions between the valence and conduction bands. The considerable width of the band is thought to be due to splitting of degenerate electron states of both valence and conduction bands of the crystal. Note that presently we have no convincing evidence that would allow us to attribute the band to a specific transition in the molecular spectrum. Since there are no transitions of such intensity in this range of the electron spectrum, the band is thought to be connected with forbidden molecular transitions that are allowed in the crystal due to a change in molecular positional symmetry.

We suggest, however, that this band is due to a weak dipole-allowed transition in the molecular spectrum whose intensity increases considerably in a crystal owing to its mixing with a stronger electron transition on the high-energy side. Similar mixing of the molecule electron states due to the crystal field was detected in exciton absorption spectra of anthracene and naphthalene molecular crystals, and described by Craig¹⁸ and McClure and Schnepp.¹⁹ Later research demonstrated²⁰ that the band intensity in this case is also changed considerably by hydrostatic pressure applied to a crystal, since it intensifies the interaction between molecules and the effect of the crystal field.

In view of this, we have investigated in detail the band intensities in electron absorption spectra of C_{60} crystals under hydrostatic pressure. We have recorded absorption spectra of C_{60} thin crystals in the 1.7–3.8 eV range at T=300 K and at pressures up to 2.5 GPa. Alongside the red shift of



FIG. 1. Absorption spectra of a C_{60} crystal with a thickness of less than 1 μ m and of C_{60} solution in toluene at T=77 K and standard pressure.

spectral features due to pressure, which was detected earlier, notable redistribution of their intensities has been observed. The intensity of the band corresponding to the lowest direct interband transition rises monotonically with the pressure, whereas the intensity of the interband transition of the higher energy decreases. Similar changes in the intensities of these features were detected in the absorption spectrum of the C_{60} molecules dissolved in toluene in comparison with that of the crystal-field induced mixing of molecular electron states suggested by Craig and McClure.

2. EXPERIMENT

Absorption spectra were measured using C_{60} thin crystals grown from either a toluene solution or a gaseous phase. The initial material purity was higher than 99%. We selected for measurements crystals shaped as thin plates with lateral dimensions of about $100 \times 100 \ \mu$ m and a thickness less than 1 μ m. The crystal thickness was derived from the optical density obtained by comparison to the optical density of C_{60} thin films.¹⁵

Absorption spectra were recorded on a computercontrolled spectrometer built around an MDR-23 grating monochromator. Measurements were taken in a broad spectral region in the visible and ultraviolet light using highquality achromatic quartz optics. The image of a crystal placed into a high-pressure cell was magnified by a factor of about 80, processed to an intermediate plane defined by two crossed $200 \times 200 \ \mu$ m optical slits, and projected to the monochromator input slit. The crystal optical density was derived from transmission spectra normalized to the transmission spectra of the diamond anvils, which were measured at all pressures. Thus the contribution from the edge absorption of the diamond anvils, which notably changed with the pressure, could be eliminated.

High-pressure experiments were performed using a highpressure diamond anvil cell of the Merril–Basset type.²¹ The working area of the anvils had a diameter of 600 μ m, and the aperture diameter of the stainless steel gasket was 250 μ m. The pressure-transmitting medium was a 1:4 mixture of ethanol and methanol. The pressure gauge was the position of the R_1 line in the ruby luminescence spectrum.²²

3. RESULTS AND DISCUSSION

The absorption spectrum at standard pressure and T=77 K of a C₆₀ crystal with a thickness less than 1 μ m is given in the lower half of Fig. 1. On the low-energy edge, one can see a weak absorption band ranging between 1.78 and 2.2 eV (*A*-band) with clearly defined fine structure. Next is a more intense absorption band running from 2.2 to 3.0 eV

(*B*-band), and on the high-energy side there is an intense *C*-band peaking at 3.4 eV. The two most intensive bands are in the region of a diamond anvil self-absorption, its lower bound being at $\sim 4 \text{ eV}$.

The upper half of Fig. 1 shows an absorption spectrum of C_{60} dissolved in toluene plotted on the same scale. The graph clearly shows that the two spectra are, by and large, similar, although there are notable differences between them. Above all, the molecular spectrum is shifted to the highenergy side with respect to the crystal spectrum. The shift is about 0.04 eV for the fine structure of the relatively weak *A*-band, and about 0.4 eV for the strong *C*-band. Moreover, the *C*-band is considerably broader in the crystal spectrum than in the molecule spectrum. The most striking difference between the two spectra is that the crystal spectrum contains the *B*-band, which peaks at 2.8 eV, whereas no such feature can be seen in the molecule spectrum.

In this spectral range, the molecule shows the weak and narrow feature marked by an asterisk in Fig. 1. The intensity distributions are also notably different: the C-band intensity in the crystal spectrum is much lower than in the molecule spectrum. Thus, the intensity is substantially redistributed among the absorption bands in the transition from isolated molecules to the crystal: that of the C-band drops considerably, and the B-band intensity increases. Note that this fact was discussed in earlier studies of C₆₀ optical absorption spectra. Several interpretations have been suggested, and the most popular of them is the hypothesis that electron transitions forbidden by molecular symmetry are partially allowed in the crystal, since the molecule is deformed by the local crystal field. Unsuccessful attempts were also made to simulate this effect in absorption spectra of C₆₀ solutions by taking solvents with a higher polarity.

Detailed measurements of optical absorption spectra of C_{60} thin crystals in the visible and UV at high pressure show that a redistribution of intensity among the electron transition bands also occurs when crystals are compressed hydrostatically. Figure 2 shows absorption spectra of a C₆₀ thin crystal at T = 300 K, at pressures ranging from one atmosphere in the lower graph to 2.5 GPa in the upper diagram. The C-band intensity gradually decreases with pressure, and the B-band intensity increases. The spectrum is simultaneously shifted toward lower energies, and the bands become appreciably wider. These changes are reversible, and when the pressure is lifted, all typcial features of the initial spectrum come back. Note that the red shift of the C_{60} absorption bands due to high pressure was previously investigated in several experiments.^{16,23,24} In those experiments, a notable increase in the *B*-band intensity in absorption spectra of C_{60} thin crystals was detected,¹⁶ as in independent measurements of C_{60} thin film spectra at high pressure.²³ Unfortunately, this effect was not given due attention in either of these works.

Figure 3 shows the ratio between the total intensities of the *C*- and *B*-bands, I_C/I_B , due to electron absorption in a C_{60} crystal as a function of pressure. In ascertaining this behavior, we isolated the bands, fitting a Gaussian to each. The *B*-band has a side band on its low-energy edge around 2.5 eV under standard pressure. To obtain a better fit, we approximated the *B*-band as a sum of two Gaussians, and its



FIG. 2. Absorption spectra of a C₆₀ crystal with a thickness of less than 1 μ m at T=300 K and pressures of up to 2.5 GPa.

total intensity was the sum of their intensities. Empty circles in Fig. 3 represent the ratio of the total intensities, I_C/I_B , measured under increasing pressure, and filled circles show measurements taken as the pressure was decreased. The intensity ratio I_C/I_B drops by a factor of more than two as the pressure grows to 2.5 GPa, but returns to its original value when the pressure is lifted.

The intensity of the *A*-band in the region of weak edge absorption is essentially independent of pressure. This is hard to see in the absorption spectra of the thin crystal shown in Fig. 2, since the *A*-band intensity is very low in this case. Absorption spectra of a crystal with a thickness of 2.8 μ m at



FIG. 3. Ratio of total intensities of the *C*- and *B*-bands, I_C/I_B , in the absorption spectrum of the C₆₀ crystal. Empty circles show measurements taken under increasing pressure, and filled circle corresponds to decreasing pressure.



FIG. 4. Absorption spectra of a C_{60} crystal with a thickness of 2.8 μ m in the region of the *A*-band at T=300 K and various pressures: 1) 1 bar, 2) 0.9 GPa, 3) 1.6 Gpa, and 4) 2.4 GPa. The insert shows positions of the edges of *A*-band (filled squares) and *B*-band (empty circles) vs pressure.

T = 300 K and pressures up to 2.4 GPa are plotted in Fig. 4. They clearly show the A-band and the low-energy edge of the B-band, whereas the peak of the B-band and the C-band are in the region of total absorption. At room temperature the fine structure of the A-band is essentially invisible, and only a sideband can be seen in this spectral region. The B-band intensity increases with pressure, and its high-energy edge shifts towards the A-band and suppresses it. The high-energy edge of the A-band shifts to the red much more slowly than the corresponding edge of the B-band. Positions of the edges of the A- and B-bands vs pressure are shown in the insert to Fig. 4. The empty symbols correspond to the the B-band edge, defined as the crossing point between the tangent to the spectral profile and the horizontal axis. Filled symbols corresponds to the A-band edge, which is defined similarly. At a pressure of 3 GPa, the A-band is not observable, and edge absorption is due entirely to the B-band. These results indicate different origins of the A - and B-bands in the absorption spectrum of C₆₀ crystals. A similar conclusion was derived earlier from analysis of electron-phonon bands in the absorption spectra of C₆₀ molecules.¹⁴

Thus, the distinctive feature of absorption spectra of C_{60} crystals is the broad and intense *B*-band, which has no analog in the molecular absorption spectrum. At the same time, the *C*-band intensity in the crystal spectrum is much lower than in the molecular spectrum. Under hydrostatic pressure,

the C-band intensity drops further, while the B-band intensity, simultaneously increases; these changes are reversed when the pressure is lifted. The behavior of C_{60} crystal absorption spectra can be interpreted in terms of the crystalfield-induced configurational mixing of electron states in molecular crystals. As shown by Craig and McClure, this effect shows up most clearly when electron states with close energies and substantially different oscillator strengths of the respective optical transitions are mixed.^{18,19} This is the case in the electron absorption spectrum of the C₆₀ molecule, where the lowest allowed electron transition between states with symmetry ${}^{1}A_{p} \rightarrow {}^{1}T_{\mu}$, whose energy is 3.04 eV and oscillator strength $f \approx 0.015$ (*-band), is much weaker than the higherenergy transition at 3.78 eV and oscillator strength $f \approx 0.37$.¹⁴ The information concerning classification of electron transitions in the C_{60} molecule given above is based on the analysis of electron-phonon spectra of frozen C₆₀ solutions in hexane and trimethylpentane at T = 77 K,¹⁴ and is in good agreement with the most detailed calculations of the molecule's electron spectrum.⁸

We now examine in more detail Craig's discussion of the effect.¹⁸ The wave function of the lowest excited electron state of the crystal is described in the first order of perturbation theory with respect to the crystal field by the expression

$$\Psi_{1}^{1} = \Phi_{1}^{0} + \{H^{12}/(H^{11} - H^{22})\}\Phi_{2}^{0} + \dots + \{H^{1r}/(H^{11} - H^{rr})\}\Phi_{r}^{0} + \dots,$$
(1)

where $\Phi_1^0...\Phi_r^0$ are unperturbed wave functions of the various electron states of the same symmetry, $H^{11}...H^{rr}$ are the energies of these states, and $H^{12}...H^{1r}$ are the energies of interaction due to the crystal field. Equation (1) holds if

$$H^{rr} - H^{11} \gg H^{1r}, \tag{2}$$

which is a prerequisite for perturbation theory to be applicable, and holds *a fortiori* for most electron transitions in molecular crystals. In this case the energy of the lowest excited state in first-order perturbation theory is

$$\Delta E = H^{11} + \sum_{r} {}^{\prime} (H^{1r})^2 / (H^{11} - H^{rr}).$$
(3)

The transition matrix element in first-order perturbation theory is

$$M_1^1 = M_1^0 + \sum_r {}^{\prime} \{ H^{1r} / (H^{11} - H^{rr}) \} M_r^0, \qquad (4)$$

where $M_1^0...M_r^0$ are the matrix elements of electron transitions between unperturbed states. It follows from Eq. (4) that the effect of the crystal-field-induced configurational mixing of electron states on the intensity and energy of electron transition is the stronger, the higher the interaction energy H^{1r} between electron states, the larger the difference between matrix elements M_1^0 and M_r^0 , and the smaller the difference between the energies of the electron transitions, $H^{11} - H^{rr}$. This effect determines the changes in the intensities of electron transitions within a molecule when a molecular crystal is formed, and subsequent changes when the crystal undergoes hydrostatic compression. In the latter case, the interaction energy H^{1r} increases and $H^{11}-H^{rr}$ drops owing to the difference between the rates of pressure-induced shifts of electron absorption bands.²⁰

Note that first-principles calculations of the electron spectrum of the C_{60} crystal indicate that similar changes should occur in electron absorption bands of the molecule.²⁵ The calculations also predict an intense and wide *B*-band, which has not been detected in the molecule absorption spectra. Its calculated intensity is much higher than the *B*-band intensity in experimental absorption spectra of C_{60} thin films, whereas the *C*-band is absent in the calculations. The intensities of two electron absorption bands above the *C*-band are considerably lower than in experimental absorption spectra. Calculations of the C_{60} crystal absorption spectrum at high pressure by the same authors indicate that the width and amplitude of the *B*-band should increase with pressure,²⁶ whereas the intensities of electron absorption bands of higher energies should continuously decrease.

Our aggregate results suggest that the lowest interband transition between the top of the valence band and bottom of the conduction band in the C_{60} crystal is related to the *B*-band. The weak edge absorption in the region of the *A*-band has a different nature and is related, as in the case of molecular absorption, to electron-phonon replicas of forbidden electron transitions. This means that the direct band gap in the C_{60} crystal is determined by the position of the longwave edge of the *B*-band, and is about 2.1 eV at atmospheric pressure. The pressure dependence of the band gap can be derived from the position of the *B*-band long-wave edge, and is shown in the insert to Fig. 4 (empty circles). The rate of the *B*-band pressure, and yields the deformation potential of the C_{60} crystal in accordance with the formula

$$D = dE_g / d\{\ln(V_0 / V)\} = -B_0 (dE_g / dP),$$
(5)

where $B_0 = 18.1 \pm 1.8$ GPa is the bulk modulus of the C₆₀ crystal derived from x-ray diffraction measurements at high pressure.^{27,28} The deformation potential of C₆₀ derived from these data is 2.7 ± 0.3 eV. It is about twice the value given in Ref. 28, where the direct gap width was erroneously deduced from the position of the *A*-band edge. Note that our measurement of the deformation potential is in better agreement with the numerical calculation,²⁶ which yields 3.1 eV.

Thus, our experimental data suggest crystal-fieldinduced mixing of electron states in the C_{60} crystal. Crystalfield-induced mixing is the primary reason for significant redistribution of intensity among electron absorption bands, due both to formation of a crystal from molecules and hydrostatic compression of the former. The presently available data lead us to claim that the *B*-band in the absorption spectrum of a C_{60} crystal corresponds to the lowest interband transition, and the position of its long-wave edge yields a direct band gap of 2.1 eV. The deformation potential derived from the pressure-induced shift of the *B*-band edge is 2.7 ± 0.3 eV.

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