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Charge transfer state of novel molecular complex $C_{26}H_{18}Te_2 \cdot C_{60} \cdot CS_2$ detected in single crystals by photoluminescence and ESR

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Abstract

Photoluminescence (PL), time resolved PL and optical absorption spectra near the band gap energy and in the range of IR active vibration modes of a novel molecular complex of fullerene, $C_{26}H_{18}Te_2 \cdot C_{60} \cdot CS_2$ (BTX $C_{60} \cdot CS_2$), have been investigated. The new absorption band in the range 1100 cm^{-1}, and a novel broad ESR signal have been found, indicating the optically excited charge transfer transition in the complex. The shift of the PL spectrum by 0.32 Ev towards lower energies (with respect to one in the C_{60} crystal), together with a long time decay of all PL lines, allows us to assume that the recombination is also accompanied by a charge transfer. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The crystals of fullerene C_{60} and some of the C_{60}-based salts and complexes can be regarded as a novel class of organic semiconductors and metals of great interest to basic research and possible applications. The interest in such crystals has especially increased after the discovery of superconductivity in C_{60}–alkali metals salts [1], and ferromagnetism in TDAE $\cdot$ C_{60} [2] (TDAE, tetrakis (dimethylaminoethylene)). It is well known [3] that the critical temperature, T_c, of a superconducting transition increases with the fcc lattice constant. An interpretation may be provided by BCS theory, which relates to the level density at the Fermi edge with T_c. However, the C_{60} fcc lattice collapses into another structure when the lattice expansion exceeds a certain limit and as a result the superconductivity also usually vanishes [4]. Therefore, synthesis of molecule complexes without considerable charge transfer, also has an interest from the point of view of changing the crystal structure in such a way that overlap between C_{60} molecules decreases, and as a result the density of states in energy zones increases. These complexes can be used for subsequent doping with alkali metals. On the other hand, the fullerites, C_{60}, can be considered as semiconductors. In view of this, the problem of appropriate doping of this material is quite important for its possible application in electronics. Chemical donors and acceptors can be very useful for this purpose because some of them have a

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good conformation ability to the structure of C_{60} crystals.

The synthesis of the new molecular complex BTX $\cdot C_{60} \cdot CS_2$ has been reported previously [5]. Recently it has been found that this complex exhibited unusual luminescence properties [6], namely its PL spectrum was shifted to low energy. The crystal structure of the complex has been reported in [6]. Here we just mention that the characteristic feature of the structure is the existence of slightly shortened contacts of BTX $\leftrightarrow C_{60}$ type between Te and C, equal to 3.60, 3.85 and 3.84 Å, as compared to the sum of their Van der Waals radii 4 Å. In contrast, the distances between C_{60} centers are somewhat larger than the distance of 10.02 Å between the centers of nearest neighbor molecules in C_{60} crystals. This means that there is some overlapping of electron wave functions of C_{60} with BTX. Recently the split of the $F_{1u}(4)$ band in the complex has been observed at room temperature [7]. This split testifies that the symmetry of C_{60} is lowered by the strong interaction between the donor and the fullerene. Taking into account that the electronic structure of a C_{60} crystal is dominated by that of a C_{60} molecule and slightly disturbed by weak intermolecular electron transfer via π electron overlap, we can assume that due to the crystal structure change, the electron transfer between C_{60} molecules also changes. This change might be the reason for the modification of the optical properties.

Here we report the experimental results of further investigation of this complex, including IR and near IR optical absorption, time resolved PL and ESR investigations.

2. Experimental

The PL of the BTX $\cdot C_{60} \cdot CS_2$ and C_{60} crystals was measured in the temperature range from 4.2 to 280 K using a monochromator MDR-2 and a cooled germanium detector. The overall spectral sensitivity of the experimental system was calibrated by recording the spectrum of a low-voltage tungsten lamp and dividing it by the known spectral density of the lamp emission. Therefore, the experimentally measured PL spectra reported here correspond to the number of photons (in relative units) of the given energy (i.e., dN_{ph}/dE) emitted per unit time, depending on their energy E (in eV). The photoluminescence was excited by a 514.5 nm argon laser or by the 632.8 nm He–Ne laser radiation. The laser beam was focused to a spot of about 1 mm^2 on the sample. The laser beam power was 12 mW in the case of the Ar-laser and 2 mW in the case of He–Ne laser.

In the time-resolved PL measurements, the samples were excited by 40 ps pulses from a 655 nm laser diode. The emitted light was passed through a spectrometer and detected by a Hamamatsu C4334 streakscope. In the case of low-efficiency PL, the time decay of PL was evaluated using a frequency dependent amplitude obtained from a lock-in-technique described in detail elsewhere [8].

Single crystals in the form of thin plane-parallel plates with the natural habit were selected for the absorption measurements in the range of the absorption edge. The thickness of the samples ranged from 0.02 to 0.1 mm, and the other two dimensions were usually of the order of 1 mm. The samples for IR investigation were prepared by blending a microcrystalline powder of the complex with KBr powder and consequently manufacturing pellets by pressing.

The ESR measurements were performed using a Bruker X-band spectrometer equipped with a gas flow He cryostat with a quartz window for illumination of the sample.

3. Results and discussion

Fig. 1 displays the PL spectrum of the BTX $\cdot C_{60} \cdot CS_2$ single crystal at 10 K. At energies higher than

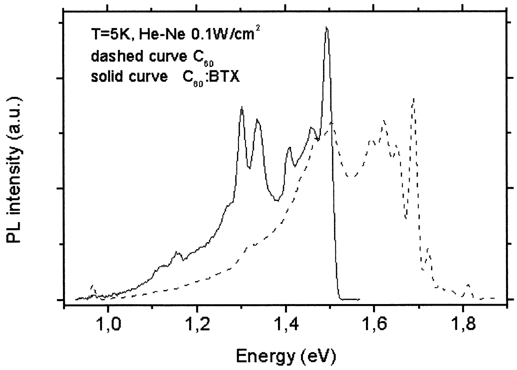

Fig. 1. PL spectra of BTX $\cdot C_{60} \cdot CS_2$ (solid line) and C_{60} (dashed line).

1.1 eV, the spectrum can be described reasonably well by a sum of 12 Gaussian lines. The energy positions of the best resolved lines calculated from the best fit, together with their relative intensities, are listed in Table 1. For comparison the PL spectrum of a pure C_{60} crystal is shown by the dashed curve. For convenience, both spectra are normalised to their integral intensity $N_{\mathrm{total}} = \int(\mathrm{d}N_{\mathrm{ph}}/\mathrm{d}E)\,\mathrm{d}E$. We have specifically checked that the BTX molecules themselves, as well as the CS_2, do not contribute to the luminescence in this energy range. We have also measured the PL in $\mathrm{BTX} \cdot C_{60}$ crystals which do not contain CS_2 molecules and obtained the same PL spectra as for $\mathrm{BTX} \cdot C_{60} \cdot CS_2$. So, the difference between the PL spectra of the complex and pure C_{60} crystal is not related to the presence of CS_2 molecules. It should be noted that there is no trace of the 0.96 eV PL line in $\mathrm{BTX} \cdot C_{60} \cdot CS_2$, while it always exists in the C_{60} spectra. This line is attributed to recombination at the singlet oxygen [9], and its absence indicates that either there is no intersystem crossing between singlet and triplet excited states of C_{60} molecules and oxygen, or the concentration of oxygen is much lower than in C_{60} crystals. Recently [10], we analysed the absorption and luminescence spectra of the C_{60} thin single crystal platelets and came to the conclusion that the first weak, high-energy PL line, with energy 1.812 eV, is caused by the no-phonon (0-0) electronic transition corresponding to the singlet Frenkel exciton. The intensity of this line in perfect C_{60} crystals is usually rather low due to the fact that this transition is symmetry forbidden. The first high-energy PL line in the complex is therefore shifted by 0.32 eV to low energies with respect to the 0-0 singlet exciton transition in the C_{60} crystal (or by about 0.16 eV with respect to the first intensive vibronic-assistant PL line in the C_{60} crystal – see Fig. 1). There are two possible explanations for the observed PL spectrum. One is that a disturbance of the energy spectrum of C_{60} by the BTX molecule is strong enough to reduce the LUMO-HOMO gap. Therefore, by analogy with C_{60} crystals, we can conclude that the PL in the $\mathrm{BTX} \cdot C_{60} \cdot CS_2$ is mainly stipulated by the recombination of Frenkel singlet excitons associated with the C_{60} molecules, but the exciton energy is decreased by about 0.16 eV (or by 0.32 eV if it corresponds to 0-0 transition) due to the interaction between the C_{60} and BTX molecules. To check this supposition we have measured the absorption near the absorption edge of the complex. Fig. 2 shows the absorption of the $\mathrm{BTX} \cdot C_{60} \cdot CS_2$ single crystal in the range 1.4 to 2 eV. For comparison, the absorption of pure C_{60} is also represented by a dashed curve. A sharp increase of absorption in the C_{60} crystal at an energy of 1.81 eV, was attributed to generation of the Frenkel exciton [10]. This transition is symmetry forbidden for the isolated C_{60} molecule, but became efficient in the solid material due to a crystal field distortion of the C_{60} molecule. One can clearly see that characteristic features of the $\mathrm{BTX} \cdot C_{60} \cdot CS_2$ absorption spectrum are quite different from those of pristine C_{60}. There is no sharp increase at the threshold, 1.81 eV, and the absorption of the $\mathrm{BTX} \cdot C_{60} \cdot CS_2$ complex grows gradually from the energy 1.85 eV. Therefore, the rapid increase of absorption in the complex starts at the energy higher than for pure C_{60}. So we can conclude that the shift of the PL spectrum does not relate to the narrowing of the forbidden gap. Another possible reason for the shift is the appearance of the new electronic state in a forbidden gap due to the interaction of the C_{60} molecule with the donor. This state might be the

Table 1
The energy positions E_{i} of PL lines in the crystals of C_{60} and C_{60}/BTX and their relative intensities

E_{i} (eV0 C_{60}	Normalized intensity	E_{i} (eV) C_{60}/BTX	Normalized intensity
1.812*	0.09	1.495	1
1.767	0.04	1.466	0.61
1.746*	0.05	1.433	0.39
1.721*	0.25	1.406	0.44
1.688	1	1.363	0.30
1.654*	0.70	1.337	0.57
1.624*	0.72	1.301	0.68
1.595	0.60	1.269	0.25
1.556	0.48	1.235	0.15
1.505	0.70	1.194	0.13
1.468	0.50	1.153	0.14
1.433	0.39	1.117	0.11
1.386	0.26		
1.327	0.18		
1.269	0.12		
0.964	0.17	0.964	0

C_{60} lines, marked with an asterisk, have the same temperature behaviour, which implies their common origin

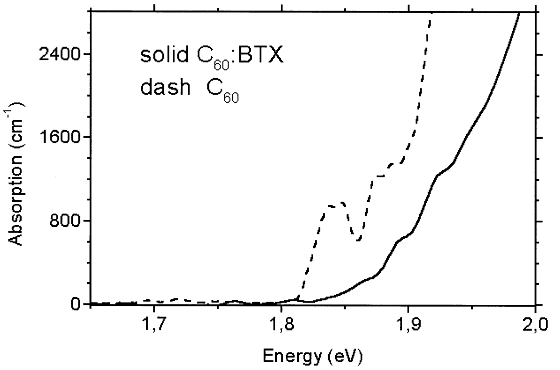

Fig. 2. The near edge absorption spectra of $BTX \cdot C_{60} \cdot CS_2$ (solid line) and C_{60} (dashed line). Spectra were recorded at 10 K.

origin of the low-energy absorption. In contrast to the PL spectrum of pristine C_{60}, the first high-energy line of the $BTX \cdot C_{60} \cdot CS_2$ spectrum is the most intense. D.J. van den Heuvel et al. [11] have shown that a reduction of the symmetry of the C_{60} molecule by either an intra- or an intermolecular perturbation leads to PL spectrum with a strong 0-0 transition and a different vibronic structure. Therefore the strong intensity of the first line in the PL spectrum of the complex supports the model of recombination at a distorted site. Besides its unusual energy position, the photoluminescence of the $BTX \cdot C_{60} \cdot CS_2$ complex has quite a different decay time. Fig. 3a illustrates the time decay of the integral PL for C_{60} and C_{60}/BTX. It is readily seen that the PL decay in C_{60}/BTX is much slower than that in pure C_{60}. Unfortunately, the low sensitivity of a streakscope does not allow us to measure the value of τ. For this purpose we used a lock-in technique. Fig. 3b shows the frequency dependence of an integral PL intensity for C_{60}/BTX. If we accept that the output signal of a lock-in amplifier is

$$\partial f/\partial t = G(1-f) - f/\tau,$$

where f is the fill factor of the radiating centres or molecules ($f = n_{\text{fill}}/n_{\text{tot}}$), an analysis of the frequency dependence will allow the decay time τ to be evaluated. The solid curve is a theoretical fit of experimental points with $\tau = 1.58$ ms. It is well known that the life time of the C_{60} singlet state is about 10^{-9} due to a very high probability of intersystem crossing between singlet and triplet excited states [12]. Therefore a time decay of the order of 1 ms can be attributed to a recombination, either through a triplet state, or due to a charge transfer excitation.

Fig. 4 shows the X-band ESR spectrum at 4.2 K. The microwave power was chosen to be in the range of linear dependence of the ESR signal on the power and was of the order of 1 mW. The total number of spines amounts to $10^{-4} \div 10^{-3}$ per molecular unit. The narrow line most probably relates to defects arising as a result of interaction of oxygen and C_{60} [13,14]. The inset shows the temperature dependence of the integral intensity. The number of spines associated with the narrow line amounts to only 10^{-3} of the whole number of spines. Therefore, the temperature dependence of the integral intensity relates

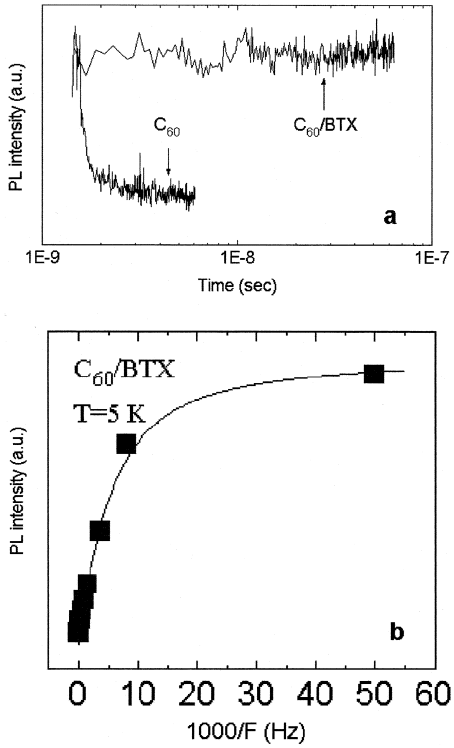

Fig. 3. The PL time decay after short pulse (40 ps) 655 nm laser diode for pristine C_{60} and $BTX \cdot C_{60} \cdot CS_2$ (a) and the frequency dependence of $BTX \cdot C_{60} \cdot CS_2$ PL intensity (b). Points, experimental values; and the solid curve is a theoretical fit of experimental points with $\tau = 1.58$ ms.

mainly to the broad part of the signal. Two models can be suggested to explain the broad part of the signal. One is that the two lines originate from the electron on the C_{60} molecule and the hole on the BTX molecule. Following this model, the whole spectra can be decomposed into three Gaussian lines with g-factors and widths $g_1 = 2.0021$, $W_1 = 4$ G; $g_2 = 2.062$, $W_2 = 80$ G; and $g_3 = 2.124$, $W_3 = 157$ G, respectively. On the other hand, describing the broad part of the signal as originating from one, but strongly anisotropic, g-factor cannot be avoided either. Indeed, since we used a powder sample, the anisotropy could produce a single, but asymmetric, non-Gaussian line. Note, that the close value of the g-factor has been observed in the complex $(Ph_4P)_2C_{70}I$ [15].

Fig. 5 shows the IR absorption spectra for pure C_{60} single crystal and BTX · C_{60} complex. The spectrum of BTX · C_{60} · CS_2 shows numerous, well separated bands attributable to four IR active vibrations of C_{60} molecules and normal vibrations of the BTX and the CS_2. Besides, there is the additional broad absorption band in the range of 1100 cm^{-1} that does not exist in pure C_{60} or in BTX. This band can be attributed to the electronic charge transfer (CT) absorption [16], although such bands are usually expected in a higher energy range [17]. The set of data presented here does not allow us to assert the model of CT between BTX and C_{60} molecules. Nevertheless, the absence of the light induced ESR signal implies that the 1100 cm^{-1} absorption band is probably related to a CT transition. Then the ESR signal can be explained as resulting from the charge transfer excitation of electrons from BTX to C_{60} by IR thermal radiation from the room temperature walls of a microwave cavity of the EPR spectrometer. We can also suggest that the low energy shift of the PL spectrum, together with a long time decay of all PL lines, can be considered as an indication for the participation of the charge transfer between BTX and C_{60} in the recombination process producing the observed PL.

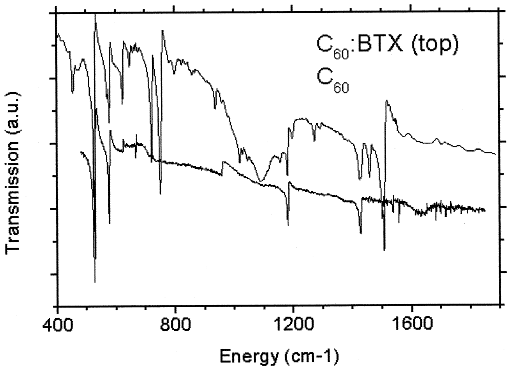

Fig. 5. Transmission spectra of KBr pellets with BTX · C_{60} · CS_2 (top curve) and C_{60} (bottom curve).

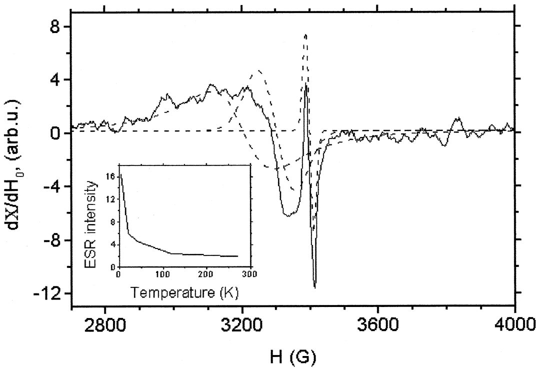

Fig. 4. The ESR signal at 4.3 K, microwave power 1 mW, and modulation amplitude 4.7 G. Solid line, experimental data; dashed lines, result of the fit. Inset shows the temperature dependence of the integral signal intensity.

4. Conclusions

In conclusion, we have measured optical and magnetic properties of the novel complex BTX · C_{60} · CS_2, in relation to the lowest excited states. ESR and absorption results imply the existence of electronic donor level at energy of 100 ÷ 150 meV below the conduction band. A small charge transfer of about 10^{-3} was discovered by the ESR technique under conditions of weak illumination of the sample by the room temperature radiation. The shift of luminescence bands to low energy probably originates from the interaction of excited the C_{60} molecule with the BTX molecule. The long decay time of all luminescence bands implies the participation of charge transfer in the recombination process.

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