

Photoinduced changes in the fundamental absorption of C₆₀ films

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An increase in the absorption in C₆₀ films near the optical transitions with 1.6 and 2.3 eV, which are forbidden in the C₆₀ molecule, has been observed upon photoinjection of electron–hole pairs. A long-wave shift of the allowed transition with 3.5 eV has been observed under the same conditions.

The photoinduced changes are explained in a model of hybridized electron states with the help of results found on the temperature dependence of the fundamental absorption of this fullerite. © 1994 American Institute of Physics.

Study of the evolution of the energy spectrum of insulating C₆₀ upon the injection of current charge carriers provides information of importance for clarifying the mechanism for the metal–insulator transition in this fullerite and for clarifying the properties of the carriers in the superconducting phase. The method of optical excitation makes it possible to create small changes in the carrier density in a crystal, in a uniform way over the volume of the crystal. We have used this method to study the restructuring of the absorption spectrum of insulating C₆₀ in the region of valence-band–conduction-band transitions.

We studied fullerite films $\approx 0.1 \mu\text{m}$ thick deposited on a sapphire substrate by vacuum sublimation of a C₆₀ powder. The quality of the films was monitored with the help of an optical microscope and through measurements of the IR transmission spectra on a Fourier-transform spectrometer. At a substrate temperature of 100–200°C we obtained films with a mirror finish (the size of the crystallites was $\leq 1 \mu\text{m}$). The IR spectrum of the films was essentially free of lines of the organic solvent, which was present in a high concentration in the original powder. The narrow absorption lines corresponded to known intramolecular phonons of C₆₀.

Spectra of the photoinduced absorption, $-\Delta I/I = (I - I_1)/I$, were measured over the spectral interval 1.4–3.8 eV with the help of a prism spectrograph and an optical multi-channel analyzer. Here $I_1(\nu)$ and $I(\nu)$ are the intensity of the light transmitted through the film respectively with and without photoinjection of carriers. The photoinjection was carried out with the help of a cw argon laser ($h\nu = 2.54 \text{ eV}$) or a pulsed XeCl excimer laser ($h\nu = 4.03 \text{ eV}$). In the latter case the pulse length was 20 ns, and the repetition frequency 20 Hz (the power density P had an average value of 60 mW/cm^2 and a peak value $\approx 150 \text{ kW/cm}^2$). In both cases we measured a time-integrated signal. To eliminate the effects of instrumental drift, we built up the difference signal ΔI during repeated cycling of the measurements of the $I_1(\nu)$ and $I(\nu)$ spectra. The cycle included a measurement which made it possible to eliminate the contribution from luminescence of

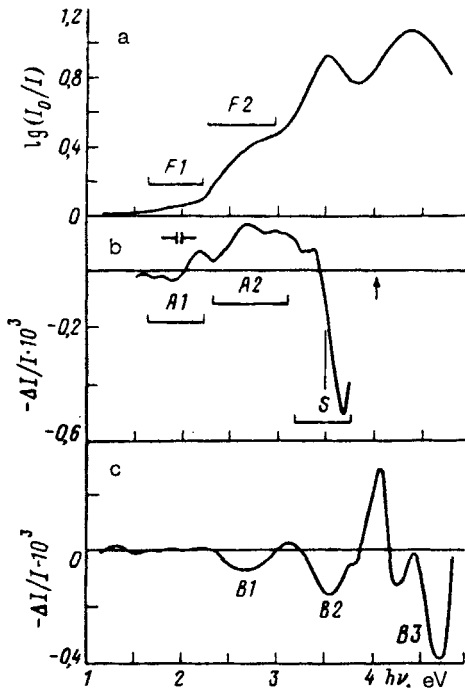


FIG. 1. Spectra of the optical density (a), the photoinduced absorption (b), and the thermal effect (c) for a C_{60} film on a sapphire substrate. Nonequilibrium carriers were excited by a pulsed XeCl laser with $h\nu = 4.03$ eV (marked by the arrow). $T = 300$ K. The thermal effect shown here corresponds to a 4° heating of the film.

C_{60} . The sample was attached to the vacuum cavity of a helium cryostat. The temperature T was varied from 300 to 20 K. We measured a thermal effect, namely the change in the optical transmission of the film as its temperature was varied by 4° , in order to identify spectral features stemming from a possible heating of the sample.

Figure 1 shows (a) a spectrum of the optical density of the fullerite film (b), a spectrum of the photoinduced absorption during excitation of nonequilibrium carriers by the pulsed laser with $h\nu = 4.03$ eV, and (c) the thermal effect, all measured at 300 K. Spectrum a is similar to spectra which have been recorded previously in several studies. It consists of transitions with 3.5 and 4.4 eV, which are allowed in the C_{60} molecule in the dipole approximation, and $F1$ and $F2$ transitions, which are forbidden in the molecule, with red boundaries of about 1.6 and 2.3 eV (Ref. 1). In the spectral interval of primary interest here, 1.2–3.8 eV, the greatest changes during the heating of the film are determined by bleaching lines $B1$ and $B2$. Comparison of spectra a and c reveals that at 300 K the thermal effect is dominated by a decrease in absorption associated with the $F2$ and 3.5-eV transitions. The photoinduced absorption is quite different from the thermal effect: Instead of the bleaching line $B1$, we see an absorption between 2.0 and 3.4 eV in the spectrum of the photoinduced absorption. There are also differences in the spectral positions of bleaching lines $B2$ and S . We can therefore ignore heating of the film by the laser excitation in this case.

The photoexcitation causes essentially no change in the transmission of a thin film between 1.4 and 1.6 eV. Corresponding to the $F1$ transition in the spectrum of the photoinduced absorption is feature $A1$. This feature consists of a slight bleaching in the

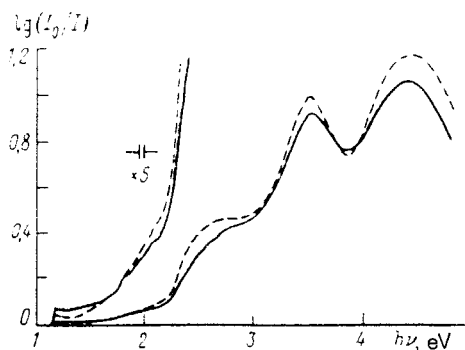


FIG. 2. Temperature dependence of the spectra of the optical absorption of a fullerite film 0.1 μm thick on a sapphire substrate. (Dashed curve) $T=20$ K; (solid curve) $T=300$ K.

region 1.6–2.0 eV which converts into an absorption line at 2.2 eV. The intense photo-induced absorption A_2 is evidence of an increase in the oscillator strength of the F_2 transition. Photoexcitation by a cw laser with $h\nu=2.54$ eV leads to the same response at $1.4 < h\nu < 2.53$ eV. Near the 3.5-eV transition, we find an S-shaped feature in the spectrum of the photoinduced absorption. The inflection point of this feature coincides with the maximum of the 3.5-eV absorption line in spectrum a. The 3.5-eV line thus undergoes a long-wave shift upon photoexcitation of the film.

It turns out that the features which are seen during photoexcitation are qualitatively similar to changes observed in the ordinary optical-density spectra of a C_{60} film as the temperature is lowered (Fig. 2). As T is lowered from 300 to 20 K, the 3.5-eV transition shifts about 30 meV in the low-energy direction. Here we can clearly see an increase in the oscillator strength of the F_2 transition. Finally, it can be seen on spectra plotted in a larger scale that near the F_1 transition the spectra of the optical density measured at 300 and 20 K intersect at $h\nu \approx 1.8$ eV. As T is lowered, the low-energy part of the F_1 transition is bleached, and there is an increase in the absorption in its high-energy part. These results are in agreement with the form of the photoinduced feature A_1 .

A vibron model^{2,3} is currently being used to explain the onset of the F_1 and F_2 transitions in crystalline C_{60} ; these transitions are forbidden in the molecule. However, the increase in the absorption associated with the F_2 transition as the temperature is lowered contradicts a phonon mechanism. Among other possible models, a likely one is a hybridization of symmetric wave functions of states, which determine the low-energy region of fundamental absorption of the fullerite with an antisymmetric function which is responsible for the dipole-allowed transition at 3.5 eV. The degree of hybridization would increase with increasing intermolecular interaction during optical excitation of electron-hole pairs. An increase in the intermolecular interaction would also result from a decrease in the distance between molecules as the temperature is lowered. On the basis of this model it is possible to explain the increase in the oscillator strength of the F_2 transition and the low-energy shift of the allowed transition at 3.5 eV, during either photoinjection of electron-hole pairs or a lowering of the temperature. This strengthening of the intermolecular interaction may be due to a photopolymerization of C_{60} , which leads to long-lived changes in the properties of this fullerite.⁴ Further study will be required to clarify the temporal parameters of the photoinduced absorption which has been observed.

In summary, this study of the fundamental absorption of a fullerite has revealed that the photoexcitation of electron-hole pairs leads to an increase in the absorption in the region of optical transitions which are forbidden in the C_{60} molecule, and that it also leads to a long-wave shift of the allowed transition at 3.5 eV. It has been established that corresponding changes occur in the fundamental absorption spectrum of the fullerite as the temperature is lowered. It has been suggested that these features can be explained on the basis of a hybridization of wave functions of electron states of the fullerite.

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