

Photoinduced transformation of luminescence centers in C_{60} crystals at high pressure

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The influence of laser irradiation on the photoluminescence spectra of perfect C_{60} crystals in the orientationally disordered phase is investigated. It is shown that irradiation of the crystals with low-power light for short durations at $T=200$ K produces radical changes in the luminescence spectrum. The pressure dependences of the spectral bands of the phototransformed and initial (without irradiation) spectra differ significantly, indicating a photoinduced structural transformation of the X centers responsible for the luminescence of C_{60} . The phototransformed C_{60} crystals are stable against further exposure to light irradiation and pressure. © 1999 American Institute of Physics.
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The low-temperature photoluminescence spectra of high-quality C_{60} crystals are known to have a line structure attributable to the radiative recombination of Frenkel excitons localized at so-called X centers.^{1,2} A C band associated with the radiative recombination of free Frenkel excitons is also observed in crystals having a relatively low density of X centers and a low luminescence quantum efficiency.³ The properties of X centers and their relationship to the structure of the luminescence spectrum of C_{60} crystals are of considerable interest and have been investigated in a number of papers. However, despite significant progress in research on the electronic states of C_{60} , the real nature of X centers remains elusive for the most part. Studies of the luminescence spectra of the purest C_{60} crystals have shown that the X centers are not associated with impurities, rather they are more likely attributable to defects of the crystal structure. Regardless of the degree of structural perfection of the investigated samples, the presence of orientational defects is a characteristic attribute of fullerite. The occurrence of an orientational ordering phase transition in C_{60} crystals at $T=260$ K and the cessation of random molecular rotation below this temperature are well known.⁴ However, the molecules execute discrete rotations between two energywise close orientational states down to 80 K, below which each molecular motion is frozen, and a phase of the orientational glass type is established.⁵

It is also known that the dimerization of molecules is observed in the orientationally disordered phase of laser-irradiated C_{60} , and polymerization of the as-grown material

takes place when the laser power is increased.⁶ Detailed studies of the optical spectra and crystal structure of C_{60} have shown that polymerization also takes place under the combined influence of pressure and high temperatures, resulting in the formation of numerous, structurally different phases.^{7,8} All these transformations are accompanied by a radical change in the initial photoluminescence spectrum.

Modification of the luminescence spectra in laser irradiation has also been observed in the orientationally ordered phase of C_{60} crystals at standard pressure and at temperatures of 5 K, 77 K and 120 K. This phenomenon was achieved by pre-irradiating local zones of the crystal with a laser beam at power densities ranging from 5 W/cm² to 50 W/cm² and then recording the photoluminescence spectra from the irradiated and control zones of the crystal at $T \sim 5$ K and an excitation power density ~ 1 W/cm². It was established that irradiation of the crystals at temperatures in the vicinity of 5 K and 77 K induces a relative variation of the intensities of the emission bands of X_2 and X_3 centers, and irradiation at 120 K is accompanied by diminution of the X_2 - and X_3 -center bands and enhancement of the intensity of the C band.⁹ Similar results on the influence of laser irradiation on the photoluminescence spectra in the low-temperature range are also reported in Ref. 10.

Consequently, the existing experimental data indicate that light has a powerful influence on the spectrum of localized electronic states of C_{60} crystals. Photoinduced processes in the orientationally ordered phase of fullerite, in particular, the low-temperature, photoinduced structural transformation of X centers, are of major interest in this regard. With the latter phenomenon in mind, in the present study we report an investigation of the combined influence of high pressure and laser irradiation on C_{60} crystals and show that a radical transformation of the photoluminescence spectra takes place in the temperature range 140–250 K. We confirm that the pressure dependence of the phototransformed and initial photoluminescence spectra differ significantly, and the phototransformed samples are stable against subsequent light irradiation and pressure. We have shown that the photoinduced structural transformation of X centers also takes place at high pressure, and when the latter is suddenly dropped to standard pressure, the photoluminescence spectra of the samples transformed at different pressures are identical.

The measurements were carried out on a large series of C_{60} crystals grown from the vapor phase. The photoluminescence spectra were recorded by means of an automated spectrometer incorporating a DFS-12 dual monochromator, a liquid nitrogen-cooled FEU-62 photomultiplier, and a 5S1 photon counting system. All the photoluminescence spectra were normalized to the calibrated spectrum of a tungsten lamp. Luminescence was excited by a helium-neon laser with its power output limited by optical filters. High-pressure measurements in liquid nitrogen or helium vapor were performed using a miniature diamond anvil cell of the Merrill–Bassett type enclosed in a helium optical thermostat. Pressure was transmitted by means of a 4:1 methanol-ethanol mixture,¹¹ and its value was determined from the position of the ruby luminescence R_1 line within ~ 0.05 -GPa error limits.¹² The measurements were performed on crystals having a mirror finish and dimensions of $100 \times 100 \times 40$ μm , which are close to the dimensions of the working volume of the high-pressure cell.

The photoinduced structural transformation was investigated over a wide range of temperatures on crystals with a relatively high photoluminescence quantum efficiency, whose spectra were dominated by the emission bands of X_3 , X_4 , and X_5 centers. They

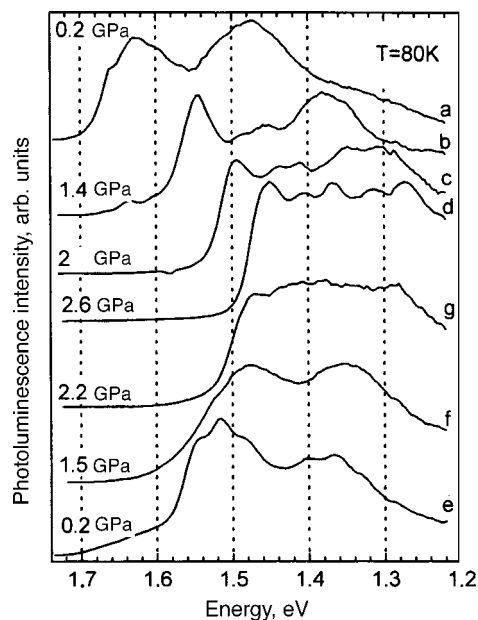


FIG. 1. Photoluminescence spectra of nonirradiated (a–d) and laser-irradiated (e–g) C_{60} crystals at a temperature $T=80$ K and pressures up to 3.0 GPa.

show that the variations of the photoluminescence spectra takes place in the temperature interval 180–240 K and are appreciable even at a very low excitation level $\cong 5 \times 10^{-3} \text{ W/cm}^2$. The temperature dependence of the phototransformation efficiency at standard pressure is bell-shaped with a maximum in the vicinity of $T \cong 200$ K. Consequently, at $T=200$ K laser irradiation of the crystal for $\cong 15$ min at a power density $\approx 0.2 \text{ W/cm}^2$ leads to radical (more than 95%) restructuring of the initial spectrum. It is important to note that direct measurements of the photoluminescence spectra were performed at $T=80$ K, i.e., at a temperature where phototransformation is frozen.

Figure 1 shows the initial (a) and phototransformed (e) photoluminescence spectra determined at a pressure ~ 0.2 GPa under the above-stated irradiation conditions. The measurements show that spectrum (e) is stable in the presence of further irradiation of the crystal over the entire temperature range up to $T=260$ K. Temperature cycling of the samples in the interval 5–300 K without irradiation by any kind of light does not produce appreciable changes in the high-temperature photoluminescence spectra. On the other hand, the irradiation of these crystals at $T=300$ K for the sample laser excitation parameters alters the low-temperature photoluminescence spectrum in connection with flare-up and pronounced broadening of the bands of the initial spectrum. Similar effects have been observed in all the C_{60} crystals at our disposal, but irradiation does not have such a pronounced influence on their photoluminescence spectra.

Figure 1 also shows the photoluminescence spectra of the as-grown and phototransformed crystals at various pressures. Spectra (a)–(d) refer to the nonirradiated crystal, and spectra (e)–(g) to a crystal preirradiated at a temperature $T=200$ K and pressure of 0.2 GPa. It is evident from Fig. 1(a–d) that, apart from an overall shift of the photolu-

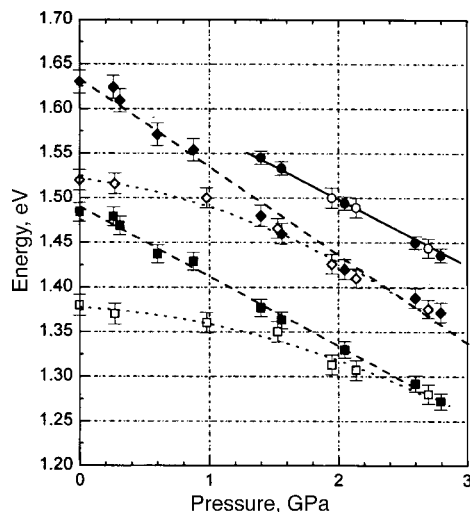


FIG. 2. Pressure dependence of the band positions in the low-temperature photoluminescence spectrum of nonirradiated (dark symbols) and irradiated (light symbols) C_{60} crystals. The dark and light dots represent the pressure dependence of the position of the C band.

minescence spectrum into the long-wavelength region, its shape also changes as the pressure is increased. At $P \geq 1.2$ GPa a band that is scarcely perceptible in the initial photoluminescence spectrum flares up in the short-wavelength region. On the other hand, fine structure becomes increasingly evident in the broad bands of the initial photoluminescence spectrum as the pressure is increased. Such changes have also been observed in the spectra of the preirradiated crystal, but are not nearly as pronounced.

Figure 2 shows the pressure dependence of the positions of the spectral bands in the photoluminescence spectra of the as-grown (dark symbols) and phototransformed (light symbols) crystals. It is evident from Fig. 2 that the pressure variations of the bands of preirradiated and nonirradiated crystals differ significantly in the low-pressure range, but then they become more alike as the pressure is increased, and at $P \geq 1.8$ GPa they essentially coincide. The difference in the pressure dependence of the photoluminescence bands of the as-grown and irradiated crystals in the initial pressure range indicates that what happens during irradiation is not merely a redistribution of the photoluminescence intensity among different luminescence centers of the as-grown crystal, but a transformation of the core structure of the crystal. At the same time, the increasing similarity of the photoluminescence spectra of the as-grown and phototransformed samples with increasing pressure suggests that the latter could be unstable under the influence of high pressure and revert to the as-grown state. It is also essential to note that pressure-enhanced band in the spectrum of the nonirradiated crystals is in the same position and exhibits the same pressure dependence as the C band, which we have previously identified with the emission of free excitons.³

We have carried out an experiment to answer the question of whether the phototransformed samples are stable and whether phototransformation takes place at high pressure; the results are shown in Fig. 3. Curves (a) and (b) in Fig. 3 represent the photoluminescence spectra of the nonirradiated crystal at a temperature $T = 80$ K and

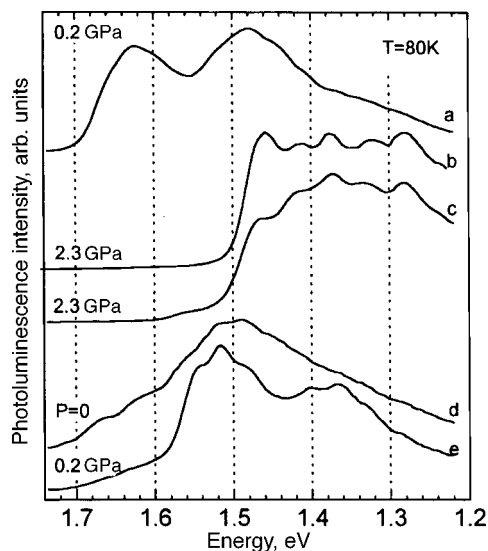


FIG. 3. Luminescence spectra of C_{60} crystals phototransformed at various pressures.

pressures of 0.2 GPa and 2.3 GPa, respectively. The crystal was then irradiated with light at the above-indicated power and duration at a pressure of 2.3 GPa and temperature $T = 200$ K. The photoluminescence spectrum of this crystal at $T = 80$ K is shown in Fig. 3(c). On the whole, its shape is quite close to that of the spectrum of the nonirradiated crystal (b) other than a certain broadening of the bands and diminution of the intensity of the short-wavelength C band. After the pressure is dropped back to the standard level the photoluminescence spectrum of this same crystal at $T = 80$ K acquires the form (d). It is evident from the figure that it is not similar to the initial spectrum (a), but is more like the characteristic spectrum (e) for the crystal preirradiated at standard pressure. The observable difference between spectra (d) and (e) is probably attributable to the presence of residual stresses in the crystal and cracking of the crystal after the pressure is dropped to the standard level, so that the spectral bands broaden, and the contribution of the initial spectrum increases somewhat. The results of the investigations show that spectrum (d) is stable against further irradiation of the crystal up to $T = 300$ K.

Consequently, the results indicate that when C_{60} crystals are irradiated by a laser beam in the temperature interval 180–240 K and at pressures up to 2.3 GPa, the photoluminescence spectra undergo a radical transformation as a result of restructuring of the radiative recombination X centers. At standard pressure this process attains its maximum efficiency at $T \cong 200$ K and falls off sharply near the point of transition to the orientationally disordered phase. The drop in efficiency of transformation of the centers at $T \geq 260$ K, when the molecules execute random rotation, is most likely indicative of the definite role played by the orientation of the C_{60} molecules during photoinduced transformation of the X centers.

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