

## Self-Trapped Polaron Exciton in Neutral Fullerene C<sub>60</sub>

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The luminescence of C<sub>60</sub> was investigated as a function of temperature between 300 and 10 K and for various oxygen concentrations. Its intensity was found to increase strongly with decreasing temperature down to about  $T_1 = 100$  K and to decrease again for a further reduction of  $T$ . Below 100 K, new structures appeared in the spectra. The experiments are described by a self-localized polaron exciton and by a diffusing free exciton above and below  $T_1$ , respectively. The important difference between the two regions is the free rotation of the C<sub>60</sub> above and the definite orientation below  $T_1$ .

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The dramatic increase of interest from material scientists in the fullerenes originates from the very unusual properties of these materials. Very high stability, many possibilities for chemical modifications, high optical non-linearity, metallic conductivity, and even superconductivity at rather high temperatures are just a few of them. Looking at all these properties and considering the quasiaromatic structure of the molecules render the fullerenes as the missing link between the various low-dimensional systems such as high-temperature superconductors, charge-transfer crystals, and conducting polymers.

From a detailed study of the luminescence of the undoped C<sub>60</sub> and C<sub>70</sub> compounds of this system we can add another relation between this material and the low-dimensional systems mentioned above. The luminescence of C<sub>60</sub> has been reported already in the early days of studying the fullerenes [1], but no satisfying interpretation of the phenomenon could be given. From a detailed study of the temperature dependence and from the influence of impurity effects on the luminescence we suggest that the luminescence originates from a self-localized exciton which is created at ambient temperature on the quasi-two-dimensional surface of the spinning C<sub>60</sub> molecules. Because of the conjugated character of the bonds this exciton can be expected to be very similar to the polaron exciton in conjugated polymers. As the temperature is lowered the spinning speed slows down or the spinning proceeds discontinuously until at the final lock-in temperature three-dimensional order is obtained. As a consequence the probability for creating a self-localized polaron exciton is reduced and the luminescence is quenched.

Thin films of standard mixtures of C<sub>60</sub>/C<sub>70</sub>, purified C<sub>60</sub>, and purified C<sub>70</sub> were grown by sublimation on a silicon wafer to a thickness of about 0.4  $\mu\text{m}$ . The C<sub>60</sub>/C<sub>70</sub> mixture was commercial and has a C<sub>70</sub> concentration of about 15%. The purification effect during the sublimation process gave a final concentration of 4% C<sub>70</sub> in the films as determined from Raman line intensities. The

luminescence spectrum was excited with various laser lines at temperatures between 320 and 10 K. In order to remove the oxygen contamination a few samples were stored in argon immediately after preparation and were further purified from remaining oxygen by laser irradiation in high vacuum before the luminescence was investigated.

The general appearance of the luminescence spectra in all samples was similar. At room temperature a broad spectrum with a peak at 1.705 eV and a shoulder extending to low energies was observed in agreement with previous results [1]. An example for the emission of a standard C<sub>60</sub>/C<sub>70</sub> composed film is shown as curve A in Fig. 1.

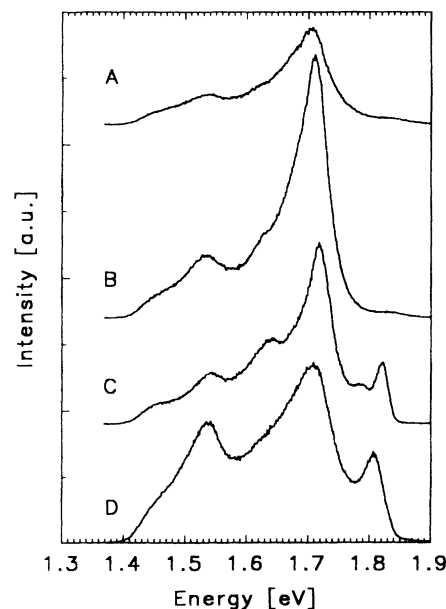


FIG. 1. Luminescence spectra of fullerenes as excited with a green laser: spectrum of a commercial C<sub>60</sub>/C<sub>70</sub> composite excited at 220 K (curve A), same material but excited at 150 K (curve B), same material but excited at 10 K (curve C), and pure C<sub>70</sub> fullerene excited at 10 K (curve D).

Whether the structure on the low-energy side of the peak emission is of vibronic or electronic origin will be discussed below. The dependence of the luminescence intensity on incident laser power was linear over 3 orders of magnitude at least at room temperature and not significantly dependent on the laser quantum energy. On the other hand, the temperature dependence of the luminescence emission is unusual. It increases strongly with decreasing temperature, goes through a maximum at about 100 K, and decreases strongly for a further reduction of  $T$ . Again, two examples for  $T=150$  K and  $T=10$  K are shown as curves *B* and *C* in the figure. The structure on the low-energy side of the main peak sharpens with decreasing temperature and it is indeed tempting to assign it to vibronic sidebands. However, the energy difference between the peaks is not coincident with the strongest phonon peak in the Raman spectrum at  $1467\text{ cm}^{-1}$  which originates from a "modified" bond alternation oscillation [2,3]. The vibronic energy as determined from the peak positions of the sidebands in the luminescence would be only  $700\text{ cm}^{-1}$ . This is not very far from the breathing mode in  $C_{60}$  at  $490\text{ cm}^{-1}$  or from a similar mode in  $C_{70}$  and could thus be the excited-state frequency of this mode.

Even more interesting than the structure on the low-energy side of the spectrum is the structure appearing on the high-energy side of the main luminescence. Simultaneously with the decrease of the main luminescence intensity two new peaks at 1.785 and 1.82 eV start to increase rapidly with decreasing temperature. Also, at temperatures below the inversion of the temperature dependence for the intensity of the main peak the energetic positions of these peaks are shifted to the blue by about 15 meV. Details concerning the correlation of the change of the temperature dependence for the main luminescence peak and the two new lines can be obtained from Fig. 2 where the integrated intensities for the main peak including the low-energy sidebands and the integrated intensity for the peaks at 1.785 and 1.82 eV are plotted versus temperature. From similar experiments with purified  $C_{60}$  it is easy to show that the luminescence at 1.82 eV originates from the  $C_{70}$  contamination since this peak is completely absent in the pure samples. On the other hand, the peak at 1.785 eV behaves in the  $C_{70}$ -free samples identically as in the standard material. The surprising feature in the spectrum *C* of Fig. 1 is that the peak from  $C_{70}$  is now very large, about 40% of the main peak even though the concentration of  $C_{70}$  is only 4%. The low-temperature spectrum of pure  $C_{70}$  is shown as curve *D* in the figure. The origin of the second luminescence peak appearing at low temperatures in the  $C_{60}/C_{70}$  samples at 1.785 eV can also be identified. Confirming previous results of Duclos *et al.* [2] we have recently observed that the strong Raman peak at  $1467\text{ cm}^{-1}$  is not intrinsic to the pristine material. However, it shows a resonance excitation at energies coincident with the well-

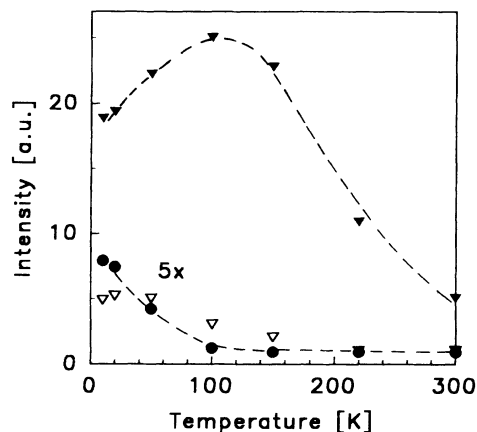


FIG. 2. Integrated intensity for the luminescence of a commercial  $C_{60}/C_{70}$  mixture vs temperature of excitation: ( $\blacktriangledown$ ) main peak including low-energy sidebands, ( $\bullet$ ) luminescence at 1.82 eV from  $C_{70}$  (multiplied by a factor of 5), and ( $\nabla$ ) luminescence at 1.785 eV from  $C_{60}^{2+}$  (multiplied by a factor of 5).

known transitions for the pristine  $C_{60}$  [4]. Thus, the species from which the  $1467\text{-cm}^{-1}$  line originates can be expected to be strongly related to the  $C_{60}$  and may be assigned as a "quasi-pinch-mode." As a matter of fact the quasi-pinch-mode is absent for highly oxygen-free samples or can be bleached by mild laser irradiation in high vacuum as described in Refs. [2,3]. In contrast to the results of Duclos *et al.* the bleaching of the quasi-pinch-mode revealed in our case two new lines at  $1462$  and  $1458\text{ cm}^{-1}$ , respectively, as shown in Fig. 3. From an extrapolation of the linear relation between charge on the molecule and frequency of the pinch mode [5] an ionization

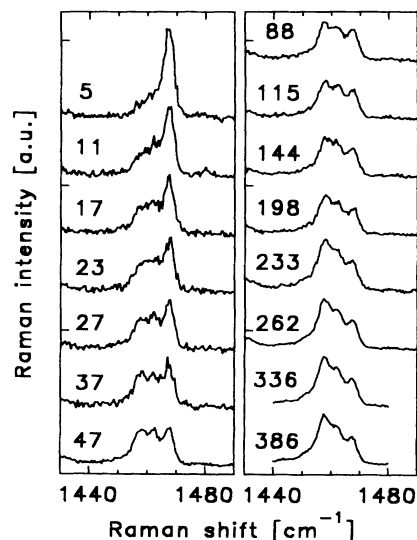


FIG. 3. Bleaching of the oxygen-induced Raman line by laser irradiation. The numbers indicate irradiation time in minutes.

state of  $1+$  and  $2+$  for the line at  $1462$  and  $1467\text{ cm}^{-1}$ , respectively, was concluded [3]. The extra positive charge is expected to originate from an oxidation of  $C_{60}$  by incorporated oxygen atoms. Interestingly, samples where the oxygen had been blown off by the method described above did not show the extra luminescence at  $1.785\text{ eV}$  at low temperature. This is clearly demonstrated in Fig. 4. Thus, the peak at  $1.785\text{ eV}$  originates from the  $C_{60}$  interacting with oxygen. Also, it is important to realize that the luminescence in the oxygen-free samples is not quenched any more at very low temperatures but rather saturates. Its temperature dependence at intermediate and ambient temperatures is, however, very similar to the one for the oxygenated samples.

The experiments demonstrate clearly that the quenching of the luminescence in the  $C_{60}/C_{70}$  samples is directly related to the appearance of the two new lines at  $1.785$  and  $1.82\text{ eV}$ . On the other hand, these two lines are demonstrated to originate from interactions of oxygen with  $C_{60}$  and from the  $C_{70}$  contamination. Any model which tries to explain the above described detailed behavior of the light emission must account for the following experimental results: (a) The emission energy is just below the forbidden gap energy [6] (or below an exciton energy if the forbidden gap is assumed at  $2.6\text{ eV}$  [7]). (b) The emission increases with decreasing temperature but it is quenched for temperatures below around  $100\text{ K}$ . (c) Simultaneous with the quenching of the main line emission new lines appear which are identified with the  $C_{70}$  contamination and with oxygen defects. (d) At least for  $C_{70}$  this emission is much stronger than expected from the low concentration of this impurity. (e) If the above characterized impurities are absent, no quenching of the luminescence is observed.

We want to demonstrate that a self-localized exciton is an appealing structure to describe the above behavior in a satisfying way. Self-trapped excitons with very strong lo-

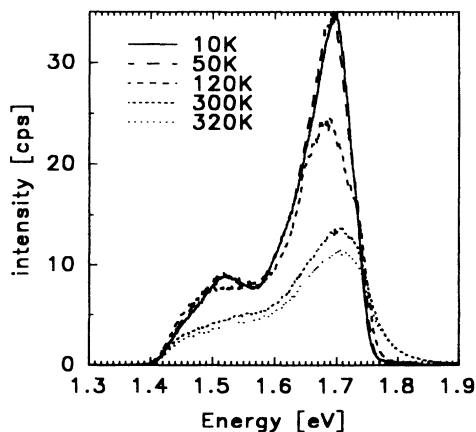


FIG. 4. Luminescence of purified  $C_{60}$  after the oxygen-induced Raman line has been bleached. The temperatures for the excitation are as indicated.

calization are well known in rare gas and alkali halide crystals [8] but have recently also been reported for conducting polymers in a luminescence diode configuration [9,10] and are expected to be less strongly localized. The dynamical behavior of a self-trapped exciton is expected to be linear with excitation intensity as observed in the experiment since the number of excitons created is proportional to the illumination intensity and each self-trapped exciton contributes to the emission. The self-trapped exciton in our particular case results from an electronic band-to-band excitation where the excited electron and the remaining hole create a local deformation of the lattice and thus localize themselves into a state below the conduction band and above the valence band. Because of the aromatic character of the carbon-carbon bonds in the fullerenes the self-localized excitons will be rather similar to those in the polymers and, accordingly, may be called polaron excitons. The generation of self-trapped states of the polaron type is favored in systems with reduced dimensionality. We can understand the luminescence in  $C_{60}$  if we consider the following scenario. The incident light excites the  $C_{60}$  somewhere above the forbidden  $h_u-t_{1u}$  (or exciton) transition at  $1.9\text{ eV}$ . The excited electrons and holes relax immediately to the bottom of the conduction band and to the top of the valence band, respectively. Both particles stay there because they cannot recombine across the forbidden gap. This means excitation energy is not relevant as observed in the experiment. Since the spinning  $C_{60}$  molecules are single molecules rather than a three-dimensional form the excited carriers will immediately trap themselves into a deformation where they are caught. In the self-trapped state selection rules are broken and radiative recombination is possible. At high temperatures the  $C_{60}$  molecules rotate rapidly, so that the overlap between  $\pi$  orbitals from neighboring molecules does not last long enough to transfer mechanical distortion. Thus, the system is really low dimensional and the excitation stays on the  $C_{60}$  molecule where it was excited. The total trapping energy for the polaron exciton is obtained from the experiment as  $170\text{ meV}$ . As the temperature is lowered the radiative recombination efficiency is increased and the luminescence increases as is quite common for radiating systems [11,12]. With decreasing temperature the angular frequency of the  $C_{60}$  molecule slows down or obtains a discontinuous character until at some low temperature  $T_1$  the orientation of the molecule is completely locked. The temperature at which the locking occurs depends on the experiment. An x-ray experiment sees it at  $250\text{ K}$  [13], whereas for NMR the spin resonance shows motional narrowing from the rotation still below  $100\text{ K}$  [14]. In neutron scattering experiments two transitions at  $250$  and at  $100\text{ K}$  are observed [15]. Thus we can expect that the change of the temperature dependence of the luminescence is correlated with the final locking of the rotating  $C_{60}$  molecules. As the rotation is quenched the system

becomes three dimensional and self-trapping becomes more and more unlikely. The excited particles stay much longer at the edges of the bands or in a nontrapped exciton state with a strongly reduced cross section for radiative recombination. They are, however, highly mobile in this state and diffuse through the crystal until they happen to meet a defect in the form of a  $C_{70}$  or an oxygen-charged  $C_{60}^{2+}$ . Since these defects are decoupled from the translational crystal they may act as luminescence centers and luminescence occurs as observed in the experiment. The upshift of the luminescence from  $C_{60}^{2+}$  as compared to the luminescence from the neutral fullerene is in agreement with the fact that the distance between the  $t_{1u}$  band and the highest occupied molecular orbital has increased due to the ionization. The scenario outlined above also explains why the luminescence from the small amount of  $C_{70}$  in the  $C_{60}/C_{70}$  material is of the same order of magnitude as the luminescence from the bulk material. Under fortunate conditions all the excitation energy is transferred to the  $C_{70}$  or to the  $C_{60}^{2+}$ . If no  $C_{70}$  and no  $C_{60}^{2+}$  is available the excitation continues to diffuse until it finally either creates a polaron exciton or decays nonradiatively. Thus, macroscopically no quenching but rather a saturation of the luminescence is observed as shown in Fig. 4. The quality of the coincidence between the temperature for the beginning of the decrease of the main luminescence and the temperature for the appearance of the  $C_{70}$  luminescence may be sample dependent. If the concentration of  $C_{70}$  is very low it may need more excited electron-hole pairs until some of them reach a  $C_{70}$  molecule. Then the luminescence from the  $C_{70}$  appears delayed on a temperature scale.

The explanation for the experimental results shown above is self-consistent if a self-localized polaron exciton is considered as the particular species from where the luminescence originates. Other explanations using more conventional forms of particular defects with a strong localization may also be used to explain the observed scenario but would require very complicated defect-defect

interactions. Thus, we feel the experiments shown give good evidence for a self-localized polaron exciton in the neutral  $C_{60}$ .

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