Dynamics of photoexcited carrier relaxation in C_{60} films

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The relaxation of photoexcited carriers in solid C_{60} films has been investigated through the measurement of their time-resolved transmissivity. A nonexponential temporal relaxation approaches an exponential decay as the ambient temperature of the sample is cooled from room temperature to 5 K. In addition, an Arrhenius-type dependence of the carrier relaxation time on the ambient temperature has been observed. This result implies that carrier trapping may play an important role in the relaxation mechanism. The dependence of the decay time on the carrier density also supports this assumption. A comparison with a simple model of the nonexponential ("stretched") decay suggests that temperature-dependent structural changes of the films also influence carrier relaxation.

The successful synthesis of pure C_{60} has spurred an intense search for the various properties of this fascinating new material.[1,2] For example, it has been reported that C_{60}, when doped with one of the alkali metals (A_xC_{60}), becomes superconducting with T_c as high as 33 K.[3] Recent experiments on an isotope effect in superconducting Rb_3C_{60} indicate the existence of strong electron-phonon interactions.[4] In this paper we report on an investigation of the time-resolved relaxation of photoexcited carriers in C_{60} films maintained in a wide range of ambient temperature (5–300 K) and in a range of excitation pulse fluence ($\sim 10-90\ \mu J/cm^2$).

Near room temperature the molecular crystal of C_{60} adopts a fcc lattice plus an orientational disorder of the molecules relative to each other.[5] Band-structure calculations suggest that pure solid C_{60} is a semiconductor with a direct gap of about 1.4 eV at the X point.[6,7] Theoretical analyses of the energy levels of the C_{60} molecule preclude, however, a direct transition from the top of the valence band to the bottom of the conduction band of the solid.[6,7] This is supported by results from optical-absorption experiments, which indicate that the observed optical gap is centered around 2 eV at room temperature.[8–10]

We have performed time-resolved transmissivity measurements on pure C_{60} films in which carriers are excited with 400-fs optical pulses at 2-eV photon energy. The ~200-nm-thick films are thermally evaporated onto sapphire substrates using C_{60} powder prepared and purified according the method described by Kratschmer.[1] Further purification of the C_{60} is achieved through vacuum distillation during the film-making procedure. The mass spectra of the films indicate a single peak at 720 amu, which is consistent with pure C_{60}. Other species of carbon fullerenes, such as C_{70}, are present in quantities less than 0.5% of the material weight, and lighter hydrocarbons are not present in detectable amounts. A lower optical damage threshold of the C_{60} films is observed in the presence of air which may be related to oxidation effects.[11] Therefore, the samples were held under vacuum during storage and during the experiments in order to prevent diffusion of other species into the films.[12] Absorption spectra of the samples are also measured from 0.3 to 1.0 μm, and found to be consistent with published data.[8–10] The linear dimension of the crystalline domains in C_{60} films, prepared in a similar process, was found to be around 6 nm.[13] This is about four times larger than the fcc lattice constant of C_{60}. In this case the existence of an optical gap in the amorphous films comparable to that in crystalline phase is expected.[14] We conclude that the most likely excitations under our experimental conditions are interband transitions near the band edge.

Standard pump-and-probe experiments were carried out with a synchronously pumped dye laser operating at a 76-MHz repetition rate.[15] The two beams were both nearly at normal incidence and perpendicular polarizations with respect to each other, and focused to a measured beam diameter of 20 ± 2 μm. The intensity of the probe beam was kept always less than 5% of that of the pump beam. In order to maintain a sufficient signal-to-noise ratio, even at low-intensity measurements, a dual modulation lock-in amplification technique is used to recover the differential transmissivity signal defined as $\Delta T/T$. The temperature of the samples were changed between 300 and 5 K using an optical Dewar previously described.[16]

The change of the differential transmission of the sample, $\Delta T/T$, as a function of the time delay between the pump-and-probe pulses, obtained at room temperature, is displayed in the main curve of Fig. 1. Similar results are obtained at several ambient temperatures from 5 to 300 K, when a small laser fluence (23 $\mu J/cm^2$) is applied in order to limit heating effects as much as possible. Additionally, the dependence of the decay of the differential transmissivity on the fluence of the excitation laser pulse is recorded at 300- and at 5-K ambient temperatures. Again, results similar to those of Fig. 1 are obtained. As can be seen in the figure, a negative change in the differential transmission of the sample is induced by the optical excitation. This phenomenon is characteristic of amorphous semiconductors. It is explained by the lack of the momentum conservation requirement for free-carrier absorption in amorphous structures.[17] Induced absorp-

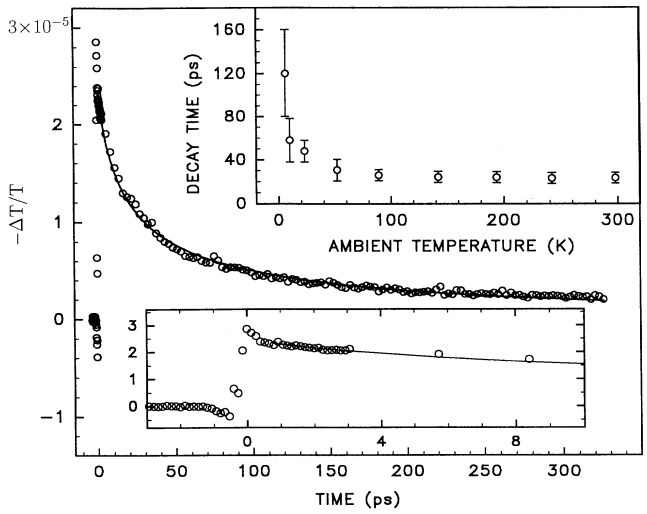

FIG. 1. The time dependence of the differential transmissivity signal, $\Delta T/T$. The experimental data are represented by open circles, the solid line is the fit of Eq. (1) with $a=2.4\times10^{-5}$, $\tau=18.6$ ps, and $\beta=0.41$. The beginning of the signal and the fit are shown in the lower inset. The upper inset displays the dependence of the differential transmissivity decay time τ on the ambient sample temperature.

tion in C_{60} has been previously reported in several papers.[18,19]

In order to characterize the temporal dependence of the transient transmissivity signal we have fit several different decay functions to the experimental data.[20] In agreement with other recent results,[18] the best fit at all temperatures and laser fluences is provided by the stretched exponential function, which is also known as the Kohlrausch relaxation law:[21]

$$\Delta T/T = a\exp(-t/\tau)^{\beta}, \quad (1)$$

where a is the amplitude of the differential transmissivity signal at $t=0$ time, τ refers to an ensemble average of decay times, and $0<\beta<1$. The Kohlrausch law has been proposed to describe a wide range of dispersive relaxation phenomena in disordered materials.[22] Since this type of temporal dependence does not provide specific information on the characteristics of the carrier relaxation, other methods are required. We chose to investigate the effect of ambient temperature on $\Delta T/T$. The temperature dependence of the decay time, τ, of the transient transmissivity, obtained by fitting of Eq. (1) to the experimental $\Delta T/T$, is shown in the upper right inset of Fig. 1. The inset in Fig. 3 displays the temperature dependence of the β parameter. The data points are average values of several experiments at the same ambient temperature; the error bars represent the standard deviations. We also observe the following: At room temperature the root-mean-square deviation of the stretched exponential fit is $\chi^2=0.04$ while the error of an exponential fit is approximately twice as much. As the ambient temperature is decreased the difference between the two fits narrows. The two types of fits become nearly equivalent at 5 K. This is equivalent to the observation that the β parameter of the stretched exponential is approaching 1 as the ambient temperature of the sample decreases (see the inset in Fig. 3).

Recently, in a similar study,[18] a Kohlrausch-type temporal dependence and a temperature-independent τ were reported above $\sim$170 K. As can be seen in the upper right inset in Fig. 1, our observations do not contradict the earlier finding. However, we observe in addition a temperature dependence of τ and β in the range below $\sim$170 K, and a temporal characteristic which approaches an exponential decay with decreasing ambient temperature. We focus further attention on these observations.

As discussed earlier, the appearance of a negative $\Delta T/T$ signal is attributed to the induced absorption of excited carriers in amorphous materials. Consequently, the decay in $\Delta T/T$ must be due to a decrease of the excited carrier population. In the absence of information to the contrary, we assume a linear correspondence between the differential reflectivity signal and the number of the photoexcited carriers.

We now discuss a possibly relevant decay mechanism of photoexcited carriers. First, we note that the temperature dependence of the carrier relaxation time on the ambient temperature is of the Arrhenius-type in the observed temperature interval, as is indeed observed in the main curve of Fig. 2. It is well established[17,23] that an Arrhenius temperature dependence is characteristic of carrier relaxation through trapping. In amorphous semiconductors, carrier trapping has been theoretically described by a multiple trapping model,[24–26] and it has been experimentally observed with exponential[27] and nonexponential[28] temporal characteristics. We also note that high-resolution subgap absorption spectra of solid C_{60} films at room temperature is strikingly similar to that of amorphous Si:H films,[10] in which carrier trapping is observed.[28] The nearly identical subgap absorption edges imply a similar trap distribution in both materials at

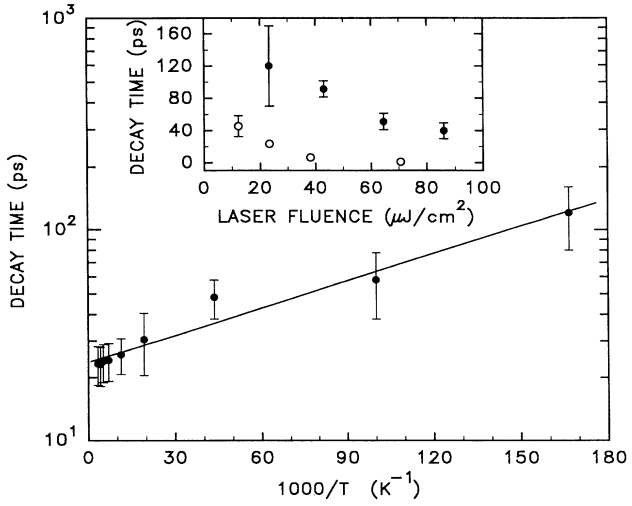

FIG. 2. The dependence of the differential transmissivity decay time τ on the ambient temperature shown in an Arrhenius-type plot. Inset: The dependence of the differential transmissivity decay time τ on the excitation laser fluence at 300-K (open circles) and at 5-K (filled circles) ambient temperatures.

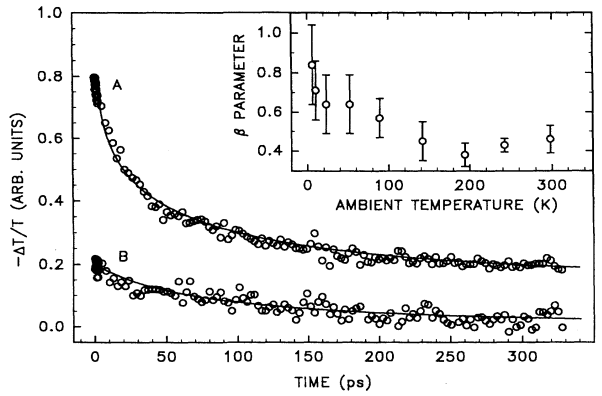

FIG. 3. *A* is the temporal dependence of the differential reflectivity signal, $\Delta T/T$, at 300 K (open circles) and the calculated $\Delta T/T$ by numerically evaluating Eq. (2) with an $F(E_{\rm tr})$ range between 0 and 150 meV. *B* is the temporal dependence of the differential reflectivity signal, $\Delta T/T$, at 5 K (open circles) and the calculated $\Delta T/T$ by numerically evaluating Eq. (2) with an $F(E_{\rm tr})$ range between 8 and 13 meV. Inset: The dependence of the β parameter on the ambient temperature of the sample.

room temperature. Based on this similarity and on the observed Arrhenius-type temperature dependence of τ, we propose that carrier trapping plays an important role in the relaxation dynamics of photoexcited carriers in C_{60} films.

According to a simplified version of the multiple trapping model,[26] excited electrons can relax through recombination or can be captured by traps. Once the electron is trapped, its mobility is drastically reduced and it is hindered from recombination. The trapped electron has two possible means for further energy relaxation. Namely, it can move towards states with deeper energy and less mobility, or it can be released from shallow traps via excitation or interaction with free carriers. Reexcited electrons can relax through recombination or can be trapped again. Deep traps are filled first in part to their limited number and in part to the low probability of carrier release.[25,26] Therefore, it is assumed that most of the observed carrier dynamics are determined by shallow traps.[25] These decay mechanisms can be considered by the following correlative point of view. The effective relaxation of photoexcited carriers can be accelerated by decreasing their immobilization time, either through thermal excitation, or through increasing the probability of free-carrier–trapped-carrier interactions. Therefore, a decrease in the relaxation time of the photoexcited electrons is expected with increasing carrier concentration, and/or by increasing the ambient temperature. Both of these effects are observed in the inset of Fig. 2. Assuming one photon absorption, the laser fluence in the two extreme cases corresponds to carrier densities from $\sim 8\times 10^{17}/\text{cm}^3$ to $\sim 6\times 10^{18}/\text{cm}^3$, respectively.

The multiple trapping model predicts a linear increase of the β parameter with increasing ambient temperature,[26,28] which is clearly not observed below $\sim$200 K (see the inset in Fig. 3). Since the theory assumes a temperature-independent trap distribution, the source of this discrepancy may lie in the recently observed temperature-dependent orientational disorder present in C_{60}.[29,30] X-ray-diffraction experiments and conductivity measurement have shown that C_{60} films possess a complete orientational disorder at room temperature. As the temperature is decreased the films undergo a phase transition at 249 K, as orientational order starts to develop. The order continuously increases as the film is cooled to liquid-helium temperatures. In the corresponding temperature interval, in the present experiment the nonexponential decay approaches a single exponential as mentioned above. The upper limit of this temperature interval corresponds to the minimum in β at $\sim$200 K in our experiment and to the phase-transition temperature at 249 K in the x-ray-diffraction experiments. The difference between these two temperatures can be, at least in part, related to thermal barriers which may be formed between the cold finger of the low-temperature Dewar and the optically excited C_{60} films. The uncertainty in the β parameter also contributes to the uncertainty in the temperature at which the minimum occurs in the inset in Fig. 3.

It is interesting to compare the experimental results with a simple but plausible model of the Kohlrausch relaxation.[31,32] In this model, the stretched exponential function is described as in integration over exponentials whose decay times are determined by the depths of the existing traps. Additionally, a simplified distribution of traps is assumed, whose density is equal to a constant value over a range of trap depths and to zero elsewhere. Specifically,

$$\Delta T/T(t,T_a) = \int F(E_{\rm tr})\exp[-t/\nu_0^{-1}\exp(E_{\rm tr}/kT_a)]dE_{\rm tr}\ . \quad (2)$$

In Eq. (2) T_a is the ambient temperature of the sample, $E_{\rm tr}$ is the depth of the traps measured from the bottom of the conduction band, $F(E_{\rm tr})$ is the trap distribution function, ν_0 [$\sim 10^{12}$ (Ref. 25)] is the "attempt-to-escape rate," and t is the time. Equation (2) is numerically evaluated with the magnitude of $F(E_{\rm tr})$ set to normalize Eq. (2) to the experimental results, while the range of $F(E_{\rm tr})$ is adjusted to obtain best fit to the temporal characteristics of the experimental $\Delta T/T$. In comparison to the data at room temperature the range of $F(E_{\rm tr})$ is found to be from 0 to 150 meV, whereas that at 5 K yields a range of 8–13 meV. The calculated curves and the experimental results are displayed in *A* and *B* of Fig. 3 at 300 and 5 K, respectively. Although this experiment yields no independent proof of any interpretation of the results, there does exist at least a plausible interpretation. We propose that the broader range of $F(E_{\rm tr})$ at room temperature reflects a spread of the trap band associated with the orientational disorder, whereas the much narrower distribution of $F(E_{\rm tr})$ at 5 K reflects a marked decrease of the disorder and approaches more closely the distinct band structure expected in the absence of the disorder.

The present experiment does not provide explicit information on the nature of the traps, however it allows some room for speculations. Since the presence of the traps is related to the temperature-dependent orientational disorder, and there are no molecular impurities present in the

samples in detectable concentrations[33] as is shown by the mass spectra, we assume that the traps are intrinsic to the C_{60} films. The relation of the traps to photoinduced dimers in the films[34,35] cannot be entirely excluded, but it is unlikely for a number of reasons. The photon energy used in the present experiment (2 eV) is considerably lower than the photon energy used in the experiments where photoinduced polymerization was observed (2.54 eV and above). Moreover, the development of the photoinduced dimers was observed after a longer ($\sim$30 min) light exposure.[34,35] If the existence of the traps is related to such a polymerization, the number of the traps would increase with increasing illumination time and, hence, a change in the carrier relaxation dynamics should be observed with increasing exposure time. No such effect was observed during the present experiments.

In summary, the relaxation of carriers excited by 2-eV laser pulses in C_{60} films was investigated through differential transmissivity measurements. The carrier relaxation possesses a nonexponential temporal characteristic at room temperature and approaches a single exponential decay as the sample is cooled to liquid-helium temperature. The temperature dependence of the decay time between 300 and 5 K indicates that trapping plays an important role in the carrier relaxation. This result is also supported by the dependence of the relaxation dynamics on the excited carrier density. The temporal characteristic of the relaxation, at 300- and 5-K ambient temperatures, is compared to a simple and well-established model of the stretched-exponential decay. The difference between high- and low-temperature behavior of the photoexcited carrier relaxation is in agreement with earlier observations of decreasing degree of disorder in C_{60} films as the ambient temperature decreases.

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