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## Decay Kinetics of Long-Lived Photogenerated Kinks in an *MX* Chain Compound

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The time evolution of the thermal bleaching of the long-lived, photogenerated midgap absorption band in a PtCl chain compound is examined in a temperature range 220–330 K. The long-lived absorption arises from kinks each confined in a segment of the PtCl chain by energy barriers of the order of 0.5 eV. Because of a random distribution of the barrier height the pair coalescence decay shows a  $\ln t$  dependence at all temperatures in the experimental range, 0–60 min, of time  $t$  after discontinuation of laser pumping. [S0031-9007(97)04131-8]

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Measurements of time-resolved optical response provide a wealth of information on the relaxation processes of self-localized excited states in low-dimensional systems. An ultrafast pump-and-probe measurement of absorption in *cis*- and *trans*-polyacetylene, for instance, has revealed that the decay of the photogenerated polaronic and solitonic kinks is dominated by their collision in the course of random walks [1]. A similar experiment on an *MX* chain compound has shown that the kinks created by a short light pulse have a lifetime of the order of 1–10 ps [2]. According to a photoluminescence measurement on a different *MX* chain compound [3], the lifetime of the charge-transfer (CT) excitons, which is of the order of 100 ps, has a unique temperature dependence that is suggestive of the presence of a relaxation channel of a CT exciton into a soliton pair.

The *MX* chain compounds consist of chainwise *M-X* bonds showing a charge-density-wave (CDW) state of *M* (Pt or Pd) ions. If the CDW state is ordered in one dimension only, the twofold degeneracy of the valence alternation allows the chains to support solitonic kinks as well as polaronic ones [4,5]. The PtCl chain compounds,  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$  and  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$ , belong to this category, where (en) signifies the ethylenediamine molecule. The photoluminescence study reported in Ref. [3] is concerned with the former compound. The two substances are very similar in the basic properties of the Pt-Cl chain bonds. In fact, in both substances the optical reflection spectrum at the fundamental Peierls gap, i.e., the CT transition between  $d_z$  orbitals of  $\text{Pt}^{2+}$  and  $\text{Pt}^{4+}$  ions, peaks around 2.8 eV [6], while a photosensitive midgap band (so-called *A* band) due to self-localized kinks appears around 1.65 eV [7,8]. Both the CT and *A* bands are optically allowed only for the polarization  $E \parallel b$  [4], where  $E$  and  $b$  are the electric field of light and the Pt-Cl chain axis of the crystal, respectively.

In this Letter we study the decay behavior of the *A* band generated by a steady pumping of the CT exciton

in the  $\text{BF}_4$  salt. Until now time-resolved studies in one-dimensional solids have primarily focused on photoexcitation dynamics in ultrafast time scales. In contrast the photogenerated *A* band in the above-mentioned PtCl chain compounds has an exceedingly long decay time. Since its photoenhancement effect was discovered, the decay time has been recognized to be much longer than 1 h below about 200 K [9,10]. Even at room temperature the decay time is several seconds in the  $\text{ClO}_4$  salt [11], while it reaches several minutes in the  $\text{BF}_4$  salt [12]. Such a long lifetime is comprehensible if the kinks are immobile. However, the motional narrowing effect of the electron paramagnetic resonance signal due to concurrently generated spins proves that the kinks are highly mobile [13]. The purpose of this work is to investigate the kinetics governing the lifetime of those kinks. The experiment is, therefore, performed in a range of delay time from 0 to 60 min at temperatures between 220 and 330 K.

Crystals which are 50–200  $\mu\text{m}$  thick and roughly  $200 \times 400 \mu\text{m}^2$  wide are used as the samples. The temperature of the sample is controlled with a nitrogen-flow optical cell (Linkam TH-600PM) mounted on the stage of an infrared microscope (Olympus IR). The 488 nm (2.54 eV) line of a cw Ar-ion laser is used to create the midgap states. The time evolution of the optical absorption spectrum is measured using a multichannel spectrometer connected to the infrared microscope through a cable of bundled silica fibers. The light of wavelength longer than 520 nm is obtained with a tungsten-halogen lamp and a glass filter. The shutter of the charge-coupled-device detector (Photometrics PM512) is synchronized with the shutter of the light source. The exposure time is chosen to be 0.3–0.6 s.

The pumping laser beam is polarized  $E \perp b$ . Its power is regulated at a level of 0.05–0.5  $\text{W}/\text{cm}^2$ . In the  $E \perp b$  polarization the laser beam is absorbed only moderately. As a consequence the CT excitons and thus the kinks are created almost homogeneously throughout the crystal

[11]. The intensity of the A band becomes stationary within 30 s–20 min, depending on the laser power and temperature, after the pumping is started. In this substance a first order phase transition from an orthorhombic to a monoclinic structure occurs at 250–255 K [14]. We keep in mind this phase transition in the experiment at low temperatures.

The pumping is discontinued when the intensity of the A band becomes almost stationary. Figure 1(a) shows a plot of the time evolution of the decay of the peak absorbance  $A_{\text{peak}}$  of the photogenerated A band for a sample (No. H6N) at various temperatures. Note that the decay is nonexponential at all temperatures. The temperature dependence of the nonexponential decay behavior differs for different samples: The experimental results for another sample (No. H8W) are shown in Fig. 1(b). For all the samples studied, the equilibrated absorption intensity increases as temperature decreases, whereas the decay slows down. Furthermore, if temperature decreases across the critical temperature of the aforementioned phase transition, a large discontinuous change occurs in both the absorption intensity and the overall decay rate.

The observed time evolution can be reproduced well in terms of a stretched exponential function of the delay time  $t$

$$A_{\text{peak}}(t) = A_0 \exp\left[-\left(\frac{t}{\tau_{1/e}}\right)^\beta\right], \quad (1)$$

where  $A_0$  is the initial peak absorbance,  $\tau_{1/e}$  is the  $1/e$  time constant, and  $\beta$  is a positive constant. A simple power function  $t^{-\alpha}$  ( $\alpha > 0$ ) does not match

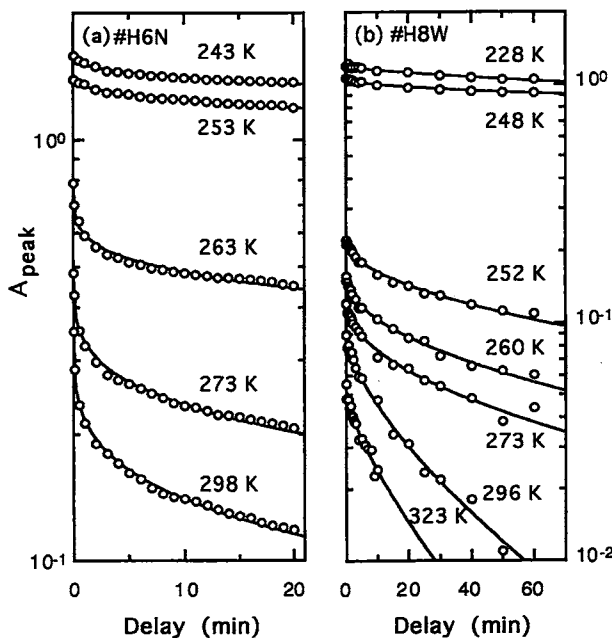


FIG. 1. Decay of the photogenerated A band at various temperatures for samples No. H6N (a) and No. H8W (b). The solid lines are the fits of Eq. (1).

the experimental results. The best-fit curves of  $A_{\text{peak}}(t)$  calculated from Eq. (1) are shown in Figs. 1(a) and 1(b) by solid lines along with the experimental points. Figure 2 shows a logarithmic plot of  $A_0$  versus  $\tau_{1/e}$ . The decay is so slow that at room temperature  $\tau_{1/e}$  reaches about 10 min, while in the low-temperature phase it exceeds 24 h. As for the argument  $\beta$ , its temperature dependence is rather weak. We obtain  $\beta = 0.2$ – $0.4$  for sample No. H6N and  $0.4$ – $0.8$  for sample No. H8W.

Within the framework of Eq. (1) the equilibrium condition at  $t = 0$  is written as

$$A_0 = a[t^{1-\beta}G(t)]_{t=0} \left(\frac{\tau_{1/e}^\beta}{\beta}\right), \quad (2)$$

where  $a$  is a constant and  $G(t)$  is the generation rate at  $t \leq 0$  of the midgap states. When  $\beta = 1$  Eq. (2) is reduced to a usual formula  $A_0 = aG(0)\tau_{1/e}$ . We see in Fig. 2 that regardless of the sample a relationship  $A_0 \propto \tau_{1/e}^\beta$  holds well, as an implicit function of temperature, for all the experimental data of  $A_0$  and  $\tau_{1/e}$ . This means that the value of coefficient  $(a/\beta)[t^{1-\beta}G(t)]_{t=0}$  is not altered significantly even by the phase transition. In addition the values of  $\beta$  (0.27 for sample No. H6N and 0.54 for sample No. H8W) are consistent with the values determined from the time evolution of  $A_{\text{peak}}(t)$ . These results show that the decay is governed by a universal nonlinear process.

We now illustrate that the observed anomalous decay can be interpreted well in terms of the pair recombination of the photogenerated kinks. Here we deal with  $1/A_{\text{peak}}(t)$  since this quantity scales with the mean distance between kinks. If a kink performing one-dimensional random walk coalesces with its antikink upon a single event of collision,  $1/A_{\text{peak}}(t)$  should evolve with  $t$  as [15]

$$1/A_{\text{peak}}(t) = \sqrt{1/A_0^2 + Dt}, \quad (3)$$

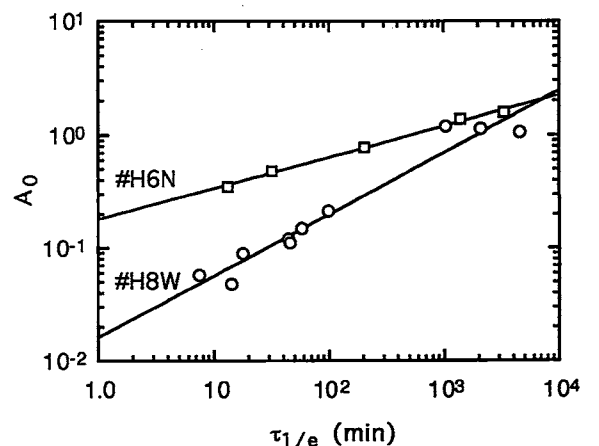


FIG. 2. The initial intensity  $A_0$  versus  $1/e$  decay time  $\tau_{1/e}$  for samples No. H6N ( $\square$ ) and No. H8W ( $\circ$ ). The solid lines are the fits of a linear line to the data.

where  $D$  is a constant proportional to the diffusion constant divided by the squared thickness of the sample. The experimental data of  $1/A_{\text{peak}}^2(t)$  of two samples are plotted in Figs. 3(a) and 3(b). The data show a good linear dependence on  $t$  for  $t > 5$  min, showing that the random walk model applies well to the present case. The slope  $D$  decreases rapidly with decreasing temperature. Figure 4 shows an Arrhenius plot of  $D$  thus obtained. In the high-temperature phase  $D$  obeys an Arrhenius law  $D = D_0 e^{-E_0/kT}$  well, where  $D_0$ ,  $E_0$ ,  $k$ , and  $T$  denote a constant parameter, activation energy, Boltzmann constant, and temperature, respectively. The kinetics of kinks turns out to be governed by a thermally activated random walk with an activation energy of  $E_0 \approx 0.5$  eV, which is much greater than the activation energy 13 meV [13] for the motion of the photogenerated spins. Upon the phase transition  $D$  decreases by 1–2 orders of magnitude. Presumably  $E_0$  is enhanced by 0.05–0.1 eV by the phase transition.

Theoretically, a solitonic kink and its antikink in an  $MX$  chain compound repel one another because the phase frustration elevates the free energy of the kinks when they come close together [16]. If this is the case a finite activation energy is needed for them to coalesce. However, the sample dependent distribution of the magnitude of  $E_0$ , which is shown below, rules out this repulsive force as the origin of  $E_0$ . The same is also true for polaronic kinks. Instead, it is natural to attribute  $E_0$  to the energy barriers due to local imperfections of the Pt-Cl bonds. Indeed, this notion gives a good basis for the long life-

time. Although the detail is unclear yet, there probably is a relaxation mechanism to leave kinks and antikinks singly in different segments of chains terminated by the barriers, while maintaining the total number of kinks in a chain to be equal to that of antikinks. Our experimental results suggest that after discontinuation of pumping a kink coalesces with an antikink when they collide in the course of random walk by surmounting barriers. The barriers are so high compared with  $kT$  that the coalescence rate is very low even if the kinks can move freely in any segment as shown by the motional narrowing effect of spins.

We note from Figs. 3(a) and 3(b) that a simple random walk model, in which  $D$  in Eq. (3) is assumed constant, does not describe the decay behavior correctly for  $t < 5$  min. In light of the optical conductivity spectrum obtained previously [17] the relative integrated intensity of the photogenerated  $A$  band is estimated to be the order of  $10^{-3}$ , at most, compared to the intensity of the CT band, showing that the density of photogenerated kinks is very low at all temperatures examined. Moreover, in the present experiment, the system is expected to be in a thermal equilibrium when pumping is discontinued. It is unlikely, therefore, that there exist particular reasons for which the Langevin and diffusion equations break down at short delays in the time scale of the present experiment. Turning our attention back to Fig. 3(a) we note that the slope of the experimental curve of  $1/A_{\text{peak}}^2(t)$  versus  $t$  decreases with increasing  $t$ , approaching a constant value  $D$ . The initial slope decreases rapidly, in the same manner as  $D$ , as temperature decreases. This fact leads us to imagine that the height of the energy barrier is not constant but has a distribution extending down to the energies below 0.4 eV.

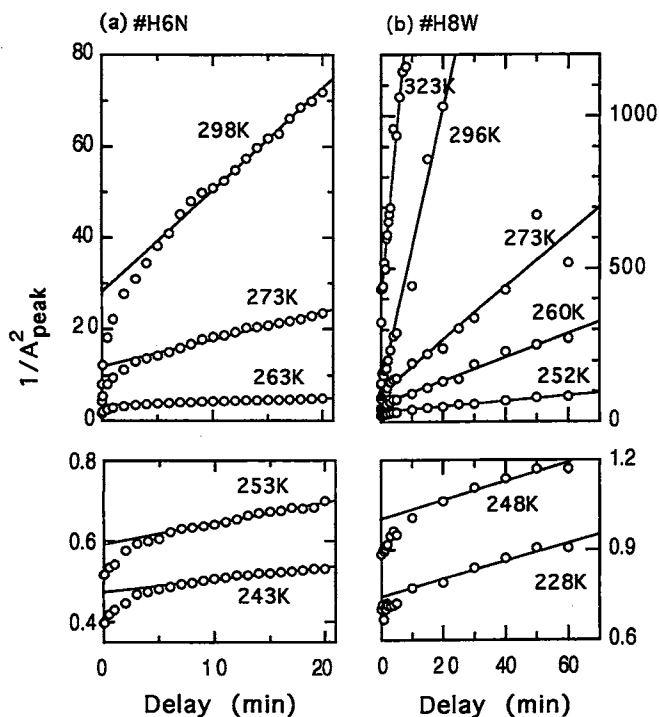


FIG. 3. Temperature dependence of the time evolution of  $1/A_{\text{peak}}^2(t)$  for samples No. H6N (a) and No. H8W (b). The solid lines are the fits of a linear line to the experimental data.

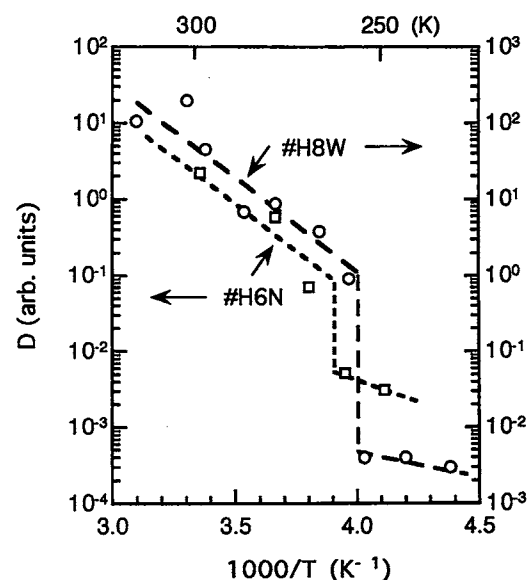


FIG. 4. Temperature dependence of the diffusion parameter  $D$  for samples No. H6N ( $\square$ ) and No. H8W ( $\circ$ ). The dotted and dashed lines are guides for the eye.

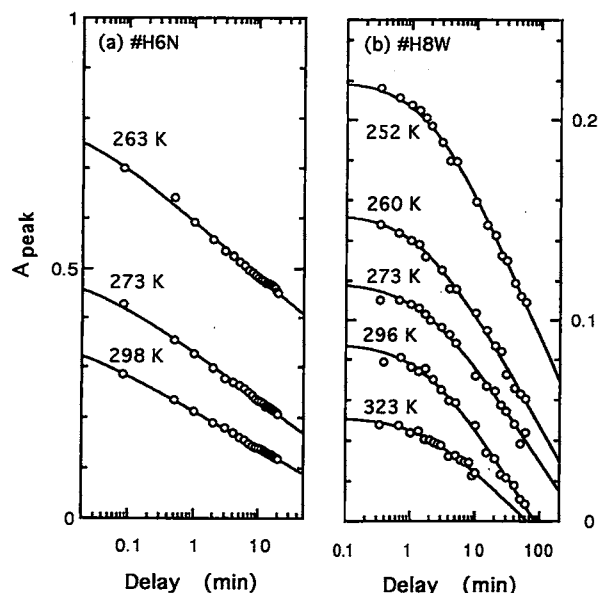


FIG. 5. Log  $t$  dependence of  $A_{\text{peak}}$ . The solid lines are the fits of Eq. (4).

In certain situations inhomogeneity of a specific barrier height causes the following logarithmic time evolution of an excited state:

$$C(t) = C_0 \left[ 1 - f \ln \left( 1 + \frac{t}{\tau_l} \right) \right], \quad (4)$$

where  $f$  is an adjustable parameter and  $\tau_l$  is a time constant. An example is the magnetic relaxation in the random-field-Ising-model (RFIM) systems [18]. An important ingredient for yielding the  $\ln t$  decay of magnetic order in the RFIM systems is the random fluctuation of the energy barriers at the interface between the stable and metastable domains [19]. The magnetic relaxation due to creep of pinned fluxes in type-II superconductors with inhomogeneous pinning energies also has a  $\ln t$  dependence [20,21]. In the RFIM and flux creep theories the quantity  $kT/f$  roughly gives the relevant barrier height, while  $\tau_l$  gives a specific waiting time for a metastable domain or a flux to jump over an energy barrier. Although there exist no theories adequate for the present case, we notice that Eq. (4) describes very well the observed absorbance  $A_{\text{peak}}(t)$  for the entire range of  $t$ , if we write  $C(t) = A_{\text{peak}}(t)$  and  $C_0 = A_0$ . Figure 5 shows the fits of Eq. (4) to the experimental data for the high-temperature phase. We obtain  $kT/f = 0.25\text{--}0.42$  eV for sample No. H6N and  $0.10\text{--}0.14$  eV for sample No. H8W, which are compared to  $E_0 \approx 0.5$  eV deduced from the temperature dependence of  $D$ .

In conclusion, a global understanding of the anomalously long lifetime of photogenerated kinks in the PtCl

chain compounds has been achieved in terms of the picture of pair coalescence of mobile kinks under the presence of large inhomogeneous energy barriers in the chain. It has emerged that this is a new nonequilibrium system that shows a  $\ln t$  decay.

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