Detection of a Precursor in a Strong First-Order Structural Phase Transition by a Fluorescence-Lifetime Measurement

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A precursor of the strong first-order structural phase transition in a resorcinol [$C_6H_6(OH)_2$] crystal was detected by measuring the lifetime of the fluorescence. A critical decrease in the lifetime and an increase in the intensity of the impurity-induced fluorescence were found to occur starting from 30 K below T_c. Large-amplitude and short-lived vibrational fluctuations associated with the phase transition are suggested as a possible origin of the precursor.

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In second-order or nearly-second-order structural phase transitions, various changes start to appear far from the transition temperature (T_c), reflecting the divergence of fluctuations of the order parameter These are considered to be the precursors of the transitions. Soft-mode spectroscopy[1,2] proved to be very powerful for detecting such precursors in second-order phase transitions. In the case of first-order structural phase transitions, the "softening" does not occur because the transitions take place discontinuously at a temperature where the free energy of one phase accidentally becomes lower than that of the other. However, even in first-order transitions, the displacements or the reorientations of molecules would not occur all at once over a macroscopic range at T_c, but local nucleations of the new phase would appear at temperatures far from T_c. Besides, the nucleation may be preceded by the momentary but large-amplitude fluctuations of molecular vibrations as a precursor. Detection of such precursors would be helpful to understand the mechanism of strongly first-order transitions. In this paper, we report that, in the α-β transition of resorcinol [$C_6H_4(OH)_2$, *m*-dioxybenzene] crystals, the fluorescence lifetime decreases critically starting from approximately 30 K below T_c. This is, to our knowledge, the first observation of a precursor in a strongly first-order phase transition.

Resorcinol is a molecular crystal with four molecules in the unit cell as shown in Fig. 1.[3,4] It undergoes an α-β transition at $T_c = 358.7$ K.[5] The space group of the two phases are the same (C_{2v}^9, *Pna*2), but at T_c the molecules drastically change their position and orientation, accompanied by a deformation of the unit cell. The network of the hydrogen bonds in the two phases is also completely changed.[3] The difference is so large that a single crystal becomes a milky-white polycrystal when it is heated above T_c. Crystals in the α phase were grown from aqueous solution by a slow evaporation method. In the course of growing, the solution gradually becomes dark reddish and the grown crystals also have a thin brown color. This coloring is probably due to some complexes and/or impurities produced by a reaction in the solution. They might be benzene complexes like fluoresein or xanthene, which have a fluorescence band in the visible region. The amount of the impurity is so scarce that no conventional chemical analytic method could assign the impurity. We took advantage of this impurity-induced fluorescence to investigate the precursor effect of the phase transition. A sample was cut from a crystal which shows relatively strong fluorescence, but the results were not dependent on the sample.

First, we measured the conventional Raman spectrum to see if there is any softening of lattice vibrational modes by slowly heating the sample to T_c. Among the Raman peaks[6-8] below 250 cm^{-1}, including the librational modes[6] at about 100 cm^{-1}, no softening was recognized. The mode frequencies change suddenly at T_c, and they again become insensitive to temperatures above T_c.

Next, the fluorescence lifetime was measured using the time-correlated single-photon counting method.[9] A pulse from a cavity-dumped dye laser at 580 nm is focused into the sample of size 3×5×8 mm. The pulse width is about 10 ps with a repetition rate of 4 MHz. The average power of the excitation is about 100 mW.

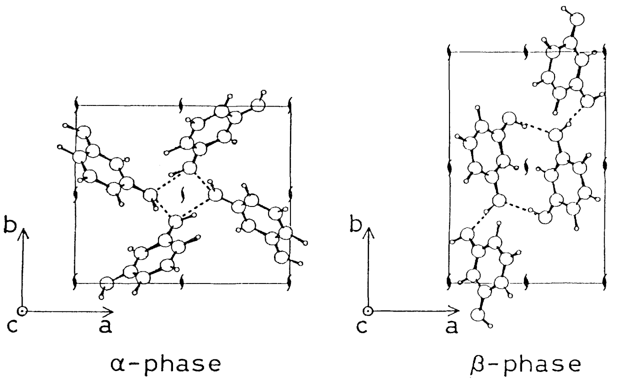

FIG. 1. Unit cell of a resorcinol crystal (Ref. 2). Large circles represent carbon and oxygen atoms. Small circles are hydrogen atoms. The unit-cell size, orientations of molecules, and the hydrogen-bond network (shown by the dotted lines) drastically change through the α-β transition.

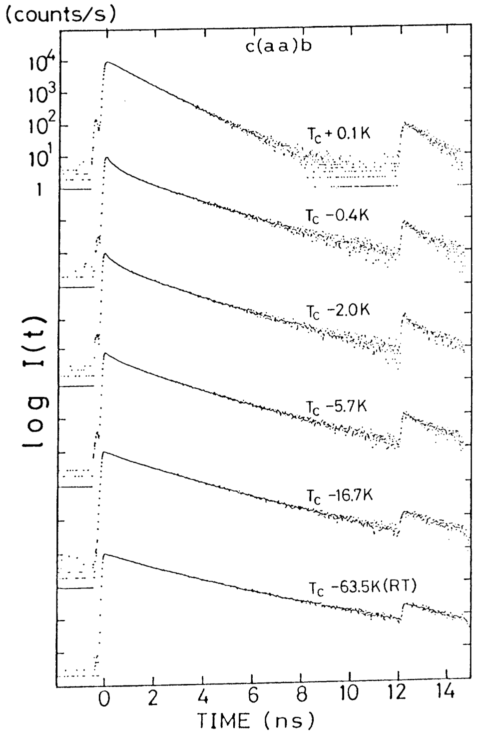

FIG. 2. Temperature dependence of the fluorescence decay in the $c(aa)b$ geometry. As $T \rightarrow T_c$ (=358.7 K), a fast decay component appears at the head of the decay curve. Note that the vertical scale is logarithmic. The second peak at about 12 ns is due to a leak of the cavity dumper for the dye laser.

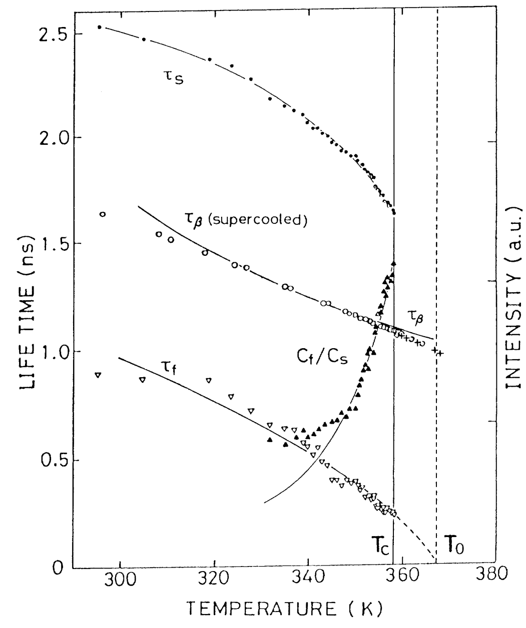

FIG. 3. Temperature dependence of the α-phase lifetimes τ_s (solid circles) and τ_f (open triangles). The β-phase lifetime τ_β just after the transition is given by crosses and the open circles are the data for the supercooled-β-phase sample on the next heating run. The solid triangles are the intensity ratio [C_f/C_s in Eq. (1) in the text]. The solid curves show the $(T_0-T)^{-1}$ dependence of Eq. (3) in the text, with $T_0=T_c+8.3$ K.

The fluorescence photon at 600 nm was detected by a photomultiplier (HTV-R1564U), and fed to a time-to-amplitude converter. The choice of the wavelength was not crucial because the fluorescence bandwidth is rather broad (about 20 nm).

Figure 2 shows the temperature dependence of the fluorescence decay curves measured in the $c(aa)b$ geometry; i.e., both the excitation and fluorescence polarization are parallel to the a axis. At room temperature (RT) the curve is well described by a single decay time of about 2.5 ns. As temperature is raised, an additional fast decay component starts to appear at the head of the decay curves. Its intensity increases and the decay time decreases significantly. (Note that the intensity is given on a logarithmic scale in Fig. 2.) The measured curves were first deconvoluted with the instrumental response function with 120-ps width, and then fitted by the following function:

$$I(t)=C_s\exp(-t/\tau_s)+C_f\exp(-t/\tau_f)\,. \qquad (1)$$

The results of the analysis are given in Fig. 3. On heating, the two lifetimes in the α phase, τ_s and τ_f for the slow and the fast decay components, respectively, become shorter and both of them tend to zero when extrapolated to about 8 K above T_c. The change in the fast component (τ_f=0.9 ns at RT to 0.2 ns at T_c) is more significant than that in the slow component τ_s (from 2.6 to 1.6 ns), and, as also shown in Fig. 3, the ratio of the intensities [C_f/C_s in Eq. (1)] critically increases as T approaches T_c.

In the β phase ($T>T_c$), the decay is well fitted by a single lifetime $\tau_\beta \sim 1.1$ ns (shown by the crosses in Fig. 3). It is approximately equal to the average of τ_s and τ_f in the α phase. Because of the large thermal hysteresis, once the sample is transformed to the β phase it remains in the supercooled β phase at RT for several days. Therefore, when heated again, the lifetime does not show any critical behavior, but decreases monotonously over a wide temperature range (given by open circles in Fig. 3).

In order to consider a possible mechanism of the precursor, the polarization dependence was studied. Decay curves at RT for various polarization geometries are shown in Fig. 4. Obviously they can be classified into two types, (aa) and (bb). The (aa)-type decay (upper half of Fig. 4) was observed for geometries such that either or both of the excitation and the fluorescence polarization are parallel to the a axis. It shows only a slow ($\tau_s \sim 2.5$ ns) decay at RT, and the temperature dependences are almost the same as those given in Fig. 2. The (bb)-type decay (the lower half of Fig. 4), on the other hand, was observed only when the polarizations are along the b or c axis. The main difference between the

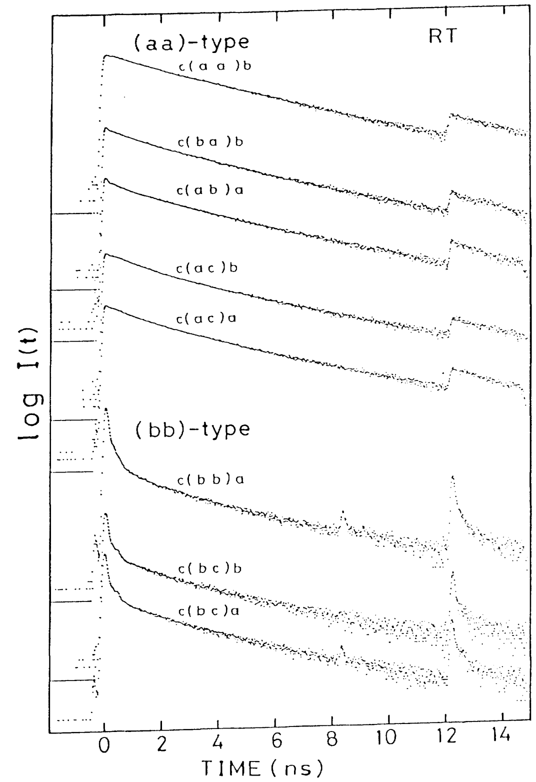

FIG. 4. Fluorescence decay for several polarization geometries at room temperature. Note that the fast decay component is absent in the (*aa*) type but it is dominant in the (*bb*) type.

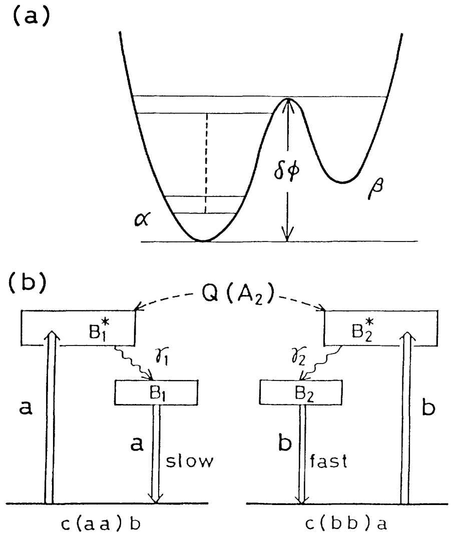

FIG. 5. (a) A schematic potential for a resorcinol vibration. The left and right wells correspond to the local α and β structures, respectively. The highly excited vibrational states close to the potential barrier $\delta\phi$ may disturb the electronic states of the impurities. (b) A model of fluorescence decay routes; a slow decay via B_1^* and a fast decay via B_2^* states. The two states are mixed by the A_2 vibration. The *a* or *b* beside the arrows represents the polarization of the light.

two types is that, in the (*bb*)-type decay curves, besides the slow decay, there is a relatively intense fast decay component ($\tau_f' \sim 0.2$ ns) already at RT. On heating, it persisted up to T_c with no significant change in intensity and lifetime. In contrast, the lifetime of the slow decay (τ_s') in the (*bb*)-type geometry decreased from 2.4 ns at RT to 1.4 ns near T_c, in a similar way to τ_s in the (*aa*)-type decay.

Taking into account the selection rules for dipole transitions in C_{2v} symmetry, the above polarization dependences at RT (Fig. 4) can be interpreted as follows [Fig. 5(b)]: The fluorescence from the B_1^* state which is excited in the (*aa*)-type geometries shows only the slow decay fluorescence τ_s, while the B_2^* state must be involved for the fast decay fluorescence in the (*bb*)-type geometries. In other words, the relaxation rate from B_1^* to the lower states (B_1, B_2, and A_1) is much slower than the rate from B_2^* to the lower B_2 and A_1 states.[10] Based on these results, the observed behavior of the precursor could be explained by the following mechanism. From the structure shown in Fig. 1, a resorcinol molecule is considered to be in a deep asymmetric double-well potential as shown in Fig. 5(a), which schematically represents the local potential as a function of the normal coordinate of vibration. For $T \ll T_c$, a molecule stays in the deep α-phase well, and as the temperature is raised, it is excited to the higher vibrational levels. When the average vibrational energy becomes comparable to the potential barrier $\delta\phi$, large displacements and reorientations of the molecules would give rise to a nucleation of the β phase. However, even long before the average energy exceeds $\delta\phi$, it is probable that, due to statistical fluctuations, the local vibrational energy surpasses the barrier momentarily. Then large-amplitude vibrations are induced, which, in turn, perturb the crystal field. Since the excited electronic states are readily influenced by such a momentary perturbation on the crystal field, the fluorescence lifetime would also be affected. In other words, the momentary large-amplitude vibration can manifest itself in the fluorescence as the precursor of the phase transition at temperatures far from T_c, where the averaged vibrational fluctuations or nucleations would not yield any detectable effect yet.

More specifically in the present case, the fluctuation of an A_2-symmetry vibration $Q(A_2)$ causes a mixing between the B_1^* and B_2^* electronic states of the impurities:

$$\langle B_2|H'|B_1\rangle = \langle B_2|dV/dQ|B_1\rangle\langle Q(A_2)\rangle\,, \qquad (2)$$

where V is the adiabatic crystal-field potential. (Similarly, B_1-symmetry vibrations may mix the B_1^* and A_1^* electronic states.) Because of this mixing, the selection rules will be violated. Then the electrons excited by light polarized along the a axis can decay via two routes: One is via the B_1^* state and the other is through the B_2^* states [Fig. 5(b)]. Since the decay via the B_2^* state is already fast at room temperature, as shown in Fig. 4, and it remains fast up to T_c, the opening of the B_2^* route due to the mixing will make the lifetimes short. This effect may be observed, depending on the detailed form of the perturbation, as the shortening of the existing single lifetime and/or the appearance of a fast component. This mechanism, therefore, explains well the observed precursor in the $c(aa)b$ geometry as $T \rightarrow T_c$ (Fig. 3).

If this is the case, the fluctuations of the A_2 (or B_1) vibrational modes should be responsible for the critical shortening of the lifetime. Let us simply assume that the fluctuation diverges at a certain temperature T_0 as $\langle |\Delta Q|^2 \rangle \sim (T_0 - T)^{-1}$. Then, from Eq. (2), the decay rate $(1/\tau_f)$ is expected to be proportional to $(T_0 - T)^{-1}$. Taking the noncritical β-structure lifetime as the background, we found that the data could be fitted well by the following equation (solid lines in Fig. 3):

$$1/\tau_f = c/(T_0 - T) + 1/\tau_\beta = +aT + b\,, \qquad (3)$$

with $a = 5.6 \times 10^6\ (\mathrm{sK})^{-1}$, $b = -1.1 \times 10^9\ \mathrm{s}^{-1}$, $c = 3.0 \times 10^{10}\ \mathrm{K s}^{-1}$, and $T_0 = 367$ K. The intensity increase should also be ascribed to the increase of the perturbation. Actually, as shown in Fig. 3, the ratio C_f/C_s in Eq. (1) can be fitted by $(T - T_0)^{-1}$ using the same T_0 (=367 K) as obtained for $1/\tau_f$. This suggests that the local α structure would lose its stability at about 8 K above T_c.

Although the idea of the divergence of $\langle |\Delta Q|^2 \rangle$ looks similar to the mean-field theory for the second-order phase transitions,[11] it is not the same because in the present case the relevant vibration is a localized one instead of a long-wavelength phonon. Therefore, the detection of the precursor in this work is consistent with the absence of a soft mode. Furthermore, if the precursor were simply due to the local increase of the vibrational amplitude, it should also be observed as a change in the internal-mode Raman spectra. However, no change was observed experimentally. This is reasonable if we assume that the origin of the precursor is not simply the localized vibration but is the momentary highly excited vibration. Since only the electronic (fluorescence) states can respond to such a fast perturbation, it could not be detected by the conventional Raman (phonon) spectra.

In conclusion, it was shown that a precursor in a strongly first-order phase transition can be detected as a change in the fluorescence lifetime. The present method might be useful for the investigation of the dynamical mechanisms of other first-order phase transitions.

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