Initial process of photoluminescence dynamics of self-trapped excitons in a β-Ga$_2$O$_3$ single crystal

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We investigate the photoluminescence (PL) dynamics of self-trapped excitons (STEs) in a β-Ga$_2$O$_3$ single crystal from the viewpoint of the transition process from the free exciton to the STE. We succeed in measuring the PL rise time ($\sim$24 ps) at 8 K corresponding to the tunneling time through the barrier between the free exciton and STE states in the adiabatic potential. From the analysis of the PL rise time of the STE based on perturbation theory for the tunneling time considering exciton-phonon interactions, we obtain the following results. Acoustic phonons near the Brillouin zone center contribute to the tunneling process. This suggests that the wave function of the STE is still spatially extended at the final state in the tunneling process. Furthermore, we investigate temperature dependence of the PL rise time of the STE. It is found that the PL rise time decreases with increasing temperature. The PL rise times in the temperature range from 8 to 100 K can be quantitatively explained by an adiabatic theory for the tunneling process. Consequently, the self-trapping process is dominated by the tunneling process at low temperatures.

I. INTRODUCTION

One of the group-III semiconductor oxides, β-Ga$_2$O$_3$, has a wide band-gap energy of $\sim$4.7 eV [1,2] and has recently attracted much attention for high-power field-effect transistors [3] and optoelectronic devices in a deep ultraviolet (UV) region such as transparent conductive substrates [4,5] and photodetectors [6]. Moreover, low-cost and large-scale β-Ga$_2$O$_3$ substrates can be fabricated with a solution method such as a floating-zone growth method [7]. Monoclinic β-Ga$_2$O$_3$ with lattice parameters of $a = 12.23$ Å, $b = 3.04$ Å, $c = 5.80$ Å, and $\beta = 103.7°$ [8] has anisotropic polarization along all of the crystal axes [2]. It was reported that photoluminescence (PL) spectra of β-Ga$_2$O$_3$ exhibit three broad bands: UV, blue, and green PL bands [9–14]. Theoretical [9] and experimental [10–14] studies support that the origin of the broad UV band is the self-trapped exciton (STE) consisting of a self-trapped hole (STH) and a bound electron. According to a theoretical calculation for β-Ga$_2$O$_3$ based on hybrid functional calculations [9], holes tend to form localized small polarons, and the STH is mainly on a single O site with a shape characteristic of an O $2p$ orbital. In our previous work on a β-Ga$_2$O$_3$ single crystal, we demonstrated that the STE is a stable state relative to the free exciton from the analysis of temperature dependence of Urbach tails [14].

The initial process of self-trapping was considerably studied in alkali halides [15,16], rare-gas solids [17], and molecular crystals [18]. According to the theoretical study of excitons interacting with longitudinal acoustic phonons [19], the free exciton and STE states are separated by an adiabatic potential barrier, leading to the coexistence of the free exciton and STE. The dynamical process of the STE formation is described as follows. Nonthermal excitons rapidly relax to the bottom of the exciton band via longitudinal optical (LO) phonon scattering, and then the exciton transforms to the STE through the adiabatic potential barrier via a quantum-mechanical tunneling

process and/or thermal activation [20–24]. At low temperatures, it is expected that the tunneling process dominates the self-trapping process because the thermal activation process is negligible. Thus, under a nonresonant excitation condition, the PL rise time of the STE at low temperatures is determined by the following three processes: (1) rapid relaxation into the free-exciton band via the LO phonon scattering, (2) tunneling from the bottom of the free-exciton band to the intermediate state of the STE in the adiabatic potential, and (3) relaxation to the bottom of the STE state. Since relaxation processes (1) (under a UV excitation condition) and (3), which are of the order of subpicoseconds, are sufficiently faster than the tunneling process (2), the PL rise time of the STE at low temperatures is mainly determined by the tunneling time [21–23,25]. Víllora *et al.* reported a long PL rise time, of the order of subnanoseconds, of the STE band under an x-ray excitation condition in β-Ga$_2$O$_3$; however, this originates from the relaxation process of nonthermal electrons with an extremely high kinetic energy [26]. Thus, there has been no clear report on the initial process of the PL dynamics of the STE in β-Ga$_2$O$_3$ from the aspect of the tunneling process. Note that the free-exciton PL has not been observed until now. A possible reason for no free-exciton PL is that the radiative lifetime of the free exciton is much longer than the tunneling time to the STE state. Very recently, Mengle *et al.* reported that the fundamental band gap is indirect, the energy of which is only 29 meV lower than the direct gap based on the first-principles calculation [27]. According to this calculation, it is expected that the radiative lifetime of the free exciton is of the order of microseconds because of the indirect transition nature. Such a long radiative lifetime of the free exciton prevents the appearance of free-exciton PL.

In this work, we investigate the PL rise process of the STE at 8 K in a β-Ga$_2$O$_3$ single crystal to reveal the initial process of the PL dynamics from the viewpoint of the transition process from the free exciton to the STE. The PL rise time is analyzed based on perturbation and nonadiabatic theories for the tunneling time reported by Sumi [22] and Nasu [23]. It is found that the interacting acoustic phonon associated with

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the tunneling process can be attributed to phonons near the Brillouin zone center. This reflects that the wave function of the STE is still spatially extended at the final state of the tunneling process. We also investigate the temperature dependence of the PL rise time of the STE. The PL rise time decreases with increasing temperature, which is analyzed based on an adiabatic theory reported by Ioselevich and Rashba [24].

II. EXPERIMENT

The sample used was a (010)-oriented undoped β-Ga$_2$O$_3$ single crystal with a thickness of 0.60 mm grown by an edge-defined film-fed growth method, which was prepared by the Tamura Corporation. In the PL measurements, the excitation light source was a mode-locked Ti:sapphire laser with a pulse duration of 110 fs. For the measurement of the PL dynamics, the energy of the fundamental laser light was doubled to 2.87 eV for two-photon excitation. Note that the two-photon energy (5.74 eV) is higher than the PL excitation peak energy (4.87 eV) of the STE band, which is attributed to the free-exciton energy at 10 K [14]; namely, two-photon excitation corresponds to nonresonant excitation. The excitation fluence was ∼8 μJ/cm^2. A streak-camera system with a spectral resolution of 3.5 nm and time resolution of 18 ps was used to detect time-resolved PL spectra. To reduce pileup of temporal profiles due to slow decay components, the repetition rate was fixed at 4.75 MHz using a pulse picker in the measurement of the PL rise time. To measure the PL decay profile, the repetition rate was set to 100 kHz to detect slow decay components, where the time resolution was 64 ns. A short-pass filter was used to cut off the scattering laser light. Steady-state PL spectra were detected with a cooled charge-coupled device attached to a single monochromator with a resolution of 1.5 nm. For reference, we measured the steady-state PL spectrum under one-photon excitation using the fifth-harmonic-generation light (213 nm) of a pulsed yttrium aluminum garnet laser as the excitation light. We measured the temperature dependence of the PL rise time of the STE at temperatures from 8 to 290 K. The sample temperature was controlled using a closed-cycle helium cryostat.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the steady-state PL spectra at 8 K under the two-photon and one-photon excitations. It was revealed that the PL band under the one-photon excitation originates from the STE [14]. In our previous work [14], we also demonstrated that the PL excitation spectrum of the STE clearly exhibits a free-exciton band. This fact phenomenologically suggests that the relaxation process to the STE state starts from the free-exciton state. If a self-trapping process of free holes is considerable, it is expected that the PL excitation efficiency of the STE will become remarkable in the energy region of the exciton continuum state. However, the PL excitation spectrum in Ref. [14] exhibits a steep decrease from the exciton peak energy, which suggests that the self-trapping process of free holes is negligible. Figure 1(b) shows the integrated PL intensity as a function of excitation fluence under the two-photon excitation. It is evident from the fitted line that the integrated PL intensity exhibits the square dependence on
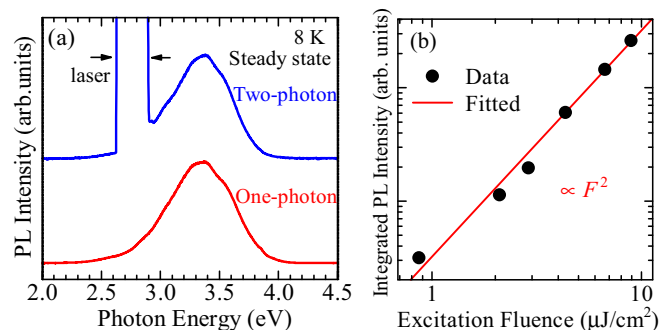

FIG. 1. (a) Steady-state PL spectra at 8 K under the one-photon and two-photon excitations in the β-Ga$_2$O$_3$ single crystal. (b) Integrated PL intensity of the STE under the two-photon excitation at 8 K as a function of excitation fluence F. The solid line indicates the fitted result based on the square dependence.

the excitation fluence, which demonstrates the occurrence of the two-photon excitation. As shown in Fig. 1(a), the PL spectrum under the two-photon excitation is the same as that under the one-photon excitation. This fact indicates that the two-photon excited PL band is attributed to the STE.

Figure 2 shows the PL decay profile (open circles) of the STE detected at the PL peak (∼3.35 eV) under the two-photon excitation. The temporal profile exhibits fast and slow decay components; therefore, the following equation was used to analyze the temporal PL profiles:

$$I_{PL}(t) = I_f \exp(-t/\tau_f) + I_s \exp(-t/\tau_s), \tag{1}$$

where the subscripts f and s indicate the fast and slow decay components, respectively. The solid curve in Fig. 2 indicates the fitted result using Eq. (1). The fast and slow decay times under the two-photon excitation were estimated to be 110 ns and 2.1 μs, respectively.

Figure 3(a) shows the temporal PL profile of the STE detected at the PL peak (∼3.35 eV) at 8 K in the time range up to 160 ns, where the PL intensity has a logarithmic scale and the open circles indicate the experimental results. The solid curve depicts the fitted result using the convolution analysis
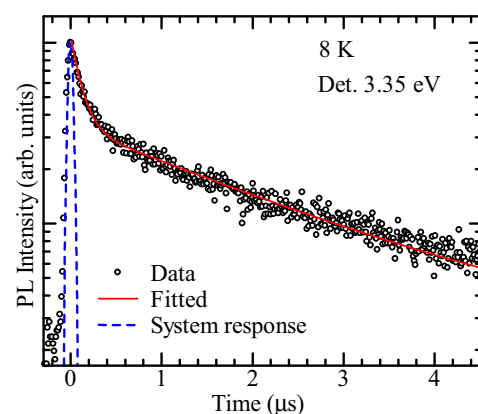

FIG. 2. PL decay profile of the STE at 8 K detected at the PL peak energy in the β-Ga$_2$O$_3$ single crystal, where the open circles indicate the experimental results and the solid curve depicts the fitted result using Eq. (1). The system response is shown by the dashed curve.
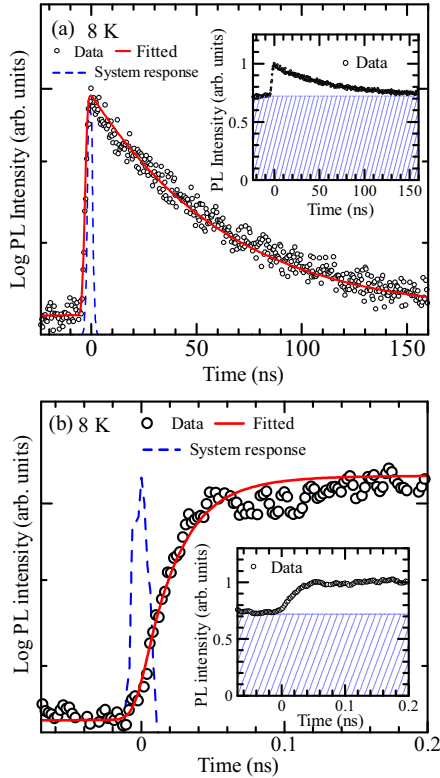
FIG. 3. Temporal PL profiles (open circles) of the STE in the time range up to (a) 160 ns and (b) 0.2 ns at 8 K detected at the PL peak energy. The dashed curve depicts the system response $I_{sys}(t)$. The solid curve shows the fitted result using the conventional convolution method for $I_{sys}(t)$ and $I_{PL}(t)$ given by Eq. (2).

of the system response shown by the dashed curve and the following equation for the temporal PL profile:

$$I_{PL}(t) = -I_r \exp(-t/\tau_r) + I_d \exp(-t/\tau_d) + I_0, \qquad (2)$$

where the subscripts r and d refer to the rise and decay components, respectively, $I_r = I_d$, and I_0 represents the pileup effect due to the slow decay component shown in Fig. 2. The inset shows the temporal PL profile in linear scale, where the pileup effect is evident. The fitted result well agrees with the temporal PL profile. The decay time τ_d was estimated to be 65 ± 5 ns, which is different from that of the fast decay component, 110 ns, estimated from Fig. 2. This difference originates because the time scale in Fig. 2, of the order of microseconds, is too long to estimate τ_f of the fast decay component accurately. To clarify the PL rise process, we show the temporal PL profile in the time range up to 0.2 ns in Fig. 3(b), where the open circles and dashed curve indicate the experimental results and system response, respectively, and the solid curve depicts the fitted result using the convolution analysis of the system response and Eq. (2). The PL rise process is obviously delayed relative to the system response. The PL rise time τ_r was estimated to be 24 ± 2 ps. Note τ_r in Fig. 3(a) is the same as that in Fig. 3(b).

Next, we discuss the PL rise time on the basis of the theories for the tunneling time from the free exciton to the STE [22,23]. Figure 4 shows the schematic diagram of the free exciton and STE energy states as a function of configuration coordinate Q.
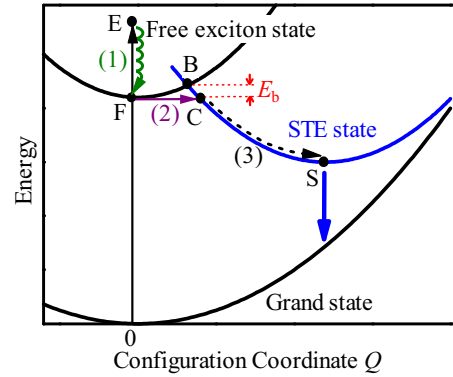

FIG. 4. Schematic diagram of the free exciton and STE energy states as a function of configuration coordinate Q.

In β-Ga$_2$O$_3$, the value of the potential barrier height E_b, which is schematically shown in Fig. 4, was theoretically evaluated to be 0.1 eV [9]; therefore, the thermal activation process is negligible at low temperatures. Consequently, the PL rise time ($\sim$24 ps) at 8 K is attributed to the tunneling time from the free exciton to the STE, which corresponds to the F $\rightarrow$ C process shown in Fig. 4. According to the perturbation theory for the tunneling rate reported by Sumi considering exciton-phonon interactions [22], the tunneling rate W_0 from the free-exciton state to the STE state at absolute zero temperature is given by

$$W_0 = 4\pi^2 \nu \overline{B}^2 \exp(-\overline{S}) \overline{S}^{\overline{S}-\overline{B}} / \Gamma(\overline{S} - \overline{B} + 1), \qquad (3)$$

where $\overline{S}$ is a lattice relaxation energy and $\overline{B}$ is the half width of an exciton band, which are scaled in units of the acoustic phonon energy $h\nu$, and Γ is the Gamma function. In this theory, a fcc structure is treated to analyze the tunneling process. The crystal structure of β-Ga$_2$O$_3$ is monoclinic; however, we analyzed the PL rise time from the aspect of the tunneling time using Eq. (3) for convenience because there is no explicit equation except for Eq. (3). Figure 5 shows the calculated result of the tunneling time using Eq. (3) as a function of acoustic phonon energy. In the calculation, the following values obtained in our previous work were used: $B = 0.15$ eV and $S = 0.83$ eV [14]. In Ref. [22], the interacting acoustic phonon is expected to be that at the Brillouin zone edge because the
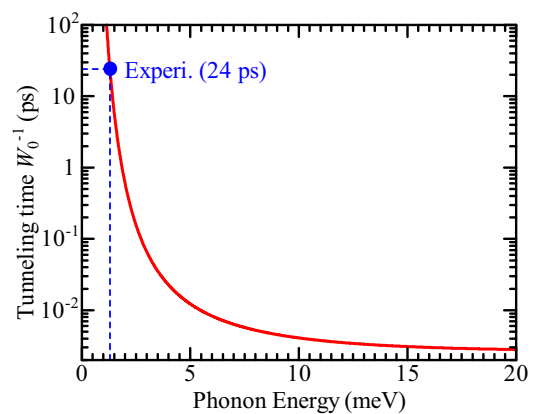

FIG. 5. Calculated result of the tunneling time from the free exciton to the STE as a function of interacting acoustic phonon energy using Eq. (3).

spatial extension of the wave function of the STE is assumed to be of the order of the lattice constant at the final state of the tunneling process. In β-Ga$_2$O$_3$, the acoustic phonon energy at the Brillouin zone edge ranges from $\sim$10 to $\sim$20 meV according to the calculation of the phonon dispersions [25,28]. As shown in Fig. 5, the calculated tunneling time using the phonon energy at the Brillouin zone edge is four orders shorter than the observed PL rise time, $\sim$24 ps. In order to explain the PL rise time, the interacting acoustic phonon energy related to the tunneling process was estimated to be $h\nu = 1.3$ meV. Although the estimated phonon energy has some ambiguity because Eq. (3) is based on the fcc structure, the four-order difference in the tunneling times described above suggests that acoustic phonons near the Brillouin zone center contribute to the tunneling process. Note that further theoretical work on the excitonic properties and exciton-phonon interactions in β-Ga$_2$O$_3$ is necessary to justify the contribution of acoustic phonons near the Brillouin zone center, which is beyond the scope of this paper.

Here, we discuss the interacting phonon mode related to the tunneling process. Nasu [23] also calculated the tunneling rate based on the nonadiabatic theory considering gradual shrinkage of the spatial extension of the wave function of the STE at the configuration coordinates, F, B, C, and S shown in Fig. 4. This is contrary to the picture in Ref. [22]. The spatial extension of the wave function of the STE at the bottom of the adiabatic potential (S) is comparable to the lattice constant, which is the fundamental nature of the STE. In contrast, the wave function of the STE is still spatially extended at the exit state (C) of the tunneling process according to Ref. [23]. Note that larger spatial extension of the wave function results in the interaction with an acoustic phonon with a smaller wave vector. Thus, the above-estimated acoustic phonon energy near the Brillouin zone center is consistent with the theory in Ref. [23]. Since the theoretical approach in Ref. [23] is numerical, we could not apply that to analyze our experimental results. In Ref. [23], the theory was applied to evaluate the tunneling time in a pyrene crystal with a phonon energy $h\nu = 3.5$ meV, which corresponds to the acoustic phonon near the Brillouin zone center.

Figures 6(a) and 6(b) show the temporal PL profiles (open circles) of the STE in the time range up to 160 and 0.15 ns, respectively, at various temperatures from 8 to 290 K and the fitted results (solid curves). The fitting procedure is the same as that used in the analysis of the temporal PL profile at 8 K in Figs. 3(a) and 3(b). The decay time τ_d was estimated from Fig. 6(a). The fitted curves well reproduce the experimental results. Figure 7 shows the temperature dependence of the PL rise time obtained from the fitted results in Fig. 6(b). It is found that the PL rise time decreases with increasing temperature. At temperatures higher than 100 K, the PL rise times are close to the system response; therefore, the PL rise times are assumed to be shorter than 18 ps. The temperature dependence of the tunneling rate of thermalized free excitons interacting with acoustic phonons was reported by Ioselevich and Rashba on the basis of an adiabatic theory [24]. Their theoretical equation was simplified by Inoue *et al.* as follows [29]:

$$W(T) = W_0(1 - T/T_D)^{-3/2} \exp[C(T/T_D)^4], \quad (4)$$

where T_D and C are the Debye temperature and a constant depending on the elastic properties of a crystal, respectively, and W_0 is the tunneling rate at absolute zero temperature. The
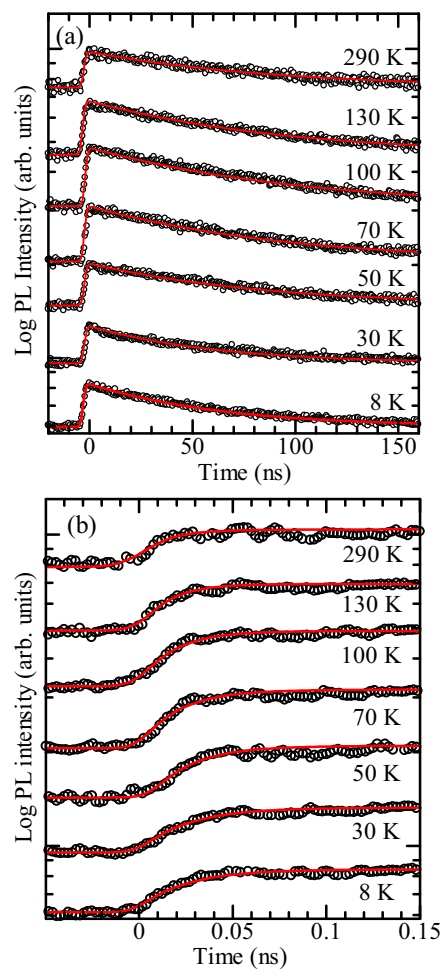

FIG. 6. Temporal PL profiles (open circles) of the STE detected at the PL peak energy in the time range up to (a) 160 ns and (b) 0.15 ns at temperatures from 8 to 290 K, where the solid curves indicate the fitted results using the same procedure as that used in Figs. 3(a) and 3(b).

value of the Debye temperature in β-Ga$_2$O$_3$ was estimated to be 872 K from the first-principles calculation [30]. In Eq. (4),
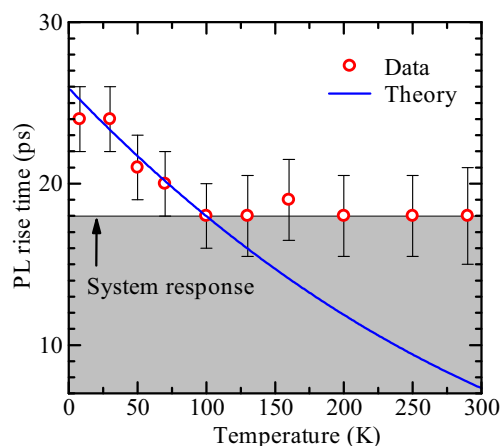

FIG. 7. Temperature dependence of the PL rise time (open circles) of the STE, where the solid curve indicates the fitted result using Eq. (4).

the temperature dependence of the exponential factor at low temperatures is negligible because of the T^4 dependence. Furthermore, the large value of the Debye temperature in β-Ga$_2$O$_3$ also leads to the weak temperature dependence; therefore, we assume that $C(T/T_D)^4$ is sufficiently smaller than unity at low temperatures: $\exp[C(T/T_D)^4] \sim 1$. Thus, the temperature dependence of the tunneling rate is determined by the preexponential factor in this assumption. The solid curve in Fig. 7 indicates the fitted result using Eq. (4) with $W_0^{-1} = 26$ ps, $T_D = 872$ K, and $\exp[C(T/T_D)^4] = 1$. Note that the estimated tunneling time at 8 K is 24 ps, which is close to W_0^{-1} in this calculation. The fitted result reproduces the experimental results at temperatures from 8 to 100 K. Consequently, the self-trapping process is dominated by the tunneling process at low temperatures in the β-Ga$_2$O$_3$ single crystal.

IV. CONCLUSIONS

We have investigated the initial process of the PL dynamics of the STE in the β-Ga$_2$O$_3$ single crystal from the viewpoint of the transition process from the free exciton to the STE. We measured the PL rise time ($\sim$24 ps) of the STE at 8 K corresponding to the tunneling time. From the analysis of the PL rise time based on the perturbation theory considering exciton-phonon interactions in Ref. [22], the phenomenological interacting acoustic phonon energy associated with the tunneling process was estimated to be $\sim$1.3 meV, which indicates that acoustic phonons near the Brillouin zone center contribute to the tunneling process. Taking into account the nonadiabatic theory in Ref. [23], the wave function of the STE is still spatially extended at the exit state of the tunneling process. This is consistent with the above conclusion for the interacting acoustic phonon. Furthermore, we investigated the temperature dependence of the PL rise time of the STE at temperatures from 8 to 290 K. It was found that the PL rise time decreases with increasing temperature. The PL rise times of the STE in the temperature range from 8 to 100 K can be quantitatively explained by the adiabatic theory for the tunneling process taking into account the Debye temperature [24,30]. Consequently, the self-trapping process is dominated by the tunneling process at low temperatures.

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