

Relaxation kinetics of a low-density exciton gas in Cu₂O

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The thermalization of a low-density gas of excitons in Cu₂O is analyzed within the phonon-assisted Boltzmann kinetics in the presence of a weak interaction with the light field. For optically quadrupole-allowed orthoexcitons, the thermalization kinetics is formulated in terms of the polariton picture. A “bottleneck” relaxation along the lower polariton branch strongly dominates over the accumulation of orthoexcitons in the energy minimum of the upper polariton dispersion branch. For paraexcitons, which are strictly forbidden in resonant optical transitions, a rather slow nonexponential occupation kinetics of the ground-state mode at temperature $T \leq T_c$ (T_c is the condensation critical temperature) prevents the development of a steady-state Bose-Einstein condensate within the optical-phonon-assisted radiative lifetime of paraexcitons. While at $T \leq T_c$ the high-energy orthoexcitons or paraexcitons quasiequilibrate into the Planck distribution (the effective chemical potential is equal to zero), the low-energy excitons in a narrow spectral band ($< 100 \mu\text{eV}$) are still far from equilibrium. This provides us with an alternative interpretation of the recent reports on the observation of quasi-steady-state Bose-Einstein condensation of excitons in Cu₂O. [S0163-1829(98)03816-8]

I. INTRODUCTION

Already more than three decades ago, a Bose-Einstein condensation (BEC) of excitons in semiconductors had been discussed for the first time.^{1,2} An exciton (x), as a bound complex of two fermions (electron and hole), has an integer spin, i.e., in the low-density limit obeys Bose-Einstein (BE) statistics. Furthermore, due to the small translational mass M_x of excitons which is typically of the order of the free electron mass, a gas of x 's becomes quantum statistically degenerate at a relatively high temperature $T \sim T_c$. Indeed, the critical temperature is given by $T_c = 2\pi\zeta^{-2/3}(3/2)(\hbar^2/M_x)n_0^{2/3} \propto 1/M_x$, where n_0 is the concentration of x 's and $\zeta(3/2) \approx 2.612$ is the Riemann ζ function. An interaction of x 's with the light field, resonant or phonon assisted, provides us with a natural optical probe of the relaxation processes towards a final quasiequilibrium state with a possible BEC. A further important advantage is that for excitons with a small radius one can approach the BEC phenomenon for an ideal Bose gas.

It seems that bulk Cu₂O is best suited for the realization of a quantum statistically degenerate system of excitons. An exciton spectrum in Cu₂O consists of two components, triply degenerate ortho- x and singly degenerate para- x , separated by 12 meV. An orthoexciton is optically quadrupole-active, i.e., interacts resonantly with the light, while a para-exciton can optically decay only by emitting an (e.g., Γ_5^- or Γ_{25}^-) optical phonon. The observation of a nonclassical BE statistics of ortho- x 's in Cu₂O has been reported in Ref. 3. Thereafter, a highly degenerate quantum gas of ortho- x 's with an extremely small chemical potential has been detected^{4,5} and the observation of BE condensation of ortho- x 's has been claimed.⁶ Moreover, a possible BEC of para- x 's in Cu₂O has been examined recently, both experimentally⁷ and theoretically.⁸

In this paper, we develop a theory of the phonon-assisted relaxation kinetics of paraexcitons and orthoexcitons in

Cu₂O. Simple estimates show that due to the small exciton radius in Cu₂O ($a_x \approx 7 \text{ \AA}$), the x scattering by longitudinal acoustic (LA) phonons strongly dominates over the x - x scattering for concentrations $n_0 \leq 10^{17} \text{ cm}^{-3}$ ($T_c \leq 3 \text{ K}$). The bath of acoustic phonons is supposed to be in thermal equilibrium at the temperature T_b . We are interested in the relaxation kinetics at $T_b > T_c$ and $T_b \leq T_c$.

The relaxation kinetics in a nonequilibrium gas of para- x 's can potentially lead to BEC in the ground-state mode $\mathbf{k} = 0$. However, a considerable slowing down of the phonon-assisted relaxation kinetics at $T_b \leq T_c$ has been proven in our previous study⁹ for an arbitrary gas of Bose-particles with quadratic dispersion. In particular, an analytic generic solution of the three-particle Boltzmann thermalization kinetics has been derived for $T_b \leq T_c$. The generic solution is independent of the initial distribution and completely defined by the ratio T_c/T_b of the critical and bath temperatures. Being applied to excitons in Cu₂O, the generic solution proves the existence of an extremely slow adiabatic stage of the LA-phonon-assisted relaxation kinetics of para- x 's. A bottleneck relaxation kinetics occurs, i.e., a jam of the relatively high-energy para- x 's together with the nonexponential occupation of the ground-state mode $\mathbf{k} = 0$. This is due to the few scattering processes into the lowest state, which are allowed by the energy-momentum conservation laws. For para- x 's with a finite lifetime of about 13 μs , the bottleneck thermalization does not allow a steady-state BEC. Moreover, during the final adiabatic stage of relaxation only the para- x 's in a close vicinity of the ground-state mode are far from equilibrium, i.e., without a condensate fraction, while a high-energy tail of the distribution of para- x 's is in a quasiequilibrium with the effective chemical potential $\mu = 0$ and the effective temperature $T = T_b + \delta T$ ($1 \gg \delta T/T_b > 0$). This result shows that the observation of zero chemical potential in the luminescence spectra with an experimental accuracy of about 100–500 μeV cannot be taken as a proof for a quasi-steady-state BE condensate.⁷

A weak, but still well developed, quadrupole polariton effect has been observed recently for ortho- x 's in Cu_2O .¹⁰ The polariton dispersion stems from the mutual hybridization and unification of the initial exciton and photon dispersion and results in the upper and lower polariton dispersion branches. While the minima of the upper polariton dispersion branch and of the initial quadratic excitonic dispersion refer to $\mathbf{k}=0$ and coincide for the quadrupole-allowed ortho- x 's, the lower polariton branch starts from zero energy. The polariton picture strongly modifies the conventional treatments of the relaxation kinetics formulated in terms of the quadratic dispersion of ortho- x 's. The lower polariton branch gives rise to a "polariton bottleneck" relaxation kinetics, which had been developed initially for the excitons with strong dipole coupling with the light field.¹¹ The ortho- x 's occupy predominantly the lower polariton states that lie below the initial excitonic dispersion unperturbed by the polariton effect, rather than the mode $\mathbf{k}=0$, which refers to the local minimum of the upper polariton branch. Our numerical simulations of the LA-phonon-assisted relaxation, done within the quadrupole polariton picture, clearly indicate such a thermalization kinetics for ortho- x 's. Therefore, we conclude that the polariton effect prevents a steady-state BE condensation of ortho- x 's in Cu_2O .

In Sec. II, we develop the phonon-assisted relaxation kinetics of paraexcitons in Cu_2O at $T_b > T_c$ and $T_b \leq T_c$. For $T_b \gg T_c$ the thermalization completes within a few scattering times τ_{sc} . For $T_b \rightarrow T_c$ from above, we describe the thermodynamic critical slowing down that results in a nonexponential thermalization of para- x 's. At $T \leq T_c$, the relaxation kinetics consists of a transient stage, which correlates with an initial distribution and lasts a few τ_{sc} , and the following slow adiabatic stage. For the adiabatic stage, we apply the generic solution⁹ of the phonon-assisted Boltzmann kinetics at $T_b \leq T_c$ and show that even in the μs time scale the low-energy para- x 's are far from the equilibrium, i.e., without a macro-occupation of the ground-state mode $\mathbf{k}=0$. At the end of this section, we present numerical calculations of the relaxation kinetics in the presence of an optical-phonon-assisted decay of para- x 's. A quasi-steady-state BEC of para- x 's is not found.

In Sec. III, we discuss the LA-phonon-mediated relaxation kinetics of ortho- x 's within a quadrupole-allowed polariton picture, i.e., in terms of "polariton \pm LA-phonon \leftrightarrow polariton" scattering. A criterion of the coexistence of a weak polariton effect and a quasi-steady-state BEC in the relative energy minimum of the upper polariton branch is proposed and tested for Cu_2O . The well-developed polariton bottleneck relaxation kinetics along the lower polariton dispersion branch rather than an effective accumulation of orthoexcitons at the upper polariton branch is found in numerical simulations.

In Sec. IV, we apply our results to give an alternative interpretation of the experimental data on the search for a quasiequilibrium BE condensation of para- x 's (ortho- x 's) in Cu_2O . A brief discussion of the importance of the exciton-exciton interaction is given with respect to the BEC phenomenon.

In the Appendix, we derive some important thermodynamic relationships between a change of the chemical poten-

tial $\delta\mu$ and the corresponding change of the temperature δT of a gas of bosons at $T \gg T_c$ and $T \rightarrow T_c$ from above.

II. PHONON-ASSISTED KINETICS OF PARAEXCITONS

The Boltzmann kinetics of a spatially homogeneous gas of para- x 's coupled to a bath of LA phonons and in the presence of a weak LO-phonon-assisted radiative decay of para- x 's is given by

$$\begin{aligned} \frac{\partial}{\partial t} N_{\mathbf{k}} = & -\frac{2\pi}{\hbar^2} \sum_{\mathbf{p}} |M_{x\text{-ph}}(\mathbf{p}-\mathbf{k})|^2 \{ [N_{\mathbf{k}}(1+n_{\mathbf{k}-\mathbf{p}}^{\text{ph}})(1+N_{\mathbf{p}}) \\ & - (1+N_{\mathbf{k}})n_{\mathbf{k}-\mathbf{p}}^{\text{ph}}N_{\mathbf{p}}] \delta(e_{\mathbf{k}} - e_{\mathbf{p}} - \hbar\omega_{\mathbf{k}-\mathbf{p}}) \\ & + [N_{\mathbf{k}}n_{\mathbf{p}-\mathbf{k}}^{\text{ph}}(1+N_{\mathbf{p}}) - (1+N_{\mathbf{k}})(1+n_{\mathbf{p}-\mathbf{k}}^{\text{ph}})N_{\mathbf{p}}] \\ & \times \delta(e_{\mathbf{k}} - e_{\mathbf{p}} + \hbar\omega_{\mathbf{p}-\mathbf{k}}) \} - N_{\mathbf{k}}/\tau_{\text{opt}}, \end{aligned} \quad (1)$$

where $e_{\mathbf{k}} = \hbar^2 k^2 / (2M_x)$ and $\hbar\omega_{\mathbf{p}-\mathbf{k}} = \hbar v_s |\mathbf{p}-\mathbf{k}|$ are the para- x 's and LA-phonon energies, respectively, $N_{\mathbf{k}}$ and $n_{\mathbf{p}-\mathbf{k}}^{\text{ph}} = 1 / [\exp(\hbar\omega_{\mathbf{p}-\mathbf{k}}/T_b) - 1]$ (we put $k_B = 1$) are the para- x 's and phonon occupation numbers, respectively, $M_{x\text{-ph}}(\mathbf{p}-\mathbf{k})$ is the matrix element of the x -LA-phonon deformation potential interaction, and τ_{opt} is the radiative lifetime of para- x 's. The x -LA-phonon coupling is given by $|M_{x\text{-ph}}(\mathbf{p}-\mathbf{k})|^2 = \hbar D^2 |\mathbf{p}-\mathbf{k}| / (2V\rho v_s)$, where D is the deformation potential, V is the crystal volume, ρ is the crystal density, and v_s is the longitudinal acoustic sound velocity.

If an initial distribution of paraexcitons $N_{\mathbf{k}}(t=0)$ is isotropic in momentum space, Eq. (1) reduces to a kinetic equation for the distribution function N_e of para- x 's in energy space, where $e = \hbar^2 k^2 / 2M_x$ [see Eq. (2) of Ref. 9(a)]. In numerical simulations of the relaxation kinetics we use the energy representation, i.e., the distribution function $N_e(t)$. The characteristic scattering time of the LA-phonon-assisted Boltzmann kinetics of excitons in Cu_2O is given by $\tau_{sc} = (\pi\hbar^4 \rho) / (4D^2 M_x^3 v_s n_{e_0}^{\text{ph}})$ as the probability of anti-Stokes scattering of a para- x from the ground-state mode $e=0$. Here, $e_0 = 2M_x v_s^2 = 0.621$ meV is the energy of the partner state coupled to the ground-state mode by the emission or absorption of an acoustic phonon [see Fig. 1 of Ref. 9(a)].

In this section we (i) analyze with Eq. (1) the thermalization kinetics of paraexcitons at $T_b > T_c$ and, in particular, develop thermodynamics of the phonon-assisted critical slowing down of the quasiequilibrium relaxation at $T_b \rightarrow T_c$; (ii) apply to the paraexcitons with a finite radiative lifetime τ_{opt} the generic solution of the phonon-assisted Boltzmann kinetics at $T_b \leq T_c$ in order to show that an extremely slow nonexponential relaxation towards BE condensation does not end up with a macro-occupation of the ground-state mode $e=0$.

A. Relaxation of paraexcitons for $T > T_c$

In order to realize the general tendencies of the phonon-mediated relaxation kinetics of para- x 's, at first we analyze the thermodynamic aspects of this problem. Let us treat a relaxation transition $(\mu + \Delta\mu, T + \Delta T) \rightarrow (\mu, T)$ between two close thermodynamic states of a gas of bosons. The second state corresponds to the final BE distribution $N_e^f = N_e^{\text{eq}}(\mu, T) = 1 / \{\exp[(e - \mu)/T] - 1\}$ in equilibrium with

the phonon bath, i.e., $T=T_b>T_c$. In other words, at the beginning of this subsection we examine within kinetic Eq. (1) the phonon-assisted thermodynamic relaxation of bosons (para- x 's) initially distributed by $N_e(t=0)=N_e^i=N_e^{\text{eq}}(\mu+\Delta\mu, T+\Delta T)=1/\{\exp[(e-\mu-\Delta\mu)/(T+\Delta T)]-1\}$.

With the specified above initial and final distributions, the kinetic Eq. (1) for the ground-state mode $\mathbf{k}=0$ (the particle energy $e=0$) reduces to

$$\frac{\partial}{\partial t}N_{e=0}=\sigma(\mu)\delta TN_{e=0}, \quad (2)$$

where

$$\sigma(\mu)=\frac{1}{\tau_{\text{sc}}}\left[1-\exp\left(\frac{\mu-e_0}{T_b}\right)\right]^{-1}\left(\frac{e_0}{T_b^2}\right). \quad (3)$$

Here, we assume that the phonon-assisted relaxation occurs through a sequence of the quasiequilibrium thermodynamic states $(\mu+\delta\mu, T+\delta T)$ with $\Delta T\geq\delta T(t)\geq 0$ and $-\Delta\mu\geq-\delta\mu(t)\geq 0$. The right-hand side (rhs) of Eq. (2) indeed vanishes in the final equilibrium of bosons with the phonon bath, due to $\delta T=0$. The substitution of the corresponding BE distributions in Eq. (2) yields the thermodynamic relationship:

$$\frac{(\delta\mu)'}{T_b}-\frac{\mu}{T_b^2}(\delta T)'=\sigma(\mu)[1-e^{\mu/T_b}]\delta T, \quad (4)$$

where $f'\equiv df/\delta t$.

The further analysis depends crucially on a link between $\delta\mu$ and δT of a Bose gas with the constant concentration n_0 . For $T=T_b>T_c$ one gets (see Appendix A):

$$-\delta\mu=\left[\frac{3}{2}\left(\frac{F_1(\mu/T_b)+1}{F_2(\mu/T_b)+1}\right)-\frac{\mu}{T_b}\right]\delta T, \quad (5)$$

where $F_{1,2}(\mu/T)$ with $\mu<0$ are defined by Eq. (A4) of Appendix A. Equations (4) and (5) yield the temperature law:

$$(\delta T)'=-\delta T/\tau^* \quad (6)$$

with solution $\delta T(t)=\Delta T \exp[-t/\tau^*]$. Here, the characteristic time τ^* of the temperature relaxation is given by

$$\tau^*=\frac{3}{2}\tau_{\text{sc}}\left(\frac{F_1(\mu/T_b)+1}{F_2(\mu/T_b)+1}\right)\left(\frac{T_b}{e_0}\right)[1-e^{\mu/T_b}]^{-1}\times[1-e^{-(e_0-\mu)/T_b}]. \quad (7)$$

The corresponding occupation kinetics of the ground-state mode $e=0$ is determined by

$$\begin{aligned} N_{e=0}(t) &= N_{e=0}^f - \frac{3}{2}\left(\frac{\Delta T}{T_b}\right)\frac{e^{-\mu/T_b}}{(e^{-\mu/T_b}-1)^2} \\ &\quad \times \left(\frac{F_1(\mu/T_b)+1}{F_2(\mu/T_b)+1}\right)e^{-t/\tau^*} \\ &= N_{e=0}^f - (N_{e=0}^f - N_{e=0}^i)e^{-t/\tau^*}. \end{aligned} \quad (8)$$

The effective time τ^* is a well-defined characteristic of relaxation because it is independent of the initial value ΔT (or $\Delta\mu$). Moreover, for $T\gg T_c$ the complete relaxation indeed

occurs within a few elementary scattering times because in this case $\tau^*\sim\tau_{\text{sc}}$ according to Eq. (7).

The *exponential* cooling given by Eq. (6) originates from the proportionality $(-\delta\mu)\propto\delta T$ in accordance with Eq. (5). As it is shown in Appendix A, this thermodynamic relationship breaks for $T\rightarrow T_c$ from above ($T>T_c$). For a close vicinity of $T_b=T_c$ ($\delta T>0$), Eq. (5) changes on (see Appendix A)

$$-\delta\mu=\frac{9}{16\pi}\zeta^2(3/2)\frac{(\delta T)^2}{T_c}. \quad (9)$$

In this case, we derive from Eqs. (4) and (9):

$$(\delta T)'=-\frac{1}{2}\sigma_0(\delta T)^2, \quad (10)$$

where $\sigma_0=\sigma(\mu=0)$. The solution of Eq. (10), which satisfies the initial condition, is

$$\delta T(t)=\frac{\Delta T}{\sigma_0\Delta T t+1}. \quad (11)$$

The corresponding phonon-assisted kinetics of the ground-state mode occupation is given by

$$\begin{aligned} N_{e=0}(t) &= \frac{16\pi}{9\zeta^2(3/2)}\left(\frac{T_c}{\Delta T}\right)^2[\sigma_0\Delta T t+1]^2 \\ &= N_{e=0}^i[\sigma_0\Delta T t+1]^2. \end{aligned} \quad (12)$$

The *nonexponential* behavior given by Eqs. (11) and (12) clearly indicates a slowing down of the phonon-assisted relaxation for $T_b\rightarrow T_c$ ($\Delta T>0$). Such a *critical slowing down* of the thermodynamic processes is a general feature of the second-order phase transitions.¹² As a manifestation that the exponential kinetics of Eq. (8) becomes invalid for $T_b\rightarrow T_c$, the effective relaxation time τ^* increases smoothly with decreasing T_b towards T_c . Moreover, formally, $\tau^*\rightarrow\infty$ if $T_b=T_c$. In this limit, the denominator on the rhs of Eq. (7) approaches zero because $[F_2(\mu/T_b)+1][1-\exp(\mu/T_b)]|_{\mu\rightarrow 0}\rightarrow 0$.

The developed analysis of the phonon-assisted relaxation implies that a Bose gas evolves thermodynamically, i.e., through a sequence of the quasiequilibrium states. Such a scenario can be justified only in the presence of strong particle-particle interaction, which is conservative and equilibrates the system without change of the total energy. The energy (temperature) relaxation is solely due to the contact with a phonon thermostat. If the particle-particle interaction is considerably stronger than the particle-phonon coupling, the both kinetics can be naturally separated (see, e.g., the corresponding discussion in Ref. 13) and the developed thermodynamic approach is correct.

However, the further analysis of relaxation of a low-density system of paraexcitons within the phonon-assisted kinetics of Eq. (1) implies that the x - x interaction is neglected and that the evolution to the final equilibrium occurs through a sequence of the *nonequilibrium* states. In this case, the relaxation kinetics strongly depends upon the initial distribution $N_e(t=0)$. Some numerical modeling of the phonon-assisted Boltzmann kinetics of excitons are reported in Refs. 14 and 15. A typical example of the thermalization kinetics at $T_b\gg T_c$, which is evaluated numerically within

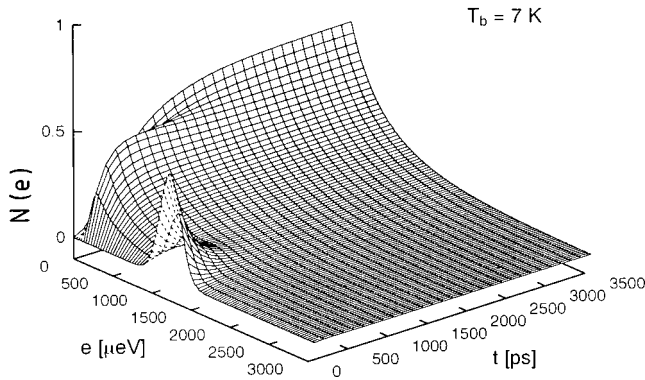


FIG. 1. Relaxation of an initial Gaussian distribution of paraexcitons in Cu_2O with the central energy $\tilde{e}=1.237$ meV, the spectral width $\Delta e=0.186$ meV, and the density $n_0=8.7\times 10^{16}$ cm^{-3} to the bath temperature $T_b=7$ K. The critical temperature $T_c=2.135$ K. The following parameters of Cu_2O have been used in numerical evaluations: $M_x=2.7 m_0$, $D=-1.38$ eV, $v_s=4.5\times 10^5$ cm/s, and $\rho=6.11$ g/ cm^3 .

Eq. (1) reduced to the kinetic equation in energy space [see Eq. (2) of Ref. 9(a)], is shown in Fig. 1. Here, the initial distribution is given by the Gaussian $N_e(t=0)=N_e^i \exp[-(e-\tilde{e})^2/(\Delta e)^2]$ with the central energy $\tilde{e}=1.237$ meV and the width $\Delta e=0.186$ meV. These parameters correspond to the concentration $n_0=0.87\times 10^{17}$ cm^{-3} .

Figure 2 summarizes the numerical modeling of the phonon-mediated relaxation kinetics into the ground-state mode $e=0$ from the different initial distributions $N_e(t=0)$ of the same concentration n_0 . In particular, the relaxation from the BE initial distributions $N_e(t=0)=N_e^i=N_e^{\text{eq}}(\mu+\Delta\mu, T+\Delta T)$ with various deviations $(\Delta\mu, \Delta T)$ are examined. Although the thermalization indeed occurs through the nonequilibrium intermediary states and depends on the initial distribution $N_e(t=0)$, typically it lasts a few scattering times τ_{sc} ($\tau_{\text{sc}}=327$ ps for $T_b=7$ K) as can be seen in Figs. 2(a,b). Moreover, the dependences $\Delta N_{e=0}(t)=N_{e=0}^f-N_{e=0}(t)$ plotted in the semilogarithmic scale [see Fig. 2(b)] clearly show an “exponential” character of the phonon-assisted relaxation at $T_b\gg T_c$.

Within the phonon kinetics of Eq. (1), the characteristic transition time $\tilde{\tau}_{\text{sc}}$ between the two BE distributions of the initial $(\mu+\Delta\mu, T_b+\Delta T)$ and final (μ, T_b) thermodynamic states can be estimated from Eq. (4) of Ref. 9(a) as $\tilde{\tau}_{\text{sc}}=(N_{e=0}^f-N_{e=0}^i)/[\sigma(\mu)\Delta TN_{e=0}^i]$. Substitution of the BE distributions $N_{e=0}^f$ and $N_{e=0}^i$ in this expression yields $\tilde{\tau}_{\text{sc}}=\tau^*$. Numerical calculations confirm this conclusion. For example, the curve of relaxation from $N_{e=0}^i$ at $T=T_b+\Delta T=7.1$ K is only “translationally” shifted from the curve, which corresponds to $T=8$ K. Moreover, both of these lines are approximately parallel to the straight reference line of the exponential law $\Delta N_{e=0}\propto\exp[-t/\tau^*]$ of Eq. (8) [see Fig. 2(b)].

B. Relaxation of paraexcitons for $T\leq T_c$

In previous subsection we have attributed the critical slowing down of the phonon-assisted relaxation thermodynamics to the change of $(-\delta\mu)\propto\delta T$ for $T_b\gg T_c$ on

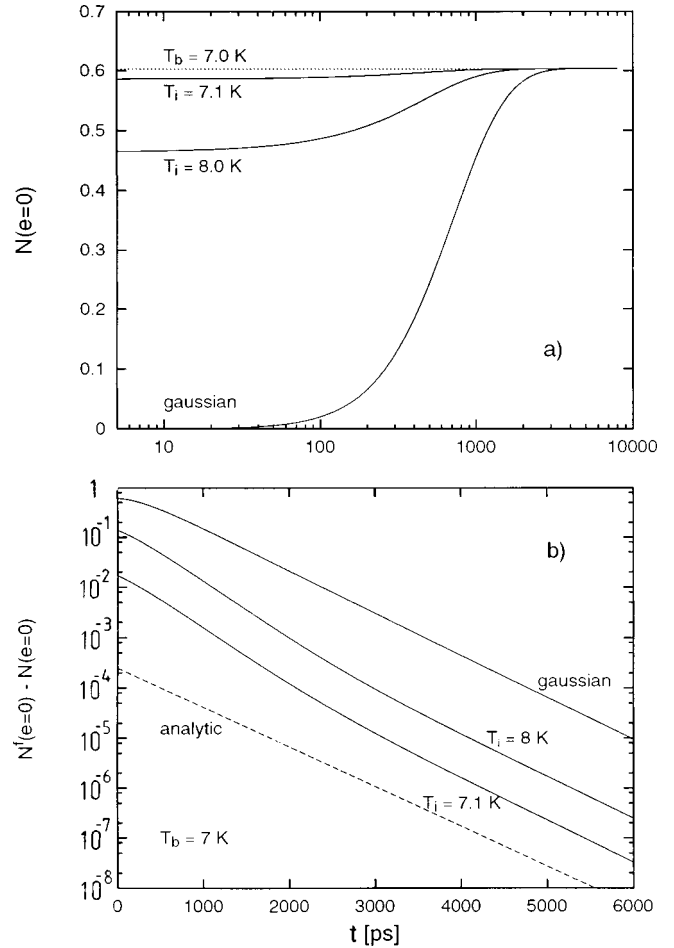


FIG. 2. (a) Occupation number $N_{e=0}(t)$ of the ground-state mode for various initial conditions versus time t (full lines). The final equilibrium occupation number $N_{e=0}^f=N_{e=0}^{\text{eq}}$ for $T_b=7$ K is shown by the dotted line. (b) Difference of the final $N_{e=0}^f$ and nonequilibrium $N_{e=0}(t)$ occupation numbers for the same initial conditions (full lines) and the analytic law of Eq. (15) (dashed line).

$(-\delta\mu)\propto(\delta T)^2$ for $T_b\rightarrow T_c$ ($T_b\geq T_c$). On the other hand, the bottleneck relaxation into the ground-state mode $e=0$ together with the need to accumulate at this mode a macroscopic number of para- x 's are responsible for the slowing down of the relaxation kinetics at $T_b\leq T_c$.⁹ The low-energy states $e\leq e_0/4=M_x v_s^2/2\approx 0.155$ meV of paraexcitons in Cu_2O couple only through anti-Stokes scattering with the corresponding phonon-separated partner modes [see Fig. 1 of Ref. 9(a)]. Moreover, the bottleneck relaxation takes place for all low-energy states $e\leq T_b$ in the close vicinity of $e=0$ ($T_b\leq T_c\leq e_0$ for the considered concentrations $n_0\leq 10^{17}$ cm^{-3}). Similar to the ground-state mode $e=0$, for these modes $N_{e=0}^{\text{eq}}\approx T_b/e\gg 1$ and simultaneously the anti-Stokes partner states have a high energy $\sim e_0$ to be nondegenerate and to suppress the stimulated relaxation, due to $N_{e=e_0}\rightarrow n_{e=e_0}^{\text{ph}}$ [see Fig. 1 of Ref. 9(a)].

A unique scenario of the relaxation kinetics of an ideal Bose gas coupled to a phonon bath at temperatures below or equal to the critical temperature T_c has been developed in Ref. 9. The high-energy states with nondegenerate statistics $N_{e=0}^{\text{eq}}\ll 1$ equilibrate first. After a few scattering times, the low-energy [$e\leq e_c(t)\leq T_b$] and the high-energy [$e>e_c(t)$]

bosons form two subsystems weakly interacting through the phonon-mediated scattering. The H theorem,¹⁶ applied to the high-energy bosons, yields a quasiequilibrium Planck distribution $N_{e>e_c} = 1/[\exp(e/T) - 1]$ with the effective temperature $T = T_b + \delta T(t)$. The effective chemical potential $\delta\mu$ of the quasiequilibrated high-energy bosons can be neglected because $(-\delta\mu) \ll \delta T$. Here, we again exploit the thermodynamic property $(-\delta\mu) \propto (\delta T)^2$ which is valid for $T_b \approx T_c$. At this adiabatic stage of the relaxation, the low-energy subsystem shrinks in energy space ($e_c(t) \rightarrow 0$), while the effective temperature T of the high-energy bosons approaches the bath temperature T_b [$\delta T(t) \rightarrow 0$]. The absence of the direct phonon-mediated interaction between the low-energy bosons results in their slow adiabatic equilibration through the resonant coupling with the high-energy quasiequilibrium states $e \sim e_0$.

During the first transient stage of the phonon-assisted relaxation at $T_b \leq T_c$, which lasts a few characteristic scattering times τ_{sc} , the initial distribution disappears. The following nonexponential relaxation towards a quantum degenerate equilibrium state with a Bose-Einstein condensate is a slow adiabatic process. For this second kinetic stage an *analytic generic solution* of the Boltzmann equation (1) with $\tau_{opt} \rightarrow \infty$ has been found.⁹ Namely, the nonequilibrium distribution of bosons is given by

$$\begin{aligned} N_e(\tau) &= \tau \int_0^1 \left[\frac{\alpha \sqrt{\tau}}{1/2 + \alpha} (u^{-\alpha-1/2} - 1) + \frac{1}{\sqrt{u}} \right] e^{-\tau \varepsilon (1-u)} du \\ &= \frac{\alpha \sqrt{\tau}}{1/2 + \alpha} \left[\frac{\tau^{3/2}}{1/2 - \alpha} e^{-\tau \varepsilon} \Phi(1/2 - \alpha, 3/2 - \alpha, \tau \varepsilon) \right. \\ &\quad \left. - \frac{\sqrt{\tau}}{\varepsilon} (1 - e^{-\tau \varepsilon}) \right] + 2 \sqrt{\frac{\tau}{e^\varepsilon - 1}} Ds[\sqrt{\tau}(e^\varepsilon - 1)^{1/2}], \end{aligned} \quad (13)$$

where $\varepsilon = e/T_b$ and $\tau = t[1 - \exp(-e_0/T_b)]^{-1} \tau_{sc}^{-1} \approx t/\tau_{sc} \geq \tau_{tr} = \Delta t_{tr}/\tau_{sc} \geq 1$ are the dimensionless energy and time, respectively, Δt_{tr} is the duration of the first transient relaxation, which depends upon an initial distribution at $t=0$, Φ is the degenerate hypergeometric function,¹⁷ and $Ds[x] = \exp(-x^2) \int_0^x dt \exp(t^2)$ is Dawson's integral.¹⁸ The corresponding fundamental law of the phonon-assisted adiabatic cooling of the high-energy quasiequilibrium bosons is

$$\delta T(\tau) = \left(\frac{T_b^2}{e_0} \right) \frac{1}{2\tau} \left[1 + \frac{1 + 2\alpha}{1 + (1/2\alpha)\tau^{-\alpha-1/2}} \right]. \quad (14)$$

The dimensionless parameter $\alpha > 0$ in Eqs. (13) and (14) is a real solution of the following transcendent equation:

$$\left(\frac{\alpha}{\alpha + 1} \right) \int_0^1 \frac{du}{(1-u)^{3/2}} [u^{-\alpha-1/2} - 1] = \zeta(3/2) \left[\left(\frac{T_c}{T_b} \right)^{3/2} - 1 \right]. \quad (15)$$

Equations (13) and (14) are the generic solution of the phonon-assisted kinetics of a Bose gas at $T_b \leq T_c$. This generic solution is completely defined by the ratio T_c/T_b of the critical and bath temperatures through the solution $\alpha = \alpha(T_c/T_b)$ of Eq. (15). Equation (15) has only one real

root $0 \leq \alpha < 1/2$ for given T_c/T_b . For $T_b \rightarrow T_c$ ($T_b \leq T_c$) the solution $\alpha \ll 1/2$ can be approximated by $\alpha = 0.25\zeta(3/2)[(T_c/T_b)^{3/2} - 1] = [\hbar^2/(2\sqrt{\pi}M_x T_b)]n_c$. Here, we have a unique example of the fundamental solution of the Boltzmann kinetics that is insensitive to an initial distribution of bosons at $t=0$. The only information from the initial distribution, which influences the total kinetics at $T_b \leq T_c$, is the duration Δt_{tr} of the first transient stage, typically a few τ_{sc} . Physically, this means that during the slow adiabatic stage, which lasts a great number of τ_{sc} , a system of bosons loses correlations with the initial distribution $N_e(t=0)$. For $\tau > \tau_{tr}$ the effective temperature $T = T_b + \delta T(\tau)$ and the distribution function of bosons asymptotically approach the generic solution (14) and (13), respectively, with α given by Eq. (15).

The generic solution (13) and (14) has been applied to the LA-phonon-assisted relaxation of para- x 's in Cu₂O modeled numerically within the initial kinetic Eq. (1) with $1/\tau_{opt} = 0$.⁹ According to Fig. 5 of Ref. 9(b), the time-dependence $\delta T = \delta T(\tau)$ of the adiabatic cooling of high-energy quasiequilibrium para- x 's is indeed described uniquely for various $T_b \leq T_c$ by the generic solution (14). The time evolution of the distributions $\sqrt{e}N_e(t)$ and $N_e(t)$ as numerical evaluation of Eq. (1) is compared with the corresponding generic solution (13) for $T_b = T_c = 2.135$ K [see Fig. 6 of Ref. 9(b)] and for $T_b = 1.5$ K $< T_c$ [see Fig. 7 of Ref. 9(b)]. These plots show that the fundamental solution (13) with α given by Eq. (15) rather well reproduces the adiabatic stage of the phonon-assisted relaxation of para- x 's in the time scale of a few μ s.

According to Eq. (13), the *nonexponential* relaxation into the ground-state mode $e=0$ is given by

$$N_{e=0}(\tau) = 2\tau + \left(\frac{\alpha}{1/2 - \alpha} \right) \tau^{3/2}. \quad (16)$$

Equation (16) shows a drastic slowing down of the entire phonon-assisted relaxation kinetics. The relaxation kinetics has a marginal character at $T_b = T_c$, i.e., for $\alpha=0$. In this case, one gets from Eq. (16) $N_{e=0}(\tau) = 2\tau$ in contrast with the phonon-assisted relaxation at $T_b < T_c$, when $0 < \alpha < 1/2$ and $N_{e=0}(\tau)|_{\tau \rightarrow \infty} \propto [\alpha/(1/2 - \alpha)]\tau^{3/2}$. The adiabatic stage of the phonon-assisted thermodynamic relaxation for $T_b \rightarrow T_c$ from above ($T_b \geq T_c$):

$$N_{e=0}(\tau) = \frac{16\pi}{9\zeta^2(3/2)} \left(\frac{e_0}{T_c} \right)^2 \tau^2 \quad (17)$$

results from Eq. (12) provided that $(\sigma_0 \Delta T)t \geq 1$. Again, Eq. (17) shows that the adiabatic stage is independent of the initial quasiequilibrium BE distribution ($\mu = \Delta\mu, T = T_c + \Delta T$). The condition $(\sigma_0 \Delta T)t \geq 1$ written in the dimensionless units yields the duration of the "transient" thermodynamic relaxation as $\tau_{tr} = T_c^2/(e_0 \Delta T)$. This transient depends upon the initial distribution through ΔT . The thermodynamic kinetics of Eq. (17) is inconsistent with Eq. (16) for $T_b = T_c$ because the phonon-assisted kinetics of a low-density gas of bosons (paraexcitons) occurs through the nonequilibrium intermediary states. In particular, in the resonantly coupled energy modes $e=0$ and e_0 of para- x 's, only the high-energy partner state is in the BE quasiequilibrium.

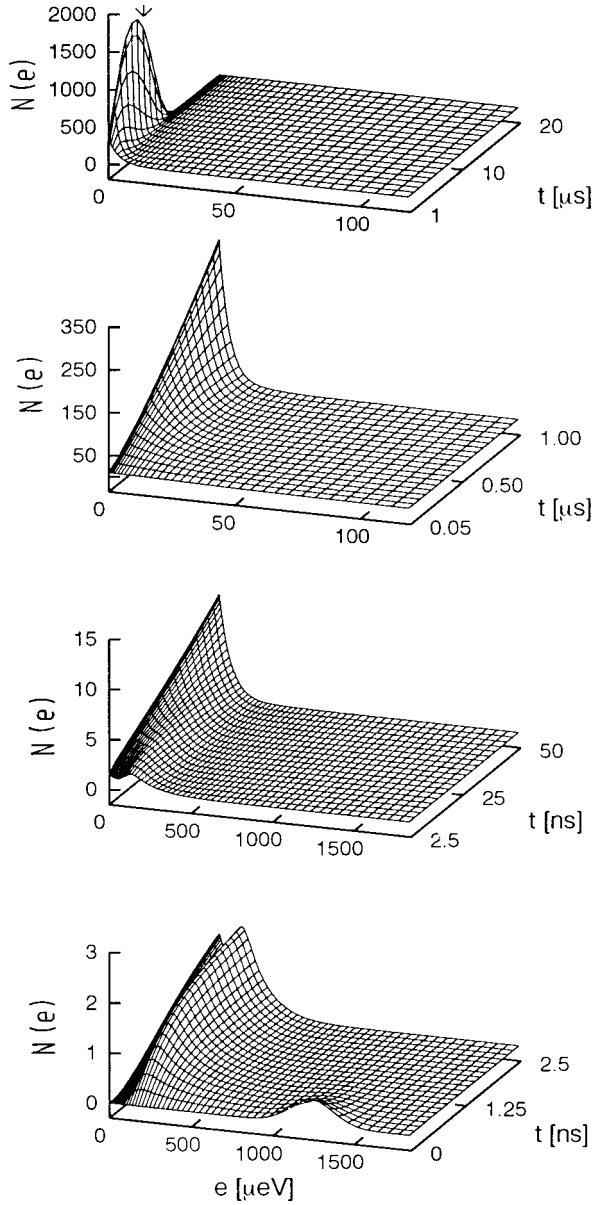


FIG. 3. Evolution of an initial Gaussian distribution with the same parameters as in Fig. 1, $T_c(t=0)=2.135$ K and the bath temperature $T_b=1.5$ K. The \perp_5 optical phonon-assisted radiative lifetime of paraexcitons $\tau_{\text{opt}}=13\mu\text{s}$. The arrow marks the transition from $T_c(t)>T_b$ to $T_c(t)<T_b$.

The generic solution given by Eq. (13) evolves to the true equilibrium distribution $N_\varepsilon^{\text{eq}}$, i.e., $N_\varepsilon(\tau\rightarrow\infty)\rightarrow N_\varepsilon^{\text{eq}}=(n_c/\sqrt{\varepsilon})\delta(\varepsilon)+1/(e^\varepsilon-1)$.⁹ On the other hand, from Eq. (13) one concludes that $\sqrt{\varepsilon}N_\varepsilon\rightarrow 0$ for $\varepsilon\rightarrow 0$ and any given $\tau>0$, while for the Planck distribution one has $\sqrt{\varepsilon}N_\varepsilon^{\text{eq}}\propto 1/\sqrt{\varepsilon}\rightarrow\infty$ for $\varepsilon\rightarrow 0$. As a result, BE condensation into the ground-state mode builds up within the phonon-assisted kinetics only at $\tau\rightarrow\infty$. The absence of the BE condensate of para- x 's ($\sqrt{\varepsilon}N_\varepsilon\rightarrow 0$ for $\varepsilon\rightarrow 0$) is traced in Fig. 6 of Ref. 9(b) up to $t=20\mu\text{s}$. Furthermore, a finite radiative lifetime of paraexcitons τ_{opt} in the μs time scale prevents a genuine BE condensation provided the absence of a condensate seed in the initial distribution $N_\varepsilon(t=0)$. Figure 3 shows a typical behavior of the phonon-assisted kinetics of para- x 's with the finite lifetime. The numerical evaluation within Eq. (1) is

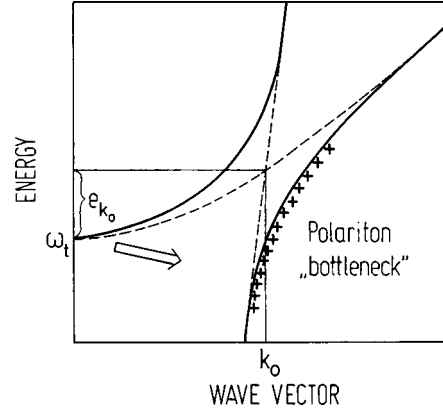


FIG. 4. Schematic picture of the polariton dispersion of quadrupole-allowed orthoexcitons.

given for $\tau_{\text{opt}}=13\mu\text{s}$, $T_b=1.5$ K and $T_c(t=0)=2.135$ K. The radiative decay of para- x 's results in a continuous decrease of $T_c=T_c(t)\propto n_0^{3/2}(t)$ with a time and the crossover $T_c(t=\Delta t_{\text{cr}})=T_b$ occurs at the dimensional time

$$\Delta t_{\text{cr}}=\frac{3}{2}\tau_{\text{opt}}\ln\left(\frac{T_c}{T_b}\right). \quad (18)$$

For $t>\Delta t_{\text{cr}}$ the gas of paraexcitons even potentially cannot condense and evolves rather quickly ($\sim\tau_{\text{sc}}$) to the classical Boltzmann quasiequilibrium distribution. The parameters of Fig. 3 correspond to the crossover point at $\Delta t_{\text{cr}}\approx 6.9\mu\text{s}$ (see the vertical arrow in Fig. 3).

III. PHONON-MEDIATED RELAXATION OF ORTHOEXCITON POLARITONS

A weak, but still well-developed, quadrupole polariton effect has been observed recently for orthoexcitons in Cu_2O by a high-precision “propagation beats” spectroscopy.¹⁰ The dispersion of quadrupole polaritons is given by

$$\frac{c^2k^2}{\epsilon_b\omega^2}=1+\frac{\Omega_c^2(k)}{\omega_t^2+\hbar\omega_t(k^2/M_x)-i\omega\Gamma^x-\omega^2}, \quad (19)$$

where $\Omega_c(k)=(fc^2k^2/\epsilon_b)^{1/2}$ is the polariton parameter of the ortho- x -photon coupling, f is the corresponding dimensionless polariton oscillator strength, ϵ_b is the background dielectric constant, $\hbar\omega_t$ is the energy of an orthoexciton at rest, and Γ^x is the damping rate. The dispersion Eq. (19) yields the upper $\omega=\omega^+(k)$ and lower $\omega=\omega^-(k)$ polariton branches (see Fig. 4). Because the quadrupole polariton parameter $\Omega_c(k)$ is proportional to the wave vector k , the upper polariton branch starts from ω_t , i.e., $\omega^+(k=0)=\omega_t$.

The polariton effect strongly influences the low-temperature relaxation kinetics and particularly the approach of a BEC phase. The x -photon coupling modifies the bare exciton mass M_x and replaces it by an effective mass M_x^+ of the upper polariton branch at $\mathbf{k}=0$. From Eq. (19) we find

$$M_x^+=\frac{M_x}{1+(fc^2M_x/\epsilon_b\omega_t)}. \quad (20)$$

For an ortho- x in Cu_2O this correction is rather small, i.e., $(M_x-M_x^+)/M_x\sim 10^{-3}$. However, for dipole-active excitons

(e.g., in CdS, CuCl, etc.) $M_x^+ = M_x / [1 + 2(\omega_l M_x c^2) / (\epsilon_b \omega_l^2)]$ and, as a result, $M_x^+ \ll M_x$ (ω_l is the longitudinal-transverse polariton splitting). If one treats the relaxation kinetics only within the upper polariton branch, a decrease of M_x^+ leads to an increase of T_c together with a decrease of the density of states of the dispersion $\omega^+(k)$ at $k \approx 0$. However, the presence of the lower polariton branch interferes with an accumulation of x 's (polaritons) at the energy minimum of $\omega^+(k)$ at $\mathbf{k} = 0$ and gives rise to the polariton bottleneck relaxation kinetics.¹¹

Within the complete, two-branch, polariton picture the dispersion $\omega^+(k)$ has only a *relative* minimum (see Fig. 4). The lower polariton dispersion branch has no energy minimum apart from $\omega^-(k=0) = 0$ and allows the polariton energies $\hbar\omega^-(k) < \hbar\omega_l$. Due to the relatively high density of states at $\omega^-(k)$, excitons (polaritons) start to occupy the lower polariton branch rather than the state $\mathbf{k} = 0$ of the upper branch. The bottleneck relaxation is a diffusion of polaritons down in energy along the lower polariton branch. This kinetics effectively slows down due to the decay of the both density-of-states and excitonic component of the lower-branch polaritons with detuning $\omega_l - \omega^-(k) > 0$. Furthermore, within a finite lifetime the bottleneck relaxation does not result in a final equilibrium thermodynamic state of the gas of polaritons.

The described relaxation picture is valid in the presence of a well-developed polariton effect. However, an effective occupation of the modes $\mathbf{k} \approx 0$ can coexist with a weak quadrupole polariton effect provided that

$$e_{\text{opt}} = \frac{\hbar^2 k_0^2}{2M_x} \gg \hbar\Omega_c(k_0), \quad (21)$$

where the wave vector k_0 corresponds to a crossover point of the unperturbed photon $\omega^\gamma = ck/\sqrt{\epsilon_b}$ and exciton $\omega^x = \omega_l + \hbar k^2/2M_x$ dispersions (see Fig. 4). In this case, the ‘‘bottleneck’’ of the lower branch $\omega^-(k)$ lies above $\omega^+(k=0) = \omega_l$ and the mode $\mathbf{k} = 0$ of the upper branch has indeed the status of a ground-state mode. The criterion (21) provides the coexistence of a weak polariton effect and a possible quasi-steady-state BEC into the ‘‘ground-state’’ mode $\mathbf{k} = 0$ of the upper polariton dispersion branch. For ortho- x 's in Cu₂O, $k_0 = 2.6 \times 10^5 \text{ cm}^{-1}$ and $e_{\text{opt}} = \hbar^2 k_0^2/2M_x = 9.8 \text{ } \mu\text{eV}$, while $\Omega_c(k_0) = 124 \text{ } \mu\text{eV}$ according to the value $f = 3.7 \times 10^{-9}$ found experimentally in Ref. 10. Therefore, inequality (21) does not hold for orthoexcitons in Cu₂O.

The scattering processes give rise to the damping Γ^x in the dispersion Eq. (19). In the presence of damping, the polariton solutions $\omega = \omega^\pm(k)$ (quasiparticle solution, k is real) and $k = k^\pm(\omega)$ (forced-harmonic solution, ω is real) are not identical.¹⁹ While the forced-harmonic solution is very sensitive to Γ^x , the quasiparticle solution is nearly independent of the damping parameter (see Figs. 3 and 4 of Ref. 19). The Boltzmann kinetics within the polariton picture operates with the quasiparticle solution. Moreover, the damping of ortho- x quadrupole polaritons in Cu₂O is rather weak, i.e., $\Gamma^x \approx 0.9 \text{ } \mu\text{eV}$ at $T = 2 \text{ K}$ according to estimates of Ref. 10. Therefore, the low-temperature relaxation kinetics of orthoexcitons in Cu₂O has to be examined within the polariton picture.

The phonon-assisted relaxation kinetics in the polariton representation is given by the following Boltzmann equation:

$$\begin{aligned} \frac{\partial}{\partial t} N_{\mathbf{k}}^i = & -\frac{2\pi}{\hbar^2} \sum_{\mathbf{p}, j = \pm} |M_{x-\text{ph}}(\mathbf{p}-\mathbf{k})|^2 \varphi^i(k) \varphi^j(p) \\ & \times \{ [N_{\mathbf{k}}^i (1 + n_{\mathbf{k}-\mathbf{p}}^{\text{ph}}) (1 + N_{\mathbf{p}}^j) - (1 + N_{\mathbf{k}}^i) n_{\mathbf{k}-\mathbf{p}}^{\text{ph}} N_{\mathbf{p}}^j] \\ & \times \delta(\omega^i(k) - \omega^j(p) - \hbar\omega_{\mathbf{k}-\mathbf{p}}) + [N_{\mathbf{k}}^i n_{\mathbf{p}-\mathbf{k}}^{\text{ph}} (1 + N_{\mathbf{p}}^j) \\ & - (1 + N_{\mathbf{k}}^i) (1 + n_{\mathbf{p}-\mathbf{k}}^{\text{ph}}) N_{\mathbf{p}}^j] \delta(\omega^i(k) - \omega^j(p) \\ & + \hbar\omega_{\mathbf{p}-\mathbf{k}}) \}, \end{aligned} \quad (22)$$

where the superscript $i(j) = \pm$ refers to the upper (+) and lower (−) polariton branches, respectively, and the x weight functions φ^\pm are determined by

$$\varphi^+(k) = \frac{\omega^+(k) - \omega^\gamma(k)}{\omega^+(k) - \omega^-(k)}, \quad \varphi^-(k) = \frac{\omega^\gamma(k) - \omega^-(k)}{\omega^+(k) - \omega^-(k)}. \quad (23)$$

These functions satisfy the conditions $1 \geq \varphi^\pm(k) \geq 0$, $\varphi^+(k) + \varphi^-(k) = 1$ and describe the distribution of an exciton state between the two polariton branches. The kinetic Eq. (23) written in terms of ‘‘polariton $\pm \pm$ LA-phonon \leftrightarrow polariton \pm ’’ scattering includes both basic interactions, the x -photon coupling (polariton effect) and the x -phonon interaction. For the polariton parameter $\Omega_c \rightarrow 0$, Eq. (23) evolves to the kinetic Eq. (1). Due to the quadrupole ortho- x -photon coupling with $\Omega_c(k) \propto k$, Eqs. (23) include this interaction only in the resonant approximation.

The previous numerical simulations^{20,21} of the phonon-assisted polariton kinetics have been done for dipole-active excitons in a CdS crystal. In this case, the polariton effect is so well developed that $e_{\text{opt}}/\Omega_c \sim 10^{-4}$. As a result, the numerical evaluations clearly indicate a polariton bottleneck relaxation kinetics, i.e., an accumulation of excitons in the x -like parts of the lower polariton branch rather than in the mode $\mathbf{k} = 0$. Here, we report our numerical analysis of the phonon-assisted thermalization of ortho- x quadrupole polaritons in Cu₂O. Similar to the analysis of Eq. (1), the kinetic Eqs. (22) reduce to two coupled equations for $N_{\omega^+}^+$ and $N_{\omega^-}^-$ in the energy space provided that an initial distribution of ortho- x 's (quadrupole polaritons) is isotropic in momentum space.

A typical phonon-assisted relaxation kinetics of ortho- x 's is plotted in Figs. 5 and 6 for an initial isotropic Gaussian distribution placed at $k = 5k_0$ of the lower polariton branch and $T_b < T_c$. Here, the critical temperature T_c refers to ortho- x 's in the absence of the exciton-photon coupling and $D^\pm(\omega^\pm)$ are the density of states of the upper and lower polariton dispersion branches, respectively. The distribution function $D^-(\omega^-)N_{\omega^-}^-(t)$ (solid line) is strongly dominant and clearly shows a quick occupation (in ns time scale) of the lower branch at the bottleneck range $\omega^- < \omega_l$. The unoccupied band right below ω_l is due to the relatively high-energy ($\hbar v_s k_0 \approx 80 \text{ } \mu\text{eV}$) LA phonons that couple the bottleneck band with a regular distribution of orthoexcitons at $\omega^\pm > \omega_l$. In particular, the double-peak distribution $D^-(\omega^-)N_{\omega^-}^-(t)$ results in a ‘‘camel-back’’ line shape of the polariton luminescence. Such a camel-back line shape has

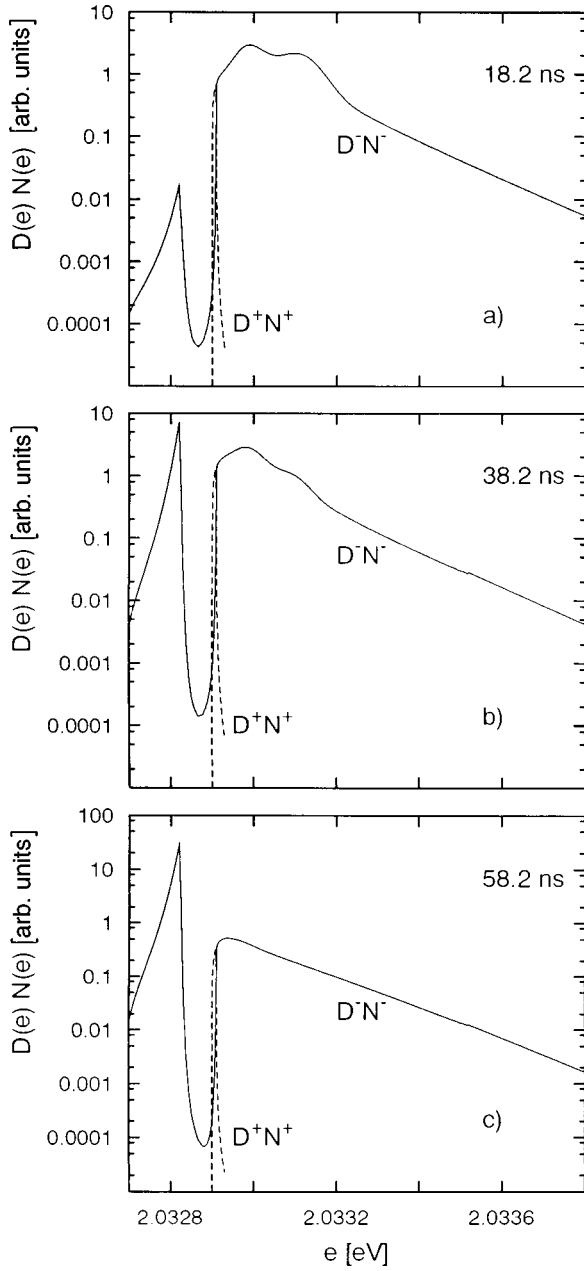


FIG. 5. Distribution functions $D^+(e=\omega^+)N^+(e=\omega^+)$ for upper (dashed line) and $D^-(e=\omega^-)N^-(e=\omega^-)$ for lower (solid lines) polariton branches at (a) $t=18.2$ ns, (b) $t=38.2$ ns, and (c) $t=58.2$ ns.

indeed been seen recently in resonant photoluminescence of low-density ortho- x 's in Cu_2O .²² On the other hand, this sharp structure is absent in the polariton bottleneck kinetics of dipole-active excitons because usually $\omega_{\text{it}} \geq \hbar v_s k_0$. Furthermore, according to Figs. 5 and 6 an effective population of the upper polariton branch is prevented. The distribution $D^+(\omega^+)N^+(t)$ (dashed lines in Fig. 5) even decays with a time at $t > 50$ ns.

While the distribution $N_{\omega^-}^-(t)$ of lower-branch polaritons is strongly nonequilibrium, it has a thermalized high-energy tail at $\omega^- \geq \omega_t$. Remarkably, the quasiequilibrated orthoexcitons can indeed be approximated by the Planck distribution [see Fig. 5(c)]. However, the effective chemical potential $\mu = 0$ of the high-energy orthoexcitons starts to decrease at

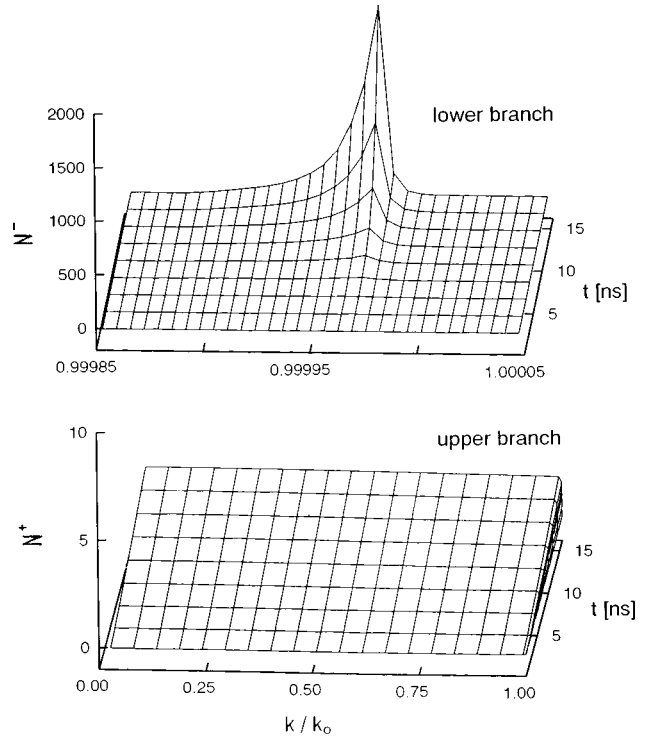


FIG. 6. Time evolution of the distributions $N^\pm(k/k_0, t)$ in the lower and upper polariton branches on a nanosecond time scale. The wave vector $k_0 = \omega_t \sqrt{\epsilon_b}/c \approx 2.6 \times 10^5 \text{ cm}^{-1}$ refers to resonant coupling between photons and orthoexcitons in Cu_2O .

some time, due to the continuous transitions of orthoexcitons in the polariton bottleneck range at $\omega^- < \omega_t$. The long-time ($1 \mu\text{s}$ time scale) polariton bottleneck relaxation kinetics is plotted in Fig. 7 for the same initial distribution as in Figs. 5 and 6. Therefore, we conclude that the weak quadrupole polariton effect indeed prevents a steady-state BEC of ortho- x 's in Cu_2O .

IV. DISCUSSION

The developed theory of the LA-phonon-assisted relaxation kinetics yields an alternative interpretation of the experiments⁴⁻⁷ on the search for x -BEC in Cu_2O . Namely,

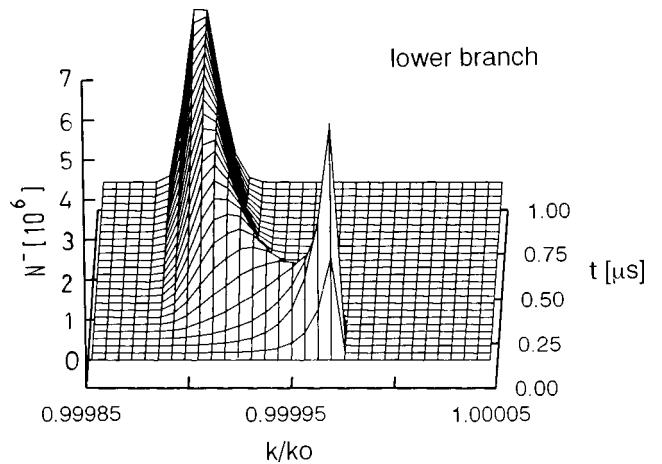


FIG. 7. Polariton bottleneck relaxation of orthoexcitons along the lower dispersion branch in a microsecond time scale.

the chemical potential $\mu=0$ found from the LO-phonon-assisted luminescence spectra is not a unique manifestation of the steady-state x -BEC. The spectral resolutions are about 100–300 μeV for ortho- x 's and about 500 μeV for para- x 's.^{4–7} According to our results, one can indeed get $\mu=0$ within the experimental accuracy in a situation where the excitons from a narrow spectral band ($<100 \mu\text{eV}$) around ω_i are still not in equilibrium and without a steady-state BEC. While in these experiments the gas of ortho- x 's or para- x 's is strongly quantum degenerate, the finite spectral resolution masks the fine nonequilibrium band of the distributions.

The x - x scattering rates in Cu_2O become comparable with those due to the x -LA-phonon deformation potential interaction at concentrations $10^{17} \text{ cm}^{-3} \leq n_0 \leq 10^{18} \text{ cm}^{-3}$ and are strongly dominant for $n_0 > 10^{18} \text{ cm}^{-3}$. In the experiments^{4–7} the concentration of excitons is in a relatively broad range $5 \times 10^{16} \text{ cm}^{-3} \leq n_0 \leq 5 \times 10^{19} \text{ cm}^{-3}$. We believe, however, that the considered above general features of the phonon-assisted kinetics are also valid in the presence of x - x scattering.

For the optically inactive para- x 's with quadratic dispersion, the search for a generic solution for the Boltzmann relaxation kinetics in the presence of x - x interaction at $T_b \leq T_c$ is a challenging problem, which recently has been solved.²⁴ The x - x scattering is important not only for the first kinetic stage of relaxation of para- x 's towards BEC. This interaction is crucial for the BEC phenomenon as a second-order phase transition. A genuine BE condensate possesses such a nonlinear property as coherence and finally develops due to the conservative x - x interaction.^{13,23} Even for an arbitrary small, finite x - x interaction U_0 , a coherent band $0 \leq e < e_{coh}$ arises due to the strong accumulation of excitons (para- x 's) in a close vicinity of the ground-state mode $e=0$. This coherent region, where the potential x - x interaction exceeds the corresponding kinetic energies $e_{\mathbf{k}}$ of para- x 's, cannot be treated within the semiclassical kinetics,²³ i.e., with the kinetic Eq. (1) valid in the random phase approximation.

For ortho- x 's in Cu_2O an increase of the x -damping Γ_x due to the x - x scattering does not destroy the polariton picture written in terms of the quasiparticle solution $\omega = \omega^{\pm}(k)$ of the polariton dispersion Eq. (19). The x - x scattering will accelerate the polariton bottleneck relaxation kinetics along the lower dispersion branch and will relax or even remove at high concentrations of the ortho- x 's the camel back structure in the distribution function $D^-(\omega^-)N_{\omega^-}$. Furthermore, the observed low-energy tail of the time-resolved LO-phonon assisted spectra of ortho- x 's (see Fig. 1 of Ref. 4) can be naturally attributed to the polariton bottleneck relaxation kinetics rather than to long-range condensate interactions²⁵ as it has been assumed in Ref. 4. The distribution $D^-(\omega^-)N_{\omega^-}(t)$ at $\omega^- < \omega_i$ (see Fig. 5) results in a low-energy tail of a few hundred μeV , as has been found experimentally.

V. CONCLUSIONS

In this work we develop the LA-phonon-assisted relaxation kinetics of a low-density gas of excitons in Cu_2O . The thermalization of the both optically quadrupole-allowed

ortho- x 's and para- x 's, forbidden in resonant optical transitions, is analyzed for temperatures above and below the critical temperature for a BEC. The following conclusions summarize our study.

(i) At $T_b \gg T_c$, the relaxation of paraexcitons from an arbitrary initial distribution is completed within a few characteristic scattering times τ_{sc} . For $T_b \rightarrow T_c$ from above, the phonon-assisted kinetics undergoes a thermodynamic critical slowing down in accordance with Eqs. (11) and (12). For $T_b \leq T_c$, the relaxation kinetics is given by the following scenario: within a few scattering times an initial distribution of para- x 's disappears and the relaxation towards a quantum degenerate equilibrium state with a Bose-Einstein condensate is a slow adiabatic process. This second kinetic stage is described uniquely by the generic solution (13) and (14).

(ii) The thermalization of orthoexcitons is treated in the presence of a weak quadrupole-allowed polariton effect. The numerical evaluations of the LA-phonon-assisted relaxation clearly indicate an effective accumulation of ortho- x 's within a narrow spectral band of the lower polariton branch below ω_i , i.e., a polariton bottleneck kinetics. This conclusion is valid for an arbitrary bath temperature T_b and stems from the fact that the upper branch of the polariton dispersion has a low density of states and does not possess an absolute minimum in energy. The criterion (21) of the coexistence of a weak polariton effect and a quasi-steady-state BEC in the ground-state mode $\mathbf{k}=0$ of the upper polariton branch indeed does not hold for ortho- x 's in Cu_2O .

(iii) The LA-phonon-assisted relaxation kinetics does not lead to a natural BEC of excitons in Cu_2O provided the absence of a laser-induced condensate seed. For para- x 's, a slow occupation of the ground-state mode given by Eq. (16) does not allow us to build up a steady-state BEC during the finite lifetime due to the LO-phonon (Γ_5^- or Γ_{25}^-)-assisted radiative decay. For ortho- x 's, the polariton effect always strongly prevents an effective population of the relative energy minimum of the upper polariton branch. The chemical potential $\mu=0$ found in the optical experiments^{6,7} with excitons in Cu_2O refers only to the distribution of relatively high-energy excitons that are in a quasiequilibrium, while a small band of low-energy excitons are far from equilibrium and without a macroscopic occupation of the ground-state mode $\mathbf{k}=0$.

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APPENDIX A: THERMODYNAMIC RELATION

$\delta\mu = \delta\mu(T, \mu, \delta T)$ FOR AN IDEAL BOSE GAS AT $T \geq T_c$

The relation $\delta\mu = \delta\mu(T, \mu, \delta T)$, which describes the infinitesimal thermodynamic transition $(\mu, T) \rightarrow (\mu + \delta\mu, T + \delta T)$ of a closed system of bosons at $T \geq T_c$, can be derived from the condition

$$\sum_{\mathbf{p}} [N_{\mathbf{p}}^{\text{eq}}(\mu, T) - N_{\mathbf{p}}^{\text{eq}}(\mu + \delta\mu, T + \delta T)] = 0, \quad (\text{A1})$$

where the occupation numbers N_p^{eq} are given by the BE distribution. This condition means the conservation of the concentration n_0 of bosons, i.e., $\delta n_0(\mu, T) = 0$.

For $T > T_c$ one gets from Eq. (A1)

$$-I_1(\mu/T)\delta T = I_2(\mu/T)\left(\delta\mu - \frac{\mu}{T}\delta T\right), \quad (\text{A2})$$

where only linear terms with respect to $\delta\mu$ and δT are kept. Here, the integrals I_1 and I_2 are given by

$$\begin{aligned} I_1(\mu/T) &= \int_0^\infty \frac{\varepsilon^{3/2} e^\varepsilon}{[e^{(-\mu/T+\varepsilon)} - 1]^2} d\varepsilon \\ &= \frac{3\sqrt{\pi}}{4} e^{\mu/T} [1 + F_1(\mu/T)], \\ I_2(\mu/T) &= \int_0^\infty \frac{\varepsilon^{1/2} e^\varepsilon}{[e^{(-\mu/T+\varepsilon)} - 1]^2} d\varepsilon \\ &= \frac{\sqrt{\pi}}{2} e^{\mu/T} [1 + F_2(\mu/T)], \end{aligned} \quad (\text{A3})$$

where

$$F_1(\mu/T) = \sum_{n=1}^\infty \frac{e^{(n\mu)/T}}{(n+1)^{3/2}}, \quad F_2(\mu/T) = \sum_{n=1}^\infty \frac{e^{(n\mu)/T}}{(n+1)^{1/2}}. \quad (\text{A4})$$

Equations (A2)–(A4) result in

$$-\delta\mu = \left[\frac{3}{2} \frac{F_1(\mu/T) + 1}{F_2(\mu/T) + 1} - \frac{\mu}{T} \right] \delta T. \quad (\text{A5})$$

A classical gas with the Maxwell-Boltzmann distribution is characterized by $-\mu/T \gg 1$ and $F_{1,2}(\mu/T) \rightarrow 0$. Therefore, for $T \gg T_c$ Eq. (A5) reduces to

$$-\delta\mu = \left[\frac{3}{2} - \frac{\mu}{T} \right] \delta T. \quad (\text{A6})$$

Equation (A6) can also be derived from the relationship $n_0(\mu, T) = (M_x T / 2\pi)^{3/2} \exp(\mu/T)$, which is valid for a classical gas. In this case, the variation $\delta n_0 = \delta [T^{3/2} \exp(\mu/T)] = 0$ leads to Eq. (A6).

For $T \rightarrow T_c$ from above ($T > T_c$), the prefactor of δT on the rhs of Eq. (A5) vanishes, because $\mu \rightarrow 0$ and $F_2(\mu/T_c \rightarrow 0) \rightarrow \infty$. In this case, the linear approximation $-\delta\mu \propto \delta T$ given by Eq. (A5) does not hold. The corresponding relationship $\delta\mu = \delta\mu(T_c, \delta T)$ for $\delta T \rightarrow 0$ and $-\delta\mu \rightarrow 0$ can be derived from the following representation of Eq. (A1):

$$-I_1(0)\delta T = \tilde{I}_2(\delta\mu, \delta T)\delta\mu, \quad (\text{A7})$$

where

$$I_1(0) = \int_0^\infty \frac{\varepsilon^{3/2} e^\varepsilon}{(e^\varepsilon - 1)^2} d\varepsilon = \frac{3\sqrt{\pi}}{4} \zeta(3/2),$$

$\tilde{I}_2(\delta\mu, \delta T)$

$$= \int_0^\infty \frac{\varepsilon^{1/2} e^\varepsilon}{(e^\varepsilon - 1) \{ [1 - (\delta\mu/T_c) - \varepsilon(\delta T/T_c)] e^\varepsilon - 1 \}} d\varepsilon. \quad (\text{A8})$$

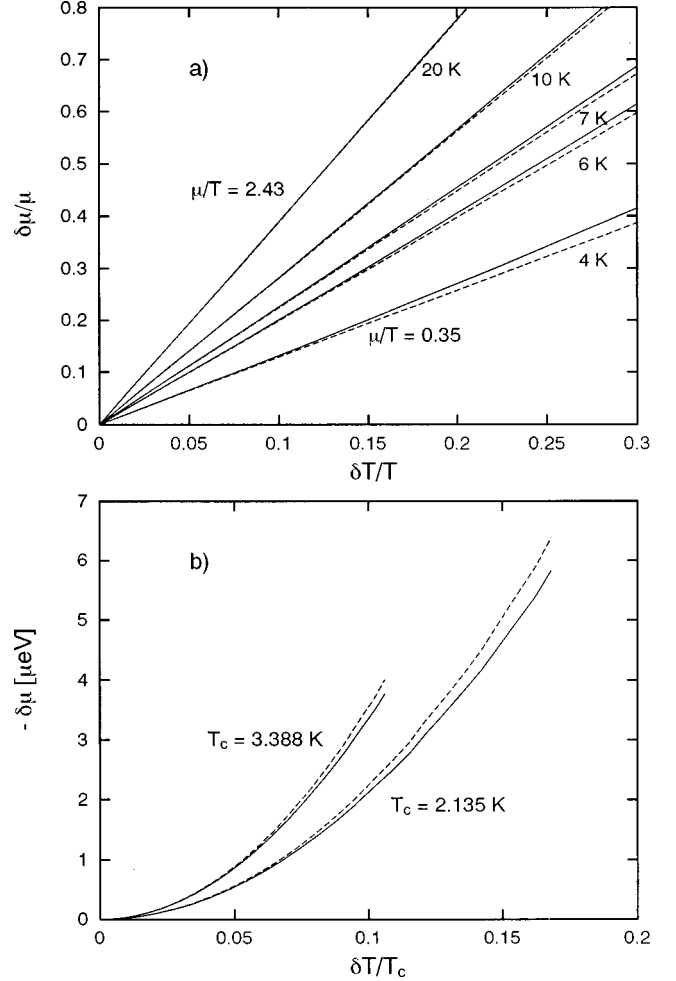


FIG. 8. Chemical potential as a function of temperature for various $T = T_b \gg T_c$ (a) and for various $T_b = T_c$ ($T = T_c + \delta T$) (b). Full lines, numerical solutions of Eq. (A1); dashed lines, analytical solutions given by Eq. (A5)(a) and Eq. (A10)(b), respectively.

For $-\delta\mu \rightarrow 0$ and $\delta T \rightarrow 0$ the main contribution to $\tilde{I}_2(\delta\mu, \delta T)$ stems from $\varepsilon \ll 1$. Making expansion with respect to ε of the numerator and denominator of the integrand, \tilde{I}_2 is approximated by

$$\tilde{I}_2(\delta\mu, \delta T) \approx \int_0^\infty \frac{d\varepsilon}{\sqrt{\varepsilon} - (\delta\mu/T_c)} = \pi \left(\frac{T_c}{-\delta\mu} \right)^{1/2}. \quad (\text{A9})$$

From Eqs. (A7)–(A9) one finally gets for $T = T_c + \delta T$:

$$-\delta\mu = \frac{9}{16\pi} \zeta^2(3/2) \frac{(\delta T)^2}{T_c}. \quad (\text{A10})$$

In this case, the chemical potential $-\delta\mu \propto (\delta T)^2$ approaches zero considerably faster than $\delta T = T - T_c$.

Figures 8(a) and 8(b) show the accuracy of the approximations given by Eq. (A5) for $T > T_c$ and by Eq. (A10) for $T \rightarrow T_c$.

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