Physical origin of the anomalous temperature dependence of the 1S yellow exciton luminescence intensity in Cu_2O

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A simple model is presented to explain the minimum in the integrated intensity of the phonon-assisted 1S yellow exciton luminescence in Cu_2O as a function of temperature. It is shown that this behavior is due to a minimum in the temperature-dependent exciton population lifetime. This model also predicts the temperature dependence of the time-resolved luminescence spectrum in Cu_2O.

Cu_2O has long been known to exhibit sharp excitonic structures[1] in absorption and luminescence and is in fact a text book example of these effects.[2] Although the details of the excitonic energy spectrum have been understood,[3] there are still aspects of the dynamic behavior of the excitons in Cu_2O which are not fully resolved. One such observation is the anomalous temperature dependence of the integrated intensity of the phonon-assisted 1S yellow exciton recombination luminescence at 16290 cm^{-1} (I_o). The intensity of this line does not exhibit a monotonic temperature dependence but has a minimum at temperature $T \sim 15$ K, as shown by the experimental data (solid circles) in Fig. 1. Although this behavior has been explained in the literature either qualitatively[4] or in a quantitative but phenomenological manner,[5] the underlying physical mechanism has not been elucidated. In this brief report we show that the temperature dependence of the intensity of the 16290-cm^{-1} luminescence line can be understood in terms of the interaction between the two exchange-split components of the 1S yellow exciton[3] (the ortho-exciton and the para-exciton) via two phonon processes involving one optic and one acoustic phonon.

Several emission peaks of the ortho-exciton have been reported[6] involving the simultaneous emission of an optic phonon. Of these emission peaks most authors have concentrated on the Γ_{12}^- (110 cm^{-1}) optic-phonon-assisted peak at 16290 cm^{-1}, since it has several desirable characteristics: The Γ_{12}^- phonon has a quite flat dispersion curve, so that the shape of the emission peak depends only on the exciton dispersion and population distribution[1,7]; it couples the ortho-exciton to the radiation field more strongly than do other phonons, and it leads to an emission peak well separated from other features in the emission spectrum. As a result the shape of the 16290-cm^{-1} line is a direct measure of the ortho-exciton population distribution function and the integrated intensity I_o is proportional to the total number of ortho-excitons N_o. Similarly, we assume the total number of para-excitions

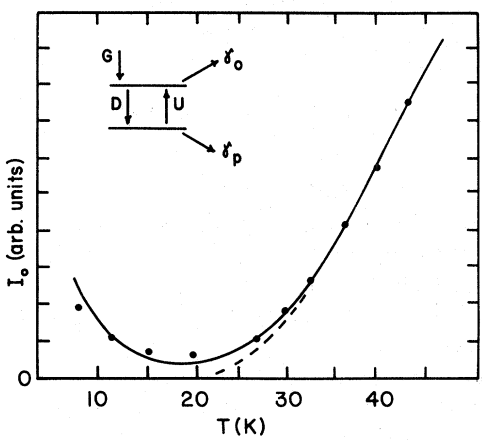

FIG. 1. Temperature dependence of the 16290-cm^{-1} luminescence line in Cu_2O. Experimental points are taken from Ref. 4. Dashed line: prediction of a naive two-level model. Solid line: calculated from a physical model proposed in the text. Inset: schematic diagram of the two-level model.

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N_p is proportional to the integrated intensity of its Γ_{25}^- (85 cm^{-1}) phonon-assisted recombination peak at 16219 cm^{-1} I_p.

We now construct a model to calculate N_o and N_p and thereby the intensity of their emission peaks I_o and I_p. Since experimentally it was found that the para-exciton lies only 96 cm^{-1} below the ortho-exciton,[8] it has been suggested that the dominant ortho-exciton decay channel is to the para-exciton. In an attempt to understand the temperature dependence of the 16290-cm^{-1} emission peak Kriengold and Makarov[4] have approximated the ortho- and para-excitons as a two-level system with energy separation, $\Delta=96$ cm^{-1}. By defining appropriate transition and loss rates, U, D, γ_o, γ_p, and G (these represent, respectively, the para- to ortho-scattering rate, the ortho- to para-scattering rate, the loss rate of the ortho-excitons due to other processes, the loss rate of para-excitons due to other processes, and the ortho-exciton generation rate due to optical pumping) as indicated schematically in the inset of Fig. 1, one can easily write down the rate equations for N_o and N_p. The steady-state solutions to these equations are

$$N_o=\frac{G(U+\gamma_p)}{U\gamma_o+D\gamma_p+\gamma_o\gamma_p}\ , \tag{1}$$

$$N_p=\frac{GD}{U\gamma_o+D\gamma_p+\gamma_o\gamma_p}\ . \tag{2}$$

If one assumes that D, γ_o, and γ_p are all temperature independent while $U=D\exp(-\Delta/k_BT)$, (where k_B is the Boltzmann constant) as required by the principle of detailed balance for a two-level system then

$$N_o(T)\propto I_o(T)\propto\exp(-96/k_BT)\ ,$$

where k_BT is expressed in cm^{-1}. This result, first proposed by Kreingold and Makarov,[4] is plotted as a dashed line in Fig. 1. Although it explains the exponential dependence of $I_o(T)$ on T for $T>15$ K, it clearly fails to account for the minimum in $I_o(T)$. By postulating a temperature dependence in D, Mysyrowicz *et al.*[15] have proposed phenomenological expressions for D and U which reproduce the observed behavior but offer little insight into their physical origin.

In order to correctly calculate the temperature dependence of U and D one must first consider the fact that both the ortho- and para-excitons consist of bands of states so that U and D really represent the *total* scattering rate summed over all initial and final states from one band to the other. Two assumption. First, that the ortho- and para-excitons have identical effective masses. Second, that the ortho- and para-exciton distribution functions are represented by Maxwell-Boltzmann distributions, i.e.,

$$N_i(E_i)\propto\sqrt{E_i}e^{-E_i/k_BT_i}\ ,\quad i=o,p$$

where the exciton energy E_i is measured relative to the zone center energy, and the exciton temperatures T_o,T_p are equal to each other and to the lattice temperatures $T_{\rm latt}$. While Mysyrowicz *et al.*[5] have shown that T_o, T_p, and $T_{\rm latt}$ are not necessarily equal, the quantitative results obtained here are insensitive to variations among T_o, T_p, and $T_{\rm latt}$ of the order of a few degrees Kelvin.

Next, the interaction responsible for the scattering must be specified. For ortho-para exciton scattering in Cu_2O, this is a two-phonon scattering process with one optic phonon and one longitudinal acoustic (LA) phonon. At the low exciton densities ($\lesssim 10^{15}$ cm^{-3}) considered here, exciton-exciton scattering will be negligible. In fact, exciton-exciton collisions can only transfer energy between the ortho and para bands. Net particle transfer between bands in a collision event is forbidden by symmetry. At the zone center, ortho-para scattering by one phonon is also symmetry forbidden, since $\Gamma_2^+\times\Gamma_{25}^+=\Gamma_{15}^+$ and no Γ_{15}^+ phonons exist in Cu_2O. Although at general points in the Brillouin zone one-phonon processes are not strictly forbidden, the exciton-phonon matrix element will still be small near the zone center. The much larger density of final states available to the symmetry-allowed two-phonon processes suggests that the latter will dominate. Of the many allowed two-phonon processes, the Γ_{12}^- + LA and Γ_{25}^- + LA are most favorable, based on the following arguments. Since emission of phonons will dominate in processes contributing to D, only ortho-excitons with kinetic energy E_o + 96 cm^{-1} greater than two-phonon energies can participate. As the number of excitons available for scattering decreases rapidly for $E_o>k_BT$, at low temperatures only the Γ_{12}^- + LA and Γ_{25}^- + LA combinations will contribute. For processes contributing to U, which require the absorption of an optical phonon, the Boltzmann factor will strongly suppress higher-energy phonons. Resonant Raman scattering results[6] indicate that the *intra*band scattering rate of an ortho-exciton by a Γ_{12}^- phonon is roughly equal to the *intra*band scattering rate of an ortho-exciton by a Γ_{25}^- phonon. On this basis, we will assume that *inter*band scattering processes involving either the Γ_{12}^- or Γ_{25}^- phonon occur with

equal probability and therefore receive equal weight in the calculations of U and D.

To calculate U and D we make the further assumption that the transition matrix element is a constant M, independent of initial wave vector, final wave vector, and temperature. Then

$$
\begin{aligned}
D = M \sum_{\vec{k}_o} \sum_{\vec{k}_p} \sum_{\vec{q}_{\mathrm{LA}}} \Bigg[& \sum_{\vec{q}_{12}} \{ \delta(E_o - E_p - \hbar\omega_{\mathrm{LA}} - \hbar\omega_{12}) \delta(\vec{k}_o - \vec{k}_p - \vec{q}_{\mathrm{LA}} - \vec{q}_{12}) \\
& + e^{-\hbar\omega_{\mathrm{LA}}/k_B T} [\delta(E_o - E_p + \hbar\omega_{\mathrm{LA}} - \hbar\omega_{12}) \delta(\vec{k}_o - \vec{k}_p + \vec{q}_{\mathrm{LA}} - \vec{q}_{12})] \} \\
& + \sum_{\vec{q}_{25}} \{ \delta(E_o - E_p - \hbar\omega_{\mathrm{LA}} - \hbar\omega_{25}) \delta(\vec{k}_o - \vec{k}_p - \vec{q}_{\mathrm{LA}} - \vec{q}_{25}) \\
& + e^{-\hbar\omega_{\mathrm{LA}}/k_B T} [\delta(E_o - E_p + \hbar\omega_{\mathrm{LA}} - \hbar\omega_{25}) \delta(\vec{k}_o - \vec{k}_p - \vec{q}_{\mathrm{LA}} - \vec{q}_{25})] \} \Bigg] , \\
U = M \sum_{\vec{k}_o} \sum_{\vec{k}_p} \sum_{\vec{q}_{\mathrm{LA}}} \Bigg[& e^{-\hbar\omega_{12}/k_B T} \sum_{\vec{q}_{12}} \{ \delta(E_p - E_o - \hbar\omega_{\mathrm{LA}} + \hbar\omega_{12}) \delta(k_p - k_o - q_{\mathrm{LA}} + q_{12}) \\
& + e^{-\hbar\omega_{\mathrm{LA}}/k_B T} [\delta(E_p - E_o + \hbar\omega_{\mathrm{LA}} + \hbar\omega_{12}) \delta(\vec{k}_p - \vec{k}_o + \vec{q}_{\mathrm{LA}} + \vec{q}_{12})] \} \\
& + e^{-\hbar\omega_{25}/k_B T} \sum_{\vec{q}_{25}} \{ \delta(E_p - E_o - \hbar\omega_{25}) \delta(\vec{k}_p - \vec{k}_o - \vec{q}_{\mathrm{LA}} + \vec{q}_{25}) \\
& + e^{-\hbar\omega_{\mathrm{LA}}/k_B T} [\delta(E_p - E_o + \hbar\omega_{\mathrm{LA}}) \delta(\vec{k}_p - \vec{k}_o + \vec{q}_{\mathrm{LA}} + \vec{q}_{25})] \} \Bigg] ,
\end{aligned}
\tag{3}
$$

where $\vec{k}_o, \vec{k}_p, \vec{q}_{12}, \vec{q}_{25}, \vec{q}_{\mathrm{LA}}$ are, respectively, the wave vector of the ortho-exciton, para-exciton, Γ_{12}^- optic phonon, Γ_{25}^- optic phonon, and LA phonon, $\omega_{12} = 110\ \mathrm{cm}^{-1}$, $\omega_{25} = 85\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{LA}} = c \mid \vec{q} \mid_{\mathrm{LA}}$ where $c = 5.12 \times 10^5\ \mathrm{cm\,s}^{-1}$, and $E_{o(p)} = (\hbar^2 k_{o(p)}^2)/2m^*$ where $m^* = 2.7 m_{\mathrm{elec}}$. Results of a numerical calculation for the terms in Eq. (3) involving the Γ_{12}^- phonon are shown in Fig. 2. Notice the increase in scattering rate with increasing T. This is due to the increasing number of excitons at higher energies, where the final density of states, and therefore the transition rate is larger. Also notice the "freezing out" of the D process at $T \sim 15$ K, where the average ortho-exciton energy falls below 14 cm^{-1} (the Γ_{12}^- phonon frequency reduced by Δ).

The solid line in Fig. 1 is a fit to the experimental intensity data obtained from Eqs. (1) and (2) with $\gamma_o (= \gamma_p)$ as an adjustable parameter, chosen to be of the magnitude indicated by the dashed line in Fig. 2. Considering the degree of approximation involved, the agreement with experiment is excellent, supporting the physical model we have proposed.

The qualitative origin of the anomalous behavior of the integrated intensity of the 16290 cm^{-1} line may now be elucidated. At temperatures above 15

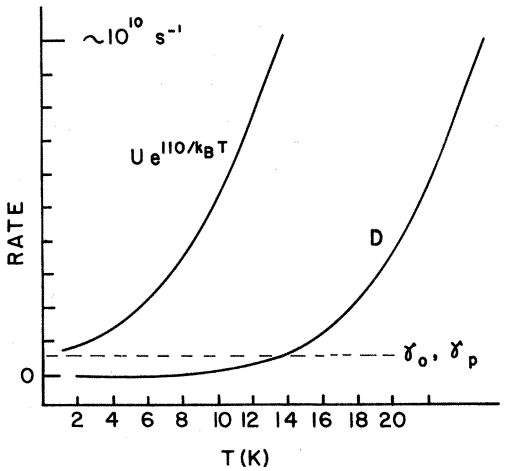

FIG. 2. Total ortho-exciton to para-exciton transition rate (D) and para-exciton to ortho-exciton transition rate (U) for processes involving the Γ_{12}^- optic phonon plus the LA phonon calculated according to the model described in the text.

K the system does behave much like a simple two-level system, with $N_o/N_p \sim U/D$ with $U \approx D\, e^{-\Delta/k_B T}$ and $\Delta \sim 96\ \mathrm{cm}^{-1}$; i.e., the ortho-exciton population is determined by thermal excitation from the para-exciton. At low temperatures U becomes negligible and $N_o \sim G/(D+\gamma_o)$ increases as D decreases, in a manner analogous to a single-level system with a temperature-dependent damping.

In conclusion we note that the model and calculation presented here are, of course, not limited to the steady-state case and can provide definite predictions for the transient behavior of N_o and N_p. Pulsed excitation experiments by Mysyrowicz *et al.*[9] show a rapid decay of I_o ($\propto N_o$) at low temperature ($T \sim 1.5$ K) which in this model would be due to ortho-para thermalization. The decay time, ~ 3 ns, would imply that full scale in Fig. 2 is on the order of $10^{10}\ \mathrm{s}^{-1}$, which is a reasonable number. Careful measurements of this decay time as a function of temperature would provide a stringent test of the model we have presented and also produce values of U, D, γ_o, and γ_p.

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