Phonon-absorption recombination luminescence of room-temperature excitons in Cu₂O

D. W. Snoke, A. J. Shields, and M. Cardona

Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany

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We observe two luminescence lines in the range 70-340 K due to exciton recombination assisted by phonon emission and phonon absorption. The luminescence line shape fits a double Maxwell-Boltzmann distribution at all temperatures, with a temperature that agrees with that of the phonons implied by the relative heights of the two lines. From the fits to the luminescence, we also deduce the variation of the band gap of Cu₂O and the exciton-phonon lifetime broadening up to room temperature. The lifetimebroadening data, when compared with time-resolved spectra and data from Ge and GaAs, indicate the existence of a strong two-phonon emission process.

I. INTRODUCTION

The semiconductor Cu₂O has several interesting properties related to the fact that the binding energy of the free excitons is relatively large, 140 meV. For example, the large binding energy allows the observation of a welldefined excitonic Rydberg series up to n = 9 in the absorption spectrum of Cu_2O .¹ Another consequence of the large binding energy is the fact that the exciton radius is small, about 7 Å. This enables the excitons to reach high densities without a Mott transition, which has allowed the observation of Bose-Einstein statistics of excitons in Cu_2O^{2-4} We report here another effect associated with the large exciton binding energy, as well as with the unique properties of the optical phonons in Cu₂O, which is the appearance in thermal equilibrium at room temperature of phonon-assisted recombination luminescence mediated by the absorption of optical phonons.

The exciton states in Cu₂O consist of the spin singlet Γ_2 "paraexciton" and the spin triplet Γ_{12} "orthoexciton," which lies 12 meV higher due to spin exchange. Direct recombination is dipole and quadrupole forbidden for the paraexciton and dipole forbidden for the orthoexciton in Cu₂O because of the inversion symmetry of the crystal. Therefore the primary luminescence mechanism is phonon-assisted recombination of the orthoexciton in-volving the 13.6-meV Γ_{12} optical phonon. Phonon-assisted luminescence involving other phonons or the paraexciton is at least a factor of 30 weaker.⁵

We observe the exciton luminescence over a wide enough range of temperature to allow us to deduce the temperature dependence of both the phonon-induced lifetime broadening and the band-gap energy. We compare the results to predictions from electron-phonon interaction theory. From the theory for the lifetime broadening, we conclude that a two-optic-phonon absorption process dominates the exciton scattering at room temperature. This is consistent with other measurements in Cu_2O and with data from Ge and GaAs.

II. STOKES AND ANTI-STOKES PHONON-ASSISTED LUMINESCENCE

At high temperature, Γ_{12} phonon-assisted recombination leads to two well-resolved luminescence peaks, one involving phonon emission and the other phonon absorption. Figures 1 and 2 show luminescence spectra of highpurity natural samples of Cu₂O at various temperatures in helium vapor. The excitons are created by photons with an energy 150 meV above the n = 1 orthoexciton energy gap, which is equal to 2.033 eV at 2 K and shifts to lower energy with increasing temperature, as discussed below. If the laser photon excess energy is substantially greater than the exciton binding energy, no exciton luminescence is seen at room temperature, indicating that the generated free electrons and holes recombine directly via band-to-band transitions without thermalizing to the exciton ground state. At lower laser photon energies, resonant reabsorption effects alter the spectrum, as discussed below. The excitation density is approximately 16 W/cm^2 in each case, except for the 335-K spectrum, which was obtained with 160-W/cm² illumination at room temperature.

The sharp direct-recombination line of the orthoexciton can be seen in the low-temperature spectra of Fig. 1 (near 2.024 eV at 74 K), along with the phononemission-assisted ("Stokes") line, whose threshold lies 13.6 meV lower in energy, and the phonon-absorptionassisted ("anti-Stokes") line, starting 13.6 meV higher. Since the phonon-assisted luminescence is allowed for all exciton momenta with approximately constant transition probability, the shape of each of the phonon-assisted lines is given simply by the kinetic-energy distribution of the excitons, which in equilibrium, at low density, is the Maxwell-Boltzmann distribution

$$n(E) \propto (E - E_0)^{1/2} e^{-E/k_B T}$$
 (1)

The relative heights of the two lines depend on the occupation number of the Γ_{12} optical phonons in the same way as Raman-scattering lines, i.e.,

$$I(S)/I(A) = (1+f)/f$$
, (2)

which, when the phonons are in equilibrium at temperature T, implies an intensity ratio fixed by the Bose-Einstein occupation number, $f = 1/(e^{E_{12}/k_BT} - 1)$, or

$$I(S)/I(A) = e^{E_{12}/k_B T},$$
(3)

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FIG. 1. Solid lines represent the luminescence spectrum of Cu_2O at three temperatures with low-power laser excitation at 150 meV above the n = 1 exciton band bottom. Dashed lines represent a fit to a sum of two Maxwell-Boltzmann distribution functions at the same temperature, with the relative heights of the two distributions fixed, assuming a Bose-Einstein occupation of phonons at the same temperature as the Maxwell-Boltzmann distribution of the fit. The direct recombination line is visible in the two low-temperature spectra; in the spectra at higher temperatures its energy position is taken as halfway between the two phonon replicas.

where E_{12} is the energy of the phonon. The fits to the luminescence data in Figs. 1 and 2 are therefore calculated using a single fit parameter T to determine both the shape of the phonon-assisted lines via the excitonic Maxwell-Boltzmann distribution [Eq. (1)] and the relative height of the lines via the phonon Bose-Einstein distribution [Eq. (3)]. As seen in these figures, the fits are quite good.

The spectra here have been obtained in a backscattering geometry, in other words, the luminescence was col-



FIG. 2. Solid lines represent the luminescence spectra of Cu_2O at three temperatures. Dashed lines represent a fit to the sum of two Maxwell-Boltzmann distribution functions as in Fig. 1. An increasing amount of spectral broadening is necessary to fit the luminescence as temperature increases. The dotted line on the 295-K data is the same fit function as given by the dashed line, but without convolution by a spectral-broadening function.

lected from the same side of the crystal as excited by the laser. Observation of luminescence through the crystal gives an altered spectrum due to the strong phononassisted reabsorption of emitted photons. Because light with energy 13.6 meV above the band bottom can be absorbed by assistance of *emission* of a Γ_{12} optical phonon, the "anti-Stokes" phonon-emission luminescence is selectively absorbed. Even in the backscattering geometry, interesting effects due to resonant reabsorption occur when the exciting laser photon energy approaches the n = 1band bottom. As the photon energy approaches the band bottom, the absorption length becomes much longer. Therefore, in a large crystal, luminescence from the excited region must traverse a longer path to leave the sample, and enhanced reabsorption of the "anti-Stokes" line occurs.

Because the exciton temperature determines the *width* of the luminescence, while the optical-phonon temperature determines the relative *heights* of the luminescence lines, the possibility exists of observing a nonequilibrium situation with excitons and optical phonons at different temperature during a pulsed exciton. This situation actually occurred in the data of Ref. 6, in which a Maxwell-Boltzmann distribution of excitons of approximately 60 K was observed in the phonon-emission line, but there was no measurable phonon-absorption line because the crystal temperature remained near 20 K.

III. LIFETIME BROADENING: EVIDENCE FOR TWO-PHONON EMISSION

As temperature increases, the double-Maxwell-Boltzmann fit function must be convolved with a homogeneous lifetime-broadening function, i.e.,

$$I(E) \propto \int n(E')g(E-E',\Gamma)dE', \qquad (4)$$

where $g(E,\Gamma)$ can be chosen as a Lorentzian with Γ half-width at half maximum (HWHM). Figure 2 shows a comparison at 295 K of fits made with and without homogeneous broadening. It can be seen that including the homogeneous broadening gives much better agreement with the luminescence curve. Consequently, a value for the homogeneous linewidth can be obtained from the fits, despite the fact that the sharp direct-recombination line cannot be resolved at temperatures above 150 K due to the strong phonon-assisted recombination. Figure 3 plots the fit values of the homogeneous broadening HWHM, Γ , at the different temperatures. The fit values of Γ at temperatures below 150 K are consistent with the width of the direct recombination line. At the highest temperature, the homogeneous linewidth of $2\Gamma = 14 \text{ meV}$ corresponds by the uncertainty principle to a lifetime of 50 fs.

The line broadening is not due to exciton recombination. We have also measured the orthoexciton lifetime via time-resolved spectroscopy in the temperature range 100-300 K, and we find that the orthoexciton lifetime increases from 100 ± 20 ns at 100 K to 350 ± 50 ns at 300 K. Although the orthoexcitons convert quickly into paraexcitons on a subnanosecond time scale at these temperatures,^{7,8} paraexcitons convert back up to orthoexcitons



FIG. 3. Solid dots represent the HWHM of the spectralbroadening function used in the fits in Figs. 1 and 2, as a function of temperature. Dashed line represents a fit of the theory for broadening due to single-phonon absorption given by Eq. (5) in the text, with $\Gamma_0=4.5$ meV and $\Theta=220$ K. Solid line represents a fit of the sum of single-phonon broadening, given by Eq. (5) with $\Gamma_0=3.5$ meV and $\Theta=220$ K, and two-phonon broadening, given by Eq. (6) with $\Gamma_0^{(2)}=1.1$ meV and $\Theta^{(2)}=160$ K.

just as fast, so that the ratio of the number of orthoexcitons to paraexcitons is given simply by the Boltzmann occupation number, $N(o)/N(p)=e^{-\Delta/k_BT}$, where $\Delta=12$ meV is the ortho-para splitting.⁹ Consequently, at high temperature, the orthoexciton and paraexciton lifetimes will be the same, equal to the fastest intrinsic rate of recombination. Because these experiments are performed at very low exciton density, the contribution of densitydependent nonradiative Auger recombination¹⁰ is negligible. Since the radiative recombination rate of the paraexcitons is known to be 500 times lower than that of the orthoexcitons,⁴ an orthoexciton lifetime of 350 ns implies that the intrinsic radiative lifetime of the paraexcitons is at least 150 μ s, ten times longer than the long liftetime reported by Mysyrowicz, Hulin, and Antonetti.⁹

The lifetime broadening can be understood as the imaginary part of the self-energy of the exciton due to the electron-phonon interaction.¹¹ For the direct gap, this can only involve phonon absorption, since energy must be conserved. If one phonon mode is dominant in the electron-phonon interaction, the broadening due to absorption of single phonons can therefore be written approximately as¹²

$$\Gamma(T) = \Gamma_0 \left[\frac{1}{e^{\Theta/T} - 1} \right] + \Gamma_1 , \qquad (5)$$

where Γ_1 is the inhomogeneous broadening and Γ_0 is a constant which depends on the phonon deformation potentials. Θ represents the dominant phonon frequency in the electron-phonon interaction ($\hbar\omega = k_B \Theta$). There is essentially no inhomogeneous broadening in these high-purity samples; the HWHM of the direct recombination line has been measured as 0.015 meV at $T = 2 \text{ K.}^3$ Consequently we take $\Gamma_1 = 0$ in fits to our data.

The dashed line in Fig. 3 shows a fit of Eq. (5) to our data, taking Θ =220 K, i.e., a phonon energy of 19 meV, which is the energy at zone center of the Γ_{15} TO phonon in Cu₂O, and allowing Γ_0 to vary. This phonon has been shown to interact much more strongly with the orthoexciton than the two optical phonons with lower energy.⁶ This gives a good fit to the data at low temperature, but substantially underestimates the broadening at room temperature. A higher value of Θ would give a better fit to the data, but we cannot realistically use a higher Θ because the next-highest-energy optical phonon in Cu₂O has an energy at zone center of 44 meV.¹³ What then produces the larger-than-expected broadening at room temperature?

Previous work has raised the possibility of a dominant two- Γ_{12} phonon interaction with energy of 28 meV.⁶ In that work, a sudden drop in luminescence intensity was observed for orthoexciton energies more than 28 meV above the energy gap. The single-optic-phonon emission processes were all observed to be quite slow, with approximately 30-ps emission time. Because the Fröhlich interaction vanishes for excitons at zone center in Cu₂O,¹⁴ and deformation-potential emission of all optic phonons is forbidden by parity at zone center, single-optic-phonon processes are expected to be slow. A two-phonon process is expected to be fast, however, because it can conserve parity and has a much larger density of states.

In Fig. 3, we fit the data to a sum of a single-phononabsorption process and a two-phonon-absorption process. The contribution of single-phonon absorption is given by Eq. (5) for the 19-meV TO phonon, while the two-phonon contribution is given by

$$\Gamma^{(2)}(T) = \Gamma_0^{(2)} \left[\frac{1}{e^{\Theta^{(2)}/T} - 1} \right]^2, \qquad (6)$$

where $\Gamma_0^{(2)}$ and $\Theta^{(2)}$ are two new constants for the dominant phonon in the two-phonon absorption process. In Fig. 3, we fix $\Theta = 220$ K and $\Theta^{(2)} = 160$ K, or 13.6 meV, for the Γ_{12} phonon, and fit the relative weights of the two contributions by varying Γ_0 and $\Gamma_0^{(2)}$. As seen in Fig. 3, the fit obtained in this way is quite good.

Further evidence for a fast 28-meV emission process comes from an examination of the time-resolved spectra to low temperature. Figure 4 shows the luminescence spectra from Cu₂O at 20 K within 10 ps of a short (5 ps) synchronously pumped dye-laser pulse, taken with a Hamamatsu streak camera, for two exciting laser photon energies. Sharp peaks are observed for the dominant phonon emission processes, as well as a broad underlying distribution which has been shown to arise from multiple LA-phonon scattering.⁶ In curve (b), the kinetic energy of the generated excitons is just below 28 meV. Emission rates of the TO and LA phonons are comparable in this case. When the laser photon energy is raised, as in curve (a), the average energy of the exciton distribution at the same time is lower, indicating that a new channel of energy loss has appeared. LA-phonon emission at this high initial kinetic energy is greatly reduced due to the $1/q^8$ high-frequency correction discussed in Ref. 6.

We can compare our values for exciton lifetime



FIG. 4. Comparison of the phonon emission rate for excitons with kinetic energy above and below the energy of the twophonon process discussed in the text. (a) The luminescence spectrum of Cu₂O within the first 10 ps of a 5-ps laser pulse with photon energy 2.090 eV. " E_{gen} " indicates the energy at which the generated excitons will appear in the luminescence. This energy is equal to the laser photon energy minus twice the Γ_{12} phonon energy, since one phonon is lost in the absorption process and another in the luminescence process. " Γ_{15} " indicates the energy of generated excitons which have emitted a single TO phonon. " $2\Gamma_{12}$ " indicates the energy of generated excitons which have emitted two Γ_{12} phonons. (b) The luminescence spectrum at the same delay after a laser pulse with photon energy 2.073 eV, just below the threshold for emission of two Γ_{12} optic phonons. The energy-loss rate is much slower, as evidenced by the higher average energy and the existence of a substantial fraction of the excitons still at the generated energy. The single TO phonon emission process is comparable to the LA phonon emission process, according to the heights of these peaks, while single Γ_{12} phonon emission is negligible.

broadening to those for carriers in other semiconductors. In germanium, the Fröhlich electron-phonon interaction is absent. Therefore the deformation-potential scattering of holes at the direct gap of Ge should be comparable to the values measured here for Cu₂O at low temperature, which is the single-phonon-scattering regime. The broadening of the splitoff Γ_7^+ valence band in Ge has been measured as $\Gamma(E_0 + \Delta_0) = 6$ meV at low temperature.^{15,16} In this case, the broadening is primarily due to phonon *emission*, instead of phonon *absorption* in the case of the direct gap of Cu₂O, because transitions to the lower-energy Γ_8^+ valence band are allowed, and phonon absorption is negligible at low temperature. The broadening for holes at the direct gap in Ge can therefore be estimated as¹⁷

$$\Gamma(E_0) = \Gamma(E_0 + \Delta_0) \frac{D(\hbar\omega) f(\hbar\omega)}{D(\Delta_0 - \hbar\omega) [1 + f(\hbar\omega)]} , \qquad (7)$$

where D(E) is the density of states in the Γ_8^+ band, taken as proportional to $E^{1/2}$, and $f(\hbar\omega)$ is the occupation number of the optical phonon with energy $\hbar\omega=35$ meV. The valence-band splitting Δ_0 is 300 meV. At k_BT equal to $\hbar\omega$, then, the direct-gap broadening should be [(35 meV)/(300 meV)]^{1/2} $e^{-1}(6$ meV)=0.75 meV. If the broadening in Cu₂O is taken to be due entirely to absorption of single Γ_{15} TO phonons, then the value found here of about 3.0 meV at 220 K, i.e, $k_B T = \hbar \omega_{15}$, seems large for deformation-potential scattering which is forbidden at zone center. From the fit shown for a sum of one- and two-phonon absorption, however, we find a broadening due to TO phonon absorption alone equal to about 1.4 meV at 220 K, which is much closer to the number for Ge.

At high temperature, we can also compare our data to that of excitons in GaAs which have a strong Fröhlich interaction. The lifetime broadening for the GaAs direct gap has been shown to fit well to Eq. (5) with Θ nearly equal to the LO-phonon energy of 36.4 meV.¹⁸ At 250 K, the HWHM for GaAs is reported as approximately 3 meV. This is essentially the same as found here at the same temperature for two-phonon absorption. Thus the two-phonon emission process in Cu₂O seems to have a rate comparable to that of Fröhlich emission of single phonons in GaAs at the same temperature.

A detailed study of the temperature dependence of the linewidths of the direct and indirect excitons should be performed for Ge, in order to ascertain whether in this case, without Fröhlich interaction, the linewidths at room temperature are also determined by two-phonon processes. The importance of two-phonon electron-scattering processes has been amply documented in the literature.¹⁴

IV. BAND-GAP SHIFT WITH TEMPERATURE

The band gap of Cu₂O has already been reported to shift to lower energy with increasing temperature.⁹ From the fits presented here, we extend this data up to room temperature. We present a measurement of the orthoexciton band gap of Cu₂O at room temperature, which we find to be 1.956 eV. Assuming that the exciton binding energy is independent of temperature, i.e., 140 meV (equal to the direct band-gap energy 2.173 eV minus the n = 1 orthoexciton gap energy 2.033 eV at T = 2 K) gives the direct band gap at room temperature as 2.096 eV.

Figure 5 shows the energy of the direct-recombination line as a function of temperature, including the data from Refs. 2 and 9. The shift of the band gap can be fit with the empirical relation proposed by Varshi, ¹⁹

$$E_g = E_0 - \frac{\alpha T^2}{T + \beta} , \qquad (8)$$

where α and β are fit constants taking into account the effects of thermal expansion and electron-phonon interaction. The fit shown as the dashed line in Fig. 5 yields $\alpha = 4.8 \times 10^{-4}$ eV/K and $\beta = 275$ K. These values of α and β are typical for semiconductors.¹⁹

A somewhat more realistic function for the shift of the band gap is given by a form similar to Eq. (5), which assumes a single dominant phonon frequency in the calculation of the exciton self energy¹²

$$E(T) = E_0 - a \left[1 + \frac{2}{e^{\Theta/T} - 1} \right], \qquad (9)$$

where $(E_0 - a)$ and Θ are two fit parameters. Both emis-



FIG. 5. Solid circles represent the position of the direct recombination line as a function of temperature, from the fits of Figs. 1 and 2. Solid squares represent data from Ref. 2. Open circles represent data from Ref. 9. Solid line represents a fit of the theory for the shift of the band gap due to electron-phonon interaction given by Eq. (9) in the text. Dashed line represents a fit of the empirical law of Varshi given by Eq. (8) in the text.

sion and absorption of phonons are now considered because the band-gap shift can include contributions from non-energy-conserving intermediate states,¹¹ although this alters the energy shift from the form for the phonon emission only by a constant. As seen in Fig. 5, the fit to this equation is not quite as good as that to Varshi's equation. The solid line is a fit with $E_0 = 2.0563$ eV, a = 0.023eV, and $\Theta = 145$ K. The value of Θ in this case need not be equal to that found in the fit of Fig. 3, because the real part of the self-energy responsible for the energy gap shift involves virtual, energy-nonconserving intermediate states. The parameter Θ in this case represents a weighted average of phonon contributions.

V. SUMMARY

To summarize, we report phonon-assisted excitonrecombination luminescence in Cu_2O up to 340 K, which is possible due to the large exciton binding energy. Both phonon-emission and phonon-absorption lines are seen, with a phonon temperature implied by the relative line heights which is consistent with the exciton temperature obtained from a fit of both lines to a Maxwell-Boltzmann distribution. We must introduce spectral lifetime broadening in order to get good fits, with a width increasing with temperature consistent with an electron-phonon scattering mechanism. The fits also yield the shift of the direct band gap in Cu_2O up to 340 K.

From an analysis of the spectral broadening in terms of phonon-electron interaction theory, we find evidence to support the claim that a parity-conserving two-phonon scattering process occurs in Cu₂O at a rate comparable to Fröhlich scattering of LO phonons in GaAs. Timeresolved spectra, as well as a comparison to lifetimebroadening data from Ge and GaAs, support this view.

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