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# Study of photoluminescence in $Cu_2O$

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We have studied the photoluminescence spectrum of $Cu_2O$ using a tunable dye laser. We found that most of the luminescence peaks can be identified as due to recombination of the $1s$ yellow exciton of $Cu_2O$ or its phonon replica. These phonon replicas showed asymmetric broadening with increase in temperature. A few of the lines showed very strong temperature dependence disappearing rapidly at high temperature. The origins of these lines are still a matter of speculation. The luminescence excitation spectrum of $Cu_2O$ is also presented and interpreted.

## I. INTRODUCTION

Photoluminescence is a well-established technique for studying optical properties of solids. One optically excites electron-hole pairs (or excitons if the electron and hole are correlated by Coulomb interaction) in a solid, and detects the outgoing photons emitted by radiative recombination of electron-hole pairs after they have attained thermal equilibrium. Photoluminescence in $Cu_2O$ has been studied by a number of authors using Hg arc lamps[1] or Ar-ion lasers as the excitation sources.[2] In this paper we have made a detailed study of photoluminescence in $Cu_2O$ excited by a tunable dye laser. Part of our results used to test out the two theories[1,3] on the possible formation of excitonic molecules in $Cu_2O$ has been reported earlier.[4] Here, we shall discuss in general the characteristics of the various luminescence lines and the identification of each of them.

## II. ELECTRONIC AND LATTICE VIBRATIONAL PROPERTIES OF $Cu_2O$

$Cu_2O$ has been studied extensively and several review articles on its properties exist in the literature.[5,6] It crystallizes in a cubic lattice with two molecules per unit cell and space group symmetry $O_h^4$. Because of inversion symmetry, its lattice vibration modes and electronic wave functions all have definite parity.

At low temperatures its absorption spectra exhibit several series of sharp excitonic peaks which have been termed yellow, green, blue, and indigo excitons (Fig. 1). The yellow exciton series consists of up to 13 peaks satisfying the Rydberg relation[6]:

$$\nu_n = 17525 - 786 n^{-2} \text{ cm}^{-1}, \quad n = 2, 3, \ldots . \qquad (1)$$

The $n = 1$ line of the series at 16 399.5 $\text{cm}^{-1}$ (referred to as the $1s$ yellow exciton in the rest of the paper) does not obey Eq. (1), and is very weak. Elliott[7] proposed that the lowest conduction band ($\Gamma_6^+$) and the top valence band ($\Gamma_7^+$) in $Cu_2O$ have the same parity so that electric dipole transition is forbidden and the $1s$ exciton line is due to electric quadrupole transition. Electric dipole transitions involving the $1s$ yellow exciton are, however, possible with the assistance of odd-parity phonons and are responsible for the rising steps in the absorption continuum beginning at ~16 490 $\text{cm}^{-1}$ (4.2 °K).[8] Group-theory analysis dictates that[7] the phonons involved must have symmetry $\Gamma_{25}^-$, $\Gamma_{12}^-$, $\Gamma_{15}^-$, and $\Gamma_2^-$. Experimentally it was found that the $\Gamma_{12}^-$ phonon has the strongest coupling to the $1s$ yellow exciton.[1,8,9]

It has been shown[10,11] that $Cu_2O$ has 15 zone-center optical phonons with symmetries: (i) $\Gamma_{15}^{-(1)}$ and $\Gamma_{15}^{-(2)}$ (TO and LO), which are infrared active; (ii) $\Gamma_{25}^-$, $\Gamma_{12}^-$, and $\Gamma_2^-$, which are silent modes; (iii) $\Gamma_{25}^+$, which is the only Raman-active mode. The frequencies of these modes, obtained by various methods, are listed in Table I.

## III. EXPERIMENTAL SETUP

The apparatus used in this experiment consists of a conventional Raman spectrometer, a cooled photomultiplier tube, and a photon-counting system. The luminescence was excited by the output of a cw dye laser (Spectra Physics model 70, or Coherent Radiation model 490). The linewidth of the laser can be as narrow as 0.1 Å. The same system was used in studying resonance Raman scattering and has been described elsewhere.[12] The sample was either immersed in liquid helium, cooled by helium exchange gas, or placed on a cold finger in contact with liquid helium. In the latter two cases, the temperature of the sample was measured by thermometers (calibrated carbon resistor or thermocouple) placed in the vicinity of the sample. The difference between the measured temperature and the actual sample temperature will be discussed later.

## IV. EXPERIMENTAL RESULTS

We have performed measurements on unoriented $Cu_2O$ samples prepared by two different methods:

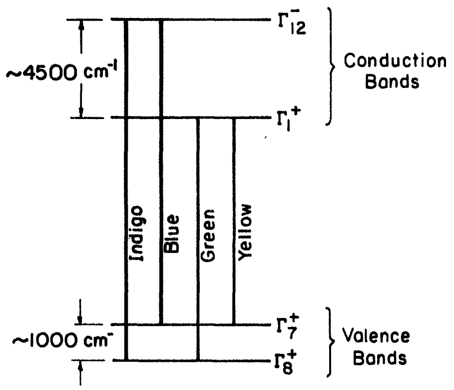

FIG. 1. Energy levels of the two top valence bands and the two bottom conduction bands of $Cu_2O$ at the Brillouin-zone center ($\Gamma$). Electrons in the conduction bands and holes in the valence bands form four series of excitons: yellow, green, blue, and indigo.

I, by oxidation of high-purity copper in oxygen and II, grown from melt using an arc image furnace.[13]

We found significant difference between the luminescence spectra of these two types of samples. Type-I samples have weaker luminescence intensities than type-II samples by roughly two orders of magnitude. The linewidths of the phonon-assisted 1*s* exciton emission peaks in type-II samples vary with temperature. The corresponding linewidths in type-I samples are less sensitive to temperature and are much broader. In Fig. 2, we show two typical luminescence peaks for the two types of samples. The $E_1$ peak at 16 400 cm$^{-1}$ due

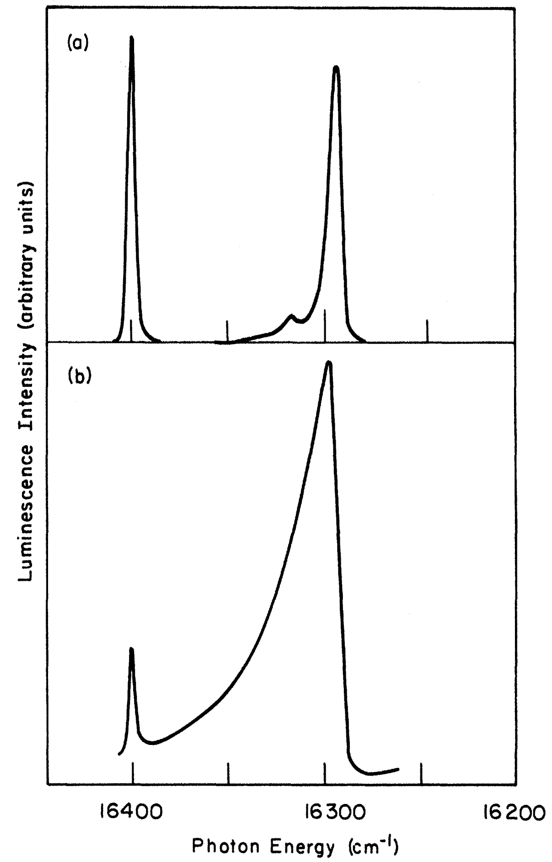

FIG. 2. Luminescence spectra of $Cu_2O$ at 1.8 °K between 16 250 and 16 450 cm$^{-1}$ for two samples; (a) type II and (b) type I. The intensity scale in (a) is 50 times larger than in (b).

TABLE I. Phonon energies of $Cu_2O$ obtained by various techniques.

| Symmetry assignment of phonons | Infrared[a] absorption (room temp.) | Phonon energies (cm$^{-1}$) obtained by: Optical[b] absorption | Raman[c] scattering | Luminescence[d] | Theoretical[e] calculation |
|---|---|---|---|---|---|
| $\Gamma_{25}^-$ | | 88 | 86 | 87 | 98.6 |
| $\Gamma_{12}^-$ | | 110 | 109 | 110 | 110 |
| $\Gamma_{15}^{-(1)}$ (TO) | 146.3 | | 153 | 152 | 143 |
| $\Gamma_{15}^{-(1)}$ (LO) | 149.3 | | | 154.4 | 159 |
| $\Gamma_2^-$ | | | 350 | 350 | 307 |
| $\Gamma_{25}^+$ | | | 515 | 515 | 549 |
| $\Gamma_{15}^{-(2)}$ (TO) | 609 | | 635 | 633 | 608 |
| $\Gamma_{15}^{-(2)}$ (LO) | 638 | | 665 | 662 | 639 |

[a] From Ref. 17.
[b] From S. Brahms and M. Cardona, Solid State Commun. 6, 733 (1968).
[c] From Refs. 9, 12, 16, 18, and 19.
[d] This work.
[e] From Ref. 11.

to $1s$ exciton recombination with no phonon appears to be equally sharp in both spectra, but the $B$ peak at ~16 293 cm$^{-1}$ due to recombination of the exciton with emission of a $\Gamma_{12}^-$ phonon is much broader in type-I samples. When excited by photons of energy higher than ~2.2 eV, type-I samples show new peaks in their luminescence spectra at 17 325, 17 430, 17 466, and 17 487 cm$^{-1}$. These peaks, due to radiative recombination from the excited states of the yellow excition ($2p$, $3p$, $4p$, and $5p$, respectively), are absent in type-II samples. The luminescence spectra of our type-I samples are very similar to that reported by Compaan and Cummins.[2]

The appearance of the $2p$, $3p$, ..., exciton peaks in the luminescence spectra and the broader temperature-insensitive linewidth suggests that the photoexcited excitons in the type-I Cu$_2$O samples are not in thermal equilibrium when they radiatively decay.[14] This could be due to the presence of more defects (associated with nonstoichiometry or impurities) in type-I samples. Collisions of excitons with these defects could enhance the nonradiative decay and suppress the $1s$ exciton luminescence. This explains the lower luminescence efficiency in these samples. Since the luminescence spectrum of type-I samples probably depends on extrinsic properties of the crystal and is not well understood, we will consider only photoluminescence of type-II Cu$_2$O samples in this paper.

Figure 3 shows the visible luminescence spectrum of a type-II Cu$_2$O sample at 1.41 °K, excited by a 7.5-mW laser beam at 16 610 cm$^{-1}$. We have labeled the peaks as $E_1$, $A$, $B$, $C$, ..., and so on.[4] The lines denoted by $R$ are Raman lines since their frequencies shift with the exciting laser frequency. Table II summarizes the positions and our identification of the observed luminescence peaks. Figure 4 shows the dependence of the $E_1$ and $B$ peaks as a function of temperature, and Table III lists the linewidths of various peaks at several different temperatures. Figure 5 gives the luminescence excitation spectrum (LES) of the $E_1$ peak. It should be pointed out that this LES is representative of *all* the other luminescence peaks, showing that they all involve the $1s$ yellow exciton.

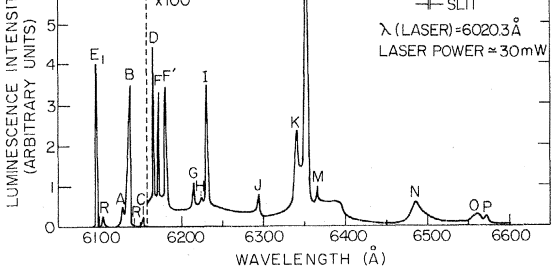

FIG. 3. Luminescence spectrum of Cu$_2$O at 1.41 °K excited by a laser beam at 6020.3 Å.

TABLE II. Luminescence peaks of Cu$_2$O at $T = 1.8$ °K.

| Peak | Peak energy (cm$^{-1}$) | Peak separation from $E_1$ (cm$^{-1}$) | symmetry assignment of phonon (S) involved |
|---|---|---|---|
| $E_1$ | 16 400 | | |
| $A$ | 16 315 | 85 | $\Gamma_{25}^-$ |
| $B$ | 16 293 | 107 | $\Gamma_{12}^-$ |
| $C$ | 16 250 | 150 | $\Gamma_{15}^{-(2)}$ (TO) |
| | | 152 | $\Gamma_{15}^{-(1)}$ (LO) |
| $D$ | 16 219 | 181 | extrinsic (?) |
| $F$ | 16 200 | 200 | $\Gamma_{12}^- + \Gamma_{25}^-$ |
| $F'$ | 16 179 | 221 | $2\Gamma_{12}^-$ |
| $G$ | 16 089 | 311 | $2\Gamma_{12}^- + \Gamma_{25}^-$ |
| $H$ | 16 067 | 333 | $3\Gamma_{12}^-$ |
| $I$ | 16 052 | 348 | $\Gamma_2^-$ |
| $J$ | 15 888 | 512 | $\Gamma_{25}^+$ |
| $K$ | 15 770 | 630 | $\Gamma_{15}^{-(2)}$ (TO) |
| $L$ | 15 740 | 660 | $\Gamma_{15}^{-(2)}$ (LO) |
| $M$ | 15 709 | 692 | extrinsic |
| $N$ | 15 421 | 979 | |
| $O$ | 15 237 | 1162 | |
| $P$ | 15 217 | 1185 | |

## V. DISCUSSION

It has been pointed out[15] that in studying photoluminescence excited by an intense laser source the temperature of the photoexcited exciton system is not necessarily the same as that of the lattice. If the lifetime of the exciton is not long enough to allow the excitons to achieve thermal equilibrium with the lattice, the exciton system can attain a quasithermal equilibrium with temperature considerably higher than that of the lattice. The temperature of the lattice can often be measured directly with a thermometer, but the temperature of the exciton system has to be inferred indirectly. Leheny *et al.*[15] have used the line shape of the phonon-assisted exciton luminescence in CdS to deduce the exciton temperature. We will adopt the same approach in this paper.

The peak we use to deduce the $1s$ yellow exciton temperature is the $B$ peak. As pointed out in Refs. 1 and 2 this peak is due to recombination of the $1s$ yellow exciton with simultaneous emission of a $\Gamma_{12}^-$ phonon. It can be shown[2] that the frequency dependence of the emitted photon intensity $I_{em}$ for the $B$ peak is given by

$$I_{em} \sim (\Delta\omega)^{1/2} e^{-\Delta\omega / kT_E} \quad , \tag{2}$$

with $\Delta\omega = \omega - \omega_1 + \omega_{12}$, $\omega_1$ being the energy of the

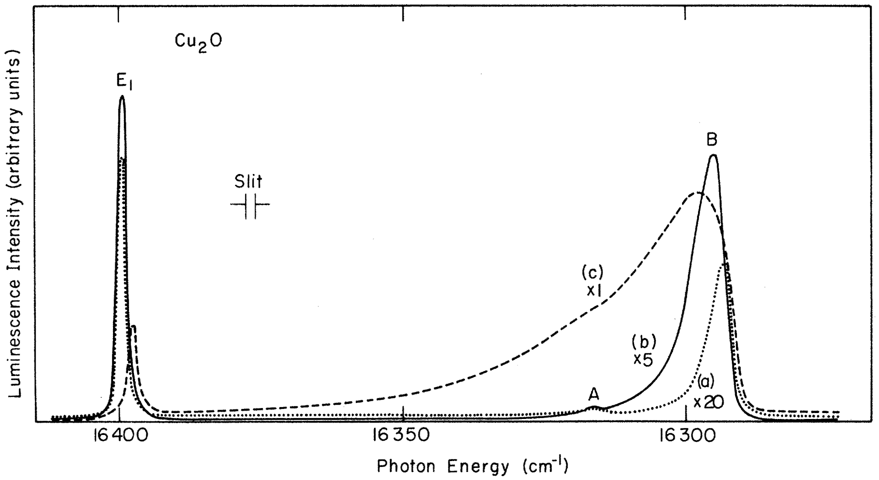

FIG. 4. Luminescence spectra of $Cu_2O$ between 16 270 and 16 410 $cm^{-1}$ at three different temperatures, showing the temperature dependence of peaks $E_1$, $A$, and $B$: (a) 1.8 °K, (b) 4.2 °K, and (c) ≃ 18 °K.

1$s$ exciton at the zone center and $\omega_{12}$ the energy of the $\Gamma_{12}^-$ phonon; $k$ is the Boltzmann constant and $T_E$ is the temperature of the exciton system.

We have used Eq. (2) to fit the line shape of the $B$ peak by adjusting $T_E$. In general the fit is good as can be seen from Fig. 6. The temperature $T_E$ obtained in this way is always higher than the measured temperature of the sample but there is no simple relationship between the two. This is partly because of local heating of sample by laser (minimized by using cylindrical lens for focusing). There was no evidence of "hot"-phonon effects though. With such a temperature $T_E$, we find that most of the observed luminescence peaks of $Cu_2O$ can be fitted by an expression of the form

$$I_{\text{em}} \sim (\Delta\omega)^m e^{-\Delta\omega/kT_E} , \tag{3}$$

with $m$ as an adjustable parameter.

TABLE III. Full width at half-maximum in $cm^{-1}$ of the various luminescence peaks of $Cu_2O$ at several different exciton temperatures $T_E$.

| Peak $T_E$ (°K) | 4 | 7 | 25 | 28 |
|---|---|---|---|---|
| $E_1$ | $\lesssim 1.2$ | $\lesssim 1.2$ | $\lesssim 1.2$ | |
| $B$ | 5 | 8 | 28 | 32 |
| $C$ | 7 | 9 | 21 | 22 |
| $D$ | | 6 | 21 | 25 |
| $F$ | $\lesssim 1.2$ | disappeared | | |
| $F'$ | $\sim 2.5$ | | | |
| $I$ | 6 | 9 | 29 | overlaps $G$, $H$ |
| $J$ | 11 | 12 | 42 | 51 |
| $K$ | $\sim 11$ | 15 | overlaps $L$ | |
| $L$ | 12 | 15 | 34 | 38 |
| $N$ | 53 | 53 | disappeared | |
| $O, P$ | 40–50 | | broadens into one broad peak | |

We shall now discuss the identification and lineshape of the individual luminescence peaks of $Cu_2O$.

### $E_1$ peak

This peak occurs at the same frequency as the electric-dipole-forbidden 1$s$ yellow exciton line in the absorption[6] and has been identified as the no-phonon recombination line of the 1$s$ exciton.[1] Compaan and Cummins[16] have reported a linewidth of 0.75 $cm^{-1}$ for this line, so the linewidth of this peak we listed in Table III is probably limited by the spectrometer resolution. As the temperature $T_E$ is increased, its width remains resolution limited but its intensity decreases (see Fig. 4). These behaviors are consistent with typical intrinsic exciton luminescence.

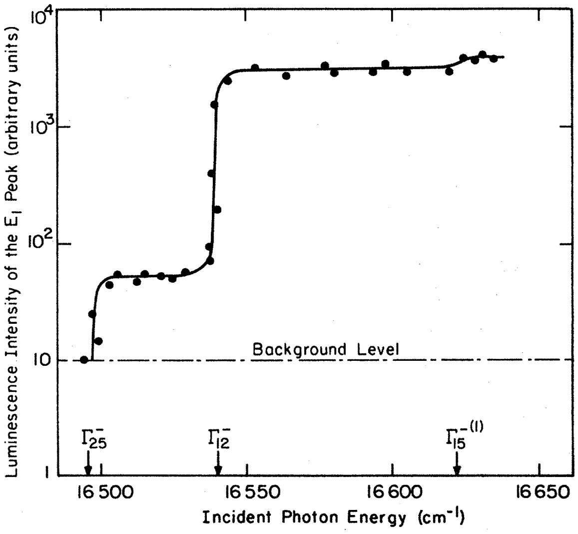

FIG. 5. Luminescence excitation spectrum of the $E_1$ peak of $Cu_2O$ at 1.8 °K. The energies of a 1$s$ yellow exciton plus a $\Gamma$ phonon are indicated by arrows.

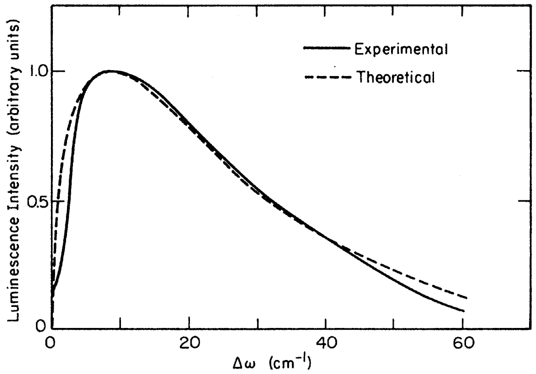

FIG. 6. Line shape of the *B* peak. The theoretical curve is described by $(\Delta\omega)^{1/2}e^{-\Delta\omega/kT_E}$ with $\Delta\omega=\omega-\omega_1+\omega_{12}=\omega-16290\ \mathrm{cm}^{-1}$ and $T_E=25\ ^\circ\mathrm{K}$.

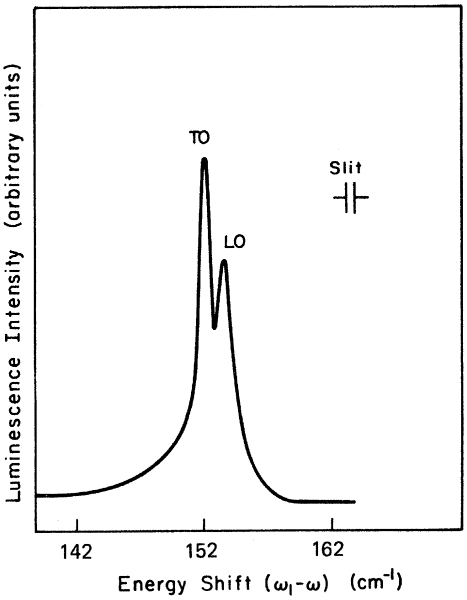

FIG. 7. Luminescence and Raman lines of $Cu_2O$ at $1.8\ ^\circ\mathrm{K}$ with an energy shift of $\sim 152\ \mathrm{cm}^{-1}$ from the $E_1$ peak obtained by a laser excitation at $16\,400\ \mathrm{cm}^{-1}$. The doublet is due to LO–TO splitting of the $\Gamma_{15}^{(1)}$ phonon mode.

### Peaks *A*, *B*, *C*, *I*, *J*, *K*, and *L*

These peaks will be considered together since they are all identified as due to recombination of the 1*s* yellow exciton with emission of a phonon (Table II). The identification is based mainly on the fact that the frequency shifts of these peaks from the $E_1$ peak agree well with the phonon frequencies deduced from other measurements.[16–18]

The infrared-active $\Gamma_{15}^{-(1)}$ mode, which gives rise to the phonon-assisted luminescence peak *C*, is expected to have a small splitting between its LO and TO components due to its weaker effective charge. Using a stable dye laser to excite the 1*s* yellow excitons directly (in this case, the observed luminescence is partly due to resonant Raman scattering), we have now succeeded in observing a doublet in peak *C* in our high-resolution measurements (Fig. 7). The results yield phonon energies of 152 and $154.4\ \mathrm{cm}^{-1}$ for $\Gamma_{15}^{-(1)}$ (TO) and $\Gamma_{15}^{-(1)}$ (LO). We also note in Fig. 7 that the TO component appears to be stronger. This is not surprising, since the macroscopic electric field associated with the $\Gamma_{15}^{-(1)}$ phonon is rather weak so the exciton-phonon interaction will be predominantly of the deformation type rather than the Fröhlich type.

We have tried to fit the line shapes of these luminescence peaks with Eq. (3), where $T_E$ is determined by fitting the *B* peak with Eq. (2). The *A* peak due to emission of a $\Gamma_{25}^{-}$ phonon is only 5% as strong as the *B* peak. Its line shape is difficult to measure accurately since the peak appears only as a shoulder on the *B* peak. The same is true for the *K* peak. For the other peaks, we find that peaks *I* and *L* roughly obey Eq. (3) with $m=\frac{1}{2}$, just like the *B* peak. The *J* peak, however, obeys Eq. (3) with $m=1$, as shown in Fig. 8. We have found no simple obvious reason why the *J* peak should have such a line shape. A possible explanation is that since the $\Gamma_{25}^{+}$ phonon has an even parity, the radiative recombination of the 1*s* exciton by dipole transition with emission of a $\Gamma_{25}^{+}$ phonon is forbidden by parity. The transition would be allowed if two phonons were emitted, namely, a $\Gamma_{25}^{+}$ phonon and a longitudinal-acoustic (LA) phonon. Since the LA phonon has very small energy[19] the frequency of this peak would be the same as emission of a single $\Gamma_{25}^{+}$ phonon. The electron–LA-phonon matrix element is known to be dependent on the phonon momentum $q$ as $q^{1/2}$.[19,20] The absorption

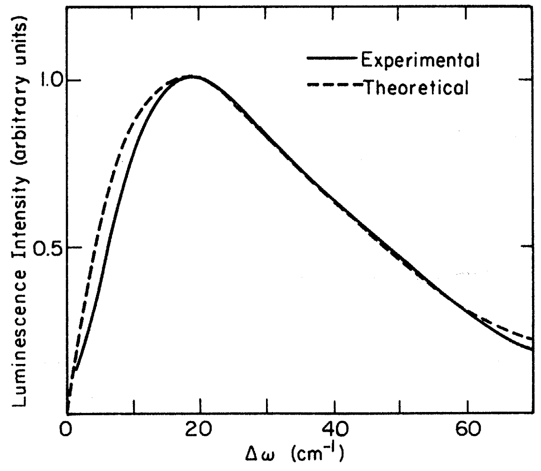

FIG. 8. Line shape of the *J* peak. The theoretical curve is described by $\Delta\omega\, e^{-\Delta\omega/kT_E}$ with $\Delta\omega=\omega-\omega_1+\omega_{25}=\omega-15\,898\ \mathrm{cm}^{-1}$ and $T_E=25\ ^\circ\mathrm{K}$.

coefficient due to dipole excitation of the 1*s* yellow exciton with emission of $\Gamma_{25}^{+}$ + LA phonons would now contain, in addition to a term $[\omega - (\omega_1 + \omega_{25})]^{1/2}$ due to the 1*s* exciton density of states, another term $[\omega - (\omega_1 + \omega_{25})]^{1/2}$ $(\sim q)$ due to the square of the electron–LA-phonon matrix element. Thus, the absorption constant $\alpha(\omega) \sim \omega - (\omega_1 + \omega_{25})$ and results in $m = 1$ in Eq. (3).

Peak *C* is the superposition of two peaks due to emission of $\Gamma_{15}^{-(1)}$ (TO) and $\Gamma_{15}^{-(1)}$ (LO) phonons, as we mentioned earlier. While it is impossible to separate the two peaks unambiguously, the overall line shape of the *C* peak (in low-resolution measurements such that the doublet in Fig. 7 is not resolved) roughly obeys Eq. (3) with $m$ between $\frac{1}{2}$ and $\frac{1}{4}$. Compaan and Cummins[2] have suggested that the $\Gamma_{15}^{-(1)}$ phonons contribute to the absorption coefficient near the absorption edge in the form

$$\alpha(\omega) \sim [\omega - (\omega_1 + \omega_{15})]^{3/2} . \tag{4}$$

This would lead to an emission line shape of

$$I_{\text{em}} \sim (\Delta\omega)^{3/2}\, e^{-\Delta\omega / kT_E} \tag{5}$$

for peak *C*. Our results are in clear contradiction with their suggestion.

The strength of a one-phonon emission peak is directly proportional to the square of the exciton-phonon interaction matrix element. Therefore, from Fig. 3, we can deduce the relative strengths of the coupling between the 1*s* yellow exciton and the different phonon modes. They agree well with the results of other measurements, such as absorption and resonant Raman scattering.

### Peaks *F*, *F*′, *N*, *O*, and *P*

These peaks have strong and peculiar temperature dependence and have been discussed in some detail in a previous publication[4] in relation to the existence of excitonic molecules in $Cu_2O$. We will not repeat the discussion here. Since then, we have made additional measurements on *F* and *F*′. Some of our findings are as follows:

(i) The lines are very narrow. The width of *F* is close to that of $E_1$ ($\lesssim 1.2$ cm$^{-1}$) while the width of *F*′ is ~2.5 cm$^{-1}$.

(ii) The positions of these lines suggest that *F* and *F*′ are due to emission of $\Gamma_{12}^{-} + \Gamma_{25}^{-}$ and $2\Gamma_{12}^{-}$ phonons, respectively, in the recombination of the 1*s* yellow exciton. However, such luminescence processes are not allowed by symmetry and the lines do not have the characteristic phonon-assisted luminescence line shape.

(iii) The intensities of *F* and *F*′ vary superlinearly with the laser intensity at low-intensity levels (<0.1 W/cm$^2$) and appear to saturate quickly at high-intensity levels. As a comparison, the intensity of the $E_1$ peak was found to vary linearly with the incident laser intensity.

(iv) The excitation spectrum of *F* and *F*′ is similar to the other luminescence peaks. In particular, they show up efficiently when the laser is tuned right on the 1*s* yellow exciton line. Note that the corresponding resonant Raman processes are forbidden by parity.

These properties appear to be characteristic of phonon-assisted luminescence from recombination of a bound exciton. We suspect that *F* and *F*′ are due to emission of $\Gamma_{12}^{-} + \Gamma_{25}^{-}$ and $2\Gamma_{12}^{-}$ phonons, respectively, in the recombination of a weakly trapped 1*s* yellow exciton.

### Peaks *G*, *H*, and *M*

These three lines are all very weak and can be distinctly resolved only at low temperatures (< 4.2 °K). Furthermore, *G* and *H* overlap with the stronger *I* peak making their line shapes difficult to analyze. We have tentatively assigned *G* and *H* as due to recombination of the 1*s* exciton with emission of $2\Gamma_{12}^{-} + \Gamma_{25}^{-}$ and $3\Gamma_{12}^{-}$ phonons, respectively. This assignment is supported by the fact that such three-phonon modes have been observed in resonant Raman scattering.[12] The *M* line has a width of ~ 5 cm$^{-1}$ which is independent of temperature. This suggests that it does not involve emission of phonons like the other peaks and has probably an extrinsic origin.

### Peak *D*

The presence of the *D* line in the luminescence spectrum of $Cu_2O$ was first reported by Gross *et al.*[21] Further details of their experiments and theories were reported by Kreingol'd and Makarov.[22] In essence, these authors found that the dependence of the intensity of the *D* line on temperature was quite different from the other lines. While the intensities of the other lines had a minimum at ~ 20 °K, the intensity of the *D* line was almost constant up to 40 °K. When the $Cu_2O$ crystal was deformed by a uniaxial stress they found a new line appearing in the luminescence spectrum at ~ 96 cm$^{-1}$ below the $E_1$ line. Based on these results, they suggested that this new line was due to radiative recombination of the 1*s* yellow "paraexciton" and the *D* line was its $\Gamma_{25}^{-}$ phonon replica.

If one considers the 1*s* yellow exciton as composed of two particles (electron and hole) each of spin $\frac{1}{2}$ and zero orbital angular momentum, then the total angular momentum of the exciton would be 1 (a triplet state of symmetry $\Gamma_{25}^{+}$ or "orthoexciton") or 0 (a singlet state of symmetry $\Gamma_{2}^{+}$ or "paraexciton").[23] The orthoexciton is the state of the 1*s* yellow exciton we have been referring to so far. The paraexciton can be excited by dipole transition only with the assistance of a $\Gamma_{25}^{-}$ phonon. In the absence of exchange interaction the ortho- and paraexcitons are degenerate. Elliott[7] has estimated the exchange splitting to be ~15 cm$^{-1}$. From Gross *et al.*'s result, this splitting would be 96 cm$^{-1}$.

We have studied the temperature dependence of the luminescence spectrum of $Cu_2O$. We found that for $T_E$ between 4 and 50 °K the intensity of *all* the luminescence peaks of $Cu_2O$ decreased monotonically. Some of the peaks like *F*, *F'*, and *N* decreased faster than others. The *D* peak disappeared around 50 °K in agreement with the observation of Kreingol'd and Makarov, but there was no exponential increase in the other peaks.

If the *D* line were a $\Gamma_{25}^-$ phonon replica of the paraexciton, we would expect to see a corresponding absorption edge at ~16 390 cm$^{-1}$ due to excitation of a paraexciton with emission of a $\Gamma_{25}^-$ phonon. We have measured the absorption of a thick $Cu_2O$ sample (~2 mm) very carefully. We were able to observe an edge at ~16 490 cm$^{-1}$ corresponding to the creation of an orthoexciton with emission of a $\Gamma_{25}^-$ phonon, but we failed to observe any absorption at 16 390 cm$^{-1}$. The Leningrad group also failed to observe the paraexciton in absorption. Thus our results do not support the interpretation of the *D* line in terms of paraexcitons.

We have found that Eq. (3) with $m=\frac{1}{4}$ fits the line shape of the *D* peak quite well. Such a line shape cannot be explained by a phonon-assisted luminescence, although the position of the *D* line appears to be only a few cm$^{-1}$ above the energy expected for the $2\Gamma_{25}^-$-phonon-assisted recombination of the 1*s* yellow exciton. We suspect that the *D* line has an extrinsic origin since the *D* line appears only in some samples (for example, not in type-I samples). Furthermore, a number of authors[17,24] have reported structures around 180 cm$^{-1}$ in the infrared and Raman spectra of $Cu_2O$. Reydellet *et al.*[24] have proposed that this 180-cm$^{-1}$ mode is a resonant gap mode due to heavy substitutional atoms (probably copper) on the $T_d$ substitutional sites. Further experiments are needed to concretely establish the origin of this line.

### Excitation spectrum

The luminescence excitation spectrum (LES) of the $E_1$ peak shown in Fig. 5 shows two very sharp steps occurring respectively at the energy of the 1*s* exciton plus a $\Gamma_{25}^-$ phonon and at the energy of the 1*s* exciton plus a $\Gamma_{12}^-$ phonon. There is another much weaker step presumably due to the $\Gamma_{15}^{-(1)}$ phonon. The presence of these steps can be easily understood. The $E_1$ line results from the radiative recombination of the 1*s* yellow exciton. The 1*s* exciton can be excited by dipole transition only with the assistance of an odd-parity phonon. If the incident-photon energy $\omega$ is larger than $\omega_1+\omega_{25}$, then the 1*s* yellow exciton can be excited via emission of a $\Gamma_{25}^-$ phonon. This yields the first step in LES. However, the coupling between the 1*s* exciton and the $\Gamma_{25}^-$ phonon is rather weak so that the observed step is also weak. If $\omega$ is larger than $\omega_1+\omega_{12}$ the 1*s* exciton is created with emission of a $\Gamma_{12}^-$ phonon. The stronger coupling of the $\Gamma_{12}^-$ phonon with the 1*s* exciton produces in the LES a step which is ~60 times larger than the step due to the $\Gamma_{25}^-$ phonon. In absorption and luminescence, we found that the coupling between the $\Gamma_{12}^-$ phonon and the 1*s* exciton is ~20 times bigger than the $\Gamma_{25}^-$ phonon. Similar steps due to the other odd-parity phonons are expected to appear, but they are difficult to observe on top of the strong $\Gamma_{12}^-$ step. We note that Taylor and Weichmann[25] have observed similar steps at $\omega_1+\omega_{12}$ in the LES of the infrared luminescence of $Cu_2O$, but they did not observe the step due to the $\Gamma_{25}^-$ phonon.

Since the 1*s* yellow exciton can also be excited by electric quadrupole transition, we expect to see the same luminescence when $\omega$ is resonant with the 1*s* yellow exciton. This is indeed the case and has been reported by Compaan and Cummins.[16] We found that the luminescence spectrum excited resonantly in this way is identical to what is shown in Fig. 2, including the presence of the peaks *F*, *F'*, and *N*.

## VI. CONCLUSION

We have studied the temperature dependence and the excitation spectrum of photoluminescence in $Cu_2O$ using a tunable dye laser. We found that most of the luminescence peaks can be identified as due to recombination of the 1*s* yellow exciton with or without emission of phonons. The phonon-assisted recombination lines are characterized by a line shape of the form

$$I_{em} \sim (\Delta\omega)^m e^{-\Delta\omega/kT_E},$$

where $T_E$ is defined as the exciton temperature (which is usually higher than the lattice temperature). A few peaks have behavior different from the phonon-assisted lines. They have been tentatively assigned. A more definite assignment requires further investigation.

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