PHYSICAL REVIEW VOLUME 185, NUMBER 3 15 SEPTEMBER 1969

Role of Excitons in the Luminescence of Cuprous Oxide

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(Received 10 March 1969; revised manuscript received 2 June 1969)

Evidence is presented on the nature of the recombination center necessary for the infrared luminescence of Cu_2O. By comparing luminescence, photoconductivity, and optical absorption, the excitonic origins of the luminescent decay are confirmed, and in particular, the presence of indirect transition processes in the region of the $n=2$ exciton of the yellow series is observed. Good agreement is also found between the observed luminescence and Elliott's theory of optical absorption, with particular reference to the exciton line asymmetry. The information obtainable from the excitation spectrum of luminescence over and above the data obtained from optical absorption and photoconductivity is discussed.

INTRODUCTION

As had been established by Bloem[1,2] and by Frerichs and Liberman,[3] the infrared luminescence of Cu_2O is an extrinsic property of the material. Bloem showed that the luminescence varied with the oxygen pressure present during preparation at high temperature, while Frerichs and Liberman were able to show from studies of electroluminescence that the recombination took place at Cu^+ vacancies.

In these experiments we present further evidence along these lines and in addition, from excitation curves, the role of excitons will be brought to the fore.

APPARATUS

The sample-handling techniques were similar to those used in our earlier work and have recently been described in detail by Zielinger *et al.*[4] In brief, the sample under study was provided with sputtered platinum contacts wrapped with platinum foil, and suspended in a clear quartz tube by two sets of Chromel-Alumel thermocouples. A small electrical oven or Pyrex double Dewar could be alternatively mounted around the quartz tube containing the sample, giving a range from 1000°C down to 4.2°K.

The optical system consisted of a motor driven Bausch & Lomb Model 33-86-45-59 grating monochromator with wolfram ribbon lamp. The monochromator output was focused into the double Dewar by means of a mirror and the emitted luminescence either detected by an *S*1-response photomultiplier with interference filter, or passed through a Leiss quartz prism double monochromator for spectral analysis. For improved sensitivity the incident light was chopped at 80 Hz and the photomultiplier signal amplified by a lock-in amplifier.

ROLE OF STOICHIOMETRY

As in earlier experiments on conductivity and photoconductivity,[5] we tried to associate, in one sample, luminescent intensity for a given amount of excitation with annealing conditions at various temperatures.

A typical freshly grown sample, whether single or multicrystalline, showed a quantum efficiency of up to 5% at room temperature increasing by a factor of 4 or 5 in cooling to 4.2°K. Such samples were prepared by oxidizing 99.999% pure copper and subsequently cooling in 10^{-4}-Torr oxygen pressure from 1000°C.

The well-known changes in electrical conductivity which take place at 150°C in air or in vacuum and which are ascribed to the breaking up of complexes[6] had no effect on the luminescent efficiency. Neither was any change in efficiency observed after annealing at 300°C, at which temperature surface conductivity can be reduced to the same magnitude as the bulk conductivity.[7] However, reheating to 1000°C for 1 h and cooling under 10^{-7} Torr, which gives rise to extremely high room-temperature resistivities and consequently a high degree of stiochiometry, destroyed room-temperature luminescence completely and reduced the low-temperature luminescence by three or four orders of magnitude.

In all samples and under all preparation conditions used by us, only the infrared luminescence was observed, although a careful search was made for the luminescence in the visibile region as found by others.[1,8–10] For conductivities ranging between 10^{-6} and $10^{-10}\ \Omega^{-1}\ cm^{-1}$ at room temperature, the luminescence was restricted to a single bell-shaped emission peaked at 1.0 μ with a half-width of 0.12 μ.

The temperature dependence of the luminescent intensity for constant incident wavelength was measured for a number of samples, and the intensity was seen to increase strongly with decreasing temperature. An attempt was made to fit the curves to standard models for luminescence, bearing in mind that Cu_2O is a *p*-type material. A good fit was found only for a

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[10] E. F. Gross and F. I. Kriengol'd, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiya **7**, 281 (1968) [English transl.: Soviet Phys.—JETP Letters **7**, 218 (1968)].

model in which the thermal population of the lower state varied with temperature.

The luminescence was therefore given by

$$L \propto N_e[1-f(E')], \tag{1}$$

where N_e is the number of excited states which are here assumed to be a function of wavelength only, $f(E')$ is the Fermi distribution function governing the population of the lower state, and E' is the energy of the lower state relative to the Fermi level. From (1), E' was found to be about 0.1 eV in the samples investigated.

Tolstoi and Abramov[11] had found the luminescence at 0.93 μ to be nonlinear with respect to incident light intensity. This effect was investigated for our samples using a 2-mW He-Ne laser as incident light source, and a nonlinearity was observed at maximum laser intensities. The luminescence is believed to be a result of an exciton decay and, since the response time for our samples was found to be faster than 10^{-7} sec regardless of temperature and it is known that the 1s exciton has a lifetime of greater than 10^{-6} sec at 77°K,[12] it is suggested that the nonlinearity is due to a saturation of the lower state rather than pair annihilation of the excited state.[11]

LUMINESCENCE AND PHOTOCONDUCTIVITY

The optical absorption and photoconductivity in Cu_2O have long been known to exhibit fine structure due to exciton formation.[13–17] It was therefore no great surprise that this fine structure was also present in the luminescent intensity-versus-incident exciting wavelength curves. It is of interest, however, to note that in spite of strong similarities in the excitation of luminescence and photoconductivity there are significant differences. One important difference is that the luminescence cannot be excited for wavelengths longer than 0.65 μ, whereas extensive photoconductivity is still detectable to wavelengths of 2 μ.[18] In addition, however, we will here be concerned with detailed comparisons between luminescence, photoconductivity, and absorption.

The curves of luminescent intensity versus incident wavelength for a sample of strong luminescent response are shown in Fig. 1 for temperatures of 300, 77, and 4.2°K. The position of the peak and long-wavelength edge are seen to shift to shorter wavelengths with decreasing temperatures, which can be attributed to the shift in the absorption edge and hence in the band structure of the material.[19] A photoconductivity curve for this sample is shown in Fig. 2 with a thin sample luminescence curve for comparison. The exciton structure is clearly visible.

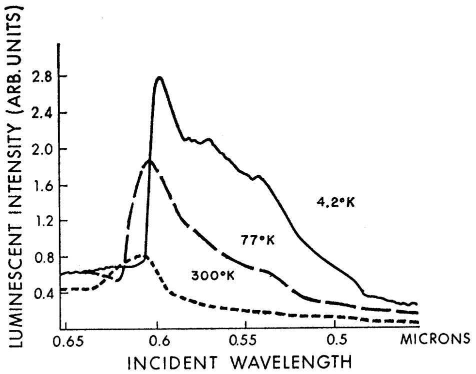

FIG. 1. Luminescence-excitation curves for a strongly luminescing sample at temperatures of 300, 77, and 4.2°K. These curves and all others shown are not normalized to constant intensity of incident light.

This sample was then heated *in situ* under vacuum to 1000°C and allowed to cool at a pressure of 10^{-6} Torr and better. The luminescence was now undetectable at room temperature, and in the low-temperature excitation curves the peak at ~0.6 μ had decreased in magnitude relative to the structure at ~0.55 μ. A similar reduction in the 0.6-μ peak in photoconductivity was observed, establishing a strong correlation between the excitation processes for the two phenomena. This result was completely reproducible, since it is possible, under the appropriate temperature and vacuum conditions, to cycle a sample from high efficiency to low efficiency and back.

The luminescence-excitation curve for a weakly luminescent sample annealed under high-vacuum conditions is shown in Fig. 3 for a temperature of 77°K. The structure at ~0.55 μ is of relatively low magnitude in this sample and dips corresponding to the $n=2$ and $n=3$ exciton lines of the yellow series can be resolved on the short-wavelength side of the 0.6 μ peak. On the

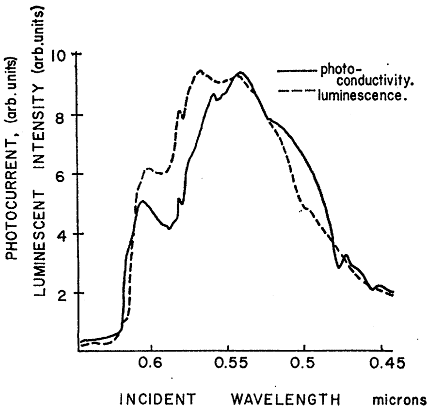

FIG. 2. Photoconductivity-excitation curve for a strongly luminescing sample shown with luminescence excitation for a thin crystal prepared from a similar sample. Temperature is 77°K.

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[11] N. A. Tolstoi and A. P. Abramov, Fiz. Tverd. Tela **9**, 3340 (1967) [English transl.: Soviet Phys.—Solid State **9**, 2630 (1968)].

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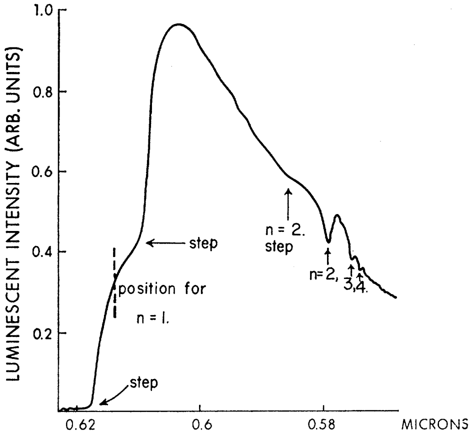

FIG. 3. Luminescence-excitation curve for a weakly luminescing sample; exciton structure is clearly visible. Temperature is 77°K.

long-wavelength side, steps are observed which correspond exactly to those occurring in the absorption coefficient at these wavelengths.[15,20]

A good over-all fit to the curve in Fig. 3 is obtained by a model in which the centers responsible for the luminescence are homogeneously distributed throughout the crystal and in which it is assumed that the luminescence is proportional to the light absorbed. The luminescence is then simply given by

$$L \propto (1/A)(1-e^{-ad}), \qquad (2)$$

where

$$A = ad \quad \text{if} \quad ad > 1$$
$$= 1 \quad \text{if} \quad ad < 1.$$

$a = a(\lambda)$ is the absorption coefficient and d is the sample thickness. The excitation-curve shapes and peak positions are thus dependent upon sample thickness, since the range of wavelengths for which luminescence occurs corresponds to a region of rapidly increasing optical absorption. The good agreement found between (2) and experiment gives further evidence for the existence of some luminescent center necessary to the decay process.

A detail of the luminescence curve of Fig. 3 is given in Fig. 4 with an uncorrected transmission curve for the same sample under identical conditions of temperature and incident radiation. In the luminescence, dips corresponding to the $n=2$ and $n=3$ exciton lines of the yellow series are observed, and the $n=4$ line can just be resolved. Most interesting is the presence of a step at 0.586 μ just before the $n=2$ dip at 0.579 μ. The luminescence is seen first to increase above background (shaded area); then, as the $n=2$ line is approached, a sharp decrease below background is observed. A detail of the $n=2$ dip under higher amplification is shown in the inset in Fig. 4. The dip is seen to be symmetrical to within the limits of experimental error. The transmission curve in the same region shows the familiar asymmetrical exciton absorption lines.[15,21]

This behavior of the luminescence is strongly reminiscent of the steps and dips seen for the blue and violet excitons in photoconductivity curves; a detail of the photoconductivity in this region at 77°K is shown in Fig. 5.

DISCUSSION

The intensity of the infrared luminescence is clearly confirmed to be dependent on the number of luminescent centers, which in Cu_2O are most easily controlled by oxygen or vacuum treatment at elevated temperatures. That these centers are distributed throughout the bulk of the material is evident from the model which relates sample thickness to luminescent output.

The fine structure of the excitation curves will now be discussed in relation to what is known about the optical absorption and the band structure.

The presence of steps on the low-energy side of the absorption curves for Cu_2O have been attributed to indirect transitions to the $n=1$ exciton level with the absorption or emission of a phonon.[20,22] On this basis the appearance of steps at identical wavelengths in the luminescent excitation (Fig. 4) indicates that the luminescence represents a decay from, or via, the 1s exciton level.

Calculations on the band structure of Cu_2O have been made by Elliott,[23] Zhilich and Makarov,[24] and a more

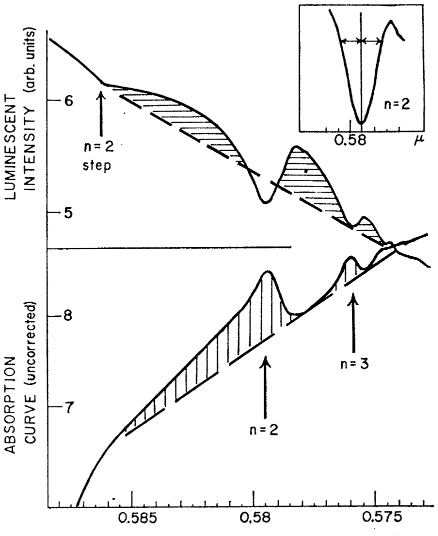

FIG. 4. Detail of a luminescence-excitation curve in the region of $n=2$ of the yellow series, with an uncorrected absorption curve in the same region for the same sample. Temperature is 77°K. Inset, detail of $n=2$ dip in luminescence showing a high degree of symmetry.

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[20] I. S. Gorban and B. V. Timofeev, Fiz. Tverd. Tela 3, 3584 (1961) [English transl.: Soviet Phys.—Solid State 3, 2606 (1962)].

[21] I. Pastrnyak, Fiz. Tverd. Tela 3, 869 (1961) [English transl.: Soviet Phys.—Solid State 3, 633 (1961)].

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[23] R. J. Elliott, Phys. Rev. 124, 340 (1961).

[24] A. G. Zhilich and V. P. Makarov, Fiz. Tverd. Tela 3, 585 (1961) [English transl.: Soviet Phys.—Solid State 3, 429 (1961)].

detailed band scheme has been computed by Dahl and Switendick.[25] It was found that the valence band has symmetry Γ_{25}' at $K=0$ while the two conduction bands, at about 2.2 and 2.7 eV above the valence band, have symmetry Γ_1 and Γ_{12}', respectively. The parity-selection rule for electric dipole transitions therefore suggests that transitions $\Gamma_{25}' \rightarrow \Gamma_1$ are forbidden,[26,27] and thus the first allowed transitions are $\Gamma_{25}' \rightarrow \Gamma_{12}'$. Transitions to the exciton levels associated with Γ_{25}' and Γ_1 will also be forbidden, and it is thus expected that indirect transitions to these levels with the absorption or emission of a phonon will be important. The theory for optical transitions to exciton states has been given by Elliott,[26] who also showed[22] that the presence of steps on the absorption edge of Cu_2O could be explained in terms of indirect transitions to the 1*s* exciton level of the yellow series with absorption proportional to

$$K=\frac{4\pi^2e^2}{\eta\, cm^2\nu}\left|\frac{\sum_i\langle 0|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|i,0\rangle\langle i,0|H_{eL}|1s,K;n_k\pm1\rangle}{E(i,0)-E(1s,K)\mp E_p(K)}\right|^2 \times\rho(1s,K)\,, \tag{3}$$

where $\boldsymbol{\varepsilon}$ is a vector parallel to the electric vector of the light, $\mathbf{p}$ is a moment matrix element, H_{eL} is the electron lattice interaction transferring the electron from the intermediate state $|i,0\rangle$ to the final state $|1s,K\rangle$, ρ is the density of states, and E_p is the phonon energy. The set of intermediate states likely to be important are at Γ_{12}', but a small contribution is expected from the $(np,0)$ exciton levels of the yellow series. It is this contribution which is responsible for the asymmetry of the $n=2, 3, 4, \cdots$ exciton-absorption lines. The steps and dips found in luminescence excitation curves agree well with Elliott's theory if the luminescence represents a decay from the $|1s,K\rangle$ exciton state only. Thus the steps and initial increase in luminescence above background before the $n=2$ line correspond to phonon-assisted transition terms in (3) to the $|1s,K\rangle$ exciton level with $|2p,0\rangle$ as intermediate state. As the energy for direct transitions to $n=2$ is approached, actual $|2p,0\rangle \rightarrow |1s,K\rangle$ transitions are possible, resulting in a finite lifetime of the 2*p* state. The absorption of light at this wavelength will therefore populate the 2*p* level, thus producing a competing process for population of the 1*s* level. Hence, a decrease in luminescence is observed and a dip produced in the excitation curve.

Luminescence studies are then seen to be a means of studying absorption processes in the material and are rendered valuable, since the 1-μ luminescence appears to be a decay from the 1*s* level only, allowing direct and indirect processes to be resolved.

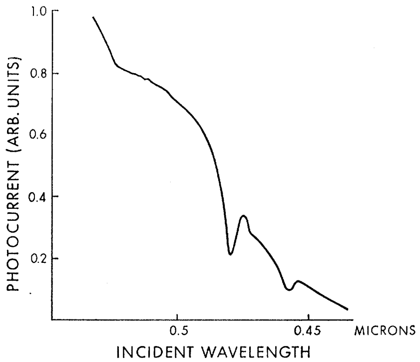

FIG. 5. Detail of a photoconductivity-excitation curve in the region of the blue and violet exciton dips. Temperature is 77°K.

The appearance of steps and dips in the blue and violet regions of the photoconductivity similar to those discussed above for the luminescence suggest that similar absorption processes may be responsible. The two photoconductivity dips at 0.48 and 0.46 μ have been attributed to excitons associated with the allowed transitions $\Gamma_{25}' \rightarrow \Gamma_{12}'$ at $K=0$.[27] The energy separation of the two dips agrees well with the spin-orbit splitting of the Γ_{25}' band which results in two bands at $K=0$ with a splitting energy of 0.13 eV. However, no steps are expected for allowed transitions, and it is therefore suggested that the steps and dips correspond to indirect transitions to the same band as given by Γ_{12}' but to the edge of the zone instead of at $K=0$, the density of available states being more favorable here than at $K=0$. The important intermediate states for the process would be at Γ_{12}'. This would also account for the wide linewidth of the dips, since the curvature of the band minimum is not as high as that at Γ_1 and the band minimum, therefore, is not as well defined.

CONCLUSION

The experimental results discussed agree well with what was previously known or postulated in Cu_2O.

Photon energy is absorbed in the crystal and, through exciton creation, transferred to copper vacancies for radiative recombinations. Whereas optical absorption gives data on all absorbed photons regardless of the later deexcitation process, we have shown that the luminescence excitation spectrum is valuable and different in that it is associated only with those absorbed photons which subsequently decay radiatively.

ACKNOWLEDGMENTS

The authors would like to express their thanks to R. K. Lomnes for help in computations, and to J. P. Zielinger for private communication of absorption data. Financial support from NATO permitted very fruitful discussions with the Strasbourg group and a research grant from the National Research Council of Canada is also gratefully acknowledged.

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