

values of the model parameters and that the data fit the model to experimental accuracy. This is the first report, to the author's knowledge, of such a complete test of Mott's model.

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⁴Crystallization was determined by looking for the onset of sharp structure in the reflectivity at 3.4 eV, the Γ -point transition in crystalline Si. This method can detect a crystallinity as small as 2% by volume.

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⁶Anneals below 225°C could be done in the measurement cryostat. By monitoring resistance versus annealing time, I found that all significant changes took place in 2 h or less.

⁷I used coplanar evaporated silver electrodes with a gap of a few hundred microns. They were removed before annealing and redeposited over a fresh part of the film after annealing.

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¹⁰Measurements of sample temperature are accurate to $\pm 0.3\%$. The uncertainty in σ is $\pm 3\%$. If the deviation of a data point from the least-squares fit with Eq. (1) is, on the average, less than 3%, we say that the data fit Eq. (1) to within experimental error.

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Luminescence of Cu_2O —Excitonic Molecules, or Not?*

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Luminescence spectra of Cu_2O excited at various temperatures by a tunable dye laser showed no evidence of the existence of excitonic molecules (or biexcitons) as suggested recently by Gross and Kreingol'd. A pair of previously unreported peaks with an exceptionally strong temperature dependence has been observed below 3°K.

The existence of excitonic molecules (or biexcitons) in a crystal was first suggested by the results of Haynes on Si.¹ Since then, the subject has attracted much attention. Recently Gross and Kreingol'd² reported the existence of excitonic molecules in Cu_2O . It is well established³ that the absorption edge of Cu_2O consists of two hydrogenic series, known as the "yellow" and the "green" series, due to the excitons formed by the lowest conduction band and the two top valence bands (split by spin-orbit coupling) at the

center of the Brillouin zone. These excitons are said to be forbidden because the conduction and valence bands involved have the same parity, so that the $n=1$ excitons cannot be excited by dipole transition. Gross and Kreingol'd² observed an inverted hydrogenic series in the luminescence spectrum of Cu_2O at 2°K, with a Rydberg constant equal to that of the green exciton series. They concluded that this inverted series in the luminescence spectrum should result from the decay of excitonic molecules, each of which was com-

posed of two $n=1$ excitons of the green series. However, the binding energy ($\sim 150 \text{ cm}^{-1}$) of the excitonic molecule obtained from this model was too large to explain the observed temperature dependence of the luminescence. L'vov and Pavinskii⁴ suggested that the excitonic molecule could be composed of one $n=1$ and one $n=2$ exciton of the yellow series with a binding energy equal to 16.9 cm^{-1} .

We have carried out the present investigation with the purpose of verifying the existence of excitonic molecules in Cu_2O and of finding evidence to support either the model of Gross and Kreingol'd,² or that of L'vov and Pavinskii.⁴ We used a cw dye laser (Spectra model 70), which is tunable from $16\,000$ to $17\,000 \text{ cm}^{-1}$ and has a linewidth of $\sim 2 \text{ cm}^{-1}$, to excite the luminescence.

The use of such a tunable laser enables us to excite selectively certain excitons only and not others. Therefore, if the excitonic molecule is composed of two $n=1$ green excitons ($17\,346 \text{ cm}^{-1}$), as suggested by Gross and Kreingol'd, the inverted series in the luminescence spectrum should disappear when the exciting laser frequency is not high enough to excite the $n=1$ green exciton. In a similar manner, in the L'vov and Pavinskii model, the inverted series should disappear if the laser only excites the $n=1$ but not the $n=2$ ($17\,328 \text{ cm}^{-1}$) yellow exciton.

The results of our investigation give no evidence of excitonic molecules in Cu_2O as Gross and Kreingol'd² have suggested. Instead, we found that most of the luminescence lines of Cu_2O result from phonon-assisted recombination of free excitons. The exceptions are three lines which appear to have much stronger temperature dependence than the rest.⁵ We have found no existing theory capable of explaining such strong temperature dependence.

The samples used in this experiment were single crystals whose absorption coefficients have been found to agree well with published data.⁶ The luminescence spectra taken at temperatures ranging from 1.4 to 30°K were analyzed by a typical Raman setup with photon-counting electronics.

In Fig. 1, we present the luminescence spectrum of Cu_2O at 1.41°K excited by a 7.5-mW laser beam at $16\,610.5 \text{ cm}^{-1}$ (6020.3 \AA). We have labeled the peaks as A, B, C, and so on. The lines denoted by R are the Raman lines of Cu_2O , since they shifted together with the exciting frequency. The positions of the luminescence peaks are listed in Table I. We found that the lumines-

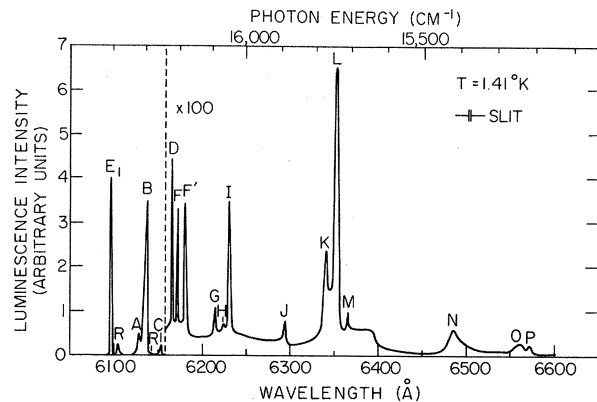


FIG. 1. Luminescence spectrum of Cu_2O at 1.41°K excited by a 7.5-mW laser beam at $16\,610.5 \text{ cm}^{-1}$ (6020.3 \AA). The temperature quoted here was obtained from the vapor pressure of the liquid helium in which the sample was immersed. The actual temperature of the sample could be somewhat higher due to local heating by the laser. The optical geometry was optimized here to give the best signal-to-noise ratio. The strong focusing of the laser beam on the sample might have caused some local heating.

cence spectrum remained unchanged as the exciting laser frequency changed from $16\,610.5$ to $17\,699 \text{ cm}^{-1}$. However, when the laser frequency was below $16\,510 \text{ cm}^{-1}$, the absorption edge of Cu_2O , the luminescence disappeared completely as expected.

Gross and Kreingol'd² reported the observation of a series of five peaks at $15\,434$, $15\,252$, $15\,210$, $15\,183$, and $15\,164 \text{ cm}^{-1}$, respectively, and suggested that they form the $n=2$ to $n=6$ members of an inverted hydrogenic series which arises from the decay of excitonic molecules. We have observed only the first three peaks of this series, namely, N, O, and P at $15\,423$, $15\,239$, and $15\,216 \text{ cm}^{-1}$, respectively [see Fig. 2(a) where the positions of the peaks reported by Gross and Kreingol'd are indicated by arrows]. We believe that the $n=5$ and 6 peaks observed by Gross and Kreingol'd could have been due to impurities or defects. As these authors mentioned in their paper, only the $n=2$ peak [i.e., peak N in Fig. 2(a)] was distinctly seen, while the higher members were superimposed on a background of defect or impurity origin. In our spectra we did not find such a background. A quantitative comparison is not possible since they did not present their spectra. The important fact, however, is that the peaks N, O, and P did not disappear, even when the exciting photon energy was below both the $n=1$ green exciton and the $n=2$ yellow

TABLE I. The photon energy of peaks in the luminescence spectra of Cu_2O obtained at 1.41°K and the energy and symmetry of the phonon(s) involved in the radiative recombination.

Peak	Energy (cm^{-1})	Energy Separation from E_1 (cm^{-1})	Phonon energy obtained by other techniques	Symmetry assignment of phonons involved
E_1	16402			
A	16317	85	88 ^(a) , 86 ^(b)	Γ_{25}^-
B	16295	107	110 ^(a) (d) (f), 108 ^(b)	Γ_{12}^-
C	16252	150	149 ^(c) , 147 ^(d)	$\Gamma_{15}^{-(1)}$ (LO)
D	16221	181	180 ^(e) , 181 ^(f)	$2\Gamma_{25}^-$
F	16202	200	197 ^(g)	$\Gamma_{12}^- + \Gamma_{25}^-$
F'	16181	221	220 ^(2, f, e)	$2\Gamma_{12}^-$
G	16091	311	306 ^(g)	$2\Gamma_{12}^- + \Gamma_{25}^-$
H	16069	333	328 ^(g) , 330 ^(c)	$3\Gamma_{12}^-$
I	16054	348		Γ_2^-
J	15890	512	510 ^(e)	Γ_{25}^+
K	15772	630	626, 3 ^(g) , 640 ^(f) 628 ^(h)	
L	15742	660	667 ^(h) , 662 ⁽ⁱ⁾	$\Gamma_{15}^{-(2)}$ (LO)
M	15710	692		
N	15423	979		
O	15239	1162		
P	15216	1185		

^aS. Brahmns and M. Cardona, Solid State Commun. **6**, 733 (1968) (electroabsorption).

^bAbsorption at 1.4°K.

^cFrom Ref. 7.

^dFrom Ref. 8.

^eFrom Ref. 9.

^fFrom Ref. 10.

^gFrom Ref. 11.

^hFrom Ref. 12.

ⁱFrom Ref. 13.

exciton energies. This is not consistent with the excitonic molecule models of Refs. 2 and 4.

In addition, we found that the peak *N* disappeared around 4.2°K but *O* and *P* did not, whereas Gross and Kreingol'd reported that their entire inverted series disappeared at 4.2°K. Figure 2(a) was taken at 1.41°K. All three peaks showed no appreciable change between 1.41 and 4.2°K. Figure 2(b) was taken after the sample had just emerged from liquid helium. The temperature was estimated to be approximately 5 to 3°K from the line shape of the *A* peak, using the theory for phonon-assisted exciton recombination of Gross, Permatoroy, and Razbirin.¹⁴ Such a strong temperature dependence indicates that *N* must come from an origin different from those of *O* and *P*. We also found that as the exciting laser power varies from 0.25 to 15 mW, the in-

tensities of these peaks are always proportional to the intensity, rather than to the square of the intensity, of the E_1 peak ($n=1$ yellow exciton line). None of these results is compatible with the idea that these peaks are produced by the decay of excitonic molecules.¹ From the observed symmetric broadening of *O* and *P* (and also the peak *M*) with increasing temperature, we assign them tentatively as emission lines involving impurities or defects. However, further investigation is needed to understand the exceptionally strong temperature dependence of the *N* peak.

All the other peaks except *F* and *F'* in Fig. 1 showed an asymmetric broadening towards the high-energy side as the temperature increased, although this was not very obvious for *H* and *K* since they were masked by the stronger neighboring lines at higher temperatures. This character-

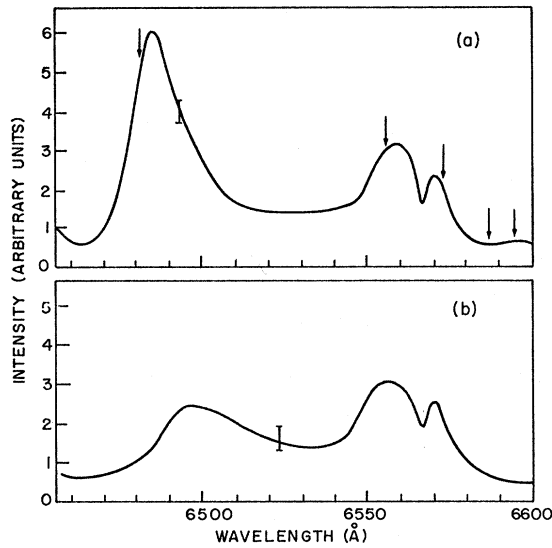


FIG. 2. Luminescence peaks N ($15\,423\text{ cm}^{-1}$, 6484 Å), O ($15\,239\text{ cm}^{-1}$, 6562 Å), and P ($15\,216\text{ cm}^{-1}$, 6572 Å) of Cu_2O excited by a 7.5-mW laser beam at $16\,611\text{ cm}^{-1}$ (6020.3 Å). The arrows give the position of the peaks observed in Ref. 2. (a) $T=1.41\text{ K}$; (b) $T=5\text{--}6\text{ K}$.

istic asymmetric broadening indicates that these peaks must originate from phonon-assisted recombination of a free exciton.¹⁴ From the earlier work on infrared absorption^{7,8,10,12,13,15} and Raman scattering in Cu_2O ,^{10,11,13} we are able to identify these various peaks as due to decay of the $n=1$ yellow exciton with simultaneous emission of a phonon or phonons as listed in Table I. The assignment is partially based on the theoretical calculation of Carabatos and Prevot.⁹ Gross, Kreingol'd and Makaroff¹⁶ have recently proposed that the D peak could be the result of decay of the $n=1$ paraexciton of the yellow series. One of the reasons for their assignment was that this peak had a very different temperature dependence from the other peaks. However, as shown in Fig. 3, we have found no appreciable temperature dependence in this peak between 1.67 and 3.02°K. At higher temperatures, the peak showed the characteristic asymmetric broadening of a phonon-assisted exciton recombination line.⁵

None of the luminescence peaks of Cu_2O showed an appreciable temperature dependence between 1.4 and 4.2°K except F and F' , which appeared to have a remarkably strong temperature dependence as shown in Fig. 3. These two peaks have never been reported earlier in the literature.^{2,16} Their intensities decreased with an increase in temperature by a factor of about 10 between 1.67 and 3.02°K. They remained proportional to the

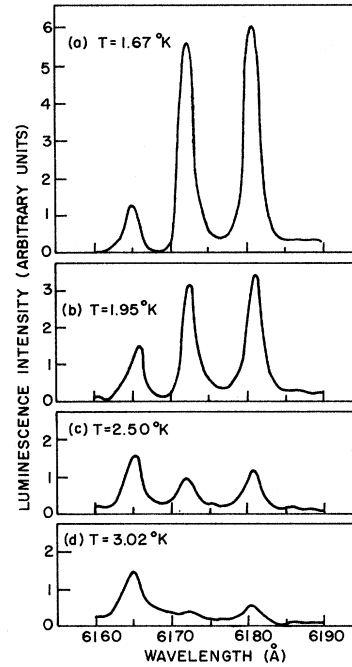


FIG. 3. Luminescence peaks D ($16\,221\text{ cm}^{-1}$, 6165 Å), F ($16\,202\text{ cm}^{-1}$, 6172 Å), and F' ($16\,181\text{ cm}^{-1}$, 6180 Å) of Cu_2O at four different temperatures, excited by a 3.8-mW laser beam at 5691.5 Å .

intensity of E_1 at low exciting power ($\leq 3.8\text{ mW}$) when local heating of the sample could be neglected. When the exciting power was too high, the intensities of F and F' would actually decrease with increasing exciting power as a result of local heating of the sample. This probably explains why Gross and co-workers^{2,16} did not observe these peaks even at 1.8°K since they used a high-power mercury lamp to excite the sample.

So far we have not been able to explain the strong temperature dependence of F and F' based on existing theories. We would just point out that these two peaks have frequencies very close to that of radiative recombination of an $n=1$ yellow exciton with simultaneous emission of two phonons, Γ_{25}^- (87 cm^{-1}) plus Γ_{25}^- (110 cm^{-1}) and $2\Gamma_{12}^-$ (220 cm^{-1}), respectively. The corresponding two-phonon lines at 197 and 220 cm^{-1} have also been seen in the Raman spectrum^{10,11,13} of Cu_2O and found to exhibit a strong resonance enhancement in their Raman cross section at the red absorption edge. Further investigation is necessary in order to elucidate the nature of this doublet.

In conclusion, we have found no evidence of the existence of excitonic molecules and paraexcitons in Cu_2O from our luminescence results. How-

ever, we noticed that there are three luminescence peaks with exceptionally strong temperature dependence, the cause of which is yet to be identified.

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Direct Observation of an Amorphous Spin-Polarization Distribution*

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Evidence is presented from neutron diffraction measurements for the existence of an amorphous spin-polarization distribution in a sputtered rare-earth-iron alloy of composition 33 at.% Tb, 67 at.% Fe.

We have made neutron diffraction measurements on a ferromagnetic sputtered sample of composition 33 at.% Tb, 67 at.% Fe, which allow the first direct observation of the spin polarization in an amorphous magnetic material.

Bulk magnetization measurements¹ show that the material is actually ferromagnetic, in the sense that a macroscopic spontaneous moment is observed. The magnetic isotherms shown in Fig. 1(a) indicate a high degree of saturation in fields of 2-3 kOe, followed by a high-field susceptibility. The zero-field intercepts are plotted versus temperature in Fig. 1(b), indicating a well-defined Curie point of 388 K. This value, as well as the spontaneous moment $\sigma(0, 0) = 2.8 \mu_B/\text{mole}$, are substantially lower than that of the crystalline TbFe_2 Laves phase (710 K and $4.7 \mu_B$, respectively).² Both these features were also found in ternary Fe-Pd-P alloys³ that are be-

lieved to be amorphous. The decrease in $\sigma(0, T)$ below 100 K in Fig. 1(b) is anomalous but may partly result from the procedure used in subtracting the susceptibility term. Prolonged annealing of the sample in the neighborhood of 650 K produces an increase in magnetization with time, providing evidence for the partial recrystallization of the TbFe_2 Laves phase at this temperature.

The neutron data were taken at the National Bureau of Standards Reactor on a disk 25 mm diam by 1 mm thick with 1.36-Å incident wavelength, the collimation being 20' in-pile, 0 between monochromator and sample, and 40' before the counter. Diffraction peak widths were unaltered by inserting 20' collimation before the counter, and therefore instrumental resolution corrections were neglected. Diffraction patterns taken at 423 and 4 K, with instrumental