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August 1972

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# LUMINESCENCE OF $Cu_2O$-BIEXCITONS, OR NOT?

Y. Petroff,* P. Y. Yu,† and Y. R. Shen

August 1972

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# Luminescence of $Cu_2O$ - Excitonic Molecules, or Not?

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## ABSTRACT

Luminescence spectra of $Cu_2O$ at various temperatures excited by a tunable dye laser showed no evidence of the existence of excitonic molecules (or biexcitons) as suggested recently by Gross et al. A pair of previously unreported peaks with an exceptionally strong temperature dependence have 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'd[2] reported the existence of excitonic molecules in $Cu_2O$. It is well-established[3] 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'd[2] 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 composed of two $n = 1$ excitons of the green series. However, the binding energy ($\sim 150\ cm^{-1}$) of the excitonic molecule obtained from this model was too large to explain the observed temperature dependence of the luminescence. L'vov and Pavinskii[4] suggested that the excitonic molecule could be composed of one $n = 1$ and one $n = 2$ excitons of the yellow series with a binding energy equal to $16.9\ cm^{-1}$.

We have carried out the present investigation with the purpose to verify the existence of excitonic molecules in $Cu_2O$ and to find 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 $16,000\ cm^{-1}$ to $17,700\ cm^{-1}$ and has a linewidth of $\sim 2\ cm^{-1}$, to excite the luminescence.

The use of such a tunable laser enables us to excite selectively only the n = 1 green exciton[3] (17,146 $cm^{-1}$) or both the n = 2 yellow exciton[3] (17,328 $cm^{-1}$) and the n = 1 green exciton. Therefore, if the excitonic molecule is composed of two n = 1 green excitons, 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, yellow excitons. With the experiment carried out by a more sensitive detection system over a wider temperature range, we can also expect to obtain more information about the luminescence spectrum of $Cu_2O$.

The results of our investigation give no evidence of excitonic molecules in $Cu_2O$ as Gross and Kreingol'd[2] 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°K 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 16610.5 $cm^{-1}$ (6020.3 Å). 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 luminescence spectrum remained unchanged as the exciting laser frequency changed from 16610.5 $cm^{-1}$ to 17699 $cm^{-1}$. However, when the laser frequency was below 16510 $cm^{-1}$, the absorption edge of $Cu_2O$, the luminescence disappeared completely as expected.

Gross et al.[2] reported the observation of a series of 5 peaks at 15434, 15252, 15210, 15183, and 15164 $cm^{-1}$ 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, however, only three peaks: N, O, and P, at 15423, 15239, and 15216 $cm^{-1}$ respectively in this region. We were not able to detect the other two peaks although, according to the hydrogenic model, the intensity of the n = 5 peak would be approximately half of that of the n = 4 peak. The fact that the peaks N, O, and P did not disappear even when the exciting photon energy was below both the n = 1 green exciton energy and the n = 2 yellow exciton energy repudiates the biexciton model of both Gross and Kreingol'd[2] and L'vov and Pavinskii.[4] In addition, we found that the N peak had a very different temperature dependence from O and P (see Fig. 2). Figure (2a) was taken at 1.41°K. All three peaks showed no appreciable change between 1.41°K and 4.2°K, but N diminished very rapidly at higher temperatures. Figure (2b) was taken after the sample has just emerged from liquid helium. The temperature was estimated to be approximately 5-6°K from the lineshape of the A peak using the theory for phonon-assisted exciton recombination of

Gross et al.[7] 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 mW to 15 mW, the intensities of these peaks are always proportional to the intensity, rather than square of the intensity, of the $E_1$ peak (n=1 yellow exciton line). All these results are not 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 characteristic asymmetric broadening indicates that these peaks must originate from phonon-assisted recombination of a free exciton.[7] From the earlier work on infrared absorption[8-13] and Raman scattering in $Cu_2O$,[12-14] we are able to identify these various peaks as due to decay of the n = 1 yellow exciton with simultaneous emission of phonon or phonons as listed in Table I. The assignment is partially based on the theoretical calculation of Carabatos and Prevot.[15] Gross et al.[16] have recently proposed that the D peak could be due to 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°K and 3.02°K. At higher temperatures, the peak showed the characteristic asymmetric broadening of a phonon-assisted exciton recombination line.[5]

All the luminescence peaks of $Cu_2O$ showed no appreciable temperature dependence between 1.4°K 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 increase in temperature by a factor of about 10 between 1.67°K and 3.02°K. They remained proportional to the intensity of $E_1$ at low exciting power ($\lesssim$ 3.8 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 et al.[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 $\Gamma_{25}^-$ (87 $cm^{-1}$) + $\Gamma_{25}^-$ (110 $cm^{-1}$) and $2\Gamma_{12}^-$ (220 $cm^{-1}$) respectively. The corresponding two-phonon lines at 197 $cm^{-1}$ and 220 $cm^{-1}$ have also been seen in the Raman spectrum of $Cu_2O$[12-14] 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. However, we noticed that there are three luminescence peaks with exceptionally strong temperature dependence, the cause of which is yet to be identified.

## ACKNOWLEDGEMENTS

Helpful discussions with Professors C. Kittel, M. L. Cohen, and L. Falicov are gratefully acknowledged. We are also indebted to Drs. J. Reydellet, M. Balkanski, and D. Trivich for sending us a preprint of their paper. This research was sponsored by the U. S. Atomic Energy Commission.

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† IBM Postdoctoral Fellow.

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## Figure Captions

Fig. 1. Luminescence spectrum of $Cu_2O$ at 1.41°K excited by a 7.5-mW laser beam at 16610.5 $cm^{-1}$(6020.3Å). 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.

Fig. 2. Luminescence peaks N (15423 $cm^{-1}$, 6484Å), O (15239 $cm^{-1}$, 6562Å), and P (15216 $cm^{-1}$, 6572Å) of $Cu_2O$ excited by a 7.5 mW laser beam at 16611 $cm^{-1}$ (6020.3Å).

Fig. 3. Luminescence peaks D(16221 $cm^{-1}$, 6165Å), F(16202 $cm^{-1}$, 6172Å), and F'(16181 $cm^{-1}$, 6180Å) of $Cu_2O$ at four different temperatures, excited by a 3.8-mW laser beam at 5691.5Å.

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] | $\Gamma_{25}^-$ |
| B | 16295 | 107 | 110[a][d][f], 108[b] | $\Gamma_{12}^-$ |
| 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 | | $\Gamma_2^-$ |
| J | 15890 | 512 | 510[e] | $\Gamma_{25}^+$ |
| 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 | | |

(a) S. Brahms and M. Cardona, Solid State Comm. 6, 733 (1968) (Electroabsorption).

(b) Absorption at 1.4°K.

(c) From Ref. 8

(d) From Ref. 9

(e) From Ref. 14

(f) From Ref. 12

(g) From Ref. 13

(h) From Ref. 10

(I) From Ref. 11

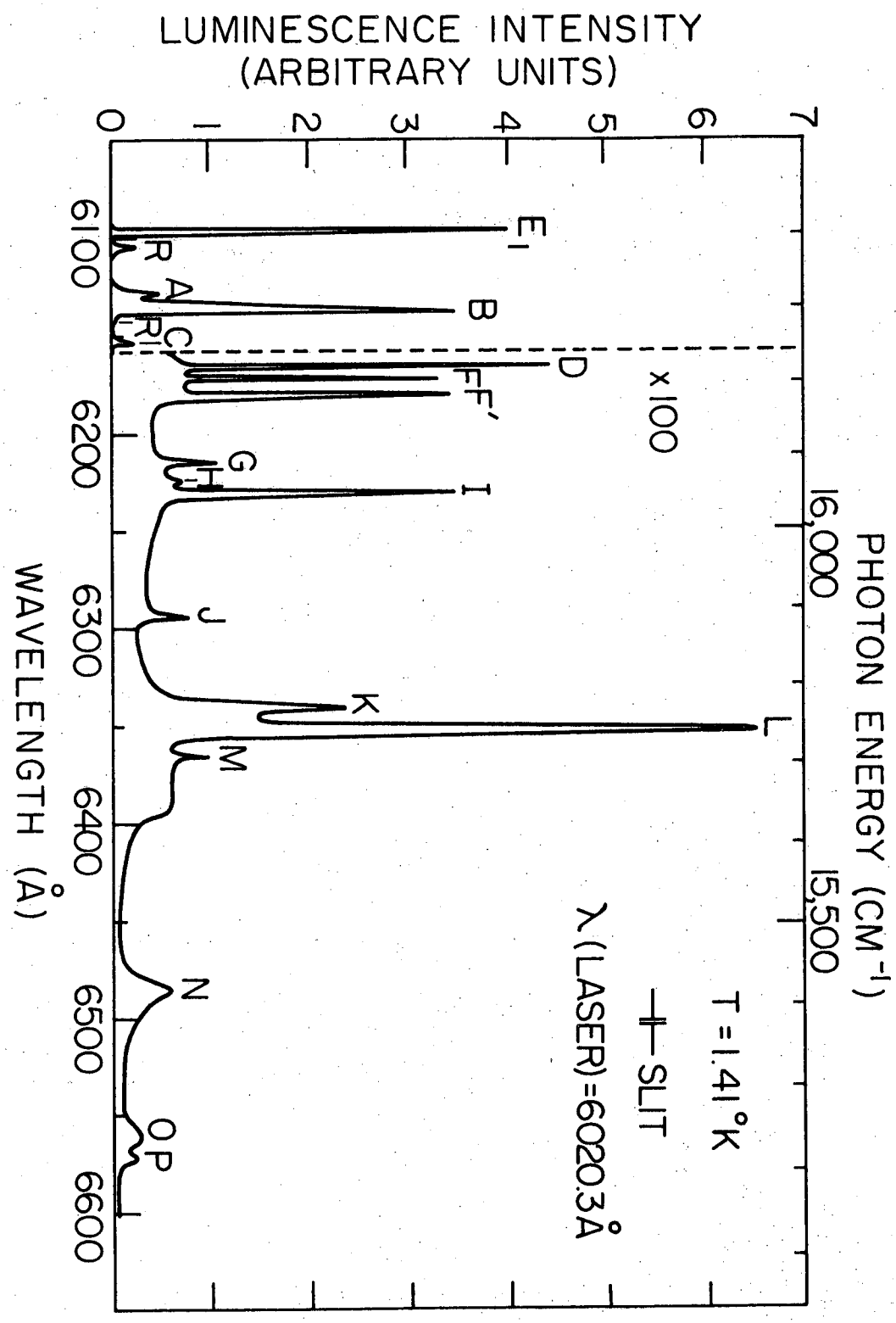


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Fig. 1

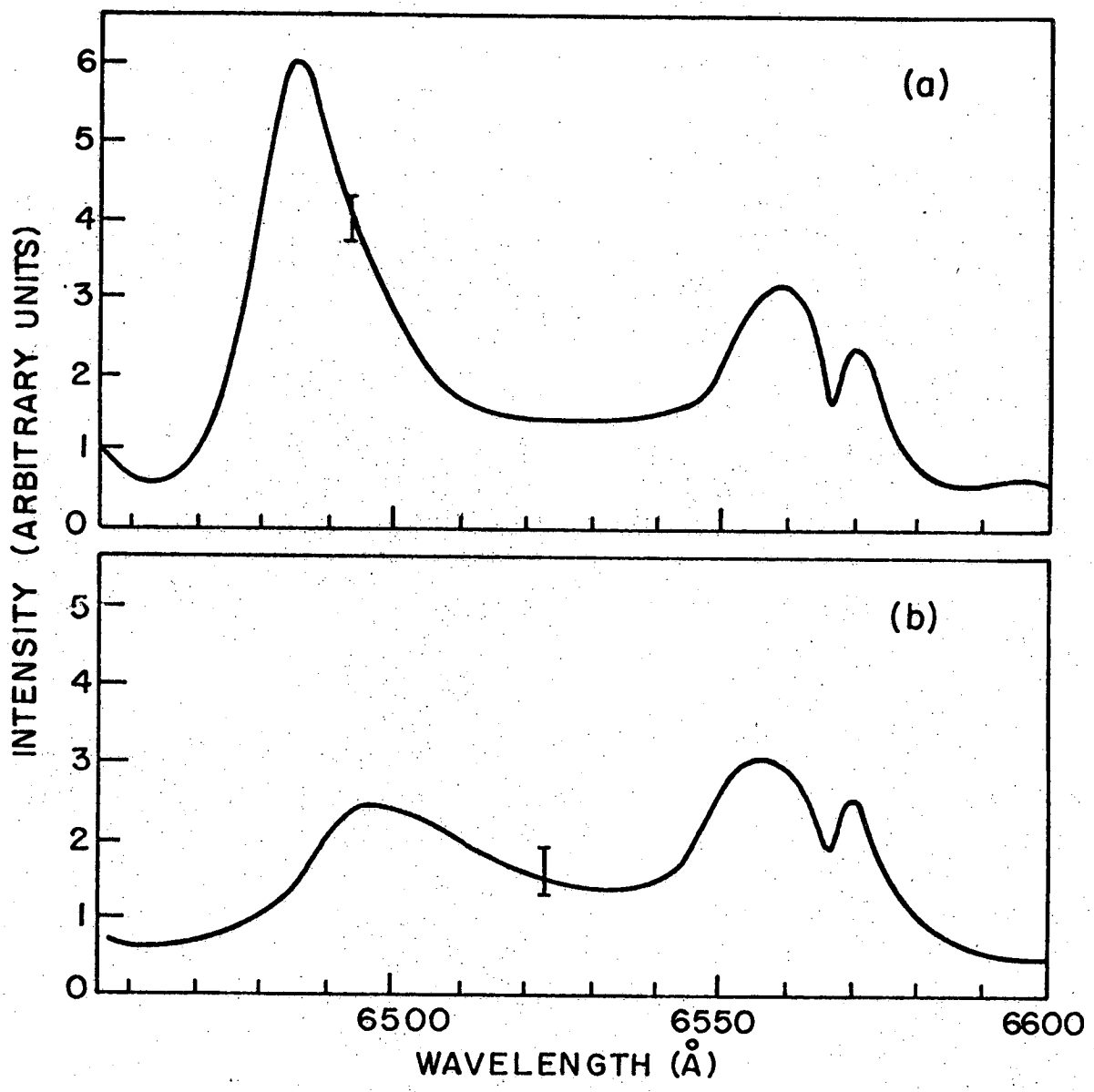


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Fig. 2

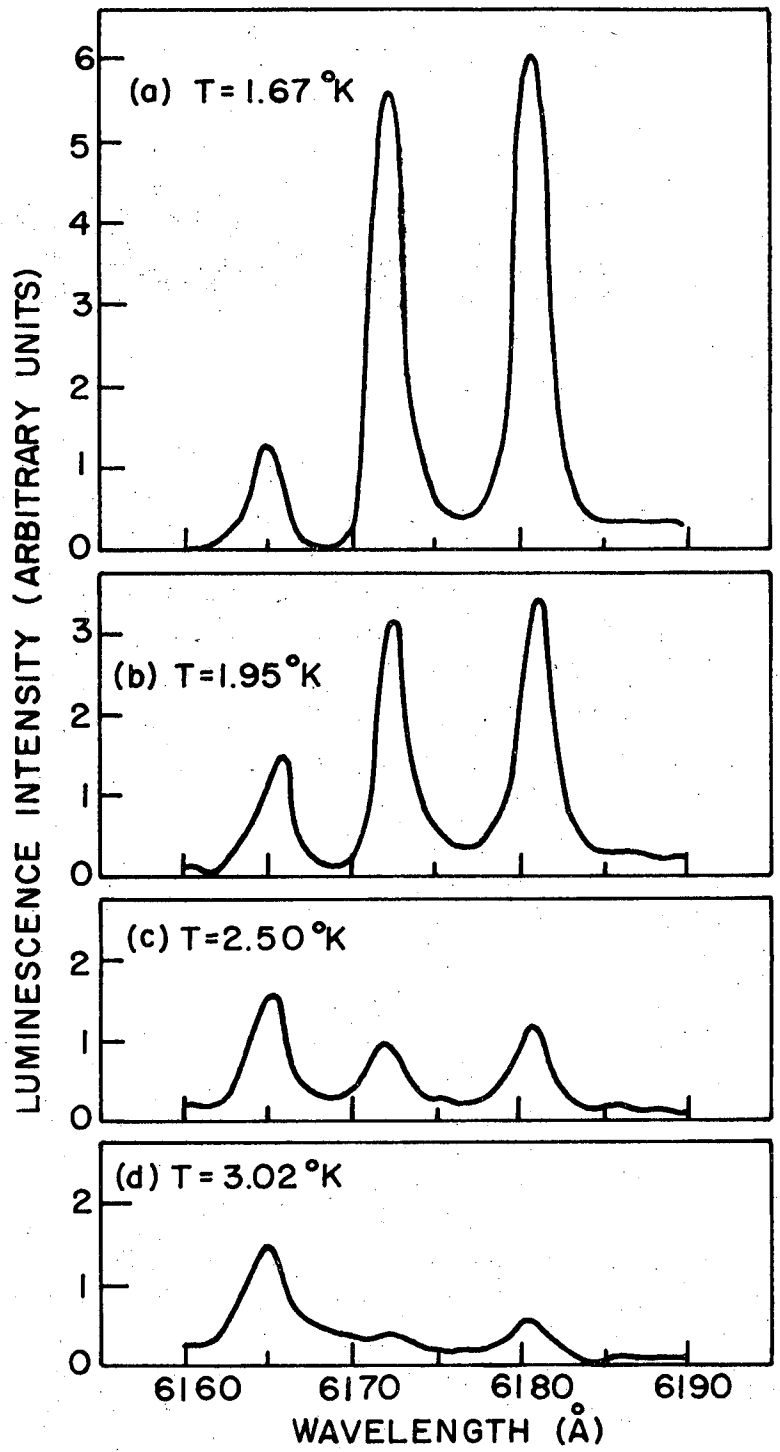
(a) T = 1.67 °K
(b) T = 1.95 °K
(c) T = 2.50 °K
(d) T = 3.02 °K
LUMINESCENCE INTENSITY (ARBITRARY UNITS)
WAVELENGTH (Å)
6160
6170
6180
6190
XBL 727 - 6674

Fig. 3

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