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Resonance Raman Scattering in Cu_2O at the Blue and Indigo Excitons

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ABSTRACT

The resonance enhancement of five Raman lines of Cu_2O has been measured in the vicinity of the blue and indigo excitons. The experimental results show qualitative agreement with the theoretical predictions.

ZUSAMMENFASSUNG

Die resonante Verstärkung des Ramaneffekts in Cu_2O wurde in der Nähe der blauen und der indigo Excitonlinie gemessen. Die experimentelle Ergebnisse stimmen qualitative mit den theoretischen Berechnungen überein.

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Resonance Raman Scattering (RRS) has been reported in a number of semiconductors in the vicinity of excitons.[1,2] In this communication, we present the first RRS results in Cu_2O near its 1s blue and indigo excitons[3] (at 20,780 and 21,800 cm^{-1} respectively). These excitons are believed to be formed by electrons in the second lowest conduction band and holes in the top spin-orbit split valence bands at the zone center.[4] We have found a strong resonance enhancement in both one-phonon and two-phonon Raman lines near the blue exciton. The corresponding enhancement at the indigo exciton is, however, much weaker. Our results are in qualitative agreement with the RRS theory of Ganguly and Birman.[5]

The Cu_2O sample used in this experiment was an unoriented single crystal prepared by oxidation of pure copper. It was mechanically polished and chemically etched before being mounted on the cold finger of a liquid helium cryostat. The sample was excited by the various laser lines (at 19,436; 19,964; 20,169; 20,492; 21,021; 21,155; 21,468; and 21,839 cm^{-1}) of a 1 W Ar^+ laser. The back-scattered light was analyzed with a Spex double monochromator and a photon counting detection system. The intensity of the scattered light was normalized against the intensity of the 283 cm^{-1} line of calcite measured under similar conditions.

Figure 1 shows a Raman spectrum of Cu_2O obtained with the 20,492 cm^{-1} (4880Å) laser line. It is essentially the same as that reported recently by Compaan and Cummins[6] except that the intensities of the 220 cm^{-1}, 515 cm^{-1}, and 625 cm^{-1} lines in our spectrum were weaker. This discrepancy can be due to different orientations of the samples. There are eight distinct lines in our spectrum at 110, 135, 150, 220, 308, 515, 665, and 819 cm^{-1}.

Only the origins of the 110, 150, 220, 515, and 665 cm^{-1} lines are known. They are due to the Γ_{12}^{-}, $\Gamma_{15}^{-(1)}$, $2\Gamma_{12}^{-}$, Γ_{25}^{+}, and $\Gamma_{15}^{-(2)}$ phonons respectively.[6-8] The Γ_{12}^{-}, $\Gamma_{15}^{-(1)}$, and $\Gamma_{15}^{-(2)}$ phonons are not Raman active but can be induced in Raman scattering by either local defects and impurities[9], or spatial dispersion effect.[10,11] The origins of the 308 and 819 cm^{-1} lines are still a matter of speculation. Based on their frequencies we assign them tentatively to $2\Gamma_{12}^{-} + \Gamma_{25}^{-}$ (88 cm^{-1}) and $\Gamma_{15}^{-(1)} + \Gamma_{15}^{-(2)}$ phonons respectively. The 308 cm^{-1} line can also be due to the Γ_{2}^{-} phonon as suggested by Carabatos and Prevot.[12]

In Figure 2 we show the observed Raman cross-section of five of the Raman lines of Cu_2O as a function of incident photon energy obtained at ~ 16°K (the data for the other lines are omitted because of poorer accuracy.) The effect of dispersion in the absorption coefficient has been corrected for in the manner described by Loudon[13] using the absorption data of Daunois et al.[3] We notice that the resonance enhancement is rather similar for all the lines with a peak close to the frequency of the blue exciton. The enhancement near the indigo exciton (only seen in case of the 818 cm^{-1} line) is, however, very weak.

Ganguly and Birman[5] have proposed a theory on RRS near an exciton. By introducing a phenomenological broadening parameter Γ into their theory, one can show that, for a one-phonon Raman process near an exciton ω_{ex}, the dispersion in the Raman cross-section $R(\omega)$ is given by

$$R(\omega) \propto \left| \frac{1}{(\omega-\omega_{ex}+i\Gamma)(\omega-\omega_{ex}-\omega_o+i\Gamma)} + A(\omega) \right|^2 \qquad (1)$$

where ω_o is the phonon frequency and $A(\omega)$ is a background term due to other optical transitions. This equation should hold also for a Raman-inactive phonon induced by local defects or impurities but not if it is induced by spatial dispersion. In the latter case $R(\omega)$ will have a stronger dispersion near the exciton than that given by Eq. (1), as has been shown in case of CdS.[11] The same equation will also apply to two-phonon Raman processes if the phonon involved can only produce interband scattering.

In Fig. 2, we have plotted a theoretical curve of $R(\omega)$ vs ω by assuming $\omega_{ex} = 20{,}780\ cm^{-1}$, $\Gamma = 425\ cm^{-1}$ (this is approximately the width of the blue exciton in the absorption spectra), $\omega_o \approx 0$ and $A \approx 0$ in Eq. (1). It is seen that there is qualitative agreement between the theoretical curve and the experimental results. The non-vanishing ω_o and A have the effects of slightly shifting and broadening the theoretical curve and making the curve somewhat asymmetric. It is possible, by proper choice of $A(\omega)$, to obtain a better theoretical fit for the experimental data. Since we have only limited data points from the limited number of discrete laser lines, a more quantitative theoretical discussion would not be very meaningful here. Further experimental work with a continuously tunable laser is clearly desirable.

The most surprising feature of our result is that the resonance enhancement of the Raman lines of Cu_2O near the indigo exciton is much weaker than that near the blue exciton, considering that in the absorption the strength of the two are roughly equal. Thus our RRS results indicate that the exciton-phonon coupling for the indigo exciton is weaker than for the blue exciton for most of the phonons in Cu_2O.

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FIGURE CAPTIONS

Fig. 1. The Raman spectrum of Cu_2O excited by the 20,492 cm^{-1} (4880Å) line of an Ar^+ laser. The spectrum is unpolarized since the crystal is not oriented.

Fig. 2. The resonance enhancement in the Raman cross-section of the 308, 150, 220, 665, and 819 cm^{-1} lines of Cu_2O in the region of the blue and indigo excitons positions (indicated by arrows). The experimental points have been connected by smooth curves as: —•—•—•—•150 cm^{-1}, ••••o •••• o •••• 220 cm^{-1}, —¤—---¤—--— 308 cm^{-1}, - x --- x -- 665 cm^{-1}, and ---Δ----Δ---- 819 cm^{-1}. the solid curve is a plot of Eq. (1) in the text.

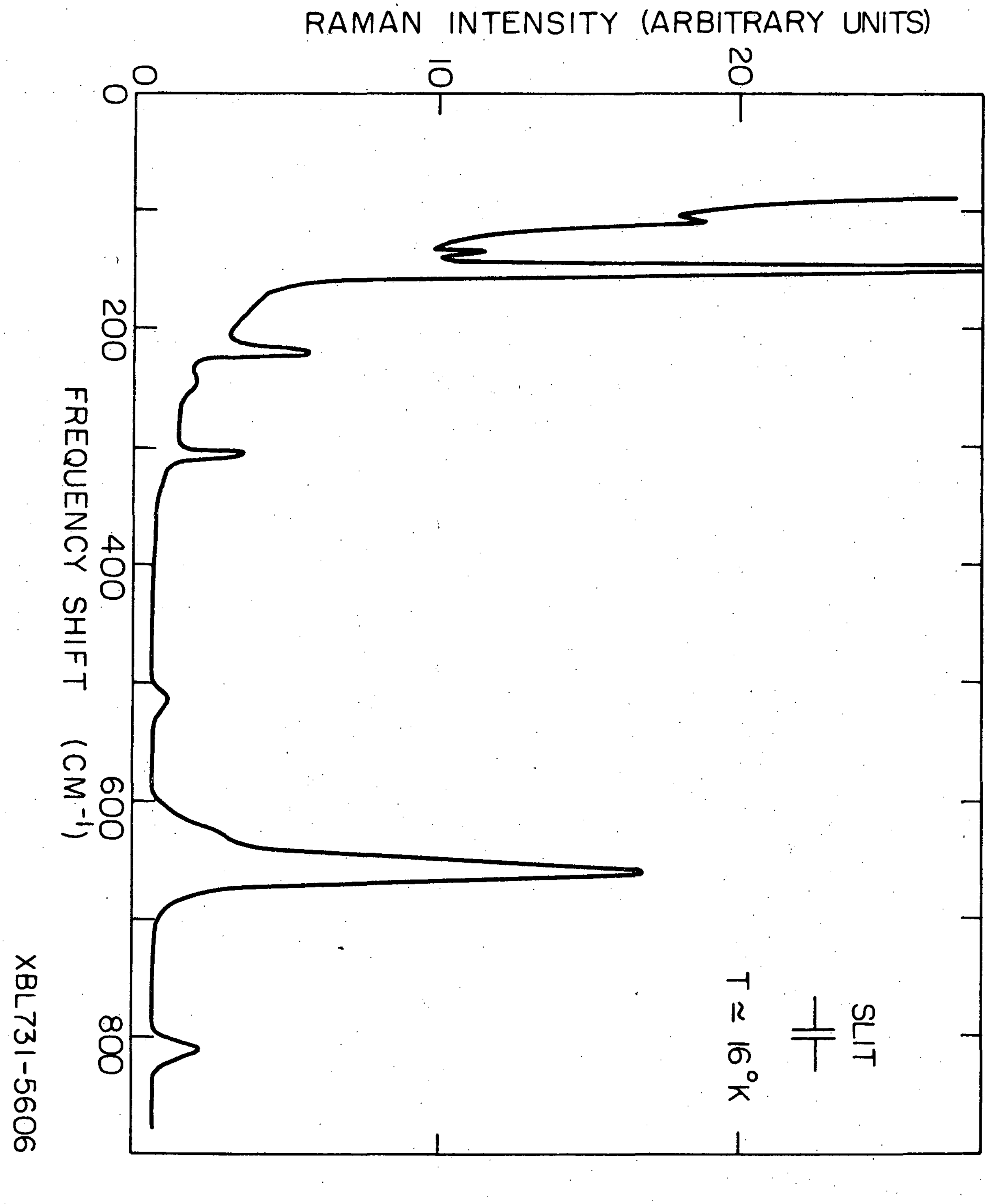
RAMAN INTENSITY (ARBITRARY UNITS)
0
10
20
0
200
400
600
800
FREQUENCY SHIFT (CM-1)
SLIT
T ≃ 16°K
XBL731-5606

Fig. 1

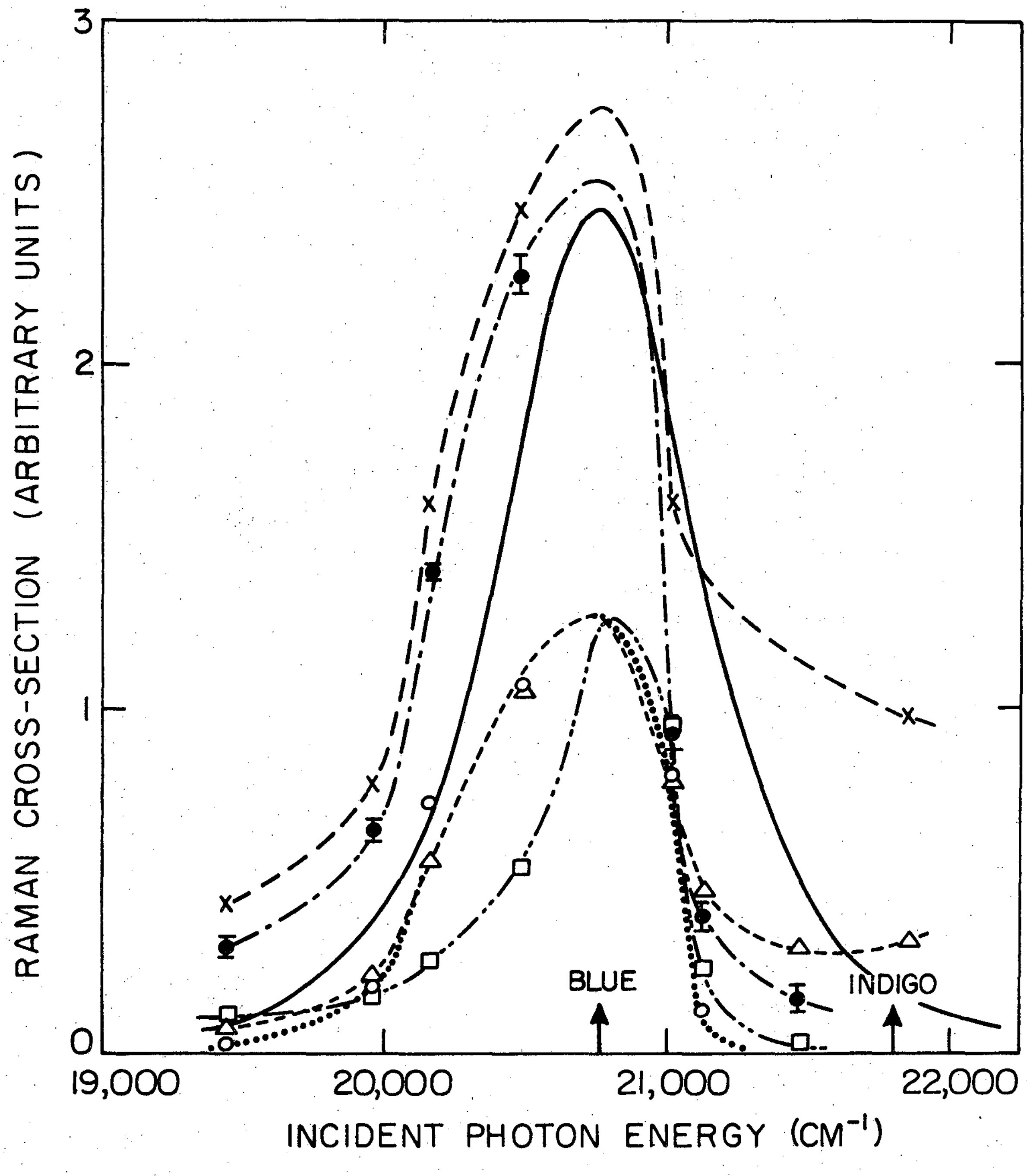

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Fig. 2

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