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[**] Supported by the National Science Foundation

# Resonance Raman Scattering at the Forbidden Yellow Exciton in $Cu_2O$

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## Abstract

We report strong resonance enhancement in the 220 $cm^{-1}$ Raman line of $Cu_2O$ at the $\Gamma_{12}^-$-phonon-assisted absorption threshold of the forbidden 1s yellow exciton. A consistent theoretical interpretation is presented. It shows that the line is due to scattering of two $\Gamma_{12}^-$ phonons and the resonance enhancement is strongly affected by the exciton lifetime. The latter

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effect has never been considered or observed before in resonance Raman scattering.

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Resonance Raman scattering (RRS) close to free or bound excitons has been the subject of a number of reports,[1] but the same effect involving a "forbidden" exciton has received little attention. We report here the results of an experimental investigation on a two-phonon RRS near a forbidden exciton line in $Cu_2O$, and the corresponding theoretical analysis which explains the unusual behavior of the observed resonance. We believe this is the first detailed RRS work involving a forbidden exciton.

The optical spectrum of $Cu_2O$ contains four series of excitons known as the yellow, green, blue and indigo excitons.[2-4] The first two are formed by electron-hole pairs in the lowest conduction band and the two top (spin-orbit split) valence bands. The blue and indigo excitons are believed to involve electrons in a higher conduction band. Electric dipole transitions are allowed for the blue and indigo series but forbidden for the 1s member of the yellow and green series.[5] At 4.2°K the yellow series has the frequencies:[2]

$$\omega_n = (17,525 - \frac{786}{n^2})\ \text{cm}^{-1} \qquad (n = 2,\ 3,\ 4,\ \ldots)$$
$$\omega_1 = 16,400\ \text{cm}^{-1} \ . \qquad (1)$$

The 1s member can be excited from the ground state through phonon-assisted electric-dipole transitions: the most important phonon has a $\Gamma_{12}^-$ symmetry and frequency[3,6,7]

$$\omega_0 = 110\ \text{cm}^{-1} \ . \qquad (2)$$

This phonon-assisted process gives rise to a band absorption threshold (insert in Fig. 1a).

We have measured RRS in $Cu_2O$ in the vicinity of its four excitons and phonon-assisted exciton absorption edge. Here we only discuss the resonance enhancement of the 220 $cm^{-1}$ line in the region of the phonon-assisted yellow exciton absorption band. The $CuO_2$ samples investigated were thin monocrystal-line plates prepared by oxidation of Cu or grown from melt. The resonance enhancement in their Raman lines were essentially the same. The samples were mechanically polished and etched with concentrated nitric acid before being placed on the cold finger of an optical dewar. The exciting radiation from a CW dye laser (Spectra Model 70) was tunable from 16,000 to 17,700 $cm^{-1}$. The back-scattered light from the sample was analyzed by a typical Raman spectrometer with photon counting electronics. Intensities of the Raman lines were normalized against the 283 $cm^{-1}$ line of calcite measured under similar conditions.

Raman spectra of $Cu_2O$ excited by discrete laser lines have been studied by several authors.[6,8-10] When the exciting laser frequency was below the absorption edge, we found lines only at 197 and 220 ($\pm$2) $cm^{-1}$; when the exciting frequency was slightly above the absorption edge we detected additional lines at 264, 280, 306, 328, 434, 626 and 774 $cm^{-1}$. All these lines, except the 197 and 220 $cm^{-1}$ lines, disappeared for exciting frequencies far above the absorption edge. This indicates resonance enhancement for all these Raman modes. The 220 $cm^{-1}$ line showed the strongest enhancement.

In Fig. 1 we show the Raman cross-section of the 220 $cm^{-1}$ line as a function of incident photon energy for two different temperatures. The effect due to dispersion in the absorption coefficient has been corrected for in the way suggested by Loudon.[11] We observe prominent resonance enhancement at two photon frequencies: (A) a very sharp rise at the phonon-assisted absorption threshold and (B) a weaker enhancement close to the edge of the yellow exciton continuum [$n = \infty$ in (1)]. Contrary to recent results[12] we found no enhancement in the 220 $cm^{-1}$ line near the 1s free exciton line, even in the presence of an electric field of up to 10 kV/cm.[7,13]

The 220 $cm^{-1}$ Raman line of $Cu_2O$ has been attributed by various authors to the $\Gamma_{25}^+$ Raman active phonon,[8] to zone boundary phonons activated by defects,[15] and to two $\Gamma_{12}^-$ phonons.[6,14] The assignment to the $\Gamma_{25}^+$ mode is not compatible with polarization studies.[9] Our observation that the Raman cross-section is essentially independent of sample preparation suggests that defects are not important. The two-phonon assignment yields a consistent explanation and good agreement between theory and the experiment.

The sharp rise in the Raman cross-section of a two-phonon mode at the absorption edge is somewhat surprising. The phonon-assisted absorption edge of $Cu_2O$ is not very strong compared to the direct absorption edges in semiconductors[15]. The reason becomes clear if we consider the detailed mechanism involved in the process.

As pointed out earlier, the absorption edge in $Cu_2O$ arises from the absorption of an incident photon with the simultaneous creation of a 1s yellow exciton of wavevector $\vec{q}$ and frequency

$$\omega_a(\vec{q}) = \omega_1 + \hbar q^2/2M \quad , \tag{3}$$

(M is the sum of the electron and hole masses of the exciton), and a $\Gamma_{12}^-$ phonon of wavevector $(-\vec{q})$ and frequency $\omega_0$ and negligible dispersion.[14] The absorption process is shown diagrammatically in Fig. 2a; it is mediated by an intermediate exciton state, labelled $\beta$.[5] Since the $a$ exciton cannot return to the ground state through an electric-dipole transition, the most probable decay mode is the simultaneous emission of a photon and another $\Gamma_{12}^-$ phonon. These two processes put together yield RRS of two $\Gamma_{12}^-$ phonons as shown in Fig. 2 b. It is now clear that the "forbidden" character of the yellow exciton makes it a suitable intermediate state for Raman processes in which two $\Gamma_{12}^-$-phonons are involved.

Standard perturbation theory of the scattering process of Fig. 2b yields for the Raman cross-section as a function of incoming photon frequency $\omega_i$

$$R(\omega_i) \sim \sum_{\vec{q}} \left|(\omega_\beta + 2\omega_0 - \omega_i)(\omega_\alpha + \omega_0 - \omega_i)(\omega_\beta - \omega_i)\right|^{-2} \qquad (4)$$

where $\omega_\beta$ is the intermediate $\beta$ exciton frequency. Eq. (4) assumes matrix elements independent of $\vec{q}$; it can be obtained directly from previously published RRS theories[16] by keeping the only two important terms.

The enhancement observed in the 220 $cm^{-1}$ line is due to the resonant denominator $(\omega_\alpha + \omega_0 - \omega_i)$ in (1). Since the $\beta$ exciton has an energy at least 0.5 eV higher than the yellow exciton $\alpha$, we can regard the non-resonant factors $(\omega_\beta + 2\omega_0 - \omega_i)$ and $(\omega_\beta - \omega_i)$ as constant. By changing the summation over $\vec{q}$ in (4) into an integral

$$R(\omega_i) \sim \sum_{\vec{q}} \left|\omega_1 + \frac{\hbar q^2}{2M} + \omega_0 - \omega_i\right|^{-2} = 4\pi \left(\frac{2M}{\hbar}\right)^{3/2} \int_0^{x_c} \frac{x^{1/2}\, dx}{\left|(\omega_1 + \omega_0 - \omega_i) + x\right|^2} \quad , \qquad (5)$$

where $x_c$ corresponds to the Brillouin zone cut-off $q_c$, it can be seen that (5) diverges for $\omega_i \geq \omega_1 + \omega_0$. This divergence is, of course, an artifact of perturbation theory and is removed by those processes which give a finite lifetime to the exciton state, and, to a lesser extent, to the $\Gamma_{12}^-$ phonon. If the exciton $\alpha$ has frequency given by (3) and a lifetime $\hbar/\gamma(\vec{q})$, then lifetime corrections to (5) are equivalent to replacing in the denominator x by $(x + i\gamma)$. It is also a good approximation to replace

$$\frac{1}{(x + a)^2 + \gamma^2} \cong \frac{\pi}{\gamma(a)}\, \delta(x + a) \quad , \qquad (6)$$

which yields

$$R(\omega_i) \sim \begin{cases} 0 & , \quad \omega_i \leq \omega_1 + \omega_0 \ , \\ \dfrac{(\omega_i - \omega_1 - \omega_0)^{1/2}}{\gamma(\omega_i - \omega_1 - \omega_0)} & , \quad \omega_i > \omega_1 + \omega_0 \ . \end{cases} \tag{7}$$

Eq. (7) states that the two-$\Gamma_{12}^-$ phonon Raman cross-section in the RRS region is given by the ratio of the density of states of the yellow exciton and the lifetime broadening of the yellow exciton at that energy.

We have calculated expressions for $\gamma(q)$ due to various decay processes. The scattering rates due to them are additive.

(a) Intraband scattering by one acoustic phonon,[17] Fig. 2c:

$$\gamma_{ac} = A_1(\omega_i - \omega_1 - \omega_0) \ ; \tag{8}$$

(b) Intraband scattering by two $\Gamma_{12}^-$ phonons, Fig. 2d:

$$\gamma_2 = A_2(\omega_i - \omega_1 - 3\omega_0)^{1/2} \qquad \omega_i > \omega_1 + 3\omega_0 \ ; \tag{9}$$

(c) Decay to the ground state by electric-dipole radiation with emission of one $\Gamma_{12}^-$ phonon, Fig. 2e:

$$\gamma_d = \epsilon_1 \ ; \tag{10}$$

($\epsilon_1$ is a constant quantity, small compared to $\gamma_{ac}$).

(d) Decay to the ground state by electric-quadrupole radiation:

$$\gamma_q = \epsilon_2 \ ;$$

($\epsilon_2$ is an even smaller constant quantity of the order of typical electric-quadrupole linewidth.)

The dashed curve in Fig. 1a is a plot of

$$R(\omega_i) \propto \begin{cases} 0 & \omega_i \leq \omega_1 + \omega_0 \\ \dfrac{(\omega_i-\omega_1-\omega_0)^{1/2}}{(\omega_i-\omega_1-\omega_0)+A}, & \omega_1+\omega_0 < \omega_i < \omega_1+3\omega_0 \\ \dfrac{(\omega_i-\omega_1-\omega_0)^{1/2}}{(\omega_i-\omega_1-\omega_0)+A+B(\omega_i-\omega_1-3\omega_0)^{1/2}}, & \omega_i > \omega_1+3\omega_0 \end{cases} \quad (11)$$

with A and B adjusted to fit the experimental points [A = 4.8 meV and B = 3.8 $(\text{meV})^{1/2}$]. It is seen that (11) fits the experiment very well up to $\omega_i \sim 2.1$ eV. At this point other scattering processes can cause an increase in $\gamma(q)$ and resulting in a $R(\omega_i)$ lower than predicted by (11). At a typical incident photon energy, say $\omega_i = 2.09$ eV, the relative magnitude of $\gamma_{ac}$, $\gamma_2$ and $(\gamma_d + \gamma_q)$ are $\sim 10$, 3, 1 respectively. The sharp increase in $R(\omega_i)$ at $(\omega_1 + \omega_0)$ is a result of the long lifetime $\hbar/\gamma(q)$ of the 1s yellow exciton at the bottom of the band $q = 0$.

It is obvious from the above theory why no appreciable enhancement appears at the frequencies corresponding to the $n = 2$ and higher members of the yellow series (1): these states have a much shorter lifetime. The weak enhancement at $n = \infty$ is due mainly to an increase in the density of states. The theory also explains why at higher temperatures the enhancement in $R(\omega_i)$ at $(\omega_1 + \omega_0)$ decreases much more than that at the continuum: as acoustic phonons become more abundant, the lifetime of the yellow exciton decreases while the density of states of the continuum remains essentially unchanged.

In conclusion, we have found strong resonance enhancement in the 220 $cm^{-1}$ line at the $\Gamma_{12}^{-}$-phonon-assisted absorption edge of $Cu_2O$. The experimental lineshape is dominated by the strong dependence of the lifetime of the 1s yellow exciton on its wavevector; the unusual strength of the enhancement is a result of the long lifetime of the "forbidden" exciton.

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## Figure Captions

Fig. 1. The Raman cross-section of the 220 $cm^{-1}$ line of $Cu_2O$ at two different temperatures: (a) $\sim 16^{\circ}K$ and (b) $\sim 80^{\circ}K$. (These temperatures represent those of the lattice obtained in (a) from the lineshape of the phonon-assisted free exciton recombination spectra and in (b) from the position of the 1s yellow exciton in the luminescence). The insert in (a) shows the absorption spectra of $Cu_2O$ at $4.2^{\circ}K$ taken from Ref. 3. The dashed curve in (a) is a plot of the theoretical expression (11).

Fig. 2. Diagrammatic representation of the following processes: (a) annihilation of a photon with creation of a 1s yellow exciton and a $\Gamma_{12}^-$ phonon; (b) resonant Raman scattering of two $\Gamma_{12}^-$ phonon with the 1s yellow exciton as the intermediate state; (c) intraband scattering of the 1s yellow exciton by acoustic phonon; (d) intraband scattering of the 1s yellow exciton by two $\Gamma_{12}^-$ phonons and (e) decay of the 1s yellow exciton into one photon and a $\Gamma_{12}^-$ phonon.

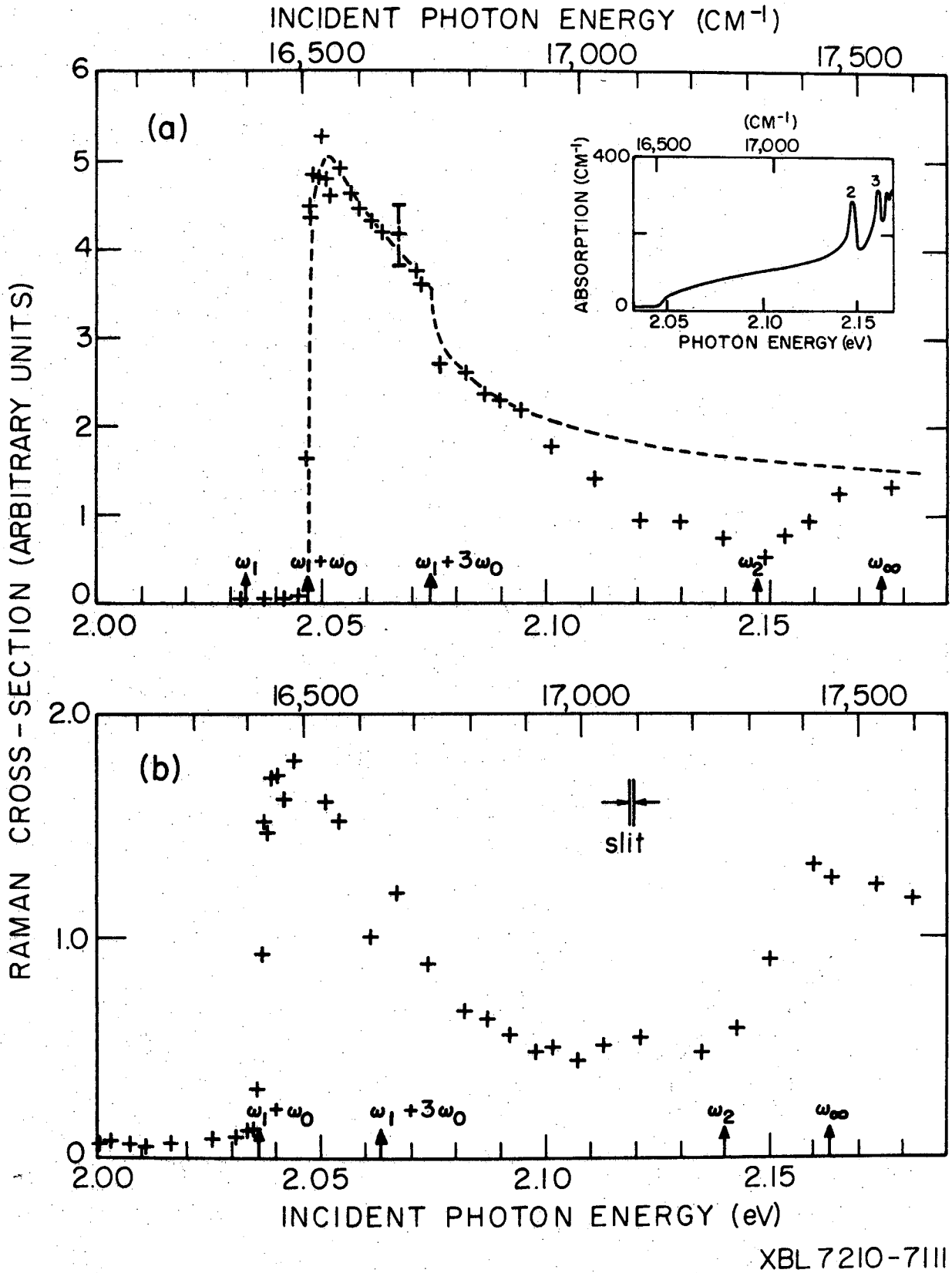
INCIDENT PHOTON ENERGY (CM⁻¹)
16,500
17,000
17,500
(a)
(CM⁻¹)
16,500
17,000
400
0
ABSORPTION (CM⁻¹)
2
3
2.05
2.10
2.15
PHOTON ENERGY (eV)
RAMAN CROSS-SECTION (ARBITRARY UNITS)
ω1
ω1+ω0
ω1+3ω0
ω2
ω∞
(b)
slit
INCIDENT PHOTON ENERGY (eV)
XBL 7210-7111

Fig. 1

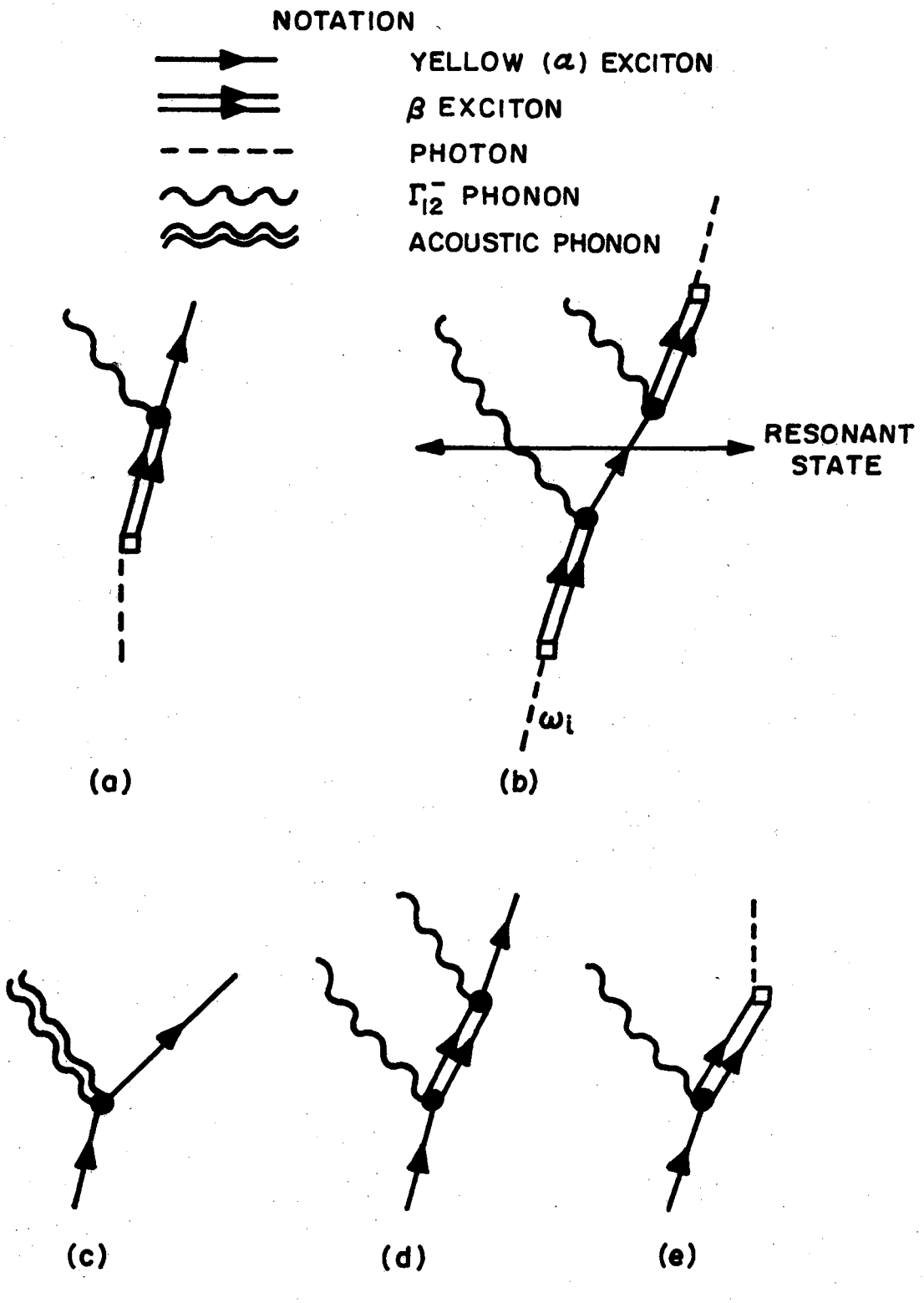
NOTATION
YELLOW (α) EXCITON
β EXCITON
PHOTON
$\Gamma_{12}^-$ PHONON
ACOUSTIC PHONON
RESONANT STATE
$\omega_i$
(a)
(b)
(c)
(d)
(e)
XBL 7210-7112

Fig. 2

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