Submitted to Physical
Review Letters

RECEIVED
LAWRENCE
RADIATION LABORATORY

LBL-1192
Preprint c.1

LIBRARY AND
DOCUMENTS SECTION

RESONANCE RAMAN SCATTERING AT THE FORBIDDEN YELLOW EXCITON IN Cu_2O

P. Y. Yu, Y. R. Shen, Y. Petroff, and L. M. Falicov

October 1972

Prepared for the U.S. Atomic Energy
Commission under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-1192
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-1192
Preprint

Submitted to Physical Review Letters

UNIVERSITY OF CALIFORNIA

Lawrence Berkeley Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

RESONANCE RAMAN SCATTERING AT THE FORBIDDEN YELLOW EXCITON IN Cu_2O

P. Y. Yu[†], Y. R. Shen, Y. Petroff[‡], and L. M. Falicov[**]

October 1972

† IBM Postdoctoral Fellow

‡ On leave from the University of Paris, France

** Supported by the National Science Foundation

Resonance Raman Scattering at the Forbidden Yellow Exciton in Cu_2O

P. Y. Yu[†*], Y. R. Shen[‡*], and Y. Petroff[‡*]

Department of Physics, University of California

and Inorganic Materials Research Division, Lawrence Berkeley Laboratory

Berkeley, California 94720

and

L. M. Falicov[**]

Department of Physics, University of California

Berkeley, California 94720

Abstract

We report strong resonance enhancement in the 220 cm^{-1} Raman line of Cu_2O at the Γ_{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 Γ_{12}^- phonons and the resonance enhancement is strongly affected by the exciton lifetime. The latter

---

[†]IBM Postdoctoral Fellow

[‡]Guggenheim Fellow, now on leave at Harvard University

[‡]On leave from the University of Paris, France

[*]Supported by the Atomic Energy Commission

[**]Supported by the National Science Foundation Grant GH 34438

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

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 $4.2^{\circ}K$ the yellow series has the frequencies:[2]

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

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

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

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 monocrystalline 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 Γ_{25}^{+} Raman active phonon,[8] to zone boundary phonons activated by defects,[15] and to two Γ_{12}^{-} phonons.[6,14] The assignment to the Γ_{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 Γ_{12}^- phonon of wavevector $(-\vec{q})$ and frequency ω_0 and negligible dispersion.[14] The absorption process is shown diagrammatically in Fig. 2a; it is mediated by an intermediate exciton state, labelled β.[5] Since the α 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 Γ_{12}^- phonon. These two processes put together yield RRS of two Γ_{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 Γ_{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 ω_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 ω_β is the intermediate β 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 β exciton has an energy at least 0.5 eV higher than the yellow exciton α, 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 Γ_{12}^- phonon. If the exciton α 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-Γ_{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 Γ_{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 Γ_{12}^- phonon, Fig. 2e:

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

(ϵ_1 is a constant quantity, small compared to γ_{ac}).

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

$$\gamma_q = \epsilon_2 \ ;$$

(ϵ_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 γ_{ac}, γ_2 and $(\gamma_d + \gamma_q)$ are ~ 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 Γ_{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.

References

1. R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters 17, 10 (1966); R. C. Leite, T. C. Damen and J. F. Scott in Light Scattering Spectra of Solids, ed. G. B. Wright, Springer-Verlag, New York (1969); T. C. Damen and J. Shah, Phys. Rev. Letters 27, 1506 (1971).
2. S. Nikitine in Optical Properties of Solids, ed. S. Nudelman and S. S. Mitra, Plenum Press, N. Y. (1969).
3. P. W. Baumeister, Phys. Rev. 121, 359 (1961).
4. E. F. Gross, Usp. Fiz. Nauk. 63, 576 (1957) [Soviet Phys. - Uspekhi 63, 782 (1957)]. E. F. Gross and K. Y. Chang, Fiz. Tver. Tela 4, 261 (1962) [Soviet Phys. - Solid State 4, 186 (1962)].
5. R. J. Elliott, Phys. Rev. 124, 340 (1961).
6. A. Compaan and H. Z. Cummins (unpublished).
7. S. Brahms and M. Cardona, Solid State Comm. 6, 733 (1968).
8. M. Balkanski, M. A. Nusimovici and J. Reydellet, Solid State Comm. 7, 815 (1969).
9. J. C. W. Taylor and F. L. Weichman, Canad. J. Phys. 49, 601 (1971).
10. M. Balkanski, J. Reydellet and D. Trivich (unpublished).

11. R. Loudon, J. Phys. Radium 26, 677 (1965).

12. J. Reydellet (unpublished).

13. J. L. Deiss, A. Daunois and S. Nikitine, Solid State Comm. 8, 521 (1970).

14. C. Carabatos and B. Prevot, Phys. Stat. Solidi 44, 701 (1971).

15. See for example E. J. Johnson in Optical Properties of III-V Semiconductors, ed. R. K. Willardson and A. C. Beer, Academic Press, N. Y. (1967).

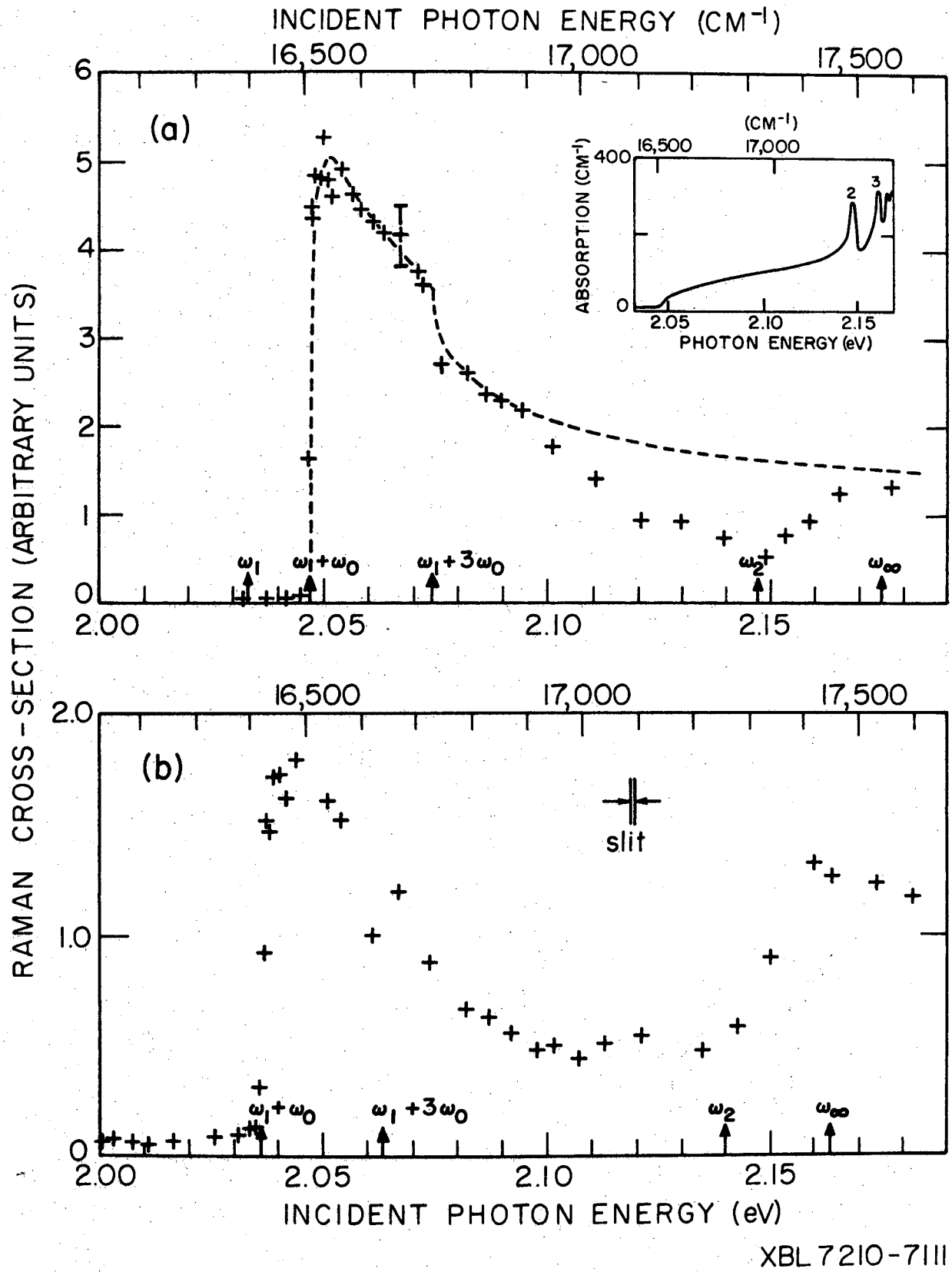
16. A. K. Ganguly and J. L. Birman, Phys. Rev. 162, 806 (1967).

17. Y. Toyozawa, Prog. Theor. Phys. 20, 53 (1958).

Figure Captions

Fig. 1. The Raman cross-section of the 220 cm^{-1} line of Cu_2O at two different temperatures: (a) $\sim 16^{o}K$ and (b) $\sim 80^{o}K$. (These temperatures represent those of the lattice obtained in (a) from the line-shape 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 $4.2^{o}K$ 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 Γ_{12}^{-} phonon; (b) resonant Raman scattering of two Γ_{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 Γ_{12}^{-} phonons and (e) decay of the 1s yellow exciton into one photon and a Γ_{12}^{-} phonon.



XBL 7210-7111

Fig. 1

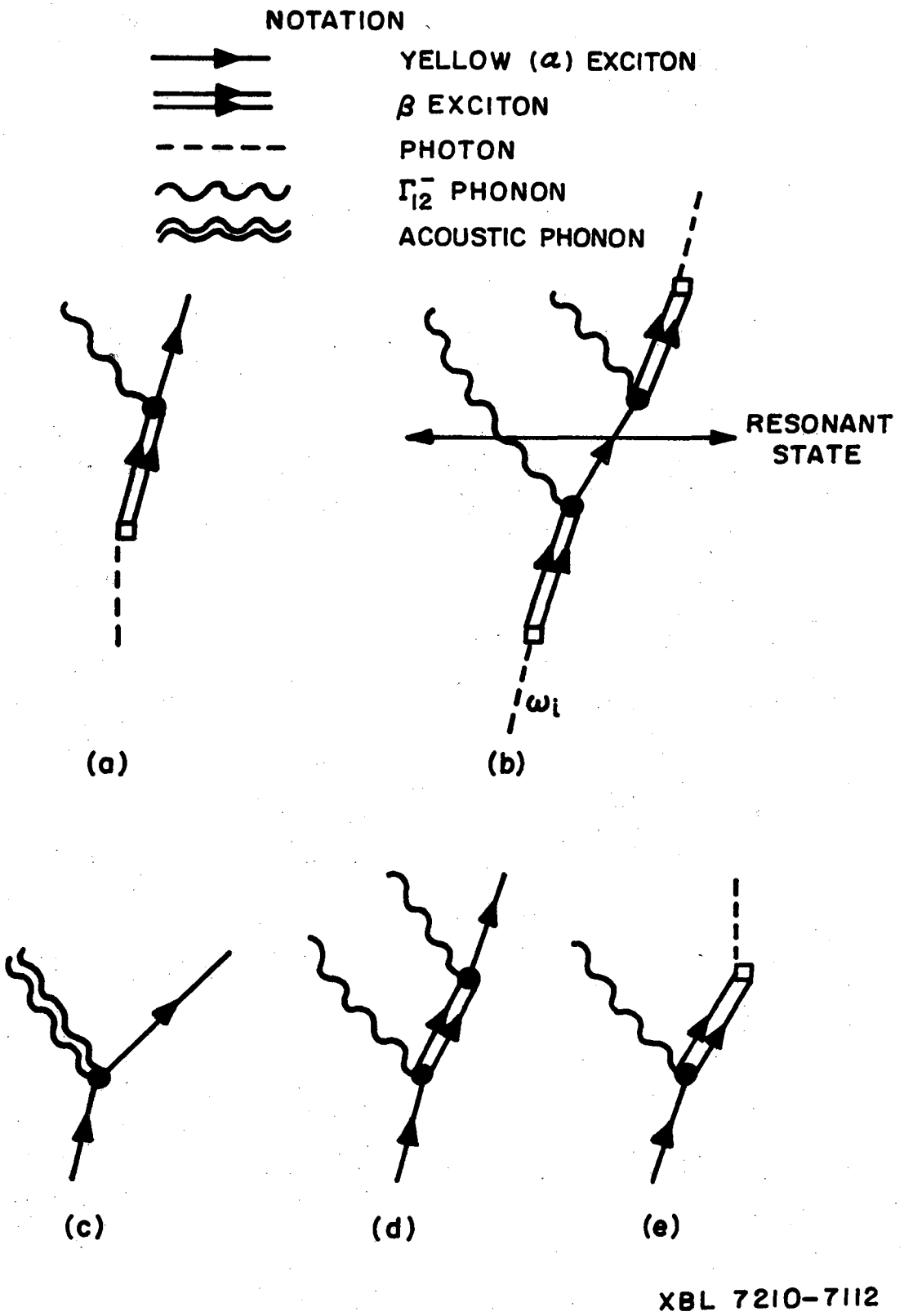

NOTATION
YELLOW (α) EXCITON
β EXCITON
PHOTON
Γ_{12}^{-} PHONON
ACOUSTIC PHONON
RESONANT STATE
ω_i
(a)
(b)
(c)
(d)
(e)
XBL 7210-7112

Fig. 2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720