Title

TIME-RESOLVED RESONANT RAMAN SCATTERING AND HOT LUMINESCENCE AT THE 1S ORTHO-EXCITON IN Cu2O

Authors

Weiner, J.S.
Yu, P.Y.

Publication Date

1984-07-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular
Research Division

Presented at the 17th International Conference on
Physics of Semiconductors, San Francisco, CA,
August 6-10, 1984

TIME-RESOLVED RESONANT RAMAN SCATTERING AND HOT LUMINESCENCE AT THE 1S ORTHO-EXCITON IN Cu_2O

J.S. Weiner and P.Y. Yu

July 1984

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

TIME-RESOLVED RESONANT RAMAN SCATTERING AND HOT LUMINESCENCE AT THE 1S ORTHO-EXCITON IN Cu_2O

J. S. Weiner[a] and P. Y. Yu

Department of Physics, University of California and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720.

The time dependence of one-phonon and two-phonon Raman modes at the 1S yellow ortho-exciton of Cu_2O is reported. In both cases it is found that these modes should be more correctly identified as hot luminescence. The data are fitted using a model which has no adjustable parameters.

Resonant Raman scattering (RRS) with tunable continuous wave (cw) lasers is a well established technique for studying electronic and vibrational transitions in various materials, ranging from semiconductors to hemoglobin.[1,2] It has been suggested that time-resolved RRS will give information about the dynamics of relaxation processes which are not provided by cw RRS measurements.[3] Also, there has been considerable debate in the literature about whether RRS, a one-step coherent process, is distinguishable from hot luminescence (HL), a two-step absorption-emission process.[3-9] It is now generally agreed that it is difficult to distinguish the two processes by cw experiments, but they can be readily distinguished by their temporal behavior after pulsed excitation.

The HL versus RRS controversy was triggered by a cw study of two-phonon Raman scattering in Cu_2O performed by Yu and Shen,[10] who found that the resonance enhancement of this mode was consistent with that expected for HL. We have studied the time dependence of both one- and two-phonon Raman modes in Cu_2O and found that they are both indeed dominated by HL. From the time dependence of the two-phonon modes we directly determine the ortho-exciton lifetime as a function of its kinetic energy. By observing the time dependence of the complete one-phonon Raman lineshape we have been able to directly observe the thermalization of the intermediate state excitons and quantitatively explain our results using an extension of the theory developed in Ref. 11.

Our resonant intermediate state is the 1S ortho-exciton in Cu_2O (w_o=16,397 cm^{-1}). The ortho-exciton is electric-dipole (ED) forbidden, but electric quadrupole (EQ) allowed. Enhancement of several one- and two-phonon Raman modes have been reported, however we will restrict ourselves to the strongest one and two Γ_{12}^- Raman modes.

The experiments were performed in a backscattering geometry with a meltgrown single crystal of Cu_2O at 2 K. The Raman modes were excited by a tunable synchronously pumped, modelocked dye laser, and detected with subnanosecond time resolution by a time-

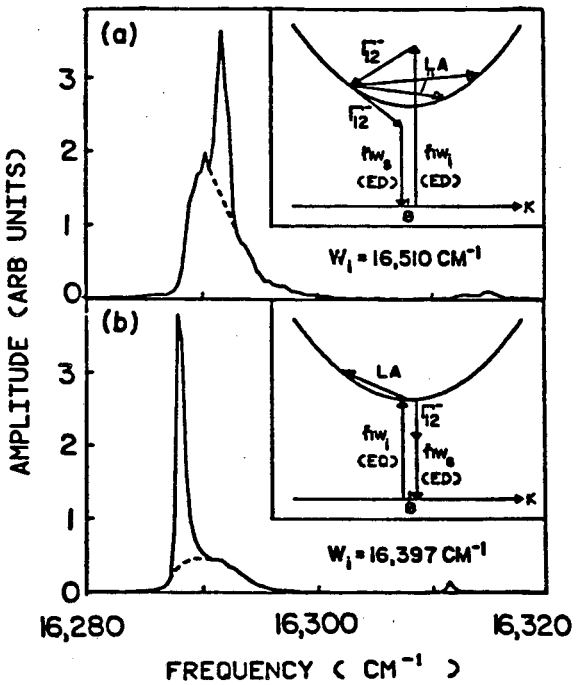

Fig. 1: Time-integrated Raman spectra of Cu_2O at 2 K. The dotted line represents the thermalized luminescence background. (a) Two-phonon Raman spectrum for E = 4 cm^{-1}. (b) One-phonon Raman spectrum. The insets in (a) and (b) are respectively the schematic diagrams of two- and one-phonon Raman scattering discussed in the text.

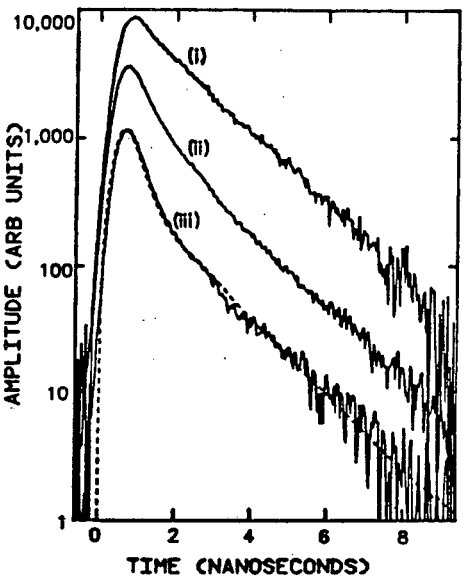

Fig. 2: Time-dependence of two-phonon RRS in Cu_2O for incident laser frequencies corresponding to $E=\hbar(w_i-w_o-w_{12})$ equal to (i) 1 cm^{-1}, (ii) 4 cm^{-1} and (iii) 7 cm^{-1} respectively. The dotted curve superimposed on (iii) represents a typical fit to the experimental curves by convolution of the system response with a decay function of the form: $0.126e^{-t/1.5ns} + e^{-t/0.26ns}$.

delayed coincidence photon counting system.[12] Using this system the lifetime of the ortho-exciton at 2 K has been determined to be 1.5 nsec.[13]

The two-phonon resonant Raman scattering process in Cu_2O, shown schematically in the inset of Fig. 1(a), involves excitation of ortho-excitons by phonon-assisted ED transitions and emission of photons also via phonon-assisted ED transitions. Because of the phonon participation, excitons with non-zero quasi-momentum can be excited. Their kinetic energy is given by $E=\hbar(w_i-w_o-w_{12})$, where w_{12} is the frequency of the dispersionless Γ_{12}^- phonon.

Fig. 1(a) shows the time-integrated two-phonon spectrum of our sample, which is similar to the cw spectra previously reported.[10] The strengths of the Raman peaks are comparable to the background, so care must be used to determine their decay times. The time dependence of the two Γ_{12}^- Raman mode for various excitation energies is shown in Fig. 2. We found that the curves in Fig. 2 show one or two decay components depending on the ortho-exciton kinetic energy E. The slow component decays with a lifetime of 1.5 nsec, which is just the population lifetime and can be explained in terms of the decay of the luminescence background. The fast component has a decay time which depends on E, and is associated with the Raman peak. Its behavior can be explained if we assume that the scattering is dominated by HL, so the variation in the decay time reflects the dependence of the ortho-exciton lifetime on exciton energy. Yu

and Shen[10] concluded from the cw two-phonon RRS in Cu_2O that for E greater than a few wavenumbers the ortho-exciton lifetime is limited by acoustic phonon scattering. Using the model and parameters presented in Ref. 11, we calculate the acoustic phonon scattering rates for E=4 and 7 cm^{-1} to be $(1.0\pm.4)x10^9$ sec^{-1} and $(2.8\pm.7)x10^9$ sec^{-1} respectively. These values are in fair agreement with the fast decay rates of $(1.8\pm.6)x10^9$ sec^{-1} and $(3.3\pm1)x10^9$ sec^{-1} deduced from curves (ii) and (iii). For E=1 cm^{-1}, however, the acoustic phonon scattering rate becomes too small to affect the lifetime, which is then dominated by the ortho- to para-exciton conversion rate,[13] hence, in curve (i) both HL and the thermalized luminescence background will decay with the same time constant of 1.5 nsec.

The one-phonon Raman modes in Cu_2O, as shown in the inset of Fig. 1(b), involve the excitation of zone center excitons by EQ transitions and emission of photons via phonon-assisted ED transitions. The important points to note are that: (i) only the zone-center phonon is excited resonantly. (ii) The EQ transition is strongly polarized for radiation incident on the [110] surface of Cu_2O in spite of the cubic symmetry of the unit cell. and (iii) the one-phonon RRS is strongly polarized.

The experimental time-dependent Γ_{12}^- Raman spectra are shown in Fig. 3 (a) and (b). They were reconstructed from the luminescence decay curves measured at frequency intervals of 1 cm^{-1} using the time-integrated luminescence intensity for normalization. We explain our results in terms of HL of an exciton population which heats up by longitudinal acoustic (LA) phonon scattering.

Our model is depicted schematically in the inset of Fig. 1(b). Excitons are created

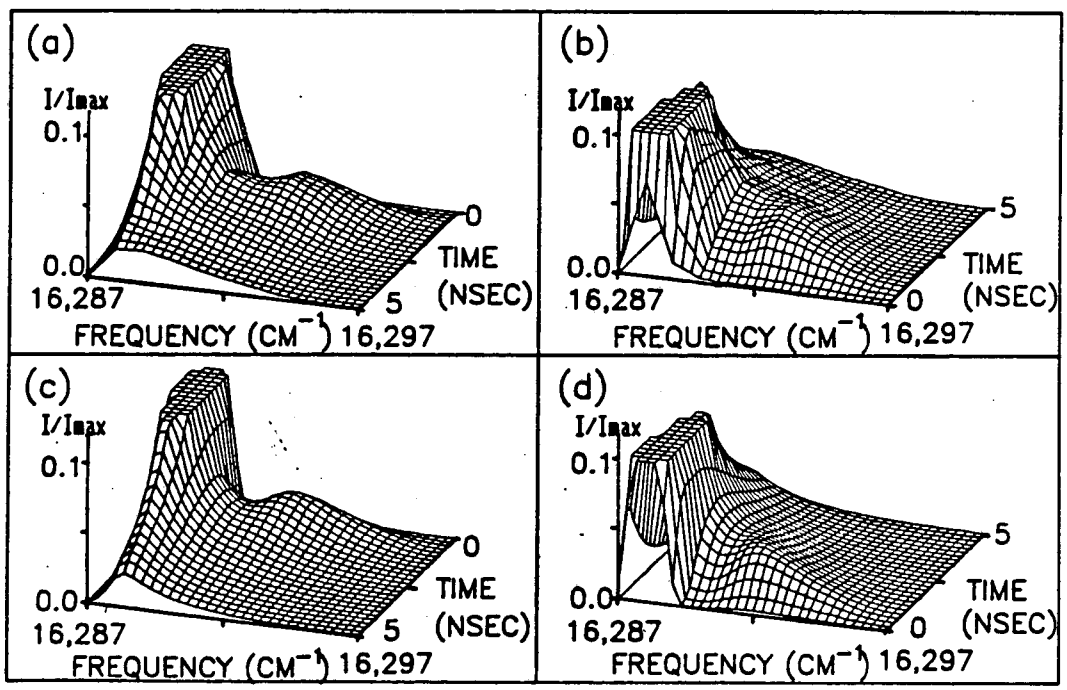

Fig. 3: Lineshape of the one Γ_{12}^- phonon Raman mode as a function of time at a temperature of 2.5 K. (a) and (b) show the measured lineshapes. The experimental points are spaced at intervals of 1 cm^{-1}. (c) and (d) show the corresponding lineshapes calculated using the model discussed in the text.

directly at k=0 by absorption. Those excitons which radiatively recombine without scattering produce the sharp peak at 16,288 cm^{-1}. The amplitude of this peak decays with time as the excitons either decay non-radiatively or are scattered by longitudinal acoustic phonons up to higher energy states. The slope of the acoustic phonon dispersion is much larger than that of the exciton dispersion near the bottom of the band due to the large effective mass of the ortho-exciton. As a result, excitons at k=0 can only be scattered by absorption of acoustic phonons of 5 cm^{-1} energy, resulting in the appearance of a broad peak at 16,293 cm^{-1}. At 2 K K_bT= 2 cm^{-1}, so the rate of this scattering process is slow. On the other hand, excitons with kinetic energy greater than 2.5 cm^{-1} can scatter by emission of acoustic phonons, which will occur much faster. The faster of the two processes will determine the risetime of the peak at 16,293 cm^{-1}, while the slower process will limit the rate at which equilibrium is reached.

The theoretical curves in Fig. 3 (c) and (d) clearly reproduce all of the features of the experimental spectrum, including the position, width and amplitude of the high energy peak, and the time needed to reach a steady state distribution. Also, by comparing Fig. 3 (b) and (d) we see that the theory correctly predicts the risetime of the high energy peak.

In conclusion, we have found that HL provides a self-consistent interpretation of all the cw and time-resolved measurements of RRS in Cu_2O. We have shown that time-dependent measurements can determine the intraband scattering rates due to acoustic phonons, which cannot be determined by cw measurements.

Acknowledgement--This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the Department of Energy under Contract Number DE-AC03-76SF00098.

[a] Present Address: AT&T Bell Laboratories, Holmdel, New Jersey 07733.

[1] See for example, Light Scattering in Solids, ed. by M. Cardona, Topics in Applied Physics, vol. 8 (Springer-Verlag, New York, 1975).
[2] See for example, Vibrational Spectra and Structure, vol 5, ed. by J. R. Durig (Elsevier, Amsterdam, 1976).
[3] T. Takagahara, Relaxation of Elementary Excitations, ed. by R. Kubo and E. Hanamura, Solid State Sciences 18 (Springer-Verlag, New York, 1980), p. 45.
[4] M. V. Klein, Phys. Rev. B 8, 919 (1973).
[5] Y. R. Shen, Phys. Rev. B 9, 622 (1974).
[6] Y. Toyazawa, J. Phys. Soc. Japan 41, 400 (1976), ibid 41, 1699 (1976).
[7] P. Saari, in Light Scattering in Solids, ed. J. L. Birman, H. Z. Cummins and K. K. Rebane (Plenum, New York, 1979), p. 315.
[8] P. F. Williams, D. L. Rousseau and S. H. Dworetsky, Phys. Rev. Lett. 32, 196 (1974).
[9] Y. Masumoto, S. Shionoya and Y. Tanaka, Solid State Commun. 27, 1117 (1978).
[10] P. Y. Yu and Y. R. Shen, Phys. Rev. B 12, 1377 (1975).
[11] N. Caswell, J. S. Weiner and P. Y. Yu, Solid State Commun. 40, 843 (1981).
[12] J. S. Weiner and P. Y. Yu, J. Appl. Phys. 55, 3889 (1984).
[13] J. S. Weiner, N. Caswell, P. Y. Yu and A. Mysyrowicz, Solid State Commun., 46, 105 (1983).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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