Resonant Quadrupole-Dipole Raman Scattering at the 1S Yellow Exciton in Cu_2O†

A. Compaan and H. Z. Cummins*
Department of Physics, New York University, New York, New York 10003
(Received 27 March 1973)

Strong first-order Raman scattering of the normally forbidden odd-parity phonons is observed in Cu_2O excited by a tunable dye laser in resonance with the intrinsic dipole-forbidden 1S yellow exciton. The resonance enhancement and the polarization behavior of these Raman lines are explained by including the electric quadrupole term of the exciton-photon interaction in the calculation of the Raman cross section.

The $n=1$ exciton of the yellow series in Cu_2O is electric-dipole forbidden and therefore it gives rise to interesting phonon-assisted electric-dipole absorption and luminescence spectra in which the odd-parity phonons participate.[1-3] Furthermore, the forbidden character of this exciton has been related to the strong enhancement of the 220-cm^{-1} two-phonon Raman line which occurs for laser frequencies at least 110 cm^{-1} *above* the 1S position.[4] We report here the appearance and strong resonant enhancement of the *first order* Raman lines of all the odd-parity phonons in Cu_2O when the laser frequency is within 5 cm^{-1} of the 1S exciton frequency. We shall show that the appearance of these odd-parity phonons, which are Raman-forbidden by the usual selection rules in a crystal with inversion symmetry, is explained by the electric quadrupole nature of the direct optical transition to the 1S exciton.

A hole from the upper valence band of Γ_7^+ symmetry and an electron from the lowest conduction band of Γ_6^+ symmetry combine to form the 1S exciton with overall symmetry Γ_{25}^+. As a consequence, the electric-quadrupole-moment operator, which transforms as $\Gamma_{12}^+ \oplus \Gamma_{25}^+$ in the point group O_h, can cause direct optical transitions to this exciton state. The polarization characteristics appropriate to the electric quadrupole operator with Γ_{25}^+ symmetry have been seen in absorption by Gross *et al.*[5] and by Nikitine, Grun, and Certier.[6] We have also verified this polarization behavior in the direct luminescence at 4°K.

Our experiments were performed on a 1-mm-thick crystal, supplied to us by R. A. Forman, which was cut from a large single-crystal boule grown by Brower and Parker[7] using a floating-zone technique. This same crystal was previously used in our studies of Raman scattering and luminescence[2] and of resonant enhancement of several Raman features at the blue and violet exciton series.[8] The data in the present experiment were obtained using a backscattering geometry from the $(1\bar{1}0)$ face with incident and scattered polarizations either [001] or [110]. The crystal was mounted in a helium exchange-gas cell in a liquid-helium "Cryo-tip" Dewar.[9] The laser source was a Spectra-Physics model 370 cw dye laser pumped with a Coherent Radiation Ar^+ laser operating at 1.5 W all lines. Using a microscope slide as an etalon, the dye-laser output was limited to two or three adjacent longitudinal modes with a total width of about 0.06 cm^{-1}. The output, filtered by a $\frac{1}{4}$-m Spex "Minimate" to reduce the fluorescence background from the dye, was constantly monitored during the experiment with a Coherent Optics model 470 piezo-scanned spherical Fabry-Perot with 0.25 cm^{-1} free spectral range. The laser frequency in each case was set with the Spex 1401 double spectrometer and is reliable to ± 0.3 cm^{-1}, corresponding to the resettability of the spectrometer. Before and after each spectral scan the laser frequency was checked with a spectrometer resolution of 0.5 cm^{-1}.

The resonant activation of odd-parity phonons in Raman scattering is demonstrated in Fig. 1. The trace in 1(a) shows a typical spectrum with the laser 10 cm^{-1} away from resonance with the 1S exciton; the only distinct Raman feature is the second-order line at 218 cm^{-1}. In 1(b), with the laser on resonance with the exciton, new Raman features appear at 86, 109, and 153 cm^{-1}. These new features correspond, respectively, to Raman scattering from phonons of symmetry Γ_{25}^-, Γ_{12}^-, and Γ_{15}^-. We also have observed resonance enhancement of the Γ_2^- mode at 350 cm^{-1} and the TO and LO components of another Γ_{15}^- mode at 640 and 660 cm^{-1}. Thus we observe the activation of all the odd-parity phonons in Cu_2O when the laser is on resonance with the 1S yellow exciton. One also expects resonant enhancement in the Raman cross section when the frequency of the scattered photon coincides with the

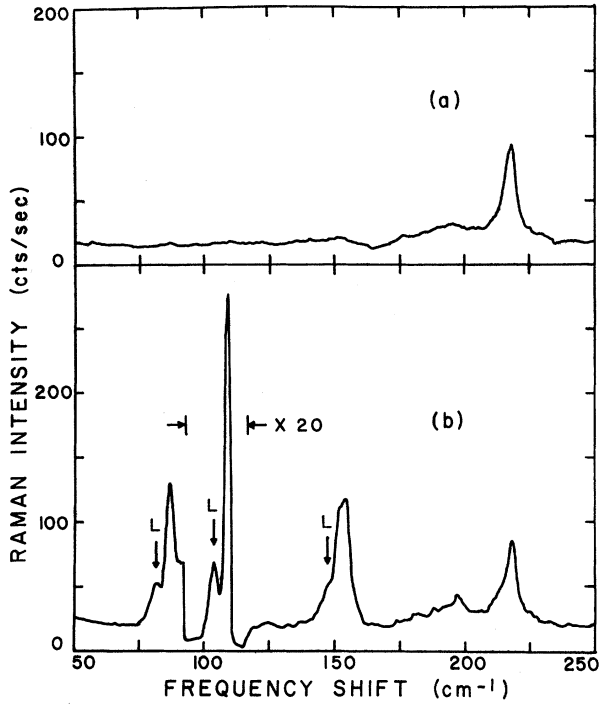

FIG. 1. Raman spectra of Cu_2O at 4°K with 12 mW incident laser power. Incident polarization, [001]; scattered polarization, [001] + [110]. Instrumental resolution, 2 cm^{-1}. (a) Laser frequency 10 cm^{-1} above the 1*S* yellow exciton frequency. (b) Laser in resonance with the 1*S* yellow exciton. The features labeled *L* are phonon-assisted luminescence as discussed in the text and in Ref. 2.

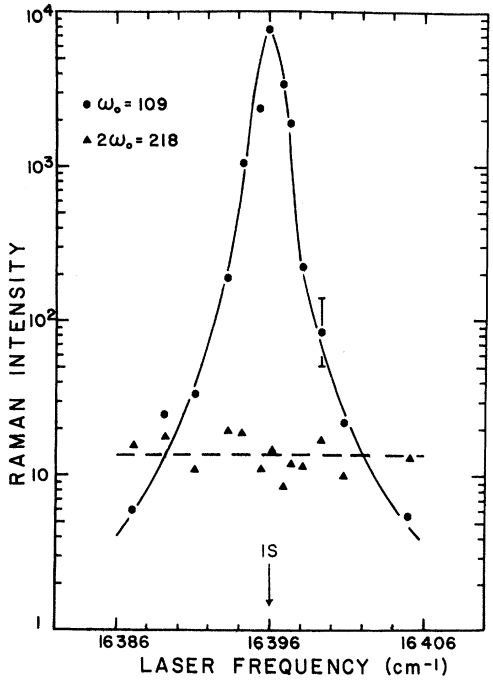

FIG. 2. Resonance enhancement of the first-order 109-cm^{-1} Γ_{12}^- Raman line and its 218-cm^{-1} second-order feature. The smooth curves through the data points are included for visibility. The frequency of the 1*S* exciton, 16396 ± 0.5 cm^{-1}, was measured in direct luminescence.

1*S* exciton (out resonance). In agreement with this prediction, we have observed strong activation of the Γ_{12}^- mode when the laser frequency is 109 cm^{-1} above the 1*S* frequency.

The three features labeled "*L*" in Fig. 1(b) arise from excitons which have been partially thermalized by collisions with phonons, acquiring a kinetic energy $\sim kT$ before decaying by phonon-assisted luminescence.[2] In principle, the luminescence features should move from the high-frequency side to the low-frequency side of the Raman lines as the laser frequency is increased above the frequency of the 1*S* exciton. In practice, however, the scattering process is only observable over a range of laser frequencies small compared to kT (as we discuss below), and no change in the relative positions of the Raman and luminescence features was actually observed.

We studied the frequency dependence of the resonant enhancement for the 109-cm^{-1} mode in more detail and the results are shown in Fig. 2.[10] Note the unusual strength of the enhancement and the narrow half-width of approximately 1.5 cm^{-1}. This is only slightly broader than the 0.75-cm^{-1} width which we have measured for the 1*S* direct luminescence. Also shown in Fig. 2 is the behavior of the second-order "Raman-allowed" feature at 218 cm^{-1}. We observe no enhancement of this feature at the 1*S* exciton frequency, in agreement with Yu *et al.*[4] We also found no resonance enhancement for the 515-cm^{-1} Γ_{25}^+ "Raman-active" mode.

In the usual perturbation-theory approach,[11] a typical matrix element for the Raman-scattering amplitude is given by

$$M = \frac{\langle 0, \omega_0 | \mathcal{H}_{ER} | e', \omega_0 \rangle \langle e', \omega_0 | \mathcal{H}_{EL} | e \rangle \langle e | \mathcal{H}_{ER} | 0 \rangle}{[\omega_L - (\omega_e + \omega_0) + i\Gamma_{e'}][\omega_L - \omega_e + i\Gamma_e]}, \quad (1)$$

where ω_L and ω_0 are the laser and phonon frequencies, and e and e' are intermediate electronic states

with frequencies ω_e and $\omega_{e'}$ and widths Γ_e and $\Gamma_{e'}$, respectively. $\mathcal{H}_{EL}$ denotes the exciton-lattice interaction; $\mathcal{H}_{ER}$, the exciton–radiation-field interaction, is given by

$$\mathcal{H}_{ER} = \hat{\epsilon}\cdot\vec{p}A_0 \exp[i(\vec{k}\cdot\vec{r} - \omega_L t)]$$
$$\simeq \hat{\epsilon}\cdot\vec{p}A_0 \exp(-i\omega_L t)[1 + i\vec{k}\cdot\vec{r} - \cdots], \quad (2)$$

where $\hat{\epsilon}$ is the polarization of the electric field with amplitude A_0 and wave vector $\vec{k}$.

The usual Raman selection rules[11,12] are obtained by taking only the zeroth-order (dipole) approximation in Eq. (2) for both operators $\mathcal{H}_{ER}$ in Eq. (1). In this case $\mathcal{H}_{ER}$ transforms like the dipole moment $\vec{p}$ or the vector $\vec{r}$ (odd under inversion) and therefore $\mathcal{H}_{EL}$, which has the symmetry of the irreducible representation of the phonon produced, must transform like the dyadic $\vec{r}\vec{r}$ with even parity in order that the overall matrix element M be a scalar. This is equivalent to the classical statement that a phonon is Raman active in first order only if its irreducible representation occurs in the reduction of the representation of the polarizability tensor.[11]

The second term in the expansion for the radiation field gives rise to electric quadrupole ($E2$) and magnetic dipole ($M1$) transitions. The corresponding operators have even parity. Thus if in Eq. (1) one of the operators $\mathcal{H}_{ER}$ corresponds to an $E2$ or $M1$ transition and the other to the usual electric dipole ($E1$) operator, then the operator $\mathcal{H}_{EL}$ must transform like the triadic $\vec{r}\vec{r}\vec{r}$ and have odd parity in contrast to the usual Raman selection rule. Near the $1S$ yellow exciton in Cu_2O, the appropriate term linear in $\vec{k}$ is the $E2$ transition of Γ_{25}^+ symmetry.[5,6] Using this form for one of the $\mathcal{H}_{ER}$ matrix elements and the usual dipole (Γ_{15}^-) form for the other (off-resonant) factor implies that now the "allowed" phonons must have a zone-center symmetry of

$$\Gamma_{ph} = \Gamma_{25}^+ \times \Gamma_{15}^-$$
$$= \Gamma_{25}^- \oplus \Gamma_{12}^- \oplus \Gamma_{15}^- \oplus \Gamma_2^-. \quad (3)$$

This mechanism, therefore, explains the observed activation and resonant enhancement of all the odd-parity phonon modes in Cu_2O. In addition, it explains the experimental observation of no enhancement for either the usual Raman-active Γ_{25}^+ phonon or the usual Raman-allowed second-order feature at 218 cm^{-1}. We note that retention of only the zeroth-order term in the expansion of $\mathcal{H}_{ER}$ has usually been justified by the fact that the second term in Eq. (2) is generally smaller by a factor of $ka \simeq 10^{-3}$ for optical transitions. (In our case a is the exciton radius.) However, as demonstrated above, this may be compensated by the smallness of the denominator very near resonance, where $\omega_L - \omega_e + i\Gamma_e \simeq i\Gamma_e$. This is especially true if the exciton state is long lived.

From the suggested form for the Raman matrix elements, one may obtain the polarization properties of the scattered light.[13] The scattering tensor is in general a third-rank tensor depending on the incident polarization $\vec{\epsilon}$ and propagation vector $\vec{k}$ and the scattered polarization $\vec{\epsilon}'$. For backscattering from a $(\bar{1}10)$ surface, $\vec{k} \parallel [\bar{1}10]$, the Γ_{12}^- mode is predicted[13] to have nonzero amplitude only for $\vec{\epsilon} \parallel [001]$ and $\vec{\epsilon}' \parallel [110]$. Experimentally we observe for $\vec{\epsilon} \parallel [001]$ a scattered polarization ratio for the 109-cm^{-1} line of

$$\hat{\epsilon}' \parallel [110]/\hat{\epsilon}' \parallel [001] \simeq 6,$$

and for $\hat{\epsilon} \parallel [110]$ the total scattered intensity is less than $\frac{1}{10}$ of that obtained with $\hat{\epsilon} \parallel [001]$. Surface roughness and finite collection-angle effects probably account for the scattered light appearing weakly in polarizations not expected theoretically. A detailed study of the enhancement and polarization properties of all the odd-parity phonon Raman lines is in progress and will be presented in a subsequent publication.

Finally, we note that recent observations of resonant enhancement of several Raman lines near the dipole-allowed blue and violet excitons in Cu_2O have been reported by Porto and Williams,[14] by Yu, Shen, and Petroff,[15] and by the authors.[8] These observations indicate large enhancement for the polar Γ_{15}^- phonons and may be explained by the mechanism proposed by Martin.[14,16] This mechanism, which assumes the usual dipole coupling for both exciton-photon matrix elements, achieves symmetry breaking through higher-order terms in the expansion of the Fröhlich exciton-phonon coupling and is therefore important only for the LO components of the infrared-active polar phonons, and for laser frequencies near resonance with dipole-allowed excitons.

In conclusion, we have observed strong resonance Raman scattering involving all odd-parity phonons near an intrinsic forbidden free-exciton state in Cu_2O and have shown the apparent selection-rule violation to be a consequence of the electric quadrupole nature of the exciton-radiation interaction near the $1S$ yellow exciton.

We wish to thank Professor J. Birman for many helpful discussions throughout this work,

and Professor R. J. Elliott and Dr. Richard Forman for several discussions on the properties of cuprous oxide. We also wish to thank Dr. Forman, W. S. Brower, Jr., and H. S. Parker for the generous loan of the crystal used in our experiments.

†Work supported by the National Science Foundation.

*Alfred P. Sloan Research Fellow.

[1]E. F. Gross, Usp. Fiz. Nauk 76, 433 (1962), and 103, 431 (1971) [Sov. Phys. Usp. 5, 195 (1962) and 14, 104 (1971)].

[2]A. Compaan and H. Z. Cummins, Phys. Rev. B 6, 4753 (1972).

[3]Y. Petroff, P. Y. Yu, and Y. R. Shen, Phys. Rev. Lett. 29, 1558 (1972).

[4]P. Y. Yu, Y. R. Shen, Y. Petroff, and L. M. Falicov, Phys. Rev. Lett. 30, 283 (1973).

[5]E. F. Gross, A. G. Zhilich, B. P. Zakharchenya, and A. V. Varfalomeev, Fiz. Tverd. Tela 3, 1445 (1961) [Sov. Phys. Solid State 3, 1048 (1961)].

[6]S. Nikitine, J. B. Grun, and M. Certier, Phys. Kondens. Mater. 1, 214 (1963).

[7]W. S. Brower, Jr., and H. S. Parker, J. Cryst. Growth 8, 227 (1971).

[8]A. Compaan and H. Z. Cummins, Bull. Amer. Phys. Soc. 18, 75 (1973).

[9]Air Products and Chemicals, Inc., Allentown, Pa.

[10]The data points in Fig. 2 indicate the observed Raman intensity divided by the incident laser power. Absorption corrections, which are less than 4% in this frequency range, have not been included.

[11]R. Loudon, Advan. Phys. 13, 423 (1964); J. L. Birman, "Theory of Crystal Space Groups and Infra-Red and Raman Processes in Insulating Crystals" in Handbuch der Physik, edited by S. Flügge (Springer, New York, 1973, to be published), Vol. 25, Part 2b.

[12]See, for example, M. Born and M. Bradburn, Proc. Roy. Soc., Ser. A 188, 161 (1947); L. N. Ovander, Opt. Spectrosk. 9, 571 (1960) [Opt. Spectrosc. 9, 302 (1960)].

[13]J. L. Birman, to be published.

[14]P. F. Williams and S. P. S. Porto, Bull. Amer. Phys. Soc. 18, 411 (1973); P. F. Williams, Ph. D. thesis, University of Southern California, 1973 (unpublished).

[15]P. Y. Yu, Y. R. Shen, and Y. Petroff, Bull. Amer. Phys. Soc. 18, 411 (1973).

[16]R. M. Martin, Phys. Rev. B 4, 3676 (1971).

Hopping Conductivity in Granular Metals

Ping Sheng
Institute for Advanced Study, Princeton, New Jersey 08540

and

B. Abeles and Y. Arie
RCA Laboratories, Princeton, New Jersey 08540

(Received 23 April 1973)

We present evidence that in granular metals the observed temperature dependence of the low-field conductivity, $\exp(-b/T^{\alpha})$ with $\alpha=\frac{1}{2}$, can be ascribed to a relationship sE_c = const between s, the separation of neighboring metal grains, and E_c, the electrostatic energy required to create a positive-negative charged pair of grains. This relationship results from simple considerations of the structure of granular metals. The predictions of the theory, for both the high- and the low-field electrical conductivity, are in excellent accord with experimental results in granular Ni-SiO_2 films.

The low-field electrical conductivity σ_L of many disordered materials has a temperature dependence that can be expressed in the form $\sigma_L \sim \exp(-b/T^{\alpha})$. The value $\alpha=\frac{1}{4}$, found in many of the amorphous semiconductors and semiconducting glasses, has been predicted by Mott[1] using a model of hopping conductivity between localized states. There are, however, disordered materials such as granular metals,[2-4] and some disordered semiconductors,[5] which exhibit an $\alpha=\frac{1}{2}$ behavior for which no definitive theory has been proposed. In this Letter we present evidence that in granular metals, consisting of fine metallic particles dispersed in a dielectric matrix, the $\alpha=\frac{1}{2}$ behavior can be explained by a structural effect. Furthermore, the theory we propose predicts the temperature and electric field dependences of conductivity in the high-field regime and relates the high- and low-field behaviors through a single structural parameter. We present measurements of the temperature and field dependences of the resistivities in granular Ni-SiO_2 films and find excellent agreement with the predictions of the theory.