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Symmetry-Forbidden Resonant Raman Scattering in Cu2O

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We have observed resonant Raman scattering from the two longitudinal branches of the Raman-forbidden F_{1u} modes of Cu_2O. The agreement between our measured scattering cross section as a function of excitation frequency and a calculated cross section which assumes an intraband Fröhlich electron-phonon interaction is good. This represents a quantitative confirmation of the resonant-Raman-scattering theory proposed by Martin.

There has been considerable interest in the recent literature in the breakdown of selection rules observed in Raman scattering when the frequency of the laser is nearly resonant with an electronic energy level of a crystal.[1-8] With the exception of some work reported by Anastassakis and Burstein,[4] on II-IV semiconductor compounds, the only experimentally observed breakdowns have been relatively minor, consisting of anomalously strong multiple-phonon lines,[6] or the appearance of Raman-allowed LO phonon lines in a forbidden polarization configuration.[5-7]

On the basis of such a breakdown observed in CdS, Martin examined the implications of an assumed intraband Fröhlich electron-phonon interaction and proposed it as an explanation for the polarization anomaly in CdS.[1] Unfortunately, later work showed that with 4880-Å excitation, even in more nearly perfect crystals than Martin and Damen used,[7] defect-related electronic states (bound excitons) dominate in the scattering.[5,9] These defect-related states do not experience translational symmetry, so that k conservation is not required. The lack of k conservation is quite sufficient to explain the "breakdown."[10] Martin's intraband Fröhlich interaction probably is operative in this case, but it is not required to explain the breakdown.

We report here experimental observation of the two Raman-forbidden LO phonons in Cu_2O when the laser is near resonance. Such a major breakdown of selection rules in crystals with inversion symmetry was predicted by Martin,[1] and has been observed previously in some of the II-IV semiconductors.[4] Cu_2O has been more extensively studied than the II-IV semiconductors, however, and for this reason, meaningful basic calculations of the variation of the Raman scattering efficiency become possible for Cu_2O. Comparison of the re-

sults of this calculation with the experimental data allows a meaningful test of the intraband Fröhlich mechanism and of the assumed importance of excitonic states in the resonance. We have performed such a calculation, and the results are reported here. The details of the calculation and of the experiment will be presented elsewhere. With the possible exception of the work of Gross et al.[8] these results form the basis of perhaps the first real test of Martin's breakdown mechanism, and of the relative importance of the free excitonic states in the resonance.

Cu_2O has the cuprite structure, space group O_h^4, with two molecules per unit cell. The usual symmetry considerations predict the following zone-center phonon modes: two infrared-active F_{1u} modes, one Raman-active F_{2g} mode, and an A_{1u}, an E_u, and an F_{2u} mode, all silent in both infrared and Raman spectra. Since the crystal has inversion symmetry, the infrared-allowed modes are Raman forbidden and vice versa.

Infrared-absorption experiments have placed the LO phonons belonging to the F_{1u} representation at 645 cm^{-1} and at 149 cm^{-1}. The TO associated with the upper LO is at 611 cm^{-1}, and the lower TO is at 146 cm^{-1}.[11] Balkanski et al. have attributed a feature seen in the Raman spectrum at 220 cm^{-1} to the Raman-active phonon.[12] We observe a similar feature in the Raman spectrum at 220 cm^{-1}, but we do not observe the correct polarization character for that feature.[13]

The spectra we report here were taken using a standard Raman scattering setup. The scattering geometry was similar to that of Balkanski et al.,[12] except that the polarization of the laser was always parallel to the sample face. The sample was cooled using an Air Products Cryotip cryostat. The sample surface was chemically polished, since mechan-
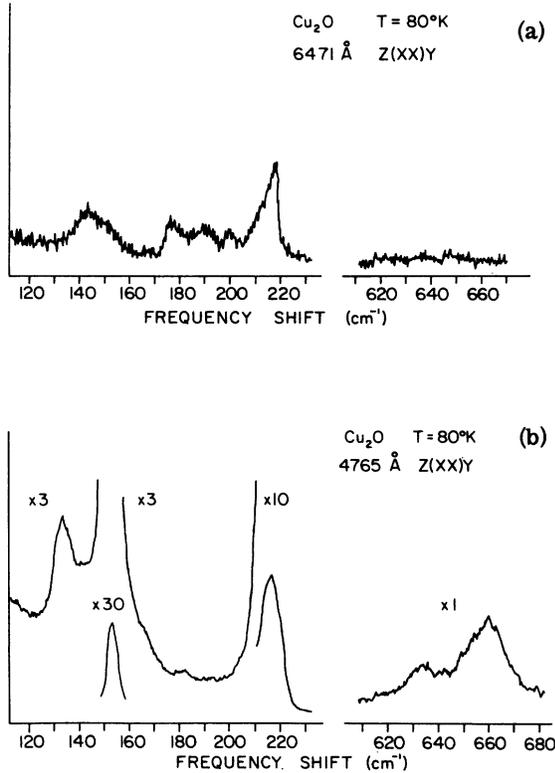
FIG. 1. (a) Polarized Raman spectrum of Cu_2O taken with a 6471-Å laser. (b) Polarized Raman spectrum of Cu_2O taken with a 4765-Å laser. The small numbers indicate scale changes and give the full scale intensity (in arbitrary units) for that scale. Resolution is 4 cm^{-1} for both spectra.

ical polishing destroyed much of the electronic structure observed with the chemically polished surface.

Figure 1 shows two typical polarized Raman spectra of Cu_2O, one taken with a 6471-Å laser below resonance with any band gap, and the other taken with a 4765-Å laser well into resonance. In the 6471-Å spectrum, the broad feature between 130 and 160 cm^{-1} is probably the result of defect-induced scattering from phonons not at the zone center. In spectra taken with the 6328-Å laser, a strong and sharp peak appears at 185 cm^{-1} and another much weaker peak appears at 140 cm^{-1}. This structure is not observed with any of the other laser lines. Additionally, the intensity of the structure seems to be somewhat dependent on the location on the sample surface of the focused laser beam. There are a number of defect-associated electronic states in the region between 6000 and 6300 Å.[14] These features probably result from near resonance with one or more of these states. The observed Raman spectrum remains little changed with lower frequency excitation, at least down to 7000 Å.

In the resonant spectrum the appearance of a sharp peak at 154 cm^{-1} and of a much broader one at 660 cm^{-1} is quite evident. Because the LO phonons are not observed directly in infrared absorption and because the reported infrared spectra were obtained at room temperature, the frequencies of the peaks observed in the resonant Raman spectra are consistent with the reported infrared data. The width of the 154-cm^{-1} line at 80 °K is about 1.5 cm^{-1}, and less than 1 cm^{-1} at 6 °K. These are polarized spectra. In resonance the structure disappears completely in the depolarized spectrum indicating a diagonal "forbidden" tensor.

Additionally, we have measured the Raman scattering efficiency as a function of laser frequency for the two Raman-"forbidden" lines. The observed Raman intensities were corrected for sample absorption and reflection. Because the absorption of Cu_2O is so high in the region of interest, it can be measured directly only by using thin films. Comparison of the reflectivity spectrum of these films with the reflectivity of bulk crystals reveals that the features are badly broadened in the thin films.[15-17] For this reason the absorption data obtained from these films are not of much use in correcting the observed Raman intensities for absorption. Because of this problem we have measured the reflectivity spectrum of our sample, and from that determined the absorption spectrum in the region of interest using a slightly modified Kramers-Kronig analysis, to be described elsewhere. The resulting absorption spectrum is shown in Fig. 2.

The experimental results for the relative Raman scattering efficiency for the 154-cm^{-1} phonon are shown in Fig. 3; the results for the 660-cm^{-1} are shown in Fig. 4. Also shown in these figures are the results of a theoretical calculation of the expected relative scattering efficiency for these two phonons. The calculation is very similar to Martin's.[1] The Raman scattering amplitude W is written as the usual third-order perturbation expression,

$$W = \sum_{ee'} \frac{\langle 0 | \vec{P} \cdot \vec{A} | e' \rangle \langle e' | V_p | e \rangle \langle e | \vec{P} \cdot \vec{A} | 0 \rangle}{(\omega_e' - \omega_R)(\omega_e - \omega_L)} + \cdots . \qquad (1)$$

Here $| e \rangle$ and $| e' \rangle$ are excited electronic states, V_p is the electron-phonon interaction (taken as the intraband Fröhlich), and $\vec{P} \cdot \vec{A}$ is the electron-radiation interaction. ω_e and ω_e' are the energies (over $\hbar$) of the corresponding excited electronic states and ω_L and ω_R are the frequencies of the laser and Raman-shifted light. Higher-order terms and terms with less strongly resonant denominators were ignored. In the summation over electronic states, only the free intrinsic excitonic states (both continuum and discrete) are considered.

Martin was able to evaluate the summation in Eq. (1) by noting that it is the same as an expres-
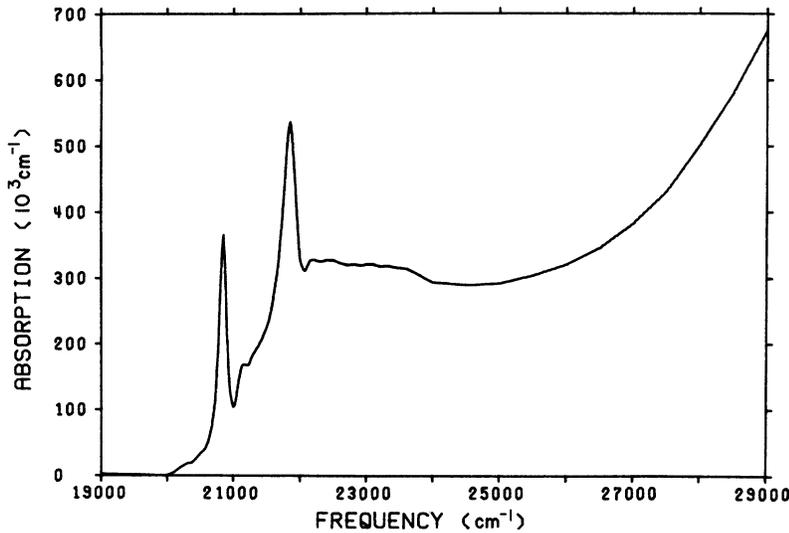
FIG. 2. Kramers—Kronig calculated absorption spectrum of Cu_2O sample. The sample temperature was 80 °K and the surface was chemically polished.

sion for the Coulomb Green's function. He encountered difficulties, however, in numerically evaluating this function for laser above the band gap. We have been able to avoid this difficulty by evaluating the matrix elements and then performing the summation directly. The $\vec{P} \cdot \vec{A}$ matrix elements between the ground electronic state and an excited state with one exciton created are taken as proportional to $\Psi_n(0)$, Ψ_n being the appropriate hydrogenic

wave function.[18] The Fröhlich matrix element is given by $(1/q)\langle \Psi_n | e^{i\vec{q}\cdot\vec{r}_e} - e^{-i\vec{q}\cdot\vec{r}_h} | \Psi_m \rangle$. For matrix elements in which both Ψ_n and Ψ_m describe discrete states, the matrix element can be evaluated exactly (if the excitons are hydrogenic) using a standard method.[19] The matrix elements for which one state is a discrete state and the other a continuum state can also be evaluated exactly by using a method similar to one described by Sommerfeld and Schur.[20]
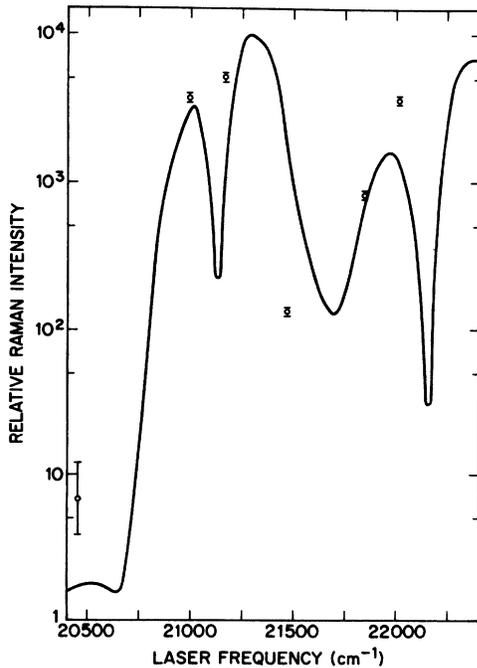
FIG. 3. Theoretical and experimental results for the relative Raman scattering efficiency for the 154-cm⁻¹ LO phonon.
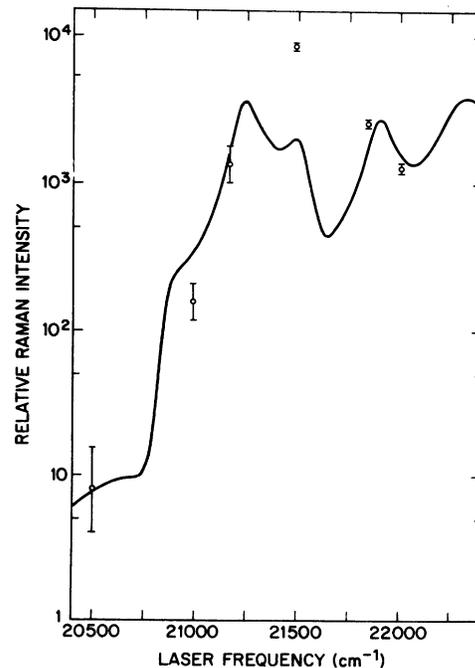
FIG. 4. Theoretical and experimental results for the relative Raman scattering efficiency for the 660-cm⁻¹ LO phonon.

The matrix element involving two continuum states was evaluated by approximating these states by plane waves. Finally, the total transition amplitude was evaluated in a straightforward manner by performing the summation of states numerically on a computer. Damping of the electronic states was included by adding a $+i\Gamma$ term in the energy denominators of the perturbation summation.

The smallest two dipole-allowed band gaps in Cu_2O are in close energy proximity (21 220 and 22 275 cm^{-1})[15-17] so that the excitonic states resulting from each of the two gaps must be considered. Since only intraband transitions are assumed, this is accomplished by adding the independently calculated transition amplitudes for each of the series.

Defect states such as bound excitons are not expected to contribute significantly to the observed Raman intensities for two reasons. First, these states are not observed in the absorption spectrum of Fig. 2. From this one can conclude that with density-of-states considerations, the effective $\vec{P}\cdot\vec{A}$ matrix element for the intrinsic states is dominant over the effective $\vec{P}\cdot\vec{A}$ element for the hypothetical defect states. The defect state could only make a contribution if there were an unusually strong electron-phonon interaction for that state. Second, bound exciton states would be expected to lie lower in energy than the intrinsic $1s$ state. For the "yellow" exciton series (dipole forbidden), the highest-lying bound exciton state observed by Gross and Kreingol'd was about 150 cm^{-1} below the $1s$ intrinsic state.[14] Such a shift does not seem compatible

with the experimental data.

The experimentally determined constants, such as exciton binding energies, required in the calculation are all related to the appropriate two exciton series and are fairly well known from independent experimental evidence.[15-17] The value of the electronic damping was determined from the observed widths of the two $1s$ exciton absorption lines seen in Fig. 2. Since only relative scattering-efficiency measurements were made, the results of Figs. 3 and 4 were obtained with an adjustable scale factor. This was the *only* adjustable parameter used.

We feel that the agreement with experiment is good. The intraband Fröhlich interaction leads to a transition amplitude proportional to the radius of the intermediate electronic state.[1] For this reason it gives more weight to scattering involving the 2s and higher discrete exciton states than does an interband interaction. If these higher-lying discrete states are neglected in the calculation the agreement with experiment is significantly degraded.

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