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Two-Photon Absorption in Cu_2O Due to Transitions to Higher-Energy Excitons

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The two-photon absorption spectrum of Cu_2O is measured at 77 °K in the frequency range corresponding to transitions between bands of opposite parity. The main features are well explained on the basis of existing theories. However, we also observe an additional structure associated with the 1*s* exciton which lies on a strongly interfering continuum. Using Fano's theory of configuration interaction, we estimate the auto-ionization lifetime of the 1*s* exciton to be $\sim 10^{-14}$ sec.

In this paper we report our results on the two-photon absorption spectrum of Cu_2O due to electronic transitions to excited states near the bottom of the second conduction band c_2. An inversion symmetric crystal with point-group symmetry O_h, Cu_2O provides an ideal material for studying excitonic transitions for several reasons. First, its band structure can be well approximated by simple parabolic bands with energy extrema at $\vec{k} = 0$. Second, the one-photon excitonic spectrum, studied experimentally in great detail,[1] is well explained on the basis of Elliot's theory.[2] Finally, the smallest band gap of 2.1 eV between the conduction and valence bands (see Fig. 1) permits two-photon spectroscopy covering two valence and two conduction bands, such that all photon energies lie in the visible or near-infrared regions.

Our experiments were performed at 77 °K on a single crystal of Cu_2O, grown by the arc-image furnace technique. Details of the experimental setup have been described earlier.[3] We measured $\alpha^2(\omega_1, \omega_2)$, the coefficient of absorption of a light beam of continuously variable frequency ω_2 in the presence of a laser beam (frequency ω_1) incident in a direction perpendicular to that of the test beam. In Figs. 2 and 3, we show α^2 as a function of $\hbar\omega_1 + \hbar\omega_2$ for $\hbar\omega_1 = 0.810$ eV and $\hbar\omega_1 = 0.655$ eV, respectively. The two laser frequencies were obtained by stimulated Raman scattering of the 1.06-μ line of a pulsed Nd-glass laser in CH_4 and H_2, respectively.

The frequency range covered by our experiments can be conveniently divided into three regions as shown in Figs. 2 and 3. Region I corresponds to $\hbar\omega_1 + \hbar\omega_2$ lying in the energy range

$$E_{c_1} - E_{v_2} < \hbar\omega_1 + \hbar\omega_2 \lesssim E_{c_2} - E_{v_1} - E_B ,$$

where $E_B = 0.0457$ eV denotes the binding energy of the lowest excitonic state associate with the highest valence band v_1 and the second conduction band c_2. In agreement with Loudon's theoretical predictions,[4] α^2 shows only a slight frequency dependence in this region.

A much sharper increase in α^2 is observed in the region III. This is associated with transitions from the ground state to the bound and ionized *p* excitonic states of the band pair v_1, c_2, mainly via *s* excitonic levels of the same bands as intermediate states. These transitions and their contribution to the two-photon absorption spectrum have been considered

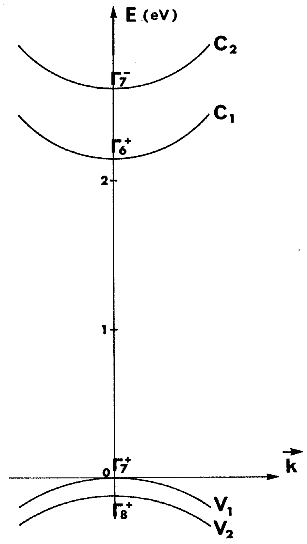

FIG. 1. Band scheme of Cu_2O near the center of the Brillouin zone (after R. J. Elliot, see Ref. 2). The irreducible representation characterizing the various bands at $\vec{k} = 0$ are indicated in the notation of G. F. Koster, J. D. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (The M. I. T. Press, Cambridge, Mass., 1963).

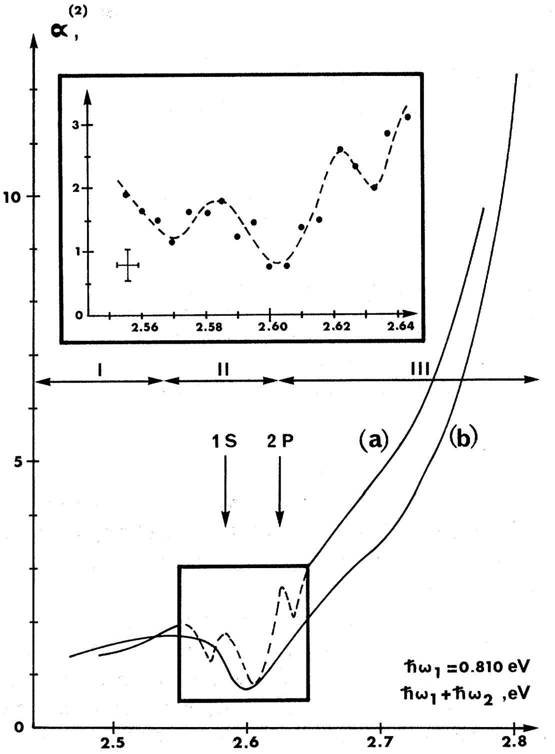

FIG. 2. Two-photon absorption coefficient $\alpha^{(2)}(\omega_1, \omega_2)$ in arbitrary units for $\hbar\omega_1 = 0.810$ eV. The curves (a) and (b) correspond, respectively, to the two photon beams parallel and perpendicular to each other.

in detail by Mahan.[5] At photon energies $\hbar\omega_1 + \hbar\omega_2 \gtrsim E_{c2} - E_{v1}$ the observed spectral dependence of α^2 is well reproduced by the theoretical formulas.[5] Also, the experimental and theoretical values of the ratio $\alpha_\perp^2 / \alpha_\parallel^2$, between the two-photon absorption coefficients in the two configurations (b) and (a) (see Fig. 2), respectively, are in good agreement (within 15–20%) with each other. For lower photon energies $\hbar\omega_1 + \hbar\omega_2 \simeq (E_{c2} - E_{v_1} - \frac{1}{4}E_B)$ the comparison of our results with Mahan's theory is made difficult by the lack of accurate information about the excitonic line shapes. Nevertheless, we have observed a structure at the position of the $n = 2$ excitonic bound state for $\hbar\omega_1 = 0.810$ eV, when the two beams were polarized parallel to each other. This structure corresponds to two-photon transitions to the 2 p excitons.

In region II the spectral dependence shows some interesting features: A structure appears at the position of the 1s excitonic line, as observed in the linear optical experiments.[1,6] Such a line is *not* expected in the two-photon absorption spectrum because of parity arguments. Also, the absorption coefficient in this region decreases below its average value in Loudon's continuum (region I). This effect is particularly evident in Fig. 2(b). To discuss this fact, we recall that the 1s excitonic level lies on a continuum of energy levels of the first conduction band. Fano[7] has shown that in such a case the interference between the discrete state and the continuum may strongly modify the shape of the spectrum. This occurs because the degenerate bound and continuum states are mixed by the "configuration interaction."[8] Then it is necessary to consider the transition probability to the mixed state. Even a small transition probability to the unperturbed (by configuration mixing) bound state leads to a highly asymmetric line shape for the mixed state. A nonvanishing probability of transitions to the "unperturbed" 1s excitonic state could arise from effects which are usually neglected in the theory of excitonic transitions, e.g., the central cell corrections. The spectral dependence in Fig. 2(b) is very similar to that calculated, in a model case, by Fano[7] for small negative values of the parameter q, which is a measure of the relative probability of transitions to the bound state. From the observed width of the structure it is possible to estimate the auto-ionization lifetime τ of the 1s exciton. We obtain a value $\tau \sim 10^{-14}$ sec which is consistent with the observed width of the 1s line in Fig. 3.

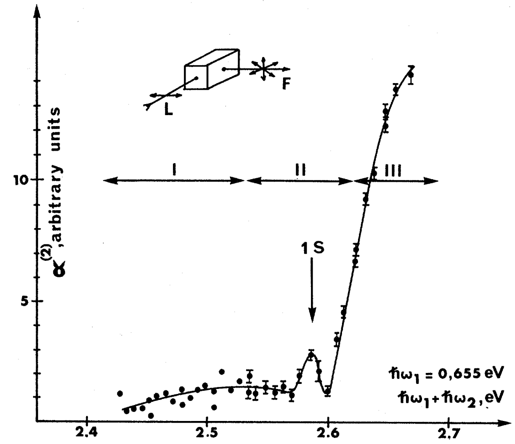

FIG. 3. Spectral dependence of $\alpha^{(2)}(\omega_1, \omega_2)$ for $\hbar\omega_1 = 0.655$ eV. The polarizations and directions of propagation of the laser beam L and the test beam F are also shown.

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[8] The configuration mixing in the case of excitonic bound states degenerate with a continuum of states has been considered earlier. See, e.g., D. L. Greenaway and G. Harbeke, *Optical Properties and Band Structure of Semiconductors* (Pergamon, New York, 1968), Chap. 8.

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Far-Infrared Optical Constants of KI[†]

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The far-infrared optical constants of KI were studied in the vicinity of the TO($\vec{k}=0$) phonon frequency $\nu_0 = 101$ cm^{-1} (in wave-number units). Experimental values of the optical constants at $T = 300$ °K were determined from transmission and reflection measurements employing a Michelson interferometer operated in the asymmetric mode. Theoretical values were calculated from a theory which utilizes thermodynamic Green's functions to include the effects of the interaction of the optically active phonon with other phonons because of cubic anharmonicity. Phonon-dispersion data for the calculation were generated from a shell model, with parameters selected by Dolling to give the phonon frequencies as determined from neutron-diffraction experiments. Good agreement for the optical constants in the region approximately 20–175 cm^{-1} was obtained by using a nearest-neighbor central-force model and adjusting the third derivative of the K$^+$-I$^-$ bond potential to $\Phi'''(r_0) = -3.6\times10^{12}$ erg/cm^3.

I. INTRODUCTION

The dominant interaction of infrared radiation in cubic ionic diatomic crystals is with the TO lattice-vibrational mode of the same wave vector $\vec{k}$ as the incident electromagnetic wave and with polarization in the electric field direction. This interaction results in the fundamental absorption band or reststrahl band, characterized by very high absorption and reflection in the neighborhood of the TO($\vec{k}=0$) phonon frequency or "eigenfrequency" ν_0 ("frequency" here measured in wave-number units cm^{-1}). To account for the detailed shape of the band, one must consider the dampening effect of the anharmonic parts of the interionic forces on the optically active vibrational mode. Theoretical studies of this effect have been carried out by Cowley,[1] Gurevich and Ipatova,[2] and Wallis, Ipatova, and Maradudin.[3] These authors, using theromodynamic Green's-function techniques, have derived expressions for the lattice contribution to the complex dielectric susceptibility. Their expressions differ from that calculated on the basis of a purely harmonic model in that a complex self-energy term is added to the denominator. This term expresses the effect of three- and four-phonon interactions due to cubic and quartic terms in the anharmonic potential, respectively.

In view of the theoretical effort mentioned above, the availability of phonon-dispersion data for many crystals of the NaCl structure type, and recent advances in far-infrared spectroscopy, we have undertaken detailed measurements of the optical constants n and k, the index of refraction and the extinction coefficient, respectively, of some of these crystals in the neighborhood of their eigenfrequencies. The results for KCl and KBr have already been published.[4] In this paper we present the experimental results for KI at $T = 300$ °K, along with a calculation of the optical constants including only the effects of cubic anharmonicity. KI was chosen because of the availability of phonon-dispersion data based on actual neutron-diffraction experiments[5] at 77 °K and because its absorption band falls in the optimum region for employment of the experimental technique used in this work. The room-temperature eigenfrequency of KI is $\nu_0 = 101$ cm^{-1}.

The optical constants were determined from transmission and reflection experiments using a Michelson interferometer operated in the asymmetric mode, as described by Bell[6] and by Russell and Bell.[7] In the asymmetric mode the sample is placed in one of the arms of the interferometer. With the sample removed from its position, an interferogram, or detector signal as a function of