TWO-PHOTON ABSORPTION SPECTRUM OF CdS

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Two-photon absorption spectroscopy involving the interaction of incoherent light with a laser beam has proven important in obtaining information about molecular states, exciton states, and band properties near the fundamental absorption edge in insulating crystals.[1-3] A theory of two-photon excitation of interband transitions has been developed by Braunstein[4] from the general theory first given by Göppert-Mayer.[5] The theory with simplifying assumptions has been applied to the results of an experiment on CdS.[6] However, since only a laser source was used in the experiment and the two-photon absorption was detected by laser-induced luminescence, only a qualitative agreement between theory and experiment was found and no spectrum was obtained. We have measured the two-photon absorption spectrum of single-crystal CdS using polarized light and precise geometry. This has allowed us to compare theory quantitatively with experiment.

The experimental technique is similar to that used in previous two-photon spectroscopy experiments.[1-3] Two light beams were used, one from a Q-switched Nd glass laser, and the other from a pulsed xenon flash lamp. Two-photon absorption was detected as a change in absorption coefficient of the CdS sample for the xenon flash-lamp light, when exposed to the laser pulse. A CdS single crystal in the form of a plate (1 cm$\times$1 cm$\times$2 mm) with the c axis normal to the face of the plate was obtained from the Eagle-Picher Company. The unfocused laser beam was directed along the c axis of the crystal and the incoherent radiation normal to the c axis. Both beams uniformly illuminated the crystal. Absorption of the xenon lamp light in the presence of the laser pulse was detected by a silicon photodiode through a grating monochromator. The signal from the diode was observed either directly on an oscilloscope using a cathode follower probe (Fig. 1) or through a high-pass filter. Observing the signal directly permitted the time dependence of the absorption pulse (with an electronic bandpass of 25 Mc/sec) and the percent of laser-induced absorption to be measured directly. However, in measuring the spectrum it was found more conveneint to use the high-pass filter although the high-pass filter slightly distorted the induced absorption signal. The use of a high-intensity probe beam (10^{17} photons/sec) and a high-current photodiode allowed us to have a good signal-to-noise ratio. The minimum detectable absorption coefficient using the sample described above was 2×10^{-3} cm^{-1} in the region where laser-scattered light was not present. This limitation was due to amplifier noise rather than shot noise. When the high-pass filter was not used, the signal-to-noise ratio was necessarily less in order to avoid saturation of the system. The laser pulse had a peak power of 12 MW with a 40-nsec pulse half-width. A Glan-Thompson prism introduced into the probe beam allowed us to study the dependence of the spectra on the polarization of the probe beam with respect to the optic axis of the CdS. The laser beam was polarized perpendicular to the c axis.

The dependence of the induced absorption coefficient was found linear on the laser as well as xenon flash-lamp radiant flux. The lack of saturation with respect to the laser flux together with the time evolution of the pulse (Fig. 1) strongly indicate that the effect is not due to a two-step excitation process with transitions between an impurity level, valence band, and conduction band.[8]

The spectra obtained at room temperature

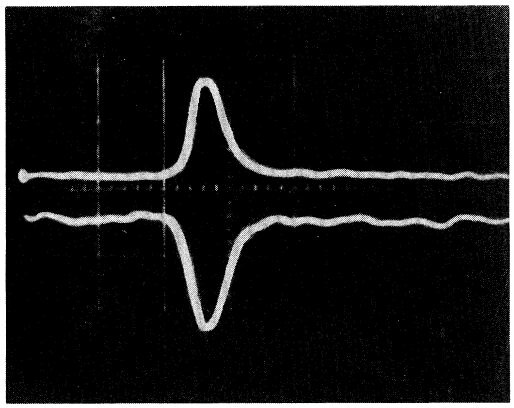

FIG. 1. Top, laser pulse; bottom, two-photon absorption signal (both 0.1 μsec/cm).

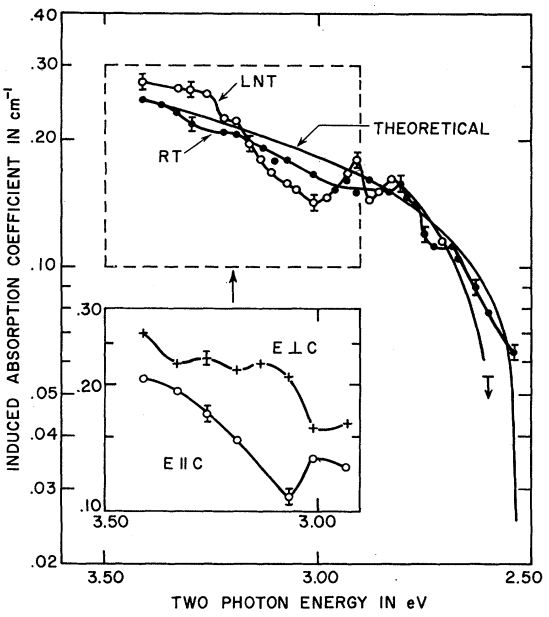

FIG. 2. Two-photon spectra at room temperature (RT) and liquid nitrogen temperature (LNT) using unpolarized light. The dichroism observed at room temperature is also indicated. The optical bandpass was 100 Å.

and liquid-nitrogen temperature are shown in Fig. 2. The fluctuation of data points was less than ±5%, hence the observed structure is greater than the estimated error. Also shown is the theoretical spectrum (multiplied by 2.7) obtained using the Braunstein theory[6] for allowed-allowed transitions. The absorption coefficient, for the probe beam, calculated from this theory for the final state at 3.4 eV is 0.10 cm^{-1}. We obtained an experimental absorption coefficient of 0.27 cm^{-1} corresponding to a nonlinear cross section of 2×10^{-49} cm^4 sec. The fit between theory and experiment, evident in Fig. 2, indicates that the model proposed by Braunstein represents the two-photon absorption process in CdS.

The discrepancy in the experiment of Braunstein and Ockman (off by a factor of ~60) was attributed to the fact that coherent effects were neglected and to the large error involved in the calculation of quantum yield for luminescence. In the present experiment neither of these sources of error is present: The probe beam is incoherent and the two-photon absorption is measured directly as an attenuation of the probe beam.

The initial and final states of the two-photon transition are the same states involved in one-photon spectroscopy and are known to have symmetry Γ_7, Γ_7, Γ_9, and Γ_7 at $k=0$, respectively. The intermediate state cannot be identified directly on the basis of the two-photon spectrum obtained with unpolarized light because the magnitude and spectral dependence of the calculated induced absorption coefficient is not strongly sensitive to the energy of the intermediate state in the range 3-6 eV. The dichroism shown in Fig. 2 indicates that the intermediate state could well be the upper conduction band at[7] 6 eV with symmetry Γ_9, Γ_7, and Γ_7. In fact, if we assume that symmetry at points near the center of the Brillouin zone does not differ significantly from the symmetry at $k=0$, the selection rules indicate that, for the probe beam polarized perpendicular to the c axis, eight transitions are allowed between the initial and the final state, using as intermediate state the upper conduction band. For the probe beam polarized parallel to the c axis only five transitions are allowed between the same states.

The lack of an effective Nd-laser rejection filter made the two-photon absorption spectrum near the absorption edge difficult to study because of scattered laser light. The scattered light problem is currently being studied in the attempt to search for fine structure in the exciton region.

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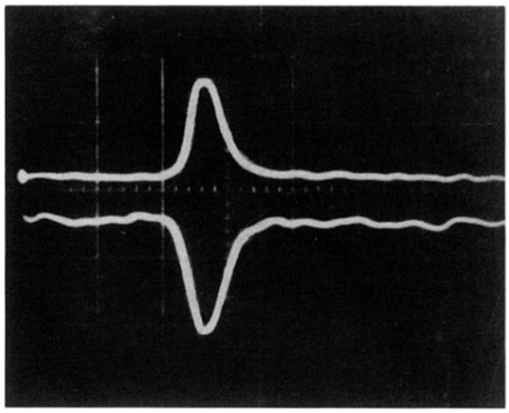

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