

FIG. 3. The calculated shape of the neutron scattering at a reciprocal lattice point. The resolution function is taken to be a spherically symmetric Gaussian of half-width σ (reciprocal lattice units), but infinitely sharp in energy.

fore be interpreted as giving a phonon frequency of 3.1. In view of the approximations made

in the present theory, by replacing the ellipsoidal band structure and resolution function by spheres, the agreement with the experimental value of 3.24 is reasonable. Excellent agreement can be obtained if we take $m^* = 0.055m_0$, or if the resolution function of the spectrometer is increased by about 10%, as shown in the upper curves of Fig. 3.

Calculations of the neutron scattering away from reciprocal lattice points have also been made, neglecting the change in the unscreened vibrational frequencies and eigenvectors of the LO mode with wave vector, and the calculated dispersion curve for the LO modes gives reasonable agreement with experiment.

The authors are grateful to Professor W. Cochran for interesting them in PbTe and for helpful correspondence, and also to Dr. D. J. Huntley, who performed the electrical measurements.

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OPTICAL QUENCHING OF PHOTOCONDUCTIVITY NEAR THE BAND EDGE IN CdS†

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(Received 25 February 1965)

We have observed the optical quenching of photoconductivity at photon energies slightly less than the band gap in undoped CdS crystals. The purpose of this Letter is to present the results and suggest an explanation.

Previous work¹⁻⁵ on the optical quenching of photoconductivity in CdS reports two "bands" at about 0.9 and 1.4 eV, well separated from the band gap at approximately 2.5 eV. The 0.9-eV band, observed only at higher temperatures, is considered to arise from the optical excitation of a trapped hole from its ground

state to an excited state close to the valence band. The hole, then, may ionize thermally and subsequently recombine with a trapped electron, emptying an electron trap. The emptied trap is then able to capture a free electron leading to a decrease of photocurrent. The 1.4-eV band, observed at lower temperatures as well, is due to the same mechanism except that the free hole is provided by the direct optical ionization of a trapped hole. The trapped electrons and holes are supplied by previous and simultaneous excitation of the crystal with

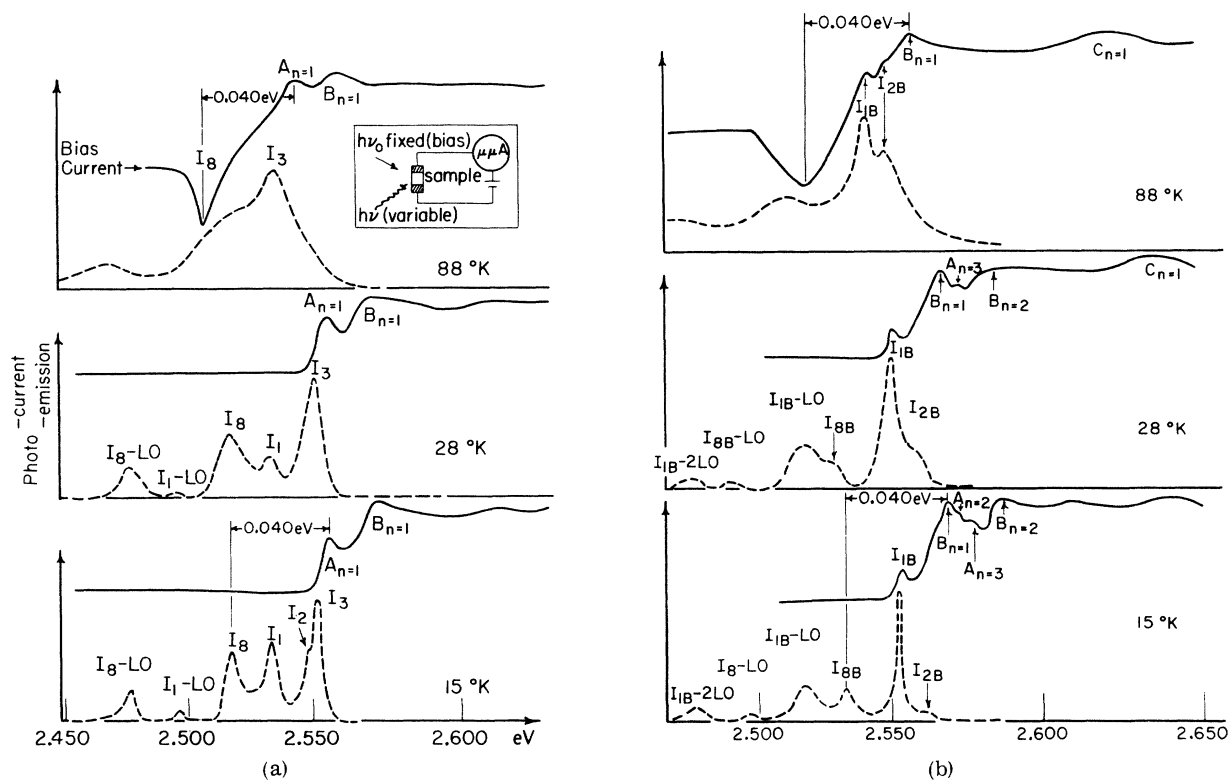


FIG. 1. Spectral dependence of photocurrent (solid curve) and photoemission (dashed curve) at 15, 28, and 88°K. (a) E vector perpendicular to c axis; (b) E vector parallel to c axis. Inset in (a) shows arrangement for recording photocurrent: Monochromatic radiation of energy $h\nu_0$ (3 eV in data) larger than band gap and of constant intensity is used as a bias light; $h\nu$ (variable) is then superposed and the change of current is recorded. A , B , and C without and with subscript are ground and excited states of intrinsic excitons, respectively, identified from D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962); and Y. S. Park and D. C. Reynolds, Phys. Rev. **132**, 2450 (1963). Emission is always less for $E \parallel c$ than for $E \perp c$; the curves are normalized to give equal maximum emission. I_1 , I_2 , I_3 , I_{1B} , and I_{2B} are bound excitons identified from Thomas and Hopfield, *loc. cit.* I_8 and I_{8B} are assumed to arise from a bound exciton. LO is the energy of a longitudinal optical phonon 0.037 eV. Monochromator slits are set for a spectral width of 0.004 eV.

a "bias light" of photon energy larger than the band gap.

Briefly, we propose that the mechanism for quenching near the band edge is, as above, due to the recombination of a free hole with a trapped electron. The free hole, however, is furnished by thermal ionization from an exciton complex created by the "quenching" radiation. This mechanism is basically similar to that responsible for the 0.9-eV band in that the free hole is primarily supplied by the thermal ionization from an optically excited defect: an exciton weakly bound to a defect in this case, an excited acceptor state in the other case.

The results to be described have been verified on several crystals; the data shown were taken on one sample. Figures 1(a) and 1(b)

show the spectra of photocurrent (solid curve) and photoluminescence (dashed curve) at 15, 28, and 88°K when the E vector is parallel and perpendicular to the c axis of the crystal, respectively. At 4.2°K the emission is completely polarized⁶ with $E \perp c$ because the population of holes in the other bands (see Fig. 2) is negligible. At 15°K this is no longer the case. Focusing attention first on the emission, the lines labeled I_1 , I_2 , and I_3 are identified from the work of Thomas and Hopfield⁷ who showed that they result from the radiative decay of an exciton bound to a neutral acceptor (I_1), neutral donor (I_2), and an ionized donor (I_3), respectively. In each case the exciton arises from a hole in the A valence band (see Fig. 2). I_{1B} and I_{2B} are the corresponding lines in which

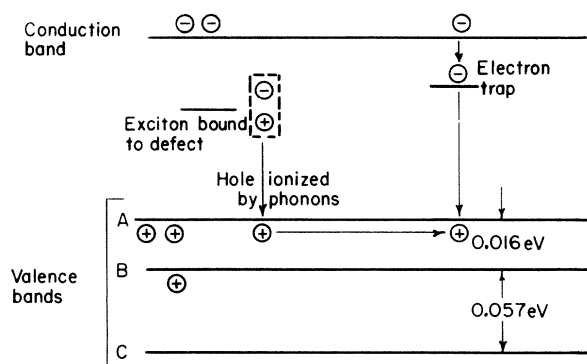


FIG. 2. Suggested model for the quenching of photocurrent near the band edge of CdS. Data on the energy band structure, shown at $k=0$, is taken from Thomas and Hopfield.⁶ A, B, and C are doubly degenerate valence bands. Optical dipole selection rules are given in reference 7 and in R. G. Wheeler and J. O. Dimmock, Phys. Rev. **125**, 1805 (1962), for free and bound excitons, respectively. A "bias" light produces free and trapped electrons and holes, in particular, a filled electron trap which is easily emptied by a free hole. Addition of the "quenching" radiation, then, directly produces an exciton bound to a defect. From the exciton "complex" thus created, a hole is thermally ionized which recombines with a trapped electron. A free electron captured by the trap, thus emptied, leads to a decrease of photocurrent.

the hole originates in the B band.⁷ The lines labeled I_8 and I_{8B} have not been reported and will prove to be an essential clue for an explanation of the mechanism of quenching. They may be peculiar to the crystals which show the effect since such crystals are, indeed, the exception rather than the rule. I_8 and I_{8B} are separated by 0.016 eV, the separation between the A and B valence bands, as one would expect if they are caused by the radiative recombination of A and B excitons bound to the same defect. At 88°K, I_1 and I_8 (I_{1B} and I_{8B}) are no longer distinct because of phonon broadening. This, in fact, is already the case at 40°K.

As for the photoconductivity spectra, our results are similar to those of Gross et al.⁸ and Park and Reynolds,⁹ who, unlike the author, worked without a bias light. The latter identified the spectra which consist of the ground and excited states of the intrinsic excitons A, B, and C as well as bound excitons. They are identified in Figs. 1(a) and 1(b). We observe, in addition, the quenching of photoconductivity shown for 88°K. Characteristic features of the quenching are the following: (a) It is ob-

served only at temperatures above about 70°K. (b) Sensitivity to polarized radiation is as shown. The minima are separated by 0.016 eV for $E \perp c$ and $E \parallel c$. (c) The "bands" are located 0.040 eV from the intrinsic excitons shown, as are the emission lines I_8 and I_{8B} , respectively. (d) The "band" is wider for $E \parallel c$ than for $E \perp c$.

We assume that the basic mechanism for quenching is the same as that previously proposed,¹⁻⁵ i.e., the recombination of a freed hole with a trapped electron. We assume further that the emission line I_8 (I_{8B}), seen clearly at 15°K, is due to the radiative decay of an exciton bound to a crystal defect, and that above 70°K the thermal ionization of a hole from this complex competes with radiative decay. The mechanism for the quenching of photoconductivity near the band gap is then visualized (see Fig. 2) as the creation of the exciton complex I_8 (I_{8B}) by the "quenching" radiation; above 70°K a free hole, supplied by thermal ionization from the complex, recombines with electrons in traps filled by the "bias" radiation causing a decrease of photocurrent. I_8 and I_{8B} arise from exciton complexes which are made up from the A and B hole bands, respectively; however, the hole is not necessarily ionized to the band from which the exciton is created. Thomas and Hopfield⁷ have pointed out that a bound B hole can convert itself into a bound A hole spontaneously, emitting a phonon. They estimate this process to be sufficiently rapid to cause lifetime broadening. The larger width of the quenching band for $E \parallel c$ than for $E \perp c$ may be due to this mechanism of hole conversion.

The quenching might also be explained by an Auger-type recombination^{10,11} in which an exciton near a hole trap is annihilated ionizing the hole. This is rejected because it is not obvious that this mechanism involves a temperature dependence observed experimentally. It should be mentioned that Halsted and Segall¹² proposed the thermal ionization of a hole from an exciton complex, in this case an exciton bound to a singly ionized double acceptor, to explain the shift to lower energy of the "green emission" with decreasing temperature.

I wish to express my gratitude to A. B. Dreeben of the Radio Corporation of America for his generous supply of these unusual crystals. D. E. Poland and R. C. Keezer were helpful during the initial stages of the experiment, and A. H. Kahn contributed through discussions.

†Research supported in part by the U. S. Office of Naval Research.

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LATTICE DYNAMICS OF WHITE TIN

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(Received 8 March 1965)

Dispersion relations for lattice vibrations in white tin with wave vector along the $[00\xi]$ direction of the reduced zone and along its continuation, the $[10\xi]$ direction, have been measured at 100 and 296°K. The results were obtained by the method of the inelastic scattering of slow neutrons, using the Chalk River triple-axis spectrometer, largely in the "constant- \vec{Q} " mode of operation. The results bear little resemblance to curves in the literature calculated on the basis of estimates of the interatomic force constants made using the experimental elastic constants. The frequencies for similar wave vectors are larger at 100°K than at 296°K, by varying amounts of the order of 3%. The results correlate well with the superconducting tunneling measurements of Rowell and Kopf. Sharp anomalies provide evidence for interference effects in the electron-phonon interaction.

White tin (β -Sn) has a body-centered tetragonal lattice with basis atoms at $(0, 0, 0)$ and $(0, a/2, c/4)$. The lattice constants have been measured at various temperatures by Rayne and Chandrasekhar¹; by interpolation of their results at 100°K, $a = 5.815$ Å and $c = 3.164$ Å; and at 296°K, $a = 5.832$ Å and $c = 3.183$ Å. For this structure, the $[0, 0, \xi]$ direction is the intersection of two equivalent mirror planes. This implies that phonons with wave vector along this direction are purely longitudinal or transverse, and that the transverse branches are doubly degenerate. The (010) plane of the reciprocal lattice of β -Sn is shown in Fig. 1, with the first Brillouin zone about each lattice

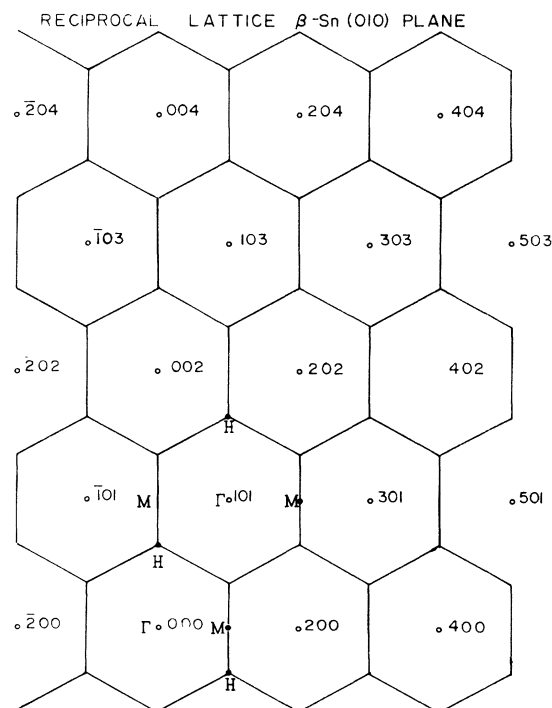


FIG. 1. The (010) plane of the reciprocal lattice of β -Sn with the first Brillouin zone about each point, and some symmetry points labeled.

position and symmetry points labeled in the notation of Koster.² From this diagram, it is obvious that the $[10\xi]$ line from H to M is the continuation of the $[00\xi]$ line from Γ to H ; henceforth, we shall include both when we refer to the $[00\xi]$ direction. The measurements were taken with the (010) plane of the specimen horizontal; i.e., in the plane of the spectrom-