OSCILLATORY PHOTOCONDUCTIVITY AND ENERGY-BAND PARAMETERS OF ZnTe†

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(Received 6 July 1966)

Measurements of photoconductivity, absorption, and reflection have been made on ZnTe single crystals at helium temperatures. The photoconductivity spectrum shows oscillations. From the results, the intrinsic energy gap and the effective masses of electrons and holes are determined. The crystals used were undoped, *p* type with room-temperature carrier concentrations ranging from 10^{16} to 10^{17} cm^{-3}. They were grown using a Bridgeman method in this laboratory by Klose.

The exciton energy in ZnTe has been determined by other workers from measurements of optical absorption, luminescence, and reflectivity. An exciton peak was observed in the absorption spectrum of single-crystal ZnTe at helium temperature between 2.385 and 2.390 eV by Loh and Newman.[1] On evaporated films, Aten, Van Doorn, and Vink[2] observed an exciton absorption peak at 2.375 eV at 4°K. In luminescence spectra of crystals, an exciton line was identified at 2.374 eV at 4.2°K by Gross, Suslina, and Livshits[3] and at 2.375 eV at 20°K by Halsted and Aven.[4] Sobolev[5] reported exciton luminescence lines at 2.375 and 2.373 eV at 4.2°K from two different types of evaporated layers. Exciton structure in reflectivity spectra has been studied by several groups of workers at helium temperatures. The common feature of the spectra is a sharp minimum observed variously at ~2.363 eV,[1] ~2.381 eV,[6] and ~2.382 eV.[2] The measurement giving 2.381 eV was made with the sample under applied stress which produced some shift of the spectrum.

Aten, Van Doorn, and Vink[2] observed an additional weak structure in the reflectivity which they attributed to the $n=2$ exciton state. From the $n=1$ and $n=2$ exciton energies, a value of 2.391 eV was deduced for the energy gap. The weak $n=2$ exciton structure has not been observed by other workers, and there are no other experimental determinations of the energy gap at low temperatures. Estimates[7,8] have been made by adding to the exciton energy some reasonable value, ~0.01 eV, for the exciton binding energy.

The results of our photoconductivity and absorption measurements are shown in Fig. 1. The photoconductivity at $h\nu < 2.36$ eV is apparently due to impurities. The absorption edge shows a step below $\alpha \sim 100$ cm^{-1} which corresponds to the step at ~2.33 eV in the photoconductivity spectrum. The photoconductivity extends further down to ~2.25 eV, though a low-energy threshold is not clearly defined. Thus it seems that more than one impurity level is involved. According to Aven and Segall,[9] zinc vacancies in ZnTe give acceptor levels with an ionization energy of 0.05 eV. The step at ~2.33 eV may be due to this level.

The steep rise of photoconductivity occurs at higher $h\nu$ than the absorption edge. Evidently, the shift is an indication for the energy difference between exciton and band-to-band excitations. The onset of exciton absorption reduces the photon absorption by impurities, causing a drop of impurity photoconductivity at the absorption edge. In the rise following this drop, a step can be seen. The step occurs near the exciton energy and seems to be produced by the exciton dissociation into free carriers.

The oscillation seen in the intrinsic photoconductivity is similar to that observed recently

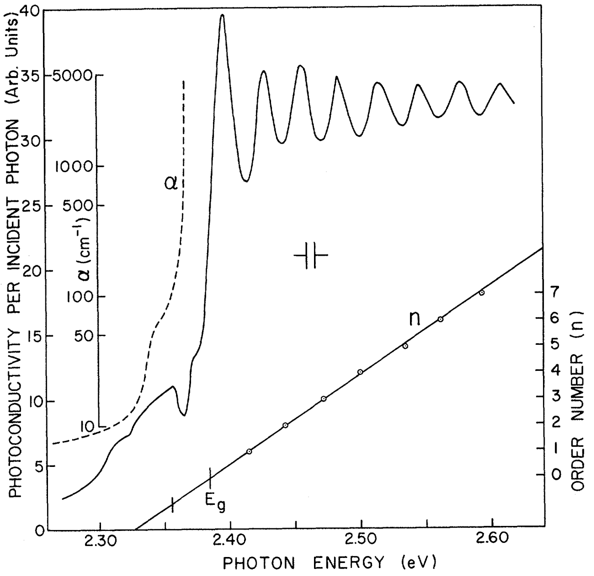

FIG. 1. Absorption (dashed curve) and photoconductivity (solid curve) spectra of ZnTe at helium temperatures. The points on the straight line give the energies of the photoconductivity minima as a function of the order numbers assigned to the minima.

in various semiconductors: p-type GaSb,[10] p-type InSb,[10,11] n-type InSb,[12] CdS,[13] and GaP.[14] It arises basically from the fact that the excited carriers interact strongly with polar optical phonons but much more weakly with acoustical phonons. The condition favorable for the oscillation is[10]: $\tau_a \gg \tau \gg \tau_{op}$, where τ_a and τ_{op} are characteristic times for the loss of carrier energy to acoustical and optical phonons, respectively, and τ is the lifetime of the excited carriers. Under this condition and direct optical excitation, the energy of the excited carriers during most of the carrier lifetime varies between 0 and $\hbar\omega_l$, according to

$$\epsilon_1 = (h\nu - Eg)/(1 + m_1/m_2) - n\hbar\omega_l,$$

where the subscripts 1 and 2 indicate the two types of carriers excited, n is the largest allowable integer, and $\hbar\omega_l$ is the energy of longitudinal optical phonons which are effective in the interaction with the carriers. No indication of indirect transitions is seen in our studies of the absorption edge. Most likely the band extrema are at the center of the Brillouin zone, with a Γ_6 conduction band and Γ_8 valence band as in other compounds of zinc-blende structure. Thus no intervalley scattering is involved, and $\hbar\omega_l$ should correspond to LO phonons with $q \sim 0$, for which a value of 0.026 eV has been found.[15]

The oscillation of carrier energy with $h\nu$ leads to an oscillation in photoconductivity. The period is $\Delta h\nu = 0.030$ eV, according to the slope of the straight line in Fig. 1. The ratio $\Delta h\nu/\hbar\omega_l$ gives an estimate of $m_1/m_2 = 0.15$. In view of this small value, it is reasonable to assume that the oscillation is produced by the contribution of electrons excited from the heavy-hole band, i.e., $m_e/m_{hh} = 0.15$. The energy $h\nu = 2.385$ eV, which is 0.030 eV below the first minimum, corresponds to the steep edge of photoconductivity. Unless this energy corresponds to the band gap, there should have been an indication of another minimum at this point. The absence of even an inflection indicates that $E_g = 2.385$ eV.

There is some spread in the exciton energy indicated by various measurements of different workers. We have made reflection measurements on the same crystals used for the photoconductivity measurements. The sample surfaces were prepared by etching. The result shown in Fig. 2 exhibits the same anomalous shape as reported by Hopfield and Thomas.[6] According to their interpretation, the exciton energy is on the low-energy side of the reflectivity minimum; the maximum which should be seen near the resonance energy is suppressed by the existence of an anomalous wave. The peak observed on the high-energy side of the minimum is presumably due to the existence of a surface barrier for excitons. The luminescence data of various workers agree in giving an exciton energy ~2.375 eV. This value seems to be consistent with the reflectivity spectrum of Fig. 2 and is also reasonable according to the absorption edge in Fig. 1. Taking the exciton energy to be 2.375 eV, we get a value of $E_g - E_{ex} = 0.010$ eV for the exciton binding energy. Using this value and $K = 10.7$ for the static dielectric constant,[2] we get $\mu = 0.08m_0$ for the exciton reduced mass.

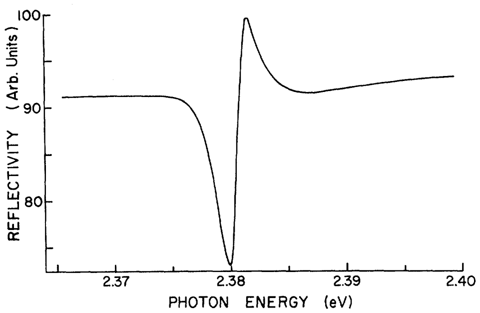

FIG. 2. Reflection spectrum of ZnTe in the exciton region at 1.7°K.

Assuming the exciton reduced mass to be determined primarily by the heavy-hole mass m_{hh} and the electron mass m_e, we obtain the two masses from the values of μ and m_e/m_{hh}: $m_e = 0.09m_0$ and $m_{hh} = 0.6m_0$. Calculations of the effective masses in ZnTe have been made by the $k \cdot p$ method. Cardona[7] obtained $m_e/m_0 = 0.17$, $m_{hh}/m_0 = 1.0$, $m_{lh}/m_0 = 0.16$, and $m_{so}/m_0 = 0.42$ for electrons, heavy holes, light holes, and the spin-orbit band, respectively. More recently, Watanabe[16] obtained the hole masses: $m_{hh}/m_0 = 1.86$, $m_{lh}/m_0 = 0.15$ and $m_{so}/m_0 = 0.31$. In the calculations, the heavy-hole mass is obtained as the reciprocal of the difference of two large numbers, and hence is not very reliable. A value of $m_{hh}/m_0 = 1.5$ was obtained by Watanabe from fitting of an observed absorption band associated with intervalence band transitions. No other experimental determinations of carrier effective masses are available in the literature.

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†Work supported in part by U. S. Army Research Of-

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NUCLEAR MAGNETIC RESONANCE AND INTERNAL OXIDATION OF Cu-Mn ALLOYS

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(Received 21 June 1966)

It is shown that vacuum annealing of comminuted Cu-Mn alloys can cause loss of Mn solute by a mechanism of internal oxidation. Some loss of Mn solute can even occur in the process of comminution. Order of magnitude errors in the true Mn solute concentration can result, leading to erroneous conclusions concerning internuclear reactions and quadrupole effects as derived from nmr measurements.

Nmr parameters of Cu-based binary alloys have been explained in terms of direct and indirect internuclear reactions and quadrupole perturbations.[1-4] Most studies in this area have been made on unannealed material containing unspecified amounts of cold work.[6-11] For binary alloys containing sufficient solute to produce second-order quadrupole interactions throughout the Cu lattice, first-order quadrupole effects arising from cold work should not be observable. In such cases, the nmr line widths, intensities, and Knight shifts, should not change with annealing heat treatment. For solute concentrations below approximately 1 at.%, first-order perturbation effects are in evidence and the effect of cold work on the nmr parameters is of significance. In this region the effect of annealing heat treatment on nmr parameters can be considerable.

Two authors, in particular, have examined the effects of heat treatment of the nmr of Cu-based alloys. Rowland[12] used samples that were generally not annealed, but he observed that, in the few (unspecified) instances when filings were annealed, the resonance intensities before and after annealing were unchanged. Chapman and Seymour,[13] however, observed that some features of the Cu^{63} resonance in Cu-Mn alloys, containing a few wt% of Mn, were widely different, depending on whether the samples were powder as filed or powder which had been annealed in vacuo at 400°C for four hours. The annealed samples showed a narrowing of the line width, an increase in the intensity, and a reduction in the Knight shift. These authors observed no significant changes for annealed Cu-Ni samples, except for a slight narrowing of the line in all cases. They further observed that a second anneal had no further effect on the Cu-Mn resonances. They therefore proposed that heat treatment produces a cluster of Mn ions, thus leaving the bulk of the material free