Eq. (A4) may be reduced to

$$C_1(t)=\hbar \sum_{i(i\neq k)} A_{ik}I_{i+}\exp[2itB_{ik}(I_{kz}-I_{iz})]I_{k-}\prod_{j(j\neq i,k)}\exp(2itI_{jz}(B_{ij}-B_{kj}))-\text{Hermitian conjugate}. \tag{A6}$$

For $I=\frac{1}{2}$, the only case considered from now on, one may use the identity in Eq. (A7) to simplify Eq. (A6).

$$\exp(i\phi I_{jz})=\cos(\phi/2)+2iI_{jz}\sin(\phi/2). \tag{A7}$$

The final result is that

$$C_1(t)=\hbar \sum_{i(i\neq k)} A_{ik}I_{i+}I_{k-}\prod_{j(j\neq i,k)}\exp[i(B_{kj}-B_{ij})I_{jz}t]-\text{Hermitian conjugate}. \tag{A8}$$

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Optical Properties of Zinc Telluride*

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The optical absorption of ZnTe single crystals grown by the Bridgeman method has been studied from visible wavelengths to 50 μ, at temperatures from 1.4 to 300°K. Lattice combination bands are observed from which assignments of zone-boundary phonon energies are made: LO = TO = 22, LA = 16, TA = 7×10^{-3} eV. The temperature dependence of the absorption is discussed. Absorption due to inter-valence-band transitions has been observed, which indicates the presence of two bands degenerate at $k=0$ and a split-off band lying 1 eV below. Infrared absorption is observed for As impurity in the range 0.05 to 0.1 eV and for a residual impurity in undoped material, probably a zinc vacancy, in the range 0.1 to 0.9 eV. For each impurity, absorption due to transitions to the split-off valence band is also observed near 1 eV. Sharp excitation lines are seen in the spectrum of the residual impurity. The lines are repeated with emission of optical phonons of energy 0.026 eV, from which the electron-phonon coupling coefficient is estimated. Some structure is observed also in the spectrum of As impurity. The intrinsic absorption edge has been measured at 1.7, 80, and 300°K. The energy gap is determined to be 2.385, 2.37, and 2.25 eV, respectively. A tail is observed at the absorption edge which shows the effect of various impurity levels in the undoped material and in the samples doped with As, In, or Fe. In two samples grown from the vapor phase, some sharp absorption lines are present in the range 2.2 to 2.35 eV. These lines are apparently due to exciton-impurity complexes.

I. INTRODUCTION

Zinc telluride is a II-VI compound semiconductor with zinc-blende structure. Undoped ZnTe turns out to be *p* type. *n*-type material with very low carrier concentration has been obtained in highly compensated form, in particular with In doping. It has been suggested that zinc vacancies acting as double acceptors give rise to self-compensation.[1,2]

The energy gap of ZnTe has been estimated to be ~2.1–2.3 eV from room-temperature optical measurements.[3–6] From low-temperature studies of oscillating photoconductivity and optical behavior near the absorption edge, we have obtained values of the carrier effective masses and the energy gap at 4.2°K: $m_e=0.09m$, $m_{hh}=0.6m$, $E_g=2.385$ eV.[7] The structure of the valence band is expected to be similar to that of the III-V compounds. Piezoresistance data[8] are consistent with such a model. Absorption bands have been observed near 1 eV in crystals doped with various impurities,[9,10] and these bands were attributed to transitions between the impurity level and the split-off valence band.

We report, in this paper, studies of optical absorption over a range from the visible region to 50 μ. The measurements were made at temperatures between 1.4°K and room temperature. Absorption bands of lattice combination modes were observed in the region between

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25 and 50 μ. The results provided an estimate of phonon energies near the zone boundary. Absorption due to inter-valence-band transitions of free holes was observed showing that the valence-band structure is in fact similar to that of III-V compounds. An estimate of the spin-orbit splitting was obtained. Absorption due to a residual acceptor in undoped material and absorption due to arsenic acceptor in doped crystals were seen at low temperature. In each case, transitions from the hole bands, as well as transitions from the split-off band, were observed.

The long-wavelength absorption edge of the residual acceptor showed a series of steps, each beginning with two prominent lines. Similar steps had been reported previously without the prominent lines.[11] The observed structure apparently corresponds to excitations and ionizations of the impurity accompanied by the emission of a successively larger number of optical phonons. The electron-phonon coupling is estimated from these results.

The intrinsic absorption edge was measured at different temperatures. The 1.7°K measurement showed a steeply rising edge indicative of a direct energy gap. The lower part of the edge was extended to long wavelengths by impurity absorption. A number of sharp lines, apparently due to exciton-impurity complexes, were observed in some samples grown from the vapor phase. They cannot be identified with various sharp-line spectra observed by other workers in absorption and emission,[12–15] and they were not seen in the crystals grown from melts.

II. RESULTS AND DISCUSSION

Single-crystal samples were used which were cut from ingots grown by the Bridgeman method in this laboratory by Klose.[16] Both undoped and As-doped materials were used. They were p type with room-temperature carrier concentrations in the range 10^{16} to 10^{17} cm^{-3} for the undoped samples and up to 10^{18} cm^{-3} for the As-doped material. With decreasing temperature, the Hall coefficient increased continuously. The hole mobility was $\sim$100 cm^2/V sec at room temperature and reached a maximum as high as 1000 cm^2/V sec at $\sim$100°K. For measurements at wavelengths less than $\sim$10 μ, samples were prepared by mechanical polishing. For longer wavelengths, etched samples were also used. A good finish with no surface film was obtained by etching for $\sim$5 sec in a solution of 3HNO$_3$:1HF:1H$_2$O. No difference in the absorption was noticed in using the etched and polished surfaces. Measurements were performed on a grating monochromator with a foreprism to remove high-order wavelengths. The resolution was better than 10^{-4} eV throughout the range studied.

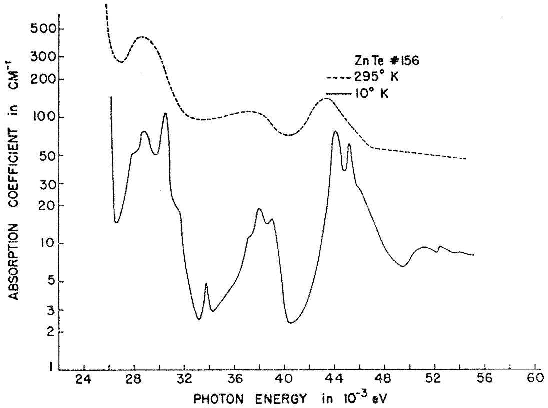

FIG. 1. Lattice absorption bands in ZnTe at room temperature and helium temperature. The background at room temperature is due to free holes.

A. Lattice Vibrations

In the range 25 to 55×10^{-3} eV, a series of absorption bands has been observed, as is shown in Fig. 1. Three bands are clearly seen in the room-temperature spectrum. In the low-temperature spectrum, some structure is resolved within each band. The strengths of these bands are of the same order of magnitude at the two temperatures. The 295°K, curve has a higher background due to free-carrier absorption, which is discussed later below. The bands observed are identical for different samples, including various undoped samples and samples doped with As. Apparently, these bands are due to the excitation of lattice vibrations.

The reststrahlen energy, the TO phonon energy at $k\sim0$, has been determined to be 22×10^{-3} eV by Mitsuishi[17] from reflection measurements on ZnTe crystals. On the other hand, an absorption measurement[18] on finely powdered ZnTe suspended in a polyethylene film gave a strong absorption band with a maximum at 23.6×10^{-3} eV, which was taken to be the TO phonon energy at $k\sim0$. Fröhlich[19] has shown theoretically that spherical particles of a dimension smaller than the wavelength give absorption at a frequency intermediate between those of the longitudinal and the transverse modes. The discrepancy between the results obtained for the crystals and the powder specimens can be understood on this basis. The energy of the TO phonon ($k\sim0$) can also be calculated from the available data for the

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static[6,20] and optical[6,21] dielectric constants:

$$\epsilon_0 = 10.4, \quad \epsilon_\infty = 7.3;$$

and the energy of the longitudinal optical phonon:

$$\text{LO } (k \sim 0) = 26 \times 10^{-3} \text{ eV}.$$

The latter was obtained from analysis of structure in the impurity absorption[11,15] and luminescence.[22] Using the Lyddane-Sachs-Teller relation,[23] a value of

$$\text{TO } (k \sim 0) = 22 \times 10^{-3} \text{ eV}$$

is obtained in good agreement with the reflection measurement on crystals.

The bands shown in Fig. 1 evidently correspond to multiphonon excitations. Of the three bands observed, the one at the highest photon energy has its maximum at 43.5×10^{-3} eV (at 295°K). This energy is approximately twice that of the TO ($k \sim 0$) phonon. Since the optical-phonon energy, in general, does not vary over a wide range, this absorption band is attributed to the excitation of two optical phonons. The other two bands are comparable in strength, and are apparently due to two-phonon excitations also. Absorption associated with the excitation of three or more phonons might be expected to be much weaker.

Multiple-phonon processes must satisfy the selection rule

$$\textstyle\sum_i q_i \approx 0,$$

where q_i represents the wave vector of the ith phonon. For two-phonon excitations, the wave vectors must be equal in magnitude and opposite in direction. A combined density of states is obtained according to this condition from the densities of states of the two-phonon branches involved. Peaks in this combined density of states give rise to peaks in the absorption spectrum. In general, the combined density of states is expected to be large near the zone boundary. Therefore, the observed bands may be related to phonons near the zone boundary.

The effective ionic charge for ZnTe, as calculated from the Szigeti equation,[24] is $e^* = 0.7e$. Keyes[25] has noted an empirical relationship between the effective charge and the ratio LO/TO of phonon energies at the zone boundary, as shown by the plot in Fig. 2. According to this trend, we should have LO≈TO near the zone boundary. Therefore, it is possible that the absorption band at 43.5×10^{-3} eV contains all possible combinations of two optical phonons: 2TO, LO+TO, 2LO. We suggest that the next absorption band with a maximum at 37.5×10^{-3} eV corresponds to the combination of one optical and one longitudinal-acoustical (LA) phonon, and that the band in the neighborhood of 29×10^{-3} eV is due to the combination of an optical and a transverse-acoustical (TA) phonon. Absorption for all the suggested combinations is allowed at least somewhere over the zone boundary.[26] With these assignments, we get the following phonon energies near the zone boundary: LO=22, TO=22, LA=16, TA=7×10^{-3} eV.

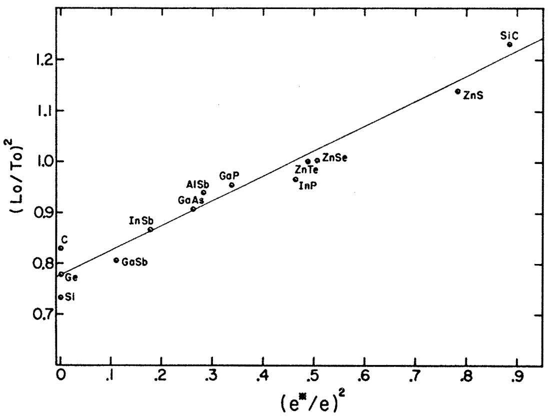

FIG. 2. Ratio of optical mode frequencies LO/TO near the zone boundary plotted versus effective charge for various materials.

1. *Sum Rule for Lattice Vibrations*

Brout[27] has shown that the sum $\sum_{i=1}^{6} \omega_i^2(q)$ is a constant independent of q for ionic diatomic crystals of NaCl structure, where each ion has Coulomb interactions with all other ions in the crystal and repulsive interactions with nearest neighbors. Rosenstock[28] has extended the sum rule to include n-atomic lattices of any type of structure. Furthermore, the rule is shown to hold for crystals with any kind of interactions between unlike atoms, but interaction between similar atoms must be electrostatic (Coulomb or multiple). Nonelectrostatic forces between like atoms contribute q dependence to the sum.

Using neutron-diffraction data, Rosenstock[28] showed that the sum rule is valid for Ge for [100] and [111] directions. The rule is apparently valid for Si also, according to the neutron-diffraction data of Dolling[29] for the points Γ, X, L. For GaAs, the data of Waugh and Dolling[30] give values of $\sum\omega^2$ differing by about 10% between Γ and X, L. According to the assignments made for ZnTe above, $\sum\omega^2$ differs by about 10% between $q=0$ and the zone boundary. This consideration lends some support to these assignments.

For zinc-blende structures, the Brout sum is given by[31]

$$\sum_{i=1}^{6} \omega_i^2(q) = \frac{16\sqrt{3} r_0 h^2}{\mu X},$$

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where r_0 is the equilibrium interatomic distance, μ is the atomic reduced mass, and χ is the compressibility at $T\approx 0°\text{K}$. Using the frequencies obtained, we get, from this equation, $\chi\approx 2.5\times 10^{-3}$ kbar^{-1}. This value compares favorably with the measured isothermal compressibility at room temperature,[32] $\chi=2.427\times 10^{-3}$ kbar^{-1}, which should not be greatly different from the value at 0°K.

2. *Temperature Dependence of Absorption*

The temperature dependence of the absorption due to a two-phonon excitation is given by

$$(n_1+1)(n_2+1)-n_1n_2=1+n_1+n_2,$$

where $n_i=[\exp(\hbar\omega_i/kT-1)]^{-1}$. The absorption bands seen at room temperature each correspond to two or three resolved peaks at helium temperature. For comparison, integrated absorption is used. In addition, it is necessary to subtract from the room-temperature absorption a background due to free holes. The ratios of integrated absorption, $\alpha(295°\text{K})/\alpha(10°\text{K})$, for the three bands are found to be within 30% of the calculated values. This may be considered reasonable agreement, in view of the accuracy involved.

3. *Fine Structure*

Consider now the resolved structure in each band at helium temperature. Structure in a two-phonon absorption spectrum is related to critical points,[33] which are defined as points where $\nabla_k[\omega_1(k)+\omega_2(-k)]$ is either zero or changes sign discontinuously. There is a distinction between two-phonon overtone states, where the two phonons have the same energy, and two-phonon combination states, where the phonons belong to two different branches. The critical points of overtone states are the same as those of the corresponding one-phonon states, except that the energy is doubled. This is not, in general, true for the two-phonon combination states. The combination of two critical points in the separate one-phonon dispersion spectra gives rise to a critical point of the two-phonon states. However, in this case, additional critical points of two-phonon states can occur where none existed in the one-phonon curves. Various types of critical points give rise to different kinds of slope discontinuities in the density of states which are reflected in the absorption spectrum. For example, there appears to be, at 37.2×10^{-3} eV (Fig. 1), a slope discontinuity of the kind given by a type of saddle point.

Critical points in the phonon spectrum occur at Γ, X, L, and W for zinc-blende structures.[26] However, there are, in general, other critical points in the Brillouin zone, which cannot be predicted from general considerations. Furthermore, three-phonon excitations may be responsible for some of the resolved structure. It is not possible to provide reliably detailed interpretation of the resolved structure without additional information.

4. *Frequency Shift with Temperature*

The lattice absorption bands in the 295°K spectrum appear to be shifted to lower energies in comparison with the low-temperature spectrum. For the band of highest frequency, the shift is most noticeable, and is of the order of 10^{-3} eV, corresponding to $\Delta\omega/\omega\Delta T\simeq 8\times 10^{-5}/°\text{K}$ for each mode. The same order of magnitude is obtained for ZnS,[34] InSb,[35] and Ge.[36] Such a shift may arise from the volume contraction of the crystal with temperature. The Grüneisen relation, based on the assumption of equal volume dependence of frequency for all modes, gives

$$-\partial\ln\omega/\partial\ln V=\gamma=\beta V/C_v\chi,$$

where γ is the Grüneisen constant, β is the thermal coefficient of volume expansion, C_v is the specific heat at constant volume, χ is the compressibility, and V is the volume/g. Using the known values of β [37] and χ [34] and a reasonable value of C_v over the present temperature range, we get an estimate of the frequency shift which is small by an order of magnitude compared with the observed result. The same situation applies also to ZnS, InSb, and Ge.

The assumption of a uniform volume dependence for the frequency of all modes is known to be oversimplified, as shown by the large temperature variation of γ observed for various materials. Furthermore, the lattice frequencies may depend on temperature directly. Loudon[38] considered the lifetime of an optical phonon as determined by the three-phonon anharmonic interaction through which the phonon decays into two other phonons. This process leads to a shift of the phonon energy which depends on the population of the modes of decay. Since this population is temperature-dependent, the phonon energy varies with temperature. This mechanism has been suggested to explain the frequency shift with temperature observed in the first-order Raman spectra of diamond[38] and III-V compounds.[39] It may be the explanation for the observed frequency shift.

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B. Inter-Valence-Band Absorption

The valence-band structure of ZnTe may be expected to be similar in nature to those of various other semiconductors of zinc-blende structure, i.e., a heavy-hole and a light-hole band which are degenerate at $k=0$ and a split-off band lying below. The piezoresistance measurements of Sagar and Lehmann[8] support this suggestion. Figure 3 shows the absorption spectra at room temperature and liquid-nitrogen temperature for undoped samples of ZnTe. The low-temperature curve will be discussed later. The room-temperature spectrum is qualitatively similar to that of p-type III-V compounds. Below about 0.8 eV, the absorption rises with decreasing photon energies, and near 0.1 eV it reaches a plateau which extends into the region of lattice absorption discussed previously. The results for the two different samples measured show that this part of the spectrum is proportional to the concentration of free holes. The structure is apparently associated with transitions between the heavy-hole and light-hole bands.

There is a small band with a maximum at 1.05 eV; the strength of this band is also proportional to the concentration of free holes, as can be seen by comparing the 300°K spectra in Fig. 3. The band is not observed at liquid-nitrogen temperature, where the hole concentration is reduced by several orders of magnitude. This band is attributed to transitions from the split-off band to the upper two valence bands, giving a spin-orbit splitting of ~1.0 eV. This is close to the value of 0.91 eV obtained by Cardona and Greenaway[5] from reflection measurements. Separate absorption bands corresponding to transitions to the heavy-hole band and light-hole band are not resolved. The absorption band seen at 1.25 eV is not associated with free holes, since it increases in strength at lower temperature, where the holes are frozen out on impurities. The nature of this band will be discussed later.

C. Impurity Absorption

Figure 3 shows that the absorption spectrum at liquid-nitrogen temperature is quite different from the room-temperature spectrum, showing a long-wavelength cutoff. The absorption has a maximum at ~0.23 eV and appears to be due to some residual impurity or defect in the undoped samples. The measured variation of Hall coefficient with temperature gives, for this sample, an activation energy of 0.14 eV, which is typical for the undoped samples. Aven and Segall[2] suggest that a zinc vacancy is a double acceptor with one level at 0.048 eV and another one in the range 0.12 to 0.16 eV from the valence band, the latter being difficult to distinguish from the 0.15-eV level of Cu impurities. However, Cherry and Allen[40] have measured Cu-doped ZnTe, obtaining an absorption peaked around 0.41 eV. Therefore, our observed absorption is more likely to be associated with zinc vacancies.

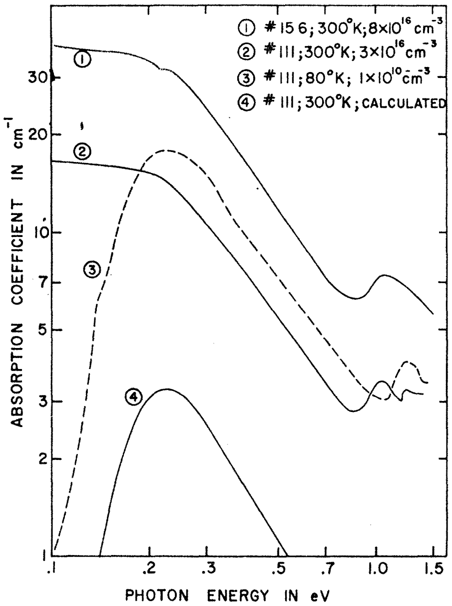

FIG. 3. Absorption spectrum of undoped ZnTe at 300 and 80°K. The temperature at which the absorption and the carrier concentration of the sample were measured are given in the figure. Curves (1) and (2) show inter-valence-band absorption. Curve (3) shows impurity absorption at the low temperature. Curve (4) shows the impurity absorption calculated for 300°K.

From the Hall data, the Fermi energy is estimated to be 0.16 eV at room temperature and 0.11 eV at liquid-nitrogen temperature by using an effective mass of $0.6m_0$ for the holes. With an ionization energy of 0.14 eV, the impurity levels should give full absorption at the lower temperature. At room temperature, the absorption is reduced by electron occupation of the levels. Curve 4 in Fig. 3 shows the calculated impurity absorption for room temperature according to the fraction of unoccupied levels. The observed absorption is dominated by free holes. The upper curve in Fig. 3 shows the room-temperature absorption curve for another sample, in which the effect of impurity absorption can be seen by the presence of a kink near 0.2 eV.

The small band at 1.25 eV in the curves of Fig. 3 seems to be due to an impurity, rather than inter-valence-band transitions, since it becomes larger at the lower temperature when the free holes are largely frozen out. The temperature dependence of this band is comparable to that of the 0.23-eV band discussed in the preceding paragraph. We suggest that the same impurity is involved for both absorption bands. The 0.23-eV band is due to transitions from the light-hole and heavy-hole valence bands, and the 1.25-eV band is due to transitions from the split-off valence band to the impurity. The peaks of the two absorption bands differ in energy by about 1 eV, which is consistent with the previous estimate of spin-orbit splitting.

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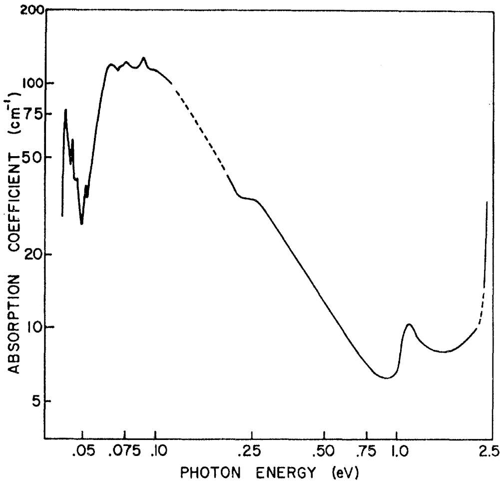

FIG. 4. Absorption spectrum of an As-doped sample at helium temperature. The absorption rising near 0.05 eV and the weak band near 1.0 eV are due to transitions from different valence bands.

Figure 4 shows the absorption spectrum at ~10°K for a sample doped with As. The peaks below ~0.05 eV are lattice vibration bands. The material was p type with $p \approx 1 \times 10^{17}$ cm^{-3} at room temperature. The Hall activation energy is 0.07 eV. The absorption in the range 0.05 to 0.2 eV arises from transitions between the upper two valence bands and the As level. The small band with a peak at 1.1 eV is given by transitions from the split-off valence band to the As impurities, similar to the 1.25-eV absorption in the undoped samples. There is a step just below 0.25 eV on the high-energy side of the As absorption. Also, an absorption tail is visible on the high-energy side of the As absorption peak at 1.1 eV. The step and the tail can be attributed to transitions from the valence bands to the residual acceptor, as observed in undoped samples.

In the present work, absorption was observed for each impurity in two different regions of the spectrum, in agreement with the spin-orbit splitting obtained from the free-carrier effect. Absorption bands in the region of 1 eV have been observed for Ag, Cu, and Au by Dietz[9] and for P by Watanabe.[10] By assuming the observed absorption to be given by transitions from a split-off band, and using the ionization energies given by electrical measurements, the authors estimated the spin-orbit splitting. The values are in agreement with our result.

D. Phonon Effects in Impurity Absorption

At helium temperatures, the absorption edge of the impurity band in undoped samples shows fine structure in the region 0.1 to ~0.25 eV (see Fig. 5). The absorption rises in steps. Two sharp lines are seen at the beginning of each step at a regular interval of 26×10^{-3} eV, which is equal to the energy of long-wavelength LO phonons. Haanstra and Haas[11] reported a similar spectrum showing steps but no prominent sharp lines. Evidently, the steps are produced by transitions involving the emission of a successively larger number of phonons. The sharp lines correspond to excitations of the impurity, with the lines at 106 and 110.1×10^{-3} eV corresponding to the zero-phonon excitations. For a particular number of emitted phonons, the excitation lines, two of which are resolved, should merge with a following ionization continuum. Gradual merging and superposition of absorptions involving different numbers of phonons make it difficult to discern the onsets of the ionizations. In a hydrogenlike impurity, the energy of the transition from the ground state to the first excited state is about 75% of the ionization energy. About the same percentage holds for shallow acceptors in Ge.[41] On this basis, we would expect an ionization energy of ~0.14 eV, assuming the 0.106-eV line to be the transition from the ground state to the first excited state. This is consistent with the Hall activation energy, 0.14±0.02 eV, of the undoped material. Accordingly, the zero-phonon ionization lies near the second pair of sharp lines. The small background in the range around 0.12 eV is then due to unresolved absorption of zero-phonon excitations. There is an additional extraneous background absorption of about 5 cm^{-1} throughout the spectrum of this sample.

The dashed curve in Fig. 5 shows the absorption due to ionizations with phonon participation. The curve is obtained from the following analysis. The steps are placed with spacing equal to the LO-phonon energy with the zero-phonon step at ~0.14 eV. In the neighborhood of 0.12 eV, the absorption of ~4 cm^{-1} above the background is ascribed to unresolved zero-phonon excitations. The strengths of absorption due to unresolved phonon-assisted excitations are then estimated accord-

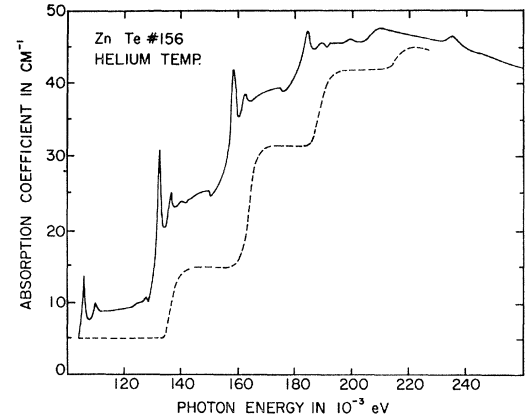

FIG. 5. Absorption spectrum of an impurity, probably a zinc vacancy, in undoped material at helium temperature. The pair of sharp lines near 0.11 eV are produced by zero-phonon excitations of the impurity. The zero-phonon ionization is shown as a step near 0.14 eV in the dashed curve. Lines and steps at higher photon energies are due to phonon-assisted transitions.

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[41] R. L. Jones and P. Fisher, J. Phys. Chem. Solids 26, 1125 (1965).

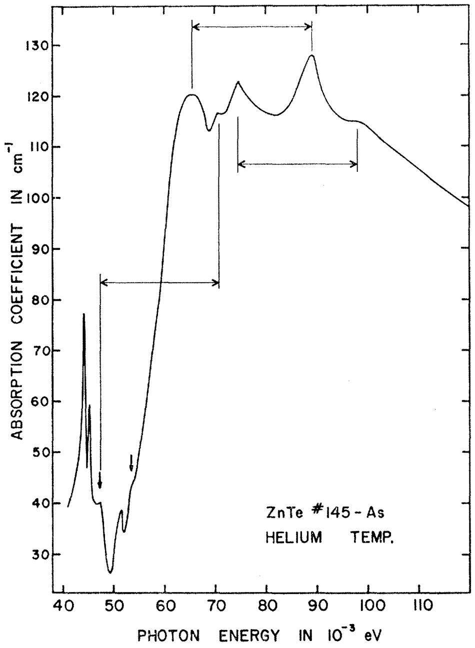

FIG. 6. Absorption spectrum of As impurity at helium temperature. The arrows show possible phonon separations of 0.023 eV. The sharp pair of lines near 0.044 eV are due to lattice vibrations. The small band near 0.05 eV occurs also in undoped samples.

ing to the relative strengths of the sharp excitation lines. The dashed curve is obtained by subtracting from the experimental curve the sharp lines and the estimated unresolved excitation absorption.

Hopfield[42] has obtained a theoretical expression for the probability of electron transitions between a localized energy level and an energy band with the emission of n phonons:

$$W_n \propto e^{-S} S^n / n!\,, \tag{1}$$

where the parameter S gives the mean number of emitted phonons. According to the theory of Huang and Rhys,[43] a similar expression applies for transitions between two localized energy levels. The ratio of n-phonon to zero-phonon absorption is given by

$$\alpha_n/\alpha_0 = S^n/n!\,.$$

The first line of each step rises sharply from the preceding step. The strengths of the lines can be estimated accurately. The series of lines can be well fitted by (1) with $S=2$. The ionization steps given by the dashed curve are better fitted with $S\sim 1.5$, but the accuracy of the analysis from which the curve is obtained is not sufficiently good to establish a definite difference.

For ionization transitions from a bound state to an energy band, the parameter S in (1) is given by[42]

$$S=\left(\frac{2\pi}{V}\frac{e^2}{\hbar\omega_l}\right)\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\sum_k |\rho_k|^2/|k|^2\,,$$

where $\hbar\omega_l$ is the energy of the longitudinal-optical phonon and ρ_k is the kth Fourier coefficient of the carrier charge density. Also for excitation transitions, the parameter may not be too different when the excited state is close to the band edge. For a bound state with a hydrogenic wave function that corresponds to an ionization energy E_i, we have[44]

$$S=\frac{5\pi}{16}\frac{\epsilon_\infty E_i}{\hbar\omega_l}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right).$$

With $E_i=0.14$ eV, we get a value of $S=1.6$, which shows that the estimate obtained in the interpretation of experimental data is reasonable.

There is also some structure in the absorption due to As impurity, as is shown in Fig. 6. The structures at 47.3, 53.8, 65.5, 70.7, 74.5, 89.0, and 97.5×10^{-3} eV are apparently due to transitions to excited states of As. The small peak near 50×10^{-3} eV appears in undoped samples also, and the two peaks near 45×10^{-3} eV are due to lattice vibrations. Absorption measurements near the intrinsic edge discussed below show a level at about 0.06 eV, and the Hall coefficient indicates an activation energy of $\sim$0.07 eV. The presence of absorption peaks at higher energies points to phonon-assisted transitions. The three peaks at 65.5, 74.5, and 47.3×10^{-3} eV are each followed by a peak at a spacing of 23.0 $\pm0.5\times10^{-3}$ eV. This energy is close to that of the LO phonon near the zone boundary. There are no peaks at higher energies which would correspond to transitions involving more than one phonon. This is in contrast to the case of undoped ZnTe in the region above 0.1 eV.

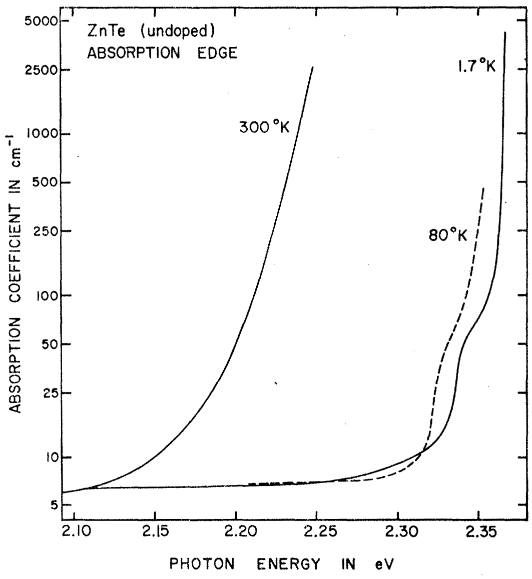

FIG. 7. The absorption edge in undoped ZnTe. At the low temperatures, impurity absorption is observed at absorption coefficients less than 100 cm^{-1}.

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[42] J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

[43] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

[44] A. Mooradian, Ph.D. thesis, Purdue University, 1965 (unpublished).

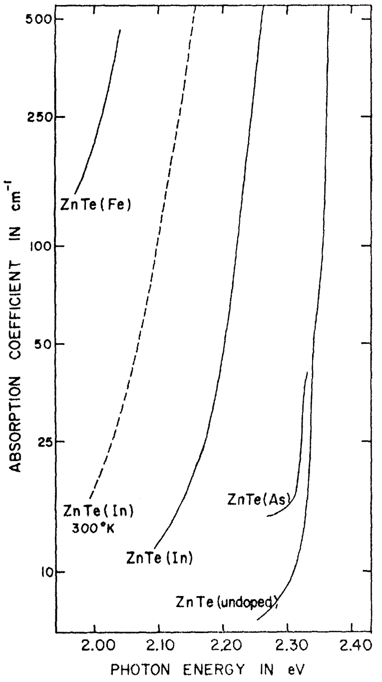

FIG. 8. The effect of impurity on the absorption edge. The dashed curve was obtained at 300°K. The other curves are for 1.7°K. The temperature shift for ZnTe(In) is the same as for undoped samples.

The difference may be due to the fact that electron-phonon coupling is weaker with a smaller ionization energy of the impurity. Also, the As spectrum may be broadened due to heavy doping.

E. Absorption Edge

The absorption edge in undoped ZnTe is shown in Fig. 7 for three different temperatures. The shift with temperature is about the same as that observed by other workers. At helium temperature, a spectral oscillation has been observed in the intrinsic photoconductivity,[7] from which the energy gap has been determined to be 2.385 eV. According to the shift of the absorption edge, the energy gap is 2.37 eV at 80°K and is about 2.25 eV at room temperature. A step, below $\alpha\sim100$ cm^{-1}, is seen at the two lower temperatures. A step was also observed at the same photon energy in the photoconductivity spectrum.[7] It is about two LO-phonon ($k\approx0$) energies from the energy gap. The step cannot be produced by direct phonon-assisted transitions, however, since phonon absorption is unlikely at the low temperature. Apparently, it corresponds to electron transitions to the conduction band from a level at $\sim$0.05 eV above the valence band. The level is probably produced by zinc vacancies. Below the step, there is a tail absorption, which, at helium temperature, rises above the background near 2.25 eV. Again, a similar effect was also observed in photoconductivity. It involves an energy level about 0.14 eV inside the energy gap. The Fermi level in this sample is about 0.06 eV from the valence band at liquid-nitrogen temperature. Evidently, the level must be 0.14 eV below the conduction band.

The absorption edge has been measured for As-, In-, and Fe-doped samples. Doping with either In or Fe had the effect of reducing the hole concentration. Figure 8 shows the results for helium temperature. A room-temperature measurement is also shown for the In-doped sample. The shift with temperature is seen to be the same, as is shown by the intrinsic edge in undoped samples. Due to the introduction of impurities, the absorption edge rises at lower energies. In the As-doped sample, the observed edge can be attributed to an As level about 0.06 eV above the valence band. The Fermi energy in this sample is near this level at low temperature. Therefore, this level may be partially filled so that it gives rise to the observed edge as well as the infrared absorption corresponding to excitation from the valence band (Fig. 6). The observed edge in the In-doped sample shows the effect of an impurity level $\sim$0.2 eV inside the energy gap. The sample has a very low hole concentration, $\sim10^{11}$ cm^{-3}, at room temperature, and electrical measurements at low temperature could not be made. The Fermi energy at low temperatures should be higher than 0.2 eV from the valence band. Thus, the level responsible for the absorption could be 0.2 eV from either band edge. The edge in the Fe-doped sample indicates the presence of an impurity level about 0.4 eV below the conduction band. The hole concentration is 2×10^{15} cm^{-3} at room temperature, corresponding to a Fermi level of 0.19 eV above the valence band. Therefore, a level at 0.4 eV above the valence band should not be occupied by electrons at low temperature, and could not give the observed absorption.

A magnetic field of up to 20 kG produced no noticeable effect on the low-temperature absorption edge. An electronic effective mass of $\sim0.09m_0$ gives $\hbar\omega_c\sim2\times10^{-3}$ eV for the spacing of Landau levels in the conduction band. With a mobility less than 10^3 cm^2/V sec, we estimate $\omega_c\tau\lesssim0.2$ at 20 kG, which is not favorable for observation of magnetic field effects.

1. Bound Excitons

Previous workers have observed sharp-line absorption and luminescence spectra in ZnTe at photon energies less than the energy gap. Dietz, Thomas, and Hopfield[15] observed absorption and luminescence structures near 2 eV. The structures in the two kinds of spectra appeared to mirror about a zero-phonon line, and they were attributed, respectively, to the formation and recombination of an exciton-impurity complex with emission of phonons. Halsted and Aven[12] observed sharp luminescence lines between 2.23 and 2.38 eV. Gross, Suslina, and Livshits[13] observed several sharp emission lines between 2.1 and 2.4 eV. Three different spectra were observed in three types of crystals. Sobolev[14] reported two different spectra of lines for two types of ZnTe films. In each of the observed luminescence spectra, some of the lines were attributed to phonon-assisted transitions. Evidently, the results depend sensitively on the impurity content of the material. It is difficult to find definite correlations among the various observations.

We did not observe, in our samples, the absorption structure near 2 eV seen by Dietz, Thomas, and Hopfield.[15] The crystals grown by the Bridgeman method, undoped as well as with As, In, or Fe doping, showed no sharp-line absorption at all. A particular crystal grown from the vapor phase showed several sharp lines between 2.25 and 2.35 eV at 1.7°K. The results are shown in Fig. 9. The width of the lines is about 10^{-3} eV. The rising background absorption apparently corresponds to the impurity step seen at the absorption edge in Fig. 7. A second vapor-grown crystal showed only one line at 2.3445 eV.

The sharpness of the lines indicates that the lines probably correspond to the formation of exciton-impurity complexes. Transition between donor-acceptor pairs do not appear to be a likely interpretation. For the latter case, we would expect a system of many lines, such as that observed in GaP,[45] which has a similar structure, and also comparable effective-mass parameters and dielectric constant.

Some of the lines in the spectrum may involve the same electronic states, but different numbers of emitted phonons. As is shown in Fig. 9, several of the lines have energy separations of $\sim 25\times 10^{-3}$ eV, which is close to the energy of LO phonons. Thus, the lines at 2.2964, 2.3215, and 2.3455 eV may be, respectively, the zero-, one-, and two-phonon transitions of a particular complex. However, the 2.3455-eV line is very close in energy to the single line observed in the second vapor-grown crystal. Thus, this line may be due to another impurity. The lines at 2.2726 and 2.2746 eV and the lines at 2.3354 and 2.3400 eV appear to be zero-phonon lines of complexes with different impurities. The nature of the impurities is not yet known. Since crystals can be obtained which do not show any lines in absorption, it should be possible to determine the impurity responsible for a given line by introducing different impurities.

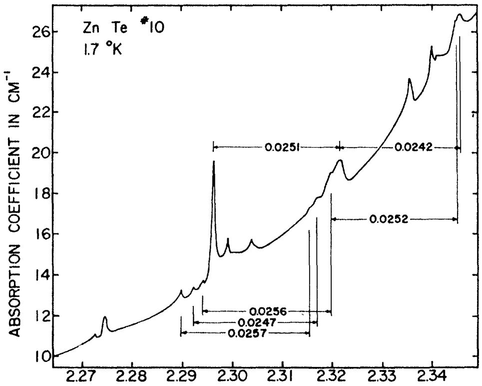

FIG. 9. Absorption of a vapor-grown ZnTe sample at 1.7°K. The lines seen are attributed to exciton-impurity complexes. The arrows indicate possible phonon separations. The rising background appears similar to the impurity absorption observed in undoped samples near the energy gap.

ACKNOWLEDGMENT

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[45] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).