Far-infrared photoconductivity measurements on tellurium in strong magnetic fields

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Photoconductivity measurements in the energy range 1–20 meV and magnetic fields up to 14.6 T for undoped tellurium single crystals and crystals doped with Bi, Sb, and As are described and analyzed. Differences in the chemical shift of the impurity ground state for different Group V impurities are clearly resolved. Unidentified deeper impurities with excitation energies of about 3 and 5.6 meV are found as residual acceptors in undoped crystals. Some impurity lines and the cyclotron-resonance transition are strongly influenced by polaron contributions.

I. INTRODUCTION

From infrared magnetotransmission[1-7] and Shubnikov–de Haas[8-10] measurements on tellurium, detailed knowledge about the valence-band structure has been obtained. All the experimental results are consistent with a $k \cdot p$ perturbation model, which leads to a camel-back structure of the valence band at the H point of the Brillouin zone.[11,12] Such a double maximum of the valence band changes the energy spectrum of the acceptors in comparison with the levels of a hydrogenic impurity; in particular, a splitting of the impurity ground state into a bonding and an antibonding state is expected.[13] The binding energies of these states are calculated to be about 1.2 and 0.9 meV.[14,15] Without magnetic field the two valleys at the points H and H' in the Brillouin zone of tellurium do not cause a valley-orbit splitting of the impurity levels, since the invariance of the Hamiltonian under the time-reversal operation (which transforms the points H and H' into each other) is not broken by the introduction of a Coulomb-type impurity potential. However, in strong magnetic fields this degeneracy is removed, and each of the impurity states, especially the ground state, should split into two levels.[16] The absolute value of this splitting is influenced by central-cell corrections, since the valley-orbit splitting depends on the impurity-envelope function close to the impurity site. Therefore different energies for the impurity levels are expected for As-, Sb-, and Bi-acceptors in tellurium. Up to now, the valley-orbit splitting and the chemical shift of the impurity levels have not been investigated in detail.

Experimentally, impurity lines have been observed in different absorption measurements.[1,2,7] However, in magnetotransmission experiments the impurity lines are mixed up with the intervalence band or cyclotron-resonance transitions, and no measurements are possible close to the reststrahlen region, where the transmission becomes very small. Moreover, without magnetic field the impurity absorption lines disappear[17] at carrier concentrations below 4×10^{20} m^{-3}.

In a previous paper we have shown that photoconductivity measurements are much more sensitive than absorption measurements and that for undoped samples ($p < 5 \times 10^{19}$ m^{-3}) at least three different impurity lines in the energy range 1–7 meV can be resolved.[18] In the present paper, these photoconductivity measurements are extended to magnetic fields up to 14.6 T. Undoped samples as well as crystals doped with Bi, Sb, and As impurities were investigated. Section II describes the experimental arrangement, in Sec. III A the results for measurements on undoped samples are presented, the corresponding data for different doped samples are summarized in Sec. III B and the results are discussed in Sec. IV.

II. EXPERIMENTAL METHOD

Samples with typical dimensions of $2 \times 2 \times 10$ mm^3 were cut from Czochralski-grown tellurium single crystals. Four electrical contacts, two current leads, and two potential leads were made by alloying thin gold wires to the specimens. At a temperature of 2 K the resistance between the potential leads was typically 1000 Ω for undoped samples and 50 Ω for samples doped with Bi, Sb, or As with an acceptor concentration of about 2×10^{20} m^{-3}. The measurements were carried out with a Beckman RIIC FS 720-Fourier spectrometer while the sample was immersed in liquid helium within the bore of a 14.6 T superconducting magnet. The experimental arrangement is shown in Fig. 1. The photoconductive signal, i.e., the change in the voltage drop across the potential leads under far-infrared (FIR) illumination, was typically 1 μV for a constant sample current of 0.5 mA. The spectra were not normalized relative to the intensity of the infrared radiation, since only the energy positions and not the absolute value of the

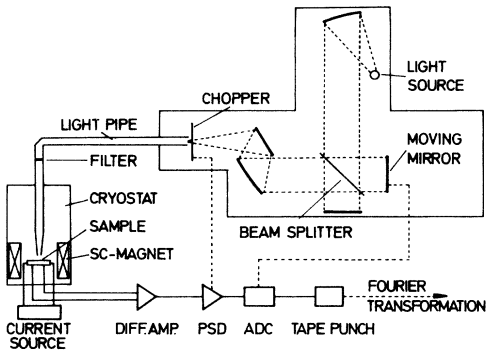

FIG. 1. Experimental arrangement for photoconductivity measurements with the Fourier spectrometer.

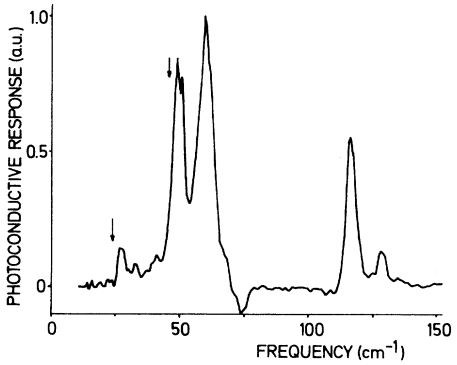

FIG. 2. Photoconductivity spectrum of an undoped tellurium sample at a magnetic field of $B = 9.8$ T. The magnetic field orientation is parallel to the c axis. The arrows mark the energy positions of the maxima in the photoconductive response at $B = 0$ T.

peaks in the photoresponse as a function of the magnetic field were analyzed. For high-resolution measurements, the Fourier spectrometer was replaced by lasers emitting radiation at 311, 337, and 496 μm. In this case, the photosignal was measured as a function of the magnetic field.

The photoresponse originates from optical transitions between discrete impurity states. In addition to the optical excitation, a thermal ionization of the excited impurity states is necessary in order to increase the free-carrier concentration and consequently the conductivity.[19] Measurements on GaAs, Si, and Ge have shown that a maximum in the photosignal is observed at sample temperatures T corresponding to $0.05E_B < kT < 0.1E_B$ (E_B = binding energy of the impurity). At lower temperatures the thermal ionization rate for carriers in the lowest excited impurity state is reduced,[20] and at higher temperatures the signal decreases due to the thermal ionization of the impurity ground state and the decreasing mobility of the carriers. For impurity binding energies of 1.2 meV, an optimal sample temperature of about 0.7–1.4 K can be calculated. Consequently, the experiments on doped samples were carried out at $T = 1.4$ K, the lowest temperature available with our cryostat. For the measurements on impurities in telluirum with binding energies of about 5 meV, as found in undoped samples,[18] a temperature of 4.2 K has been chosen. At this temperature all the impurities with a binding energy of about 1.2 meV are fully ionized and do not contribute to the photosignal, which simplifies the analysis of the spectra.

III. EXPERIMENTAL RESULTS

A. Undoped samples

Photoconductivity measurements on undoped samples show that, in addition to the "hydrogen-like" impurities with an excitation energy of about 11 cm^{-1}, a photoconductive response at about 24 and 46 cm^{-1} is found.[18] In strong magnetic fields, with the magnetic field direction parallel to the trigonal c axis, each of these peaks splits mainly into two components. In the magnetic fields above 4 T, additional structures are visible. A typical result is shown in Fig. 2. The arrows indicate the energy positions of the peaks without magnetic field. The negative signal at 74 cm^{-1} agrees with the energy $\hbar\omega_c$ for cyclotron resonance. Experimentally, the photothermal ionization of majority impurities always increases the conductivity, whereas the sign of the cyclotron-resonance signal varies for different semiconductors, depending on the energy dependence of the mobility and the energy-relaxation process of carriers excited to higher Landau levels.[21] The different sign of the photoresponse for impurity and cyclotron-resonance excitation in tellurium simplifies the interpretation of the spectra. It should be noted that an increase of the sample current by a factor of 10, corresponding to an electric field strength of about 300 V m^{-1}, changes the sign of the cyclotron-resonance signal, whereas the impurity lines remain unchanged. A summary of the experimental data is shown in Fig. 3. The dotted line characterizes the magnetic field dependence of the negative photosignal. A peculiarity is visible in the magnetic field region of 7–8 T. Coming from low-magnetic-field values, the upper two impurity lines disappear around $B = 7$ T but reappear at about $B = 8$ T at much higher energies. The parallel shift of the lines is about 20 cm^{-1}. A small splitting of about 1.6 cm^{-1} is observed for the lines in the wave number region 30–60 cm^{-1} in strong magnetic fields.

For the magnetic field orientation $B \perp c$, the experimental results for the same crystal as used

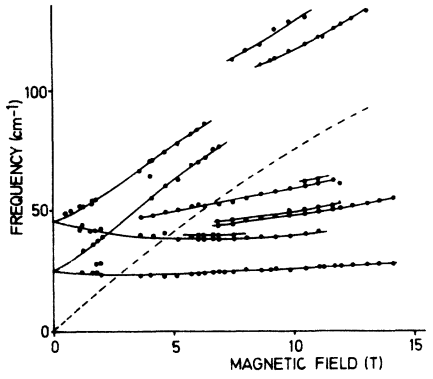

FIG. 3. Magnetic field dependence of the energies of the extrema in the photoconductive response for an undoped sample ($B \| c$). The dotted line characterizes the energy of the negative signal in the photoresponse.

for the measurements in the orientation $B \| c$ (Fig. 3) are summarized in Fig. 4. Contrary to the measurements in the orientation $B \| c$, a photosignal originating from a cyclotron-resonance (CR) transition was not visible. Only a small reduction of the photosignal by less than 10%, was observed at those magnetic field values where the CR-absorption lines cross the impurity lines. Measurements on another undoped crystal showed additional lines compared to those shown in Fig. 4. One of these additional lines is shifted approximately parallel to the line (2) to higher energies by about 10 cm^{-1} (9.5 cm^{-1} at $B = 5$ T and 11 cm^{-1} at $B = 14$ T). Another line appeared in the magnetic field range 5–14 T and is shifted by 20 cm^{-1} to lower energies relative to the line (1) plotted in Fig. 4. A systematic error in the energy position of the impurity lines of about 2 cm^{-1} at $B = 14$ T may result from an estimated misorientation of the sample, of at most $\pm 5°$. In the orientation $B \| c$, the influence of a misorientation on the energy position of the impurity lines is much smaller than that for the $B \perp c$ orientation as found from an analysis of the angular dependence of the spectra for a doped sample (see Fig. 7).

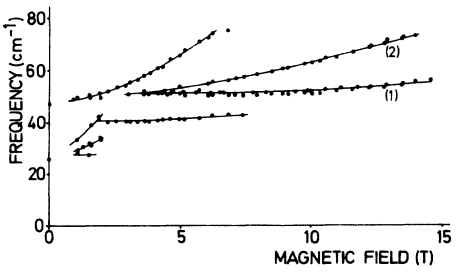

FIG. 4. Magnetic field dependence of the energies of the maxima in the photoconductive response for an undoped sample ($B \perp c$).

B. Doped samples

For the measurements on doped crystals, samples with Group V impurities at a doping level of about 2×10^{20} m^{-3} were used. Within the resolution of 1 cm^{-1} for our measurements with the Fourier spectrometer, no differences in the spectra are observed for the different crystals containing different impurities (Bi, Sb, As). The results shown in Fig. 5 ($B \| c$) are obtained for six different crystals. The dotted line is identical with the dotted line shown in Fig. 3 and corresponds to the cyclotron-resonance transition. Most of the impurity lines can be extrapolated to a common intercept at 11 cm^{-1} for $B = 0$ T; only the lines which are nearly magnetic field independent extrapolate to a lower energy value of about 9.5 cm^{-1}. For the strong impurity lines, a relatively weak satellite line shifted to higher energies is visible. At $B = 14$ T the energy difference between these two lines is 7.5 cm^{-1}.

A summary of the experimental results for the magnetic field direction $B \perp c$ is shown in Fig. 6. No significant difference is observed for measurements on differently doped samples. As for undoped samples, the CR line is visible only as a small decrease in the impurity signal, which is explained by an attenuation of the infrared radiation within the sample due to CR absorption. The dotted lines correspond to CR transitions obtained from absorption measurements.[1] The angular

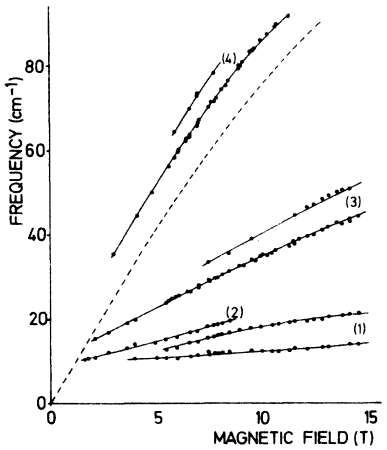

FIG. 5. Magnetic field dependence of the energies of the extrema in the photoconductive response for samples doped with Group-V impurities ($B \| c$, $T = 1.4$ K). The dotted line corresponds to the cyclotron-resonance line (negative photosignal).

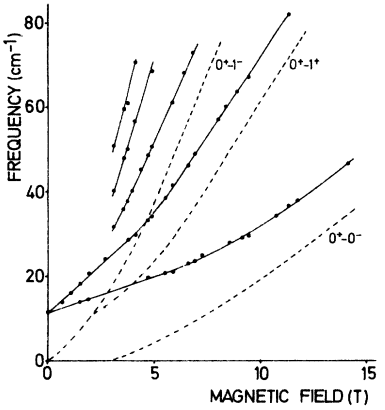

FIG. 6. Magnetic field dependence of the energies of the maxima in the photoconductive response for doped samples ($B \perp c$, $T = 1.4$ K). The dotted lines characterize the cyclotron resonance transitions from the lowest Landau level to higher Landau levels obtained from absorption measurements (Ref. 1).

dependence of the impurity lines (φ = angle between the magnetic field direction and the c axis) plotted in Fig. 7 shows that two impurity lines disappear at about $\varphi = 65°$, and only one impurity line can be traced from $B \perp c$ to $B \parallel c$.

All the experimental results presented so far do not show significant differences in the energy positions of the impurity lines for different Group V acceptors. This means that the chemical shift is relatively small. In order to resolve small differences in the impurity excitation energies for different acceptors, in addition to the Fourier spectrometer experiments, the photoresponse was measured at a constant laser excitation energy of 32.2 cm^{-1} (311 μm), 29.7 cm^{-1} (337 μm), and 20.2 cm^{-1} (496 μm) as a function of the magnetic field. The results for Bi-, Sb-, and As-doped crystals and the orientation $B \parallel c$ are shown in Fig. 8.

The magnetic field positions of the different impurity lines are summarized in Table I. The error in the magnetic field values is estimated to be about ±1%, whereas the difference in the magnetic field values of the split lines is accurate within ±0.01 T. It seems that the impurity line at B_0 (337 μm) = 7.65 T and B_0 (311 μm) = 8.68 T, respectively, is not greatly affected by a chemical shift (second and fourth columns of Table I), whereas the energy position of the other line depends strongly on the chemical nature of the impurity (first and third columns of Table I). The energy difference between the two lines is about 0.074 meV (Bi), 0.046 meV (Sb), and 0.024 meV (As) at $B = 8$ T. From a linear extrapolation, the following magnetic field dependence of the impurity lines for Bi-doped samples is obtained:

$$E_0(B) = 11.1\ \text{cm}^{-1} + 2.43\ \text{cm}^{-1} \times B/\text{T}\,, \qquad (1)$$
$$E_1(B) = 11.07\ \text{cm}^{-1} + 2.51\ \text{cm}^{-1} \times B/\text{T}\,.$$

The energy $E_0(B)$, listed in the second and fourth columns of Table I, is approximately identical for Bi, Sb, and As impurities. Within experimental accuracy the extrapolated value of 11.1 cm^{-1} for the excitation energy at $B = 0$ T is the same for the two lines.

Photoconductivity measurements with an optically pumped CH_3F laser ($\tilde{\nu} = 20.2$ cm^{-1}) on a bismuth doped sample show structures at $B = 8.4$ and 9.0 T. These peaks originate from an impurity transition which is different from that investigated with the 311 and 337 μm radiation. The calculated energy splitting of 0.08 meV at $B = 8.7$ T for this double peak (deduced from the slope of the corresponding

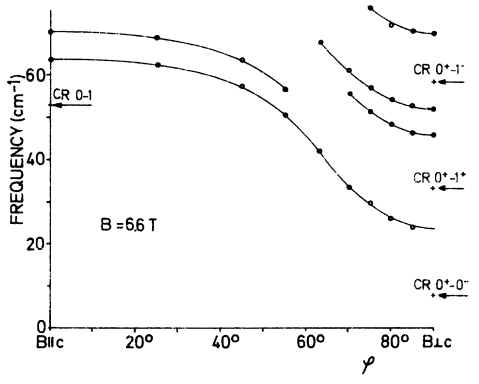

FIG. 7. Angular dependence of the energies of the maxima in the photoconductive response at a constant magnetic field of $B = 6.6$ T. The arrows mark the energy positions of the cyclotron-resonance lines in the orientations $B \parallel c$ and $B \perp c$.

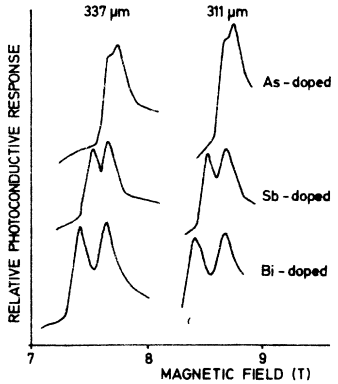

FIG. 8. Photoconductive response as a function of the magnetic field ($B \parallel c$) for differently doped samples at laser-excitation energies corresponding to 337 μm (left side) and 311 μm (right side). $T = 1.4$ K.

TABLE I. Magnetic field values in T of the maxima in the photoconductive response for differently doped tellurium samples at two excitation energies corresponding to 337 and 311 μm laser radiation (see Fig. 8).

	337 μm		311 μm	
Bi (1)	7.41	7.64	8.41	8.67
Bi (2)	7.43	7.65	8.42	8.68
Sb	7.52	7.66	8.53	8.68
As	7.68	7.75	8.68	8.75

impurity line in Fig. 5 and the observed magnetic field values of the resonance at $\tilde{\nu} = 20.2$ cm^{-1}) is identical with the splitting observed for a transition to an impurity level at higher energy (see measurements with the HCN laser). With the assumption that all the impurity lines observed at low temperatures are transitions from the ground state to different excited states, the experimental results indicate that the impurity ground state is split into two states, and all the impurity transitions shown in Fig. 5 are composed of two different transition energies which are not resolved in this figure. The absolute value of this fine-structure splitting depends on the chemical nature of the impurity and increases approximately linearly with the magnetic field. In the orientation $B \perp c$, a fine-structure splitting of the impurity lines could not be resolved.

IV. DISCUSSION

A. Magnetic field direction parallel to the c axis

The measurements on undoped single crystals show that, in addition to Group V impurities, other impurities are present with an excitation energy of about 3.0 and 5.6 meV at $B = 0$ T (Fig. 3). At low magnetic fields, $B \parallel c$, a splitting of each line into two components is observed. The energy of one of these split lines is nearly magnetic field independent; the other one is shifted approximately parallel to the cyclotron-resonance line. The agreement of the energy difference between the two impurity lines with the cyclotron energy $\hbar\omega_c$ is better than 10%. At magnetic fields above $B = 4$ T a third line can be resolved with an energy position between the split lines discussed before. Such a splitting is typical for a $1s$-$2p$ transition of a hydrogenic impurity. In a magnetic field the $2p$ state splits into three levels $2p_-$, $2p_0$, and $2p_+$, corresponding to the magnetic quantum numbers $m = -1$, 0, and +1. The energy difference $2p_+ - 2p_-$ is equal to $\hbar\omega_c$ for a parabolic band.

The experimental results shown in Fig. 3 initiated calculations[22] of the energy differences between the ground state and the first excited p states of a singly ionized heliumlike impurity in tellurium for the magnetic field orientation $B \parallel c$. Good agreement with the measured triplet starting around 46 cm^{-1} at $B = 0$ T was found in the calculations.[22] For this interpretation, one has to assume that singly ionized heliumlike impurities are present at temperatures where the thermal energy $3\,kT$ is a factor of five smaller than the first ionization energy of a heliumlike impurity. The broadband excitation with radiation energies exceeding the impurity binding energy, characteristic for measurements with the Fourier spectrometer, may be the reason for the presence of singly ionized impurities even at helium temperatures. The other lines, which are shifted parallel to lower energies and extrapolate to 24 cm^{-1} at $B = 0$ T, may be explained as an excitation of a neutral heliumlike impurity. As expected qualitatively, these lines disappear if the temperature is increased from 1.7 to 4.2 K since the impurity becomes thermally ionized at $T = 4.2$ K. Quantitative calculations for such an impurity are very difficult due to electron-electron interaction of this two-electron system and strong central-cell corrections.[23]

Theoretically, the Zeeman splitting of the first excited state is the same for a hydrogen atom, a neutral helium atom, and a singly ionized helium atom in the linear-Zeeman-effect regime, but the zero-field excitation energies are different by the ratio 1 : 2.1 : 4.[24] This behavior agrees fairly well with the experimental data. Unfortunately, it was not possible to identify the nature of these heliumlike impurities. For example, measurements on Sn-doped tellurium crystals do not show an increase in the acceptor concentration.

The anomalous behavior of the "$2p_+$" states at an energy of about 100 cm^{-1} can be explained as a polaron effect. It is known[25] that electron-LO phonon interaction results in a pinning of the $1s$-$2p_+$ transition energy close to the LO-phonon energy $\hbar\omega_{LO}$ and in a line at energies above $\hbar\omega_{LO}$ which is shifted to higher energies relative to a linear extrapolation of the $1s$-$2p_+$ line observed at energies well below the LO-phonon energy. The strength of this polaron shift is connected with the polaron-coupling constant α which, within the Fröhlich continuum model, depends on the LO-phonon frequency, the high-frequency and static-dielectric constants, and the effective mass. For tellurium a value of $\alpha = 0.14$ has been calculated.[26] A comparison of the experimental data with calculations on the basis of a simple hydrogenlike impurity[25] indicates that a polaron-coupling constant of 0.14 is too small to explain the observed polaron shift. For an accurate calculation of the polaron

Zeeman effect, the knowledge of the magnetic-field-dependent impurity eigenvalues and eigenfunctions is necessary. The extent data for a heliumlike impurity state in tellurium are not accurate enough so as to give a reliable value for the polaron-coupling constant from a fit of the experimental data with the polaron-coupling constant as a parameter. However, a relatively accurate value for the coupling constant α can be deduced from the magnetic-field-dependent cyclotron mass. The pinning of the cyclotron-resonance line at the energy of the LO phonon leads to an increase of the cyclotron mass m_c. Since in photoconductivity measurements the cyclotron-resonance transition (negative signal) can be traced to energies up to 90 cm^{-1} ($\hbar\omega_{LO} = 116$ cm^{-1}), a relatively strong influence of the polaron pinning on m_c can be observed.

The data are shown in Fig. 9. Without polaron contribution ($\alpha = 0$), the magnetic field dependence of m_c is given by the dotted line. The increase of the cyclotron mass is due to nonparabolicity. For the calculations of the energy of the Landau levels, we employed the same computer program which was used by Bangert for the interpretation of magneto-optical experiments on tellurium.[27] In these calculations, the absolute value of the cyclotron mass can be changed by varying the band-edge mass, but the magnetic field dependence of m_c is given by fixed band parameters. Therefore, the absolute value of m_c is insignificant, since all the calculated curves are fitted to the experimental m_c value at $B = 8$ T. The polaron contribution to the cyclotron-resonance energy can be approximated by the following equation[28]:

$$\Delta E = \hbar\omega_c - \alpha\hbar\omega_{LO}\left[\frac{1}{6}\frac{\omega_c}{\omega_{LO}} + \frac{3}{20}\left(\frac{\omega_c}{\omega_{LO}}\right)^2 + 0.145\left(\frac{\omega_c}{\omega_{LO}}\right)^3\right], \quad (2)$$

where ΔE is the energy separation between the Landau levels, and $\hbar\omega_c$ the cyclotron energy without polaron contributions. This equation, which is expected to be correct for $\alpha < 0.5$, agrees with variational calculations for energies $\hbar\omega_c < 0.8\hbar\omega_{LO}$.[37] Good agreement between theory and experiment can be obtained with a coupling constant $\alpha = 0.35 \pm 0.05$. However, this coupling constant is about a factor of 2.5 higher than the value calculated within the Fröhlich continuum model.[26] Similar discrepancies are also found for CdTe,[29] and it is not clear whether the simple definition of the coupling constant given in the Fröhlich continuum model is inadequate or the values of the dielectric constants, which are necessary for the calculation of α, are grossly inaccurate.

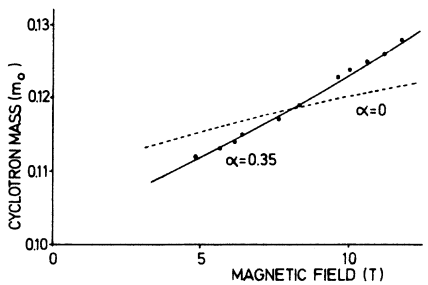

FIG. 9. Magnetic field dependence of the cyclotron mass of holes in tellurium. The lines are calculated for different polaron-coupling constants α.

For the interpretation of the impurity lines shown in Fig. 3, the splitting of the ground state into a bonding and an antibonding state has not been included, since the calculated energy separation of about 2.5 meV between these states[22] is too high for a substantial population of the antibonding state at helium temperatures. At the very least, the ratio of the intensities of the impurity lines corresponding to transitions from the bonding and antibonding state to an excited level should increase with decreasing temperature. This is opposite to the behavior found for the peaks observed at 24 and 46 cm^{-1} at $B = 0$ T.[18] Therefore the photoresponse at 24 cm^{-1} is explained as an excitation of the neutral heliumlike impurity and not as a transition from the antibonding ground state to an excited state of the singly ionized heliumlike impurity.

The observed splitting of about 1.6 cm^{-1} (0.2 meV), resolved for some lines shown in Fig. 3, may be explained by the valley-orbit splitting. This phenomenon will be discussed in connection with the following interpretation of the data obtained for doped samples (Figs. 5 and 8).

Qualitatively, the splitting of the impurity ground state in tellurium is described by the formula[16]

$$E_{1,2,3,4} = \pm\left[\left(\tfrac{1}{2}G\mu_B B\right)^2 + \Delta^2 \pm G\mu_B B|\delta|\right]^{1/2}. \quad (3)$$

2Δ is the energy difference between the bonding and the antibonding state, δ is a constant that determines the mixing of the states at H and H' ($\delta \sim 0.1\Delta$), and G is a constant ($G \sim 5$) which describes the inversion asymmetry splitting of Landau levels in a magnetic field $B \parallel c$.[30]

We believe that the small splitting of the impurity lines shown in Fig. 8 (not resolved in Fig. 5) originates from a valley-orbit splitting connected with the third term in Eq. (3). This valley-orbit splitting disappears at $B = 0$ as observed experimentally [see Eq. (1)]. However, a quantitative description of the experimental data by Eq. (3)

cannot be expected, since this equation is based on qualitative arguments. For example, preliminary variational calculations show[22] that the splitting between the bonding and the antibonding state at $B = 10$ T is about one order of magnitude smaller than the corresponding value deduced from Eq. (3).

So far, no attempts have been made to calculate the differences in the valley-orbit splittings for different impurities in tellurium. The experimental results indicate that only one of the two lines shows a strong chemical shift. A similar behavior is found in measurements on other multivalley semiconductors[31] where only the s-like ground state, which is symmetrically composed of the wave functions for the different equivalent valleys, shows a significant chemical shift. For Group V impurities in tellurium, this shift, which increases the binding energy, is largest for bismuth impurities and decreases with decreasing atomic number. At $B = 8$ T the energy difference between the split levels is 0.074 meV (Bi), 0.046 meV (Sb), and 0.023 meV (As). The absolute value of the chemical shift increases with increasing localization of the impurity wave function, which results in a larger valley-orbit splitting for heliumlike impurities than for hydrogenlike impurities. It seems reasonable to assume that the splitting of about 0.2 meV at $B = 8$ T observed for heliumlike impurities (Fig. 3) originates from the valley-orbit splitting of the impurity ground state.

Up to now, no theoretical explanation has been available for the impurity line (3) in Fig. 5 (which shifts from 20 cm^{-1} at $B = 4$ T to 45 cm^{-1} at $B = 14.5$ T), if one assumes that only transitions to excited states corresponding to hydrogenlike $2s$ and $2p$ states are included in the interpretation. The lines (1), (2), and (4) in Fig. 5 agree fairly well with transitions to $2p_-$, $2p_0$, and $2p_+$ states. Apart from the fact that the transition probability should be very small, the transition energy to the $2s$ state is about 50% larger than the excitation energy observed experimentally for line (3). It is therefore necessary to perform further variational calculations including $3p$ and $3d$ states and calculations of the transition probabilities between the four levels of the impurity ground state and the excited states.

In our model the lines attributed to $2p_\pm$ levels coincide at $B = 0$ T. This is not in contradiction to the experimental result which indicates that, deduced from a linear extrapolation to $B = 0$ T, apparently two different excitation energies of 11 and 9.5 cm^{-1} are present at $B = 0$ T. This difference originates from a strong bending of the $1s$-$2p_-$ line at low magnetic fields, which is typical for hydrogenic impurities including Stark shifts.[36]

B. Magnetic field direction perpendicular to the c axis

In the magnetic field orientation $B \perp c$, the impurity spectra are determined by the complicated Landau-level structure.[11,12] Figure 6 shows clearly that each impurity line is associated with a cyclotron-resonance line. Calculations for a simple hydrogenlike impurity in a magnetic field show[32,33] that the $1s$-$2p_+$ transition dominates in the high-field limit, and that the transition energy is given by $\Delta E = \hbar\omega_c - \epsilon(2p_+) + \epsilon(1s)$. $\epsilon(2p_+)$ and $\epsilon(1s)$ are small quantities compared with the cyclotron energy $\hbar\omega_c$ and describe the binding energies of the $2p_+$ and $1s$ states relative to the Landau levels with the quantum number $N = 1$ and 0, respectively. This relation shows that the predominant contribution to the energy of the so-called impurity-shifted cyclotron-resonance line comes from the energy difference between the Landau levels. Since no strong selection rules for cyclotron-resonance transitions in tellurium in the orientation $B \perp c$ exist,[12] a large number of impurity-shifted cyclotron-resonance lines can be observed, because the transition probability for the impurity lines are determined by the same matrix elements as for the cyclotron-resonance lines. A lower limit for the impurity binding energy ϵ $(1s)$ in strong magnetic fields can be determined from the energy difference between the impurity excitation energy and the corresponding cyclotron-resonance energy, which gives a minimum impurity binding energy for the shallow acceptors in tellurium of 1.5 meV at $B = 10$ T. The splitting of the impurity ground state in a strong magnetic field $B \perp c$ into four states (bonding-antibonding states, valley-orbit split states) is expected to be much smaller than the corresponding splittings in the orientation $B \parallel c$.[16] Experimentally no splitting of the impurity ground state could be observed, although the energy difference between the bonding and the antibonding state should be large enough to be resolved.

Measurements of the angular dependence of the impurity lines at a constant magnetic field of $B = 6.6$ T (Fig. 7) indicate that the amplitude of the transition attributed to an excitation from the bonding state to the $2p_+$ state $(B \parallel c)$ decreases with increasing angle φ between the magnetic field direction and the crystallographic c axis. This transition cannot be detected in the orientation $B \perp c$. For $B \perp c$ the impurity transitions to excited states belonging to the 1^+ and 1^- Landau levels disappear at $\varphi < 70°$, and only the line associated with the 0^+-0^- cyclotron-resonance transition $(B \perp c)$ can be followed for all angles φ. This result indicates that the ordinary cyclotron-resonance line 0-1 for $B \parallel c$ passes into the 0^+-0^- tran-

sition for $B \perp c$. Cyclotron-resonance measurements with a constant excitation energy of 2.4 meV, however, show a monotonic change from a 0-1 transition ($B \parallel c$) to a 0^+-1^+ transition ($B \perp c$),[2] whereas the analysis of the magnetophonon resonance in tellurium[34] leads to the same angular dependence of the Landau-level transitions as deduced from our measurements.

Most of the impurity lines observed for undoped samples (Fig. 4) show the same magnetic field dependence as found for doped samples and are interpreted as impurity-shifted cyclotron-resonance lines. The lines which are nearly magnetic field independent originate from transitions to a localized excited state which is correlated with the lowest Landau level. The corresponding transition is not observed for doped samples, which may be explained by the very weak intensity of the infrared source at 10 cm^{-1}, where this impurity line is expected.

It should be noted that all the impurity lines are interpreted as transitions between discrete impurity states and not by transitions to Landau levels, since the transition probability for shallow impurities from localized states to the continuum should be small.[35] Moreover, the energy differences between the different impurity-shifted cyclotron-resonance lines for $B \perp c$ are not identical with the energy difference between the corresponding cyclotron-resonance lines, which shows that the binding energies of the excited states relative to their respective Landau levels are different for different excited states.

V. SUMMARY

We have presented the results of far-infrared photoconductivity measurements on tellurium in strong magnetic fields, which show a large number of strong impurity lines. In addition, the cyclotron-resonance line is visible in the orientation $B \parallel c$ as a small negative photosignal. Most of the experiments were carried out in the orientation $B \parallel c$, because the Landau-level structure for this orientation is relatively simple and can be compared with the Landau levels of a parabolic band.

The four energetically equivalent valence-band maxima in the first Brillouin zone of tellurium cause a splitting of the impurity ground state into two pairs of states in strong magnetic fields. The large splitting originates from an interaction between the two valleys which are close together in k space (bonding-antibonding state). The small splitting, which is strongly influenced by a chemical shift, is connected with an interaction between the valleys close to the H and H' points in the Brillouin zone (valley-orbit splitting). The largest valley-orbit splitting, corresponding to the largest binding energy, is observed for Bi impurities, the smallest one for As impurities.

In the orientation $B \parallel c$, all the data obtained with doped crystals are interpreted as transitions from the four impurity ground states (which are not always resolved) to excited states. In the notation for hydrogenlike impurities, the transitions to $2p_-$ and $2p_+$ states are clearly identified. Also the transition to the $2p_0$ state obtained from variational calculations agrees fairly well with experimental data. However, one set of impurity lines, which shifts linearly with the magnetic field with a slope of $dE/dB \sim 0.3$ meV/T, could not be explained theoretically.

For pure crystals with a residual carrier concentration of $p < 5 \times 10^{19}$ m^{-3}, the strongest photosignal arises from impurities which are deeper than the impurities found for crystals doped with Bi, Sb, and As. These spectra can be explained as excitations of a heliumlike impurity. Since the excitation energy for these impurities is higher than for hydrogenlike impurities, the excitation energy reaches the LO-phonon energy within the magnetic field range of our measurements, and strong polaron effects are observed. The analysis of the magnetic-field-dependent cyclotron mass leads to a polaron-coupling constant of $\alpha = 0.35$, which is higher than expected theoretically by a factor of 2.5.

In the orientation $B \perp c$, a large number of impurity-shifted cyclotron-resonance lines are visible, since no strong selection rules for the cyclotron-resonance transition exist. In this orientation a splitting of the impurity ground state could not be observed. Measurements of the angular dependence of the impurity-shifted cyclotron-resonance line show that the single cyclotron-resonance line in the orientation $B \parallel c$, corresponding to a transition between the Landau levels with the quantum number $N = 0$ and 1, passes into a transition 0^+-0^- for the magnetic field orientation $B \perp c$, contrary to earlier cyclotron-resonance measurements.

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[1]R. Yoshizaki and S. Tanaka, J. Phys. Soc. Jpn. 30, 1389 (1971).
[2]Y. Couder, M. Hulin, and H. Thomé, Phys. Rev. B 7, 4373 (1973).
[3]M. v. Ortenberg, K. J. Button, G. Landwehr, and D. Fischer, Phys. Rev. B 6, 2100 (1972).
[4]M. v. Ortenberg and K. J. Button, Phys. Rev. B 16, 2618 (1977).
[5]N. Miura, R. Yoshizaki, and S. Tanaka, Solid State Commun. 7, 1195 (1969).
[6]D. Hardy and C. Rigaux, Phys. Status Solidi 38, 799 (1970).
[7]D. Hardy, C. Rigaux, J. P. Vieren, and Nguyen Hy Hau, Phys. Status Solidi B 47, 643 (1971).
[8]M. S. Bresler, I. I. Farbshtein, D. V. Mashovets, Yu. V. Kosichkin, and V. G. Veselago, Phys. Lett. 29 A, 23 (1969).
[9]C. Guthmann and J. M. Thuillier, Phys. Status Solidi B 38, 635 (1970).
[10]E. Braun, L. J. Neuringer, and G. Landwehr, Phys. Status Solidi B 53, 635 (1972).
[11]M. Hulin, *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970*, edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. AEC, Division of Technical Information, Springfield, Va., 1970), pp. 329–337.
[12]K. Nakao, T. Doi, and H. Kamimura, J. Phys. Soc. Jpn. 30, 1400 (1971).
[13]L. S. Dubinskaya, Fiz. Tekh. Poluprovodn. 6, 1457 (1972) [Sov. Phys. Semicond. 6, 1267 (1973)].
[14]D. Thanh, Solid State Commun. 9, 1263 (1973).
[15]K. Natori, T. Ando, M. Tsukada, K. Nakao, and Y. Uemura, J. Phys. Soc. Jpn. 34, 1263 (1973).
[16]G. L. Bir, V. G. Krigel, G. E. Pikus, and I. I. Farbshtein, Pis'ma Zh. Eksp. Teor. Fiz. 19, 48 (1974) [JETP Lett. 19–20, 29 (1974)].
[17]M. Ataka, R. Yoshizaki, and S. Tanaka, Solid State Commun. 13, 849 (1973).
[18]K. v. Klitzing and C. R. Becker, Solid State Commun. 20, 147 (1976).
[19]For a review see, e.g., E. E. Haller, W. L. Hansen, and F. S. Goulding, IEEE Trans. Nucl. Sci. 22, 127 (1975).
[20]G. E. Stillman, C. M. Wolfe, and D. M. Korn, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors*, edited by M. Miasek (PWN-Polish Scientific, Warsaw, 1972), Vol. II, pp. 863–869.
[21]P. E. Simmonds, J. M. Chamberlain, R. A. Hoult, R. A. Stradling, and C. C. Bradley, J. Phys. C 7, 4164 (1974).
[22]J. Trylski, International Conference on the Application of High Magnetic Fields in Semiconductor Physics, Oxford, 1978 (unpublished).
[23]T. H. Ning and C. T. Sah, Phys. Rev. B 4, 3482 (1971).
[24]H. A. Bethe and E. E. Salpeter, in *Quantum Mechanics of One- and Two-Electron Atoms*, edited by H. A. Bethe and E. E. Salpeter (Springer, Berlin 1957), p. 154.
[25]D. R. Cohn, D. M. Larsen, and B. Lax, Phys. Rev. B 6, 1367 (1972).
[26]K. J. Button, D. R. Cohn, M. H. Weiler, B. Lax, and G. Landwehr, Phys. Lett. 35A, 281 (1971).
[27]M. Lutz, E. Bangert, T. Mizrah, and H. Stolze, Phys. Status Solidi B 71, 523 (1975).
[28]J. Waldman, thesis, MIT, Boston, 1970 (unpublished).
[29]C. W. Litton, K. J. Button, J. Waldman, D. R. Cohn, and B. Lax, Phys. Rev. B 13, 5392 (1976).
[30]V. B. Anzin, Yu. V. Kosichkin, V. G. Veselago, M. S. Bresler, I. I. Farbshtein, E. S. Hskevich, and V. A. Sukhoparov, Solid State Commun. 8, 1773 (1970).
[31]R. L. Aggarwal and A. K. Ramdas, Phys. Rev. 140, A1246 (1965).
[32]R. R. Haering, Can. J. Phys. 36, 1161 (1958).
[33]R. F. Wallis and H. J. Bowlden, J. Phys. Chem. Solids 7, 78 (1958).
[34]M. S. Bresler and D. V. Mashovets, Phys. Status Solidi 39, 421 (1970).
[35]H. Hasegawa and R. E. Howard, J. Phys. Chem. Solids 21, 179 (1961).
[36]D. M. Larsen, Phys. Rev. B 8, 535 (1973).
[37]D. M. Larsen, J. Phys. C 7, 2877 (1974).