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Comments

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Evidence for shallow bound states in PbTe

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Data are presented showing structure in the magneto-optical absorption of thin films of *p*-type PbTe, which cannot be explained in terms of free-carrier effects alone. This structure, while having a similar form in many samples, is quantitatively different in samples with different doping. This behavior is strongly suggestive of central cell effects on bound-impurity states rather than of intrinsic many-body effects as recently suggested by McKnight and Drew.

I. INTRODUCTION

In recent years, many workers have studied the far-infrared magneto-optics of PbTe.[1–5] In these experiments, structure attributable to free-carrier cyclotron resonances has been observed together with additional fine structure close to the cyclotron resonance. Some of this structure[3,6] has been successfully explained in terms of so-called quantum effects. These effects arise because the effective masses associated with different Landau levels in a nonparabolic band are not equal. This results in the resonances between the different levels occurring at slightly different magnetic fields. Most recently Schaber and Doezema[4] have observed spin-flip transitions in the magneto-optical spectrum.

In addition to quantum and spin effects certain additional structure has been observed[2,3] which cannot be explained simply in terms of free-carrier effects. In one case Kuchar *et al.*[2] interpreted fine structure on the low-magnetic-field side of the cyclotron resonance as being due to shallow bound impurity states. Since the structure had only been observed in one sample this identification could only be tentative. McKnight and Drew[3] have interpreted similar structure, observed in their own experiments, and also re-interpreted the data of Kuchar *et al.*[2] in terms of a complex many-body effect. This effect, being intrinsic to PbTe and its band structure, should produce *identical* effects in similar samples. In this paper we present new data obtained in both reflection and transmission showing that while the additional structure is *qualitatively* similar in the samples studied, *quantitatively* it depends on the doping history of the sample. This data seems to reinforce the interpretation of Kuchar *et al.*[2] while being apparently inexplicable in terms of the model proposed by McKnight and Drew.[3]

TABLE I. Sample characteristics.

Ion dose at 300 keV (cm^{-2})	Anneal	Hole concentration (cm^{-3}) (300 K)	Mobility ($cm^2/V\,s$) (300 K)	Mobility ($cm^2/V\,s$) (77 K)
		7.0×10^{17}	640	22 000
As^+ 1×10^{13}	2 hr 280°C	1.3×10^{17}	590	
Te^+ 3×10^{13}	2 hr 280°C	1.6×10^{17}	650	11 500

II. EXPERIMENTAL DETAILS AND RESULTS

Four epitaxial thin PbTe films were investigated. Three samples were in the form of 5-μm thick films on (111) BaF_2 substrates, grown by the hot-wall technique.[7] All three samples were p type with carrier concentrations between 0.8 and 1.6×10^{23} m^{-3}; one was ion implanted with arsenic and subsequently annealed, one ion implanted with tellurium before annealing, and the third nominally undoped. The sample characteristics are shown in Table I. The samples were annealed at 280°C for two hours after implantation. This process has been found[8,9] to remove any detectable lattice damage. The implantation by Te acts to produce additional Pb vacancies after annealing.[8] The effect of a Pb vacancy is to produce two holes in the conduction band,[9] however, the exact nature and position of the vacancy level is not well known.[10] The films were studied in transmission in the Faraday geometry, using a deuterium cyanide (DCN) laser ($\lambda=195$ μm, 51.4 cm^{-1}).

The fourth sample was a high-quality (100) film (15-μm thick) of arsenic-doped PbTe grown on a bulk PbTe substrate. The sample was p type with a carrier concentration of 2.5×10^{23} m^{-3}. This structure had the advantage that any strain effects due to lattice mismatch at the film-substrate interface should be negligible. On the other hand, since the substrate is opaque, this sample could only be studied in reflection, using a TE mode stripline in the Voigt geometry. In this mode dips in the stripline transmission have been shown to correspond to cyclotron resonance absorption.[11]

The experimental data are shown in Figs. 1 and 2. Figure 1 shows the magnetotransmission of the

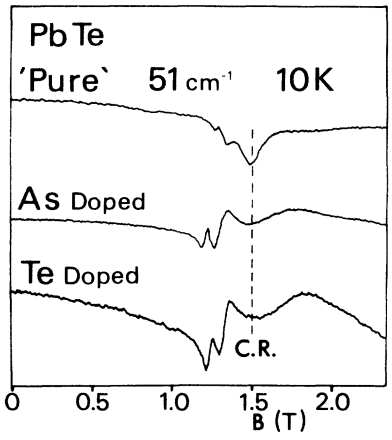

FIG. 1. Faraday geometry transmission at 195 μm as a function of magnetic field $B||\langle 111\rangle$ of the PbTe films on BaF_2 substrates. The resonance CR, which is in the same position for *all* samples, is identified as the cyclotron resonance of free carriers in the valley whose long axis is parallel to the applied magnetic field. The additional structure on the low-magnetic-field side is at different positions in different samples.

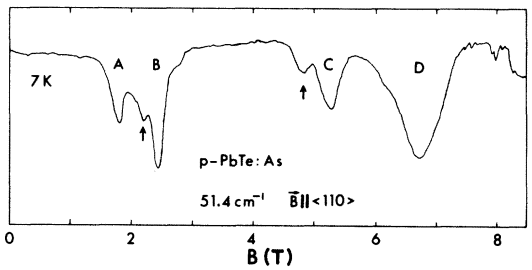

FIG. 2. Voigt geometry magneto-reflection obtained by the stripline technique, at 195 μm as a function of magnetic field $\vec{B}||\langle 110\rangle$ for the arsenic-doped PbTe film on PbTe substrate. Resonances A and C are the tilted orbit cyclotron resonances, B is the hybrid resonance, and D is the plasma-shifted cyclotron resonance. The arrowed structure is believed to be due to the As impurity.

three (111) films. The broad absorption is at the same position in all three traces and is identified as the cyclotron resonance due to transitions between adjacent Landau levels. From the position of this resonance we may calculate the cyclotron effective mass ($m_t^h = 0.025 m_0$) for free holes at the band edge. The width of this line characterizes the free-carrier transitions and is broader in the more heavily doped implanted samples. At lower magnetic field, two sharp absorption lines are observed. Since these are much sharper than the cyclotron resonance it is unlikely that the transitions observed either begin or end on Landau levels. Furthermore, since their positions are different in different samples, they cannot be simple inter-Landau level transitions, otherwise the cyclotron mass would be strongly sample dependent. The effective-mass value of $0.025 m_0$ is in excellent agreement with both the intraband and interband data reported by several authors[1,5,6,11,12] which all give $m_t^h = 0.025 \pm 0.001 m_0$. The exceptions to this are the intraband cyclotron resonance data of McKnight and Drew[3] and Foley and Langenberg,[13] where much lower values of $m_t = 0.021 m_0$ were deduced. In the case of McKnight and Drew the difference lies in the assignment of the resonances. The observation of interband magneto-absorption,[12] from which highly accurate sets of band parameters[6,12] may be deduced, makes the assignment of free-carrier hole masses of the order of $0.021 m_0$ highly implausible. The many-body final-state interactions proposed by McKnight and Drew[3] cannot cause significant shifts in the interband transition energies, where transitions between high Landau-level index hole and electron states can be observed.

The additional structure observed in Fig. 1 is not produced only by strain at the sample-substrate interface, since similar fine structure was observed on the As-doped PbTe⟨100⟩ film on the PbTe substrate (Fig. 2). The simple cyclotron resonance absorption (A) is again in excellent agreement with other measurements giving $m_t^h = 0.025 m_0$. In this case the impurity resonance appears associated with the hybrid resonance (B). This can occur since the impurity resonance will contribute to the dielectric function thus causing absorption to occur in the stripline transmission. Similar samples grown without doping were n type and did not show this structure. In Fig. 2 only one peak was observed at lower magnetic field than the cyclotron resonance. Possible reasons for this will be discussed later.

III. DISCUSSION OF RESULTS

The data in Fig. 1 strongly imply that the fine structure at magnetic fields just below the cyclotron resonance is due to the different impurity species, since other interpretations of the structure require that the structure be identical for all PbTe samples with similar carrier concentrations. Namely,

(i) quantum effects due to band nonparabolicity,

(ii) spin effects giving rise to combined and spin-flip resonances,

(iii) many-body effects, and

(iv) nonlocal effects.

Also, the data cannot be explained in terms of interference effects since the samples are strongly absorbing at this wavelength which is within the reststrahl.

By comparison of the data in Figs. 1 and 2 with that obtained for n-InSb,[14] we suggest that the fine structure is due to transitions between bound states below the zeroth and first Landau levels.

For n-type InSb the impurity-shifted cyclotron resonance occurs at magnetic fields slightly less than that for free-carrier resonance, and is due to a transition from a $1s$-like impurity ground state below the zeroth Landau level to a $2p$-like impurity level below the first Landau level. The matrix elements for the possible transitions between bound and Landau levels have been studied[15] for excitons. In the high-magnetic-field limit, the matrix elements for bound-to-bound level transitions remain finite, as do those for continuum-to-continuum transitions. However, the matrix elements between bound and continuum states vanish. Thus in order to explain the fine structure in Fig. 1 at least three bound levels are required.

The very large measured values of the static dielectric constant (ϵ) of PbTe (Refs. 13 and 16) (~ 1000) would suggest that the effective hydrogenic Rydberg (R^*) is of the order of 1 μeV, making the existence of shallow bound states seem at first rather unlikely. Use of the static dielectric constant is, however, incorrect, since it is dynamic screening which will be important for the motion of a bound carrier. This has been proved recently by Enderlein,[17] who has suggested that an effective dielectric constant in the range 80–150 should be used. Even with this change (setting $\epsilon = 100$), the effective Rydberg still remains small (~ 0.1 meV); however, at the magnetic fields employed here there is a strong shrinkage of the electron wave function, which causes an increased binding. At

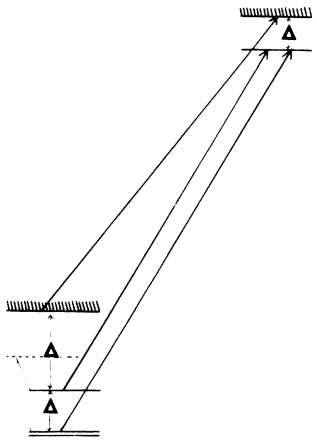

FIG. 3. Proposed energy-level scheme for a shallow-impurity center in a high magnetic field. The ground state is split due to the valley-orbit interactions.

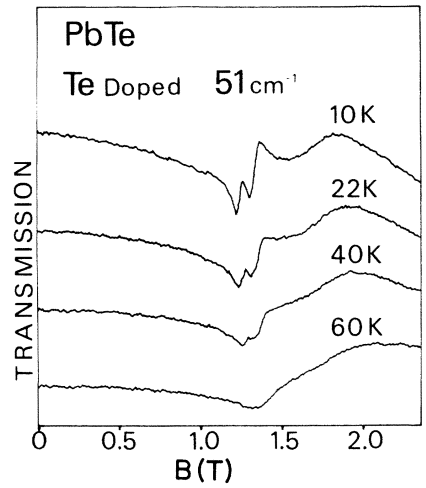

FIG. 4. Temperature dependence of the magneto-transmission of the Te-implanted PbTe sample.

1.5 T the effective magnetic field γ ($\gamma=h\omega_c/2R^*$) is of the order of 100, which has been found, in n-type InSb, to produce an increase in binding energy[18] of almost a factor of 10. This increase in binding energy will also greatly increase the importance of dynamic screening.[17] In addition, the wave function shrinkage leads to the appearance of a strong "central cell" shift.[18,19] This will be more significant than in InSb, for example, since while the wave functions in the plane of the magnetic field will be determined only by the Larmor radius, which is independent of material parameters, the effective Bohr radius for motion parallel to the field [$a_B^*=a_B^0(\epsilon/m_1^h)$] is determined by the longitudinal effective mass m_1^h ($m_1^h=0.30m_0$). Thus $a_B^*=170$ Å for PbTe, compared with the 680 Å for InSb, for which central-cell splittings of the order 0.3 meV have been observed at 8 T.[18]

Figure 3 shows a possible energy-level scheme together with the transitions observed, originating on the two valley-orbit split[20] ground states below the zeroth Landau level. It should be noted that using a level scheme such as that shown in Fig. 3 does not allow a determination of the binding energy of the 1s state attached to the zeroth Landau level. As was noted previously only one "impurity" peak was observed in the As-doped data in Fig. 2. This is most likely due to the fact that with this particular sample the width of the absorption peaks is too large for the weakest line to be detected. It should also be noted that the impurity levels for $\vec{B}||\langle 110\rangle$ will be significantly different from those for $\vec{B}||\langle 111\rangle$, due to the anisotropic nature of the valence band. The presence of strain in the film samples may also alter the spectra since the valley-orbit splitting, which is also dependent upon the positions of the nonequivalent valleys,[20] will be affected by any additional stress induced shift of these valleys.

Figure 4 shows the temperature dependence of the magnetotransmission of the Te-implanted sample. As the temperature is increased all the features on the trace broaden, although the peak absorption of the fine structure decreases more slowly than the free-carrier resonance. At a sufficiently high temperature, the free-carrier resonance becomes nothing more than a shoulder on the high-magnetic-field side of the fine structure, which itself has now broadened to form a single feature. Some reduction in the cyclotron resonance absorption may also be caused by the increasing number of free carriers[1] which, due to the negative contribution to the dielectric constant within the reststrahl, causes a decrease in the absorption strength. It is suggested that for samples of lower mobility a trace such as that obtained at higher temperatures for this sample may be the best possible. In such circumstances the single feature may be identified as the free-carrier resonance. This would lead to an incorrect assignment for the transverse cyclotron effective mass, 15% below the true value. Such values for the effective mass have been observed by other workers[13] in measurements at much lower frequencies.

This temperature dependence should be compared with that obtained by Kuchar *et al.*[2] for sample 2077. This is another nominally pure p-type sample of PbTe. The similarity between the transmission of this sample for 195-μm radiation and that obtained in this work for a nominally

pure sample is striking. Not only are the separations between the absorption peaks the same, but also the temperature dependences are similar. As the temperature increases and the resonances broaden, the free-carrier cyclotron resonance becomes the dominant feature, in contrast to the two ion-implanted samples. The fact that there is such great similarity between the spectra for these two nominally pure samples, with electron concentrations of 8×10^{16} cm^{-3} and 3.2×10^{17} cm^{-3}, in contrast to the quite different spectra from the ion-implanted samples, which have electron concentrations of 1.3×10^{17} cm^{-3} and 1.6×10^{17} cm^{-3}, is further strong evidence against many-body effects which should be determined by carrier concentration alone. This behavior is, however, similar to that found in GaAs by Cooke *et al.*,[21] where high-purity epitaxial layers grown by any one particular technique always show a characteristic "fingerprint," consisting of a specific combination of shallow donors in roughly constant relative proportions.

IV. CONCLUSION

Magneto-optical data are presented which shows sharp fine structure close to the cyclotron resonance. The position of this structure appears to depend on the nature of the dopant in the PbTe sample and so cannot be explained in terms of any intrinsic process. The data imply that shallow bound states exist associated with the impurity centers. The data cannot be explained in terms of the many-body effects recently proposed by McKnight and Drew.[3]

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