Evidence for shallow bound states in PbTe: A reply

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Line-shape calculations cast doubt on the interpretation offered by Lewis *et al.* (the preceding Comment).

In the Comment by Lewis *et al.*[1] (hereafter referred to as I), and previous publications by some of the same authors, some interesting experimental results are presented and a provocative interpretation in terms of shallow impurity levels in PbTe is advanced. This result is unexpected experimentally because PbTe does not exhibit carrier freezeout and theoretically because of the screening of the Coulomb potential by the large lattice dielectric constant ($\epsilon_l \sim 1300$) and the free carriers which are generally present in concentrations in excess of $10^{16}/cm^3$ in PbTe. The authors are publishing their paper as a Comment on a paper by McKnight and Drew (hereafter referred to as II)[2] in which similar cyclotron-resonance fine structures were reported and it was suggested that these features may arise from subband exciton modes, which in PbTe would result from the photon-mediated electron-electron interaction. In this reply, we wish to address several points raised in I, and hopefully to clarify the issue concerning shallow impurity states in PbTe.

The authors of I have not taken proper account of the profound modifications to semiconductor far-infrared magneto-optics due to magnetoplasma effects. These measurements and those of II are taken at frequencies in the reststrahlen band of PbTe, where the real part of the dielectric function is negative and the sample is nearly totally reflecting at zero field. For carrier concentrations and mobilities characteristic of the samples studied in I and II the real part of the dielectric function changes sign at the cyclotron resonance and the sample transmits (or absorbs) radiation in a narrow window at fields above the resonance. The major magnetospectral features are always the dielectric anomalies (DA) which correspond to the zero crossing of the effective dielectric function above the resonance.[3] The abrupt change from transmission to reflection at the DA when the dielectric function becomes negative again is the dominant feature in the magneto-optical spectra. The resonances, on the other hand, show up as rather small features in comparison. For smaller carrier concentrations and higher scatterings than reported in I, the dielectric function does not change sign at the resonance. Nevertheless, the index of refraction n and extinction coefficient k are still affected primarily by the behavior of the real part of the dielectric function. The spectra are characterized by transmission peaks due to the dispersion in $\mathrm{Re}\epsilon$ instead of transmission dips at the maxima of $\mathrm{Im}\epsilon$.

Line-shape calculations demonstrate this clearly as we show in Fig. 1. In the figure, the Faraday-geometry transmission spectrum of a film chosen to be very similar to those reported by Lewis *et al.* is shown together with a calculated spectrum. It is seen that the experimental trace and

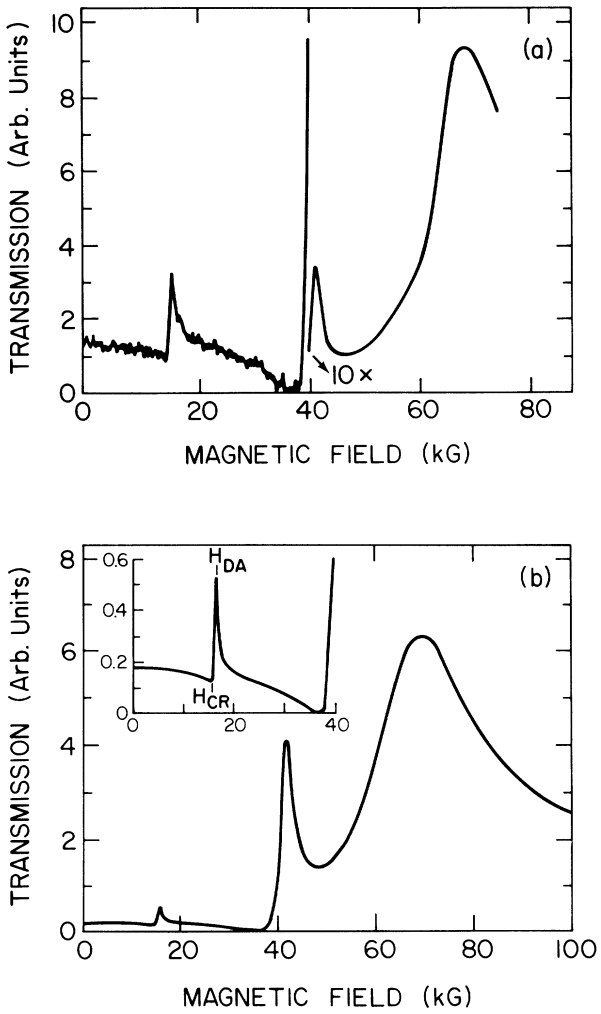

FIG. 1. (a) Faraday geometry transmission vs magnetic field for a p-type PbTe(111) epitaxial film at 171 μm. The carrier density of the film was measured at $p=2.6\times10^{17}$ and its thickness was 3.0 μm. (b) The calculated transmission spectrum with parameters adjusted for a good fit. $p=2\times10^{17}$, $m_t=0.025m_0$, $m_e=0.35_0$, $\hbar/\tau=0.1$ meV and the low-cyclotron-mass pocket was assumed to have only 5% of the carriers. This modification of the occupancy of the carrier pockets from 25% each is a consequence of the lifting of the degeneracy of the four pockets due to the effects of the substrate strain and the applied magnetic field. The inset shows the magnetic field positions of the cyclotron resonance (CR) and dielectric anomaly.

the calculated line shape are in quite good agreement with one another and the dielectric anomaly dominates the spectrum. The calculation and spectra show transmission peaks near the DA, not dips as seen in the Faraday-geometry data in I. The theoretical calculation is based on the classical model for PbTe,[4] but a full quantum calculation gives very similar results.[5] Moreover, the line shape is dominated by transmission peaks over a wide range of carrier densities at least as great as $10^{16} < n < 10^{19}$ cm^{-3} and for scattering times from $2 < \omega\tau < 100$. Measurements on a variety of films have demonstrated that this conclusion is generally valid.[6] In our measurements on p-type films from NSWC and from Lopez-Otero at Linz, we have not observed any spectra that resemble those presented in I. We have also calculated line shapes by adding extra "impurity" features into the model dielectric function in order to simulate their proposed interpretation but were unable to produce line shapes similar to those reported in their paper.

How then are we to interpret the transmission data presented in I? We can suggest two possibilities. One is that the spectra they present include radiation leakage around the sample in addition to the transmitted signal. Their data were taken at transmission levels of around 0.001% (Ref. 7) and it is difficult to prevent comparable levels of far-infrared radiation from reaching the detector around the sample. The result would be a combination of reflection and transmission spectra which might show dips at the DA positions, as in reflection, superimposed on peaks as expected in transmission. Secondly, there is the possibility of Landau-level transitions of carriers in space-charge layers at the interfaces of the sample. Schaber and Doezema[8] have observed such transitions in MIS structures on PbTe and they find that surface space-charge layers are generally present even at zero bias. In addition, Gungor and Drew[9] have found that damage or strain at the BaF_2 interface may produce an inversion layer. It may be that the Faraday transmission spectra reported in I are a superposition of the spectra from n- and p-type space-charge regions of the film with varying carrier concentrations. The varying carrier density can broaden the dielectric anomalies and multiple cyclotron resonance features can arise from the valence and conduction band and from multiple subband occupation in an inversion layer. The observed effects of doping more likely result from small variations in the carrier concentration among the samples, or to damage or inhomogeneities induced through the ion-bombardment and annealing process, than from the proposed impurity transitions. The dielectric anomalies, which will be prominent in the line shape, are quite sensitive to such changes in carrier concentration, scattering time, and sample homogeneity.

As with the Faraday-geometry transmission data, the interpretation of the Voigt-geometry strip-line data presented in I can be greatly clarified by model line-shape calculations. The calculations for this strip-line configuration are difficult, but it has been shown that transmission line spectra can be approximated by calculations of multiple reflection.[10] We have made these calculations and we find several points of interest. First, the minima in strip-line transmission correspond closely to the position of the DA's, not to the resonances as asserted in I. Second, the dip identified as a hybrid resonance is most probably the DA associated with the hybrid resonance, and the feature at slightly lower field which the authors of I have identified as an impurity feature, is very close to the position of the actual hybrid resonance. We suspect that the authors have misinterpreted the hybrid resonance and its DA as the resonance and an extra impurity transition. Certainly we reject their assertion that impurity transitions would occur associated with hybrid resonances. The hybrid resonance is a collective mode of a multicomponent electron gas which arises from the combined effects of the Hall conductivity and the requirement that there be no current normal to the sample interface.[3] This leads to an effective dielectric function proportional to $(\sigma_\perp)^{-1}$, where $\sigma_\perp$ is the diagonal component of the conductivity tensor perpendicular to the magnetic field. The hybrid resonances will thus occur at zeros of $\sigma_\perp$ between the cyclotron frequencies of the system. The presence of an impurity-level transition close to cyclotron resonance will result in an additional zero crossing of $\sigma_\perp$ between the impurity resonance and its associated cyclotron transition, but cannot induce multiple zeros in $\sigma_\perp$ near the original hybrid resonance. Third, we find that the extra feature observed below the high-field cyclotron-resonance DA appears to be split off from the DA by considerably more than would be expected for the cyclotron resonance, and probably does represent an extra feature in the spectra which is not present in the classical magnetoplasma calculation.

Interpreted in this way, the Voigt-geometry spectra presented in I are consistent with the results on bulk material at 337 μm in II since both show extra structure associated with, and at a lower field than, cyclotron resonance (compare, for example, Fig. 13 in Ref. 2). It should be pointed out that this extra structure has so far been observed only in p-PbTe: In II no n-type samples were studied at 337 μm, where the additional structure was easily apparent, and in I the undoped samples on PbTe substrates were n-type and are not reported to show unusual feature. It cannot be said, therefore, that the observation of structure in p-type As-doped films in I constitutes proof that the features are impurity related since similar undoped films were n rather than p type and a direct comparison of the effect of the As impurities is not possible.

The nature of these features is discussed at some length in II, and it was conjectured that they might be related to many-body excitonic modes associated with cyclotron resonance as found in bismuth by Verdun and Drew.[11] Impurity and space-charge effects were considered to be less likely. The key experimental finding of II was that when identical samples were studied at 337 and 119 μm the major resonance observed at 119 μm corresponded to this secondary "impurity" feature observed at 337 μm. This indicates a strong frequency dependence of the oscillator strength of these cyclotron-resonance-associated features, a finding which seems inconsistent with space-charge effects since the skin depth is roughly comparable at 337 and 119 μm. This would not be unexpected for an excitoniclike state in a phonon-mediated frequency-dependent potential.

Recently, Baldwin and Drew[12] have found clear evidence for phonon-mediated electron-electron interaction effects in bismuth in far-infrared experiments performed near the LO-phonon frequency. The experiments show many new modes developing as the cyclotron frequency approaches ω_{LO}. It seems possible that similar modes may exist in PbTe, where the electron-phonon interaction is much stronger, but the problem is also far more difficult to analyze. Although some preliminary theoretical work has been done,[13] the picture is not yet complete. Much more theoretical and experimental work will be required to sort out these interesting effects in both bismuth and PbTe.

If it is found that the extra structure is due to impurity ef-

fects, the impurity states involved may be quite interesting and deserving of further study. Calculations indicate that the major contribution to the binding energy of shallow impurities in PbTe would be the local dielectric relaxation of the lattice around the site of the defect.[14] These impurity states, if they exist, may then be similar to strongly lattice-coupled deep levels, or may represent a crossover from the hydrogenic impurity state to a deep level. It is unlikely that the simple hydrogenic picture suggested in I can be correct, even including the effects of central-cell corrections.

Finally, we would like to address the question of why the results for the effective mass derived from the data at 119 μm in II appear not to agree with much of the more recent work.[5] The possibility of misassigned resonances in II does not appear reasonable in p-type material where a feature is directly observed with a mass as low as $0.021 m_0$ (Figs. 7 and 8 in II). We note that the data in II are taken with a derivative technique that, as shown experimentally in Fig. 4 of II, can expose features that would appear only as an increased resonance width in straight reflection. It may also be that these differences are indicative of actual differences between bulk material (as in II) and thin films as those in I and Ref. 5. It appears, for example, that anisotropies measured on PbTe films are systematically lower than the results well established in bulk materials. This is particularly evident in n-type material where bulk anisotropy values[2,15] are all close to 10 while the value measured on BaF_2 films[5,6] seems to average around 6. It is known that epitaxial films of PbTe on BaF_2 are always strained at cryogenic temperatures, and, while the effect of substrate strain on the fundamental band gap does not appear large enough to account for these differences in band parameters, the changes in the interband velocity matrix elements should also be considered. These changes may be large because the substrate-induced strain may be large (typically 1%) and because the strain lowers the symmetry of the PbTe crystal from cubic to tetragonal. If the observed variation of the anisotropy is indeed an effect due to strain, it suggests that these effects on the band structure are quite sufficient to account for the mass differences between II and Ref. 5. Lastly, the idea presented in II that mass-dressing and collective-mode effects might lead to different effective masses in experiments performed at different frequencies still needs to be considered.

In conclusion, while we do not believe that the results of I constitute convincing evidence for shallow impurity states in PbTe, their transmission line results for films on PbTe substrates confirm our findings of extra structure associated with the cyclotron resonance. Whether this structure is a result of surface space-charge, impurity, or many-body effects is a subject for further experimental and theoretical investigation. It is hoped that the publication of the Comment (I) and this reply will motivate further work so that we can arrive finally at a clearer understanding of the physics of this interesting material.

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