Anomalous temperature dependence of the effective mass in *n*-type PbTe

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We have measured the cyclotron resonance in *n*-type PbTe in the temperature range between 12 and 340 K at wavelengths of 9.6 and 16.9 μm in the Faraday configuration ($\mathbf{B}\|\mathbf{k}\|[111]$) in ultrahigh magnetic fields up to 150 T. Samples of single-crystal *n*-type PbTe are grown on the $BaF_2(111)$ surface by the hot-wall technique. The effective masses measured around 20 K are explained well by the six-band model. However, the temperature dependence of the effective masses in the temperature range between 20 and 300 K is at least 2.6 times larger than the calculation taking into account the temperature dependence of the fundamental energy-band gap. The large discrepancy suggests that the conventional theory, which assumes the temperature-independent momentum matrix elements, should be reexamined, or may expose the applicable limit of $\mathbf{k}\cdot\mathbf{p}$ theory at finite temperatures.

PbTe has attracted much interest because of the small energy gap and related peculiar properties, and has been investigated for many years. The effective masses and *g* factors have been determined experimentally through measurements of cyclotron resonance, magneto-optical spectra, Shubnikov–de Haas effects, and so on.[1] Information on these band parameters is limited to low temperatures around liquid-helium temperature. Temperature dependence of the effective masses is one of the fundamental parameters of the band structure in semiconductors. In PbTe, however, only a few reports have been made on the effective masses at higher temperatures up to about 77 K.[2,3] The reason the measurements of the effective masses in PbTe has been limited to such low temperatures is partly because the mobility of carriers becomes low in temperatures higher than 20 K. In *n*-type PbTe, it is about 1×10^6 cm^2/V s at 20 K but 2×10^4 cm^2/V s at 100 K and 1×10^3 cm^2/V s at 300 K.[4] Moreover, the large magnetoplasma effect due to the large carrier concentration affects the cyclotron resonance spectra in low magnetic field range and high temperatures. In order to investigate the temperature dependence in a wider temperature range, measurements in very high fields are required.

Theoretical treatment of temperature dependence of carrier effective mass was discussed by Ehrenreich,[5] Lang,[6] and Ravich.[7] Ehrenreich took a dilational change of a fundamental gap into consideration in the framework of $\mathbf{k}\cdot\mathbf{p}$ perturbation theory. Temperature variation of the fundamental energy gap is due to both dilation of a lattice and electron-phonon interaction. Lang and Ravich found that not only the dilation change but also the change due to electron-phonon interaction of a fundamental gap contributes to temperature dependence of effective masses in narrow-gap semiconductors. In addition, they noted that Kane's formula is valid at finite temperatures if changes of the effective mass and the energy gap are small enough.

Experimentally, measurements of the cyclotron resonance or the magnetophonon resonance have been made by several workers to investigate this problem in detail. Stradling and Wood[8] reported on this subject in InSb, InAs, and GaAs using the magnetophonon effect. They compared their results with both theoretical treatments mentioned above. They found that the dilational change of its gap explains their experimental results very well in the case of InSb, but that in InAs and GaAs, its contribution was a factor of 2 smaller than the observation, whereas the consideration of the total gap change overestimated the experimental results considerably. Hazama *et al.*[9] extended the $\mathbf{k}\cdot\mathbf{p}$ method for III-V semiconductors from a three-band to a five-band model. They concluded that the agreement has been improved in the case of GaAs but there is still a large discrepancy for InAs and InP. Takita *et al.*[10] observed anomalously large temperature dependence of magnetophonon resonance peak positions of *n*-type $Hg_{1-x}Cd_xTe$ ($x=0.206, 0.305$). Mani *et al.*[11] also observed the same phenomena in $Hg_{1-x}Cd_xTe$ ($x=0.206$). These results were inexplicable even if the total temperature dependence of its fundamental gap was taken into account. Mani *et al.* found that this disagreement is resolved if the momentum matrix element *P* depends on temperature. The possibility of the temperature dependence of the momentum matrix elements was also pointed out in PbTe by Hewes *et al.*[12] through measurements of the Knight shift.

In this paper, we investigate cyclotron resonance in *n*-type PbTe under ultrahigh magnetic fields up to 150 T. Anomalously large temperature dependence of the effective masses was observed in a wide temperature range from 12 up to 340 K. Thin single crystals of *n*-type PbTe were grown on BaF_2 substrates by the hot-wall technique. Electrical properties of the samples are listed in Table I. Magnetic fields were generated using the single-turn-coil technique.[13] With coils of inner bore diameter of 10 mm, pulsed fields up to 150 T were generated. We used a CO_2 laser and a H_2O vapor laser as light sources. The former provided many lines with different wavelengths between 9.2 and 10.8 μm and the latter pro-

TABLE I. Properties of samples.

Sample number	Carrier concentration (10^{17} cm^{-3})	Mobility (cm^2/V s)	Thickness (μm)
1	1.9	39 800 (77 K)	6.6
2	1.7	29 500 (77 K)	4.5
3	2.3	45 000 (77 K)	5.7
4	1.9	40 000 (77 K)	4.7
5	5.8	1 585 (300 K)	19.8

vided a line at 16.9 μm. Transmitted light was detected by a liquid-nitrogen cooled HgCdTe photovoltage-type detector for a CO_2 laser[14] and LHe-cooled Ge(Cu) for 16.9 μm from a H_2O vapor laser.

PbTe is a multivalley semiconductor whose conduction-band mimima are located at the L points in the [111] direction. When the magnetic field **B** and the propagation vector **k** of the incident light are parallel to [111], two kinds of cyclotron resonances are expected to be observed; one is from a valley oriented to [111] (parallel to **B**) and another is from three equivalent valleys whose symmetric axes are tilted from the magnetic field by $\sim 70°$. The former is observed at lower fields than the latter. Hereafter we will label L for the Landau levels in the former valley and H for the levels in the latter valleys.

In Fig. 1, experimental recordings of the absorption spectra in n-type PbTe (sample 1) are shown for various temperature at a wavelength of 9.6 μm. Two kinds of resonance peaks are observed. As mentioned above, the peak observed at lower fields is assigned to be the transition ($L0\beta \rightarrow L1\beta$) and the other is the transition ($H0\beta \rightarrow H1\beta$). Both peaks showed a drastic shift to higher fields as the temperature was increased. We can obtain cyclotron masses from the fields of the absorption peaks.

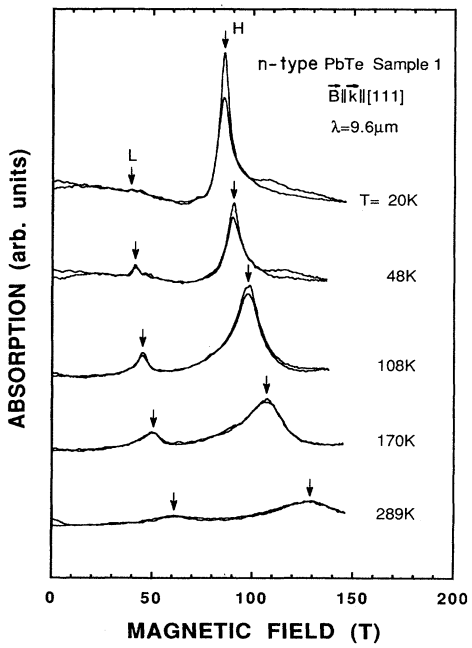

FIG. 1. Magnetoabsorption spectra for n-type PbTe (sample 1) at a wavelength of 9.6 μm at several temperatures in the Faraday configuration (**B**$\|$**k**$\|$[111]).

Figure 2 shows the transition energies ($0\beta \rightarrow 1\beta$) versus magnetic fields in n-type PbTe. Different types of points correspond to the experimental results at about 20 K on the different samples listed in Table I. The solid and broken lines are calculated using the six-band model and **k**·**p** parameters of Pascher *et al.*[15] or Hewes *et al.*,[12] respectively. As the fundamental energy gap at 20 K, a value of 193.3 meV which was calculated through the empirical relation of Grisar[16] is used. We found that the calculated transition energies using the two sets of **k**·**p** parameters deviate from each other by about 15% for the resonance $L0\beta \rightarrow L1\beta$ at 40 T and 14% for the resonance $H0\beta \rightarrow H1\beta$ at 90 T. The experimental result at 16.9 μm (transition energy 73.37 meV) is in a very good agreement with the calculation using the parameters of Pascher *et al.* At higher energies, the experimental results deviate from the calculation using the parameters of Pascher *et al.* The difference in the resonance fields between the experimental results and the calculation using the parameters of Pascher *et al.* is (11.7±0.6)% for the resonance $H0\beta \rightarrow H1\beta$ and (13.5±0.5)% for the resonance $L0\beta \rightarrow L1\beta$ at 9.6 μm. Thus we can estimate the validity of the six-band model in the energy or magnetic field regions of our measurements. Originally, the **k**·**p** method is valid only for small perturbations. At a wavelength of 16.9 μm whose photon energy is less than 40% of the energy gap, the **k**·**p** method with the six-band model using the parameters of Pascher *et al.* explains the observed resonance positions well. At wavelengths of the CO_2 laser lines, however, there is a slight discrepancy in the resonance energies between the experiment and the calculation. This fact may indicate that the experimental energy range with a CO_2 laser is beyond the validity of the **k**·**p** perturbation theory. However, it should be noted that the discrepancy is small and such an approach using the **k**·**p** theory can still give semiquantitative information for the temperature dependence of the effective masses even in the range of the CO_2 laser lines.

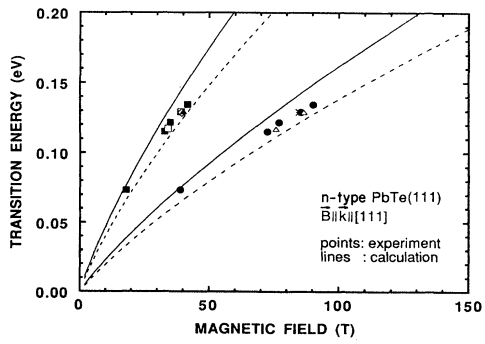

FIG. 2. Cyclotron energy vs magnetic fields in n-type PbTe. Transitions in both Landau levels L and H (see text for these notations) are shown. The points represent the experimental results (L; ■: sample 1, ▲: 3, ◇: 4, and □ 5; H; ●: 1, *: 2, and △: 5). Solid and broken lines represent the calculations using the six-band model with the parameters of Pascher *et al.* and Hewes *et al.*, respectively.

In Figs. 3(a) and 3(b), the points show the cyclotron masses measured at various temperatures at wavelengths of 9.6 and 16.9 μm, respectively, for samples listed in Table I. The lines in Fig. 3 show the temperature dependence of the cyclotron masses calculated in the framework of the six-band model under a condition of a transition energy of (a) 129 meV (9.6 μm) and (b) 73.4 meV (16.9 μm). The broken and solid lines show calculations taking account of the dilation change only and the total change of the fundamental energy gap, respectively. Here, the dilation change was calculated from the experimental data of the pressure coefficient of the gap,[17] the thermal expansion coefficient,[18] and the bulk modulus.[19] The total change was calculated from the empirical relation given by Grisar. The calculated and experimentally obtained temperature variations of the effective masses are listed in Table II.

The calculation taking only the dilation change of the energy gap is obviously inadequate to explain the experimental results. Even the calculation considering the total change of the gap is 38% of the experimental value at best at 16.9 μm. At many different lines of the CO_2 laser, up to about 10.6 μm, we have also observed temperature dependence of the effective masses similar to that at 9.6 μm. The degree of the disagreement between experimental results and calculations at 9.6 μm is larger than that at 16.9 μm. This may be attributed to the inaccuracy of the calculation in a range of the transition energy.

The elastic strain due to the difference in the thermal expansion coefficients between the PbTe film and the BaF_2 substrate causes a slight increase of the energy-band gap (less than 3 meV) in the [111] oriented valley as compared to its bulk value.[20] Correspondingly, the effective mass is increased through the $\mathbf{k}\cdot\mathbf{p}$ interaction. However, such a small effect is almost negligible in comparison to the large temperature change of the energy gap. Thus we will not take the strain effect into account in the following discussion.

In order to resolve the discrepancy in the framework of the six-band model, one can suppose the temperature dependence of the momentum matrix elements. Temperature dependence of momentum matrix elements follows temperature variation of wave functions of the band edges. In fact, there may be such possibilities in the case of PbTe. In PbTe, the Debye-Waller term in the temperature dependence of the fundamental gap greatly increases with increasing temperature. The temperature coefficient of the fundamental gap $(\partial E_0/\partial T)_p$ is $+0.44$ meV/K.[16] The Debye-Waller term contributes about half of the coefficient.[21,22] This property is quite different from other crystals such as Si and Ge. This peculiar electron-phonon interaction may cause mixture of wave functions at the band edges. In $Hg_{1-x}Cd_xTe$ with $x<0.5$, anomalous temperature dependence of the fundamental energy gap has also been reported, showing a large positive temperature coefficient.[23,24] Because the dilation term has the opposite temperature dependence,[1] electron-phonon interaction is considered to contribute greatly to the positive coefficient.[25] The fact that both materials have these common features may suggest that the peculiar contribution of electron-phonon interaction to the band gap may be responsible for the large positive temperature dependence of the effective mass.

Another possibility for temperature-dependent momentum matrix elements is temperature change of spin-orbit interaction. In PbTe, the spin-orbit coupling mixes states with L_6^- symmetry which originates from different single group wave functions. The lowest conduction-band level L_6^- is a linear combination of $L_6^-(L_2^-)$ and $L_6^-(L_3^-)$, among which the $L_6^-(L_3^-)$ function dominates the L_6^- level. This leads to the property of PbTe that the transverse mass is about ten times lighter than the longitudinal mass. If the spin-orbit coupling changes and contribution of $L_6^-(L_3^-)$ to L_6^- decreases with temperature, the momentum matrix element between the lowest conduction band and the highest valence band becomes smaller and effective masses become larger with increasing temperature.

We have estimated the temperature variance of the two-band $\mathbf{k}\cdot\mathbf{p}$ parameters P_t^2 and P_l^2 necessary to explain our experimental results. For the low-temperature parameters, we took the parameters of Pascher *et al.* and compared the calculation with the experiments at 16.9 μm because the calculation with the parameters of Pascher *et al.* agrees well with our data at 16.9 μm and at 20 K. We have found that reduction of 77% in P_t^2 and 7% in P_l^2 are necessary to explain the experiments at 300 K. These results are quite different from the values es-

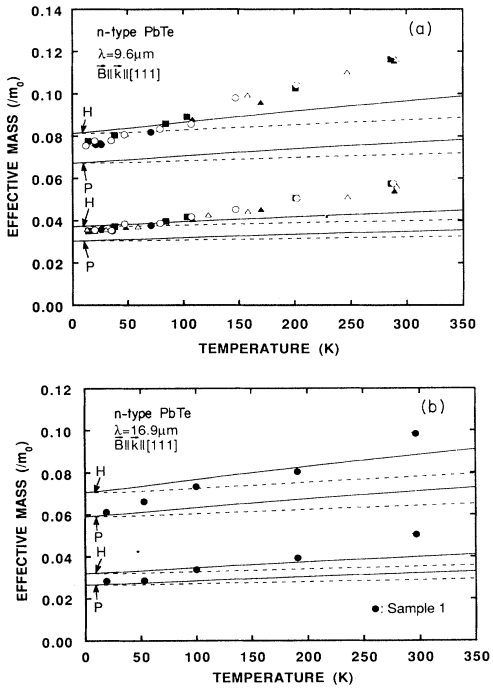

FIG. 3. Effective masses vs temperature. The points represent the experimental results measured on samples listed in Table I at wavelengths of (a) 9.6 μm (▲: sample 1; ●: 2; △: 3; ○: 4, and ■: 5) and (b) 16.9 μm. Lines are calculated results through the six-band model. Solid lines and broken lines represent calculations taking a total change and only a dilational change of the fundamental energy gap into account, respectively. Calculations using parameters of both Pascher *et al.* and Hewes *et al.* are presented (labeled as *P* and *H*, respectively).

TABLE II. Percentage change in cyclotron masses with temperature. Values per 100 K are listed. The values for 16.9 and for 9.6 μm are averages in the temperature range between 19 and 297 K and 19 and 289 K, respectively. Values in the parentheses are ratios to the experimentally measured changes.

Wavelength		Experiments (per 100 K)	Calculations (per 100 K) Pascher *et al.*	Hewes *et al.*
16.9 μm	m_L^*	28%	6.8% (24%)	7.9% (28%)
	m_H^*	22%	6.8% (32.%)	8.2% (38%)
9.6 μm	m_L^*	23%	5.2% (23%)	5.9% (26%)
	m_H^*	20%	4.8% (25%)	6.3% (32%)

timated by Hewes *et al.*[12]. They found that calculated curves of the Knight shift versus carrier concentration fit their 300-K data fairly well by reducing the two-band parameters by as little as 25%. The disagreement may be partly due to the difference of the set of $\mathbf{k}\cdot\mathbf{p}$ parameters used and partly due to the different measurement method. The cyclotron resonance gives the most direct information on the band parameters. However, because our measurements have been performed at high-energy regions comparable to half of the band gap, the electronic states we observed are largely perturbed by far bands. Therefore the temperature dependence of far band parameters in addition to the two-band parameters may be necessary to be considered in the fitting. It is difficult to discuss it quantitatively with our data on *n*-type PbTe only. More investigation, for instance on *p*-type PbTe, will be necessary.

These possibilities do not go beyond conjecture because it is not clarified that the Debye-Waller type electron-phonon interaction may modify the band-edge states, or that the spin-orbit interaction may change with temperature.

Our measurements[26] on *n*-type PbSe may be worth referring to for comparison. We have also found large temperature dependence of the effective masses in *n*-type PbSe. In this case, the six-band model using the parameters of Pascher *et al.*[15] overestimates the effective masses measured at 16.9 μm by about 10%. However, except for the absolute value of the effective masses, their temperature coefficients are well explained through the calculation taking account of the total change of the energy gap. These two lead chalcogenides have similar band structures and similar temperature dependence of the energy gaps. However, the Debye-Waller term decreases with increasing temperature in PbSe.[22] In addition, the L_6^- (L_2^-) function dominates the lowest conduction band in PbSe. These properties are opposite to those in PbTe. The comparison of the properties between PbTe and PbSe should be made carefully because the contribution of the electron-phonon interaction to the energy gap has not yet been clarified completely in PbSe (Ref. 22) and the absolute values of the effective masses derived from the calculation are still not in agreement with the experiments. Nevertheless, such comparisons between members in the same family are very useful to clarify the mechanisms of the large temperature dependence of the effective masses.

Though Lang and Ravich showed the $\mathbf{k}\cdot\mathbf{p}$ method is valid at finite temperatures, one should notice that such a treatment is justified only under the condition that $\Delta m^* \ll m^*$ and $\Delta E_g \ll E_g$. In PbTe, the fundamental energy gap changes about 60% at 300 K relative to the value around 0 K and effective masses change about 50%. These variations may be too large to be dealt with in the framework of the $\mathbf{k}\cdot\mathbf{p}$ method.

We observed an anomalously large increase of the effective masses with increasing temperature between 12 and 340 K at wavelengths of 16.9 and 9.6 μm in the Faraday configuration ($\mathbf{B}\|\mathbf{k}\|[111]$). The increase cannot be explained by the conventional $\mathbf{k}\cdot\mathbf{p}$ theory. It is suggested that the conventional assumption of temperature-independent momentum matrix elements should be reexamined, or that the large temperature variation of the band gap is beyond the applicable limit of the $\mathbf{k}\cdot\mathbf{p}$ theory.

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