Electron Spin-Flip Raman Scattering in PbTe

C. K. N. PATEL AND R. E. SLUSHER
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 8 March 1968)

We have observed electron spin-flip Raman scattering in *n*-PbTe using a 10.6-μ laser and magnetic fields up to 105 kOe. From *g*-value measurements in samples with $\langle 111\rangle$, $\langle 110\rangle$, and $\langle 100\rangle$ along **B**, we obtain $g_{\parallel}=57.5\pm2$ and $g_{\perp}=15\pm1$. The $g_{\parallel}$ is considerably larger than that deduced previously from injection-diode fluorescence and Shubnikov–de Haas measurements. The $g_{\perp}$ measurement gives the first direct observation of anisotropy of *g* values in PbTe. The magnetic field dependence of intensity of spin-flip scattering for different *g*-value transitions indicates shifting of electrons from high *g*-value valleys to low *g*-value valleys.

THE band structure of PbTe and the associated properties of its anisotropic electron gas have previously been investigated in detail both theoretically[1] and experimentally.[2,3] Conflicting and incomplete measurements of mobile electron *g* values[2,3] make the comparison between theory and experiment difficult. In the present paper we report results of Raman scattering of 10.6-μ radiation by spin flips of PbTe conduction electrons for three different orientations of **B** with respect to the crystalline axes. From these results we have obtained $g_{\parallel}$ and $g_{\perp}$ for PbTe where the electron valleys are cigar-shaped elipsoids along $\langle 111\rangle$ axes at the *L* points in the Brillouin zone.[2] This $g_{\parallel}$ is considerably larger than that deduced previously from injection diode fluorescence[3] and Shubnikov–de Haas[2] (SdeH) measurements. Our $g_{\perp}$ measurement gives the first direct observation of the anisotropy of *g* values in PbTe. Since our measurements were performed in low-carrier-concentration material, they are appropriate for comparison with theoretical calculations for band-edge *g*-values. The magnetic field dependence of intensities of spin-flip scattering for different *g* values indicates shifting of electrons from high *g*-value valleys to low *g*-value valleys. In the present experiments, we were unable to observe the Landau-Raman scattering corresponding to a change of the Landau-level quantum number, *l*, by 1 or 2 (Refs. 4 and 5). Also absent were Raman scattering from phonons and optic plasmons.

The effective-mass tensor for conduction electrons in PbTe has been relatively well established. However, a number of different measurements of *g* values give the $g_{\parallel}$ (*g* values of electrons in a $\langle 111\rangle$ valley parallel to **B**) varying from $\sim$30 to 48. The *g* value reported in Ref. 3 is for $\mathbf{B}\parallel\langle 100\rangle$ and thus it is neither the $g_{\parallel}$ nor $g_{\perp}$, but is related to them through the expression[6]

$$g_\theta=(g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{1/2}, \quad (1)$$

where θ is the angle between **B** and the $\langle 111\rangle$ direction of the electron valley of interest. The diode measurements may not represent the bulk electron *g* value because of the proximity of the junction region and because the recombination radiation measurements give an average of electron and hole *g* values. There are no direct measurements of $g_{\perp}$ in either the PbTe diode measurements or in SdeH measurements. The SdeH measurements were carried out on PbTe samples having high carrier concentrations. The nonparabolic nature of conduction bands in PbTe results in higher effective mass of electrons near the Fermi level in the high-carrier-concentration materials. Thus the SdeH measurement of *g* values represent, at best, a lower limit on the effective *g* value of electrons at the bottom of the band. In contrast, the light-scattering measurements in low-carrier-concentration PbTe can give a much better value of $g_{\parallel}$ and $g_{\perp}$ at the bottom of the band as a function of magnetic field.

The experimental setup used for the Landau-Raman scattering of 10.6-μ CO_2-laser radiation from mobile carriers in PbTe was similar to the one described earlier,[4,7] with the exception that a 105-kOe superconducting solenoid was used for the high magnetic field. The *n*-PbTe samples prepared by Schmidt[8] were grown by vapor deposition and properly annealed to have an electron concentration of 8 to 10×10^{16} cm^{-3}. The dc mobilities of the samples were in range of 10^6 cm^2 V^{-1} sec.$^{-1}$ Sample temperature was in the range of 50°K and could be monitored by the wavelength of the recombination radiation resulting from two-photon electron-hole-pair creation in the laser beam.[9] The electrons produced by the two-photon process were minimized by defocusing the laser beam and did not affect the scattering measurements. Free-carrier absorption from 4.2°

[1] L. Kleinman and P. J. Lin, *Proceedings of 7th International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), pp. 63–68; G. W. Pratt and L. G. Ferreira, *ibid.*, pp. 69–76; J. O. Dimmock and G. B. Wright, *ibid.*, pp. 77–81; J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., Phys. Rev. **137**, A1282 (1965); P. J. Lin and L. Kleinman, Phys. Rev. **142**, 478 (1966); J. O. Dimmock and G. B. Wright, Phys. Rev. **135**, A821 (1964).

[2] K. F. Cuff, M. R. Ellett, C. D. Kuglin, and L. R. Williams, *Proceedings of 7th International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), pp. 677–684.

[3] J. F. Butler and A. R. Calawa, *Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc., 1966), pp. 458–466.

[4] R. E. Slusher, C. K. N. Patel, and P. A. Fleury, Phys. Rev. Letters **18**, 77 (1967); C. K. N. Patel and R. E. Slusher, Phys. Rev. (to be published).

[5] P. A. Wolff, Phys. Rev. Letters **16**, 225 (1966); Y. Yafet, Phys. Rev. **152**, 858 (1966).

[6] L. M. Roth, Phys. Rev. **118**, 1534 (1960).

[7] C. K. N. Patel, *Proceedings of the Modern Optics Symposium, April, 1967* (Polytechnic Press, Brooklyn, N. Y., 1967), pp. 19–52.

[8] P. H. Schmidt and L. M. Rhodes (to be published).

[9] C. K. N. Patel, P. A. Fleury, R. E. Slusher, and H. L. Frish, Phys. Rev. Letters **16**, 971 (1966).

to 77°K was measured to be between 2 and 10 cm^{-1} in the wavelength range of interest. Detection apparatus and associated electronics allowed observation of scattered-light intensities as low as 10^{-9} W, which corresponds to $\sim 10^{-13}$ times the incident 10.6-μ laser intensity.

Figure 1 shows the results of frequency shift of spin-flip scattered light as a function of magnetic field for three crystal orientations: (a) $\mathbf{B} \| \langle 111 \rangle$, (b) $\mathbf{B} \| \langle 110 \rangle$, and (c) $\mathbf{B} \| \langle 100 \rangle$. For the case of $\mathbf{B} \| \langle 111 \rangle$, two $\langle 111 \rangle$ valleys lie at $\theta = 0°$ to **B** and six other $\langle 111 \rangle$ valleys are located at $\theta = 70°32'$ with respect to **B**. Thus the two distinct spin-flip scattering transitions seen in Fig. 1(a) correspond to the $\Delta s = 1$ transitions[4] in these two sets of electron valleys. The first of these gives the value of $g_{\parallel}$ directly as seen from Eq. (1) for $\theta = 0°$. For $\mathbf{B} \| \langle 100 \rangle$, all the eight $\langle 111 \rangle$ valleys are symmetrically located with respect to **B** and thus the single spin-flip transition, shown in Fig. 1(c), is to be expected. For the last case when $\mathbf{B} \| \langle 110 \rangle$, we have again two sets of electron valleys. Four $\langle 111 \rangle$ valleys lie at $\theta = 35°16'$ and the remaining four valleys are at $\theta = 90°$ to the magnetic field. The Fig. 1(b) shows the positions of these two spin-flip transitions with the latter giving the $g_{\perp}$ directly as seen from Eq. (1) for $\theta = 90°$. These g values are summarized in Table I. From these values, using Eq. (1), we find that

$$g_{\parallel} = 57.5 \pm 2\,, \quad \text{and} \quad g_{\perp} = 15 \pm 1\,, \tag{2}$$

for conduction electrons in PbTe. These g values are extrapolated to zero magnetic field and decrease with increasing field because of nonparabolic effects. g values measured for other orientations fit within experimental error using Eqs. (1) and (2) for all values of magnetic field. The g values in Eq. (2) are in disagreement with previous measurements as well as with those obtained from a number of different band-structure calculations.[1,2,3]

The scattering cross section for the spin-flip Raman process can be calculated from a simple two-band model[5] and is of the order of

$$d\sigma/d\Omega \approx (\hbar\omega_0/E_G)^2(e^2/m_s c^2)^2 \approx 10^{-23}\ \text{cm}^2/\text{sr}\,, \tag{3}$$

where ω_0 is the incident laser frequency, E_G is the band gap, and m_s is the spin effective mass. The numerical estimate is for typical PbTe parameters. For incident peak power of 30 kW, collection of ~ 0.1 sr of scattered light, and allowance for loss in sample, the observed signal to noise ratio of 30 to 1 for a 10-kHz bandwidth is in qualitative agreement with Eq. (3).

TABLE I. Summary of g-value measurements in n-PbTe.

Direction of B	Observed g values[a]
$\mathbf{B} \| \langle 111 \rangle$	$\theta = 0°$, $g = 58$; $\theta = 70°32'$, $g = 24$
$\mathbf{B} \| \langle 100 \rangle$	$\theta = 54°44'$, $g = 35.5$
$\mathbf{B} \| \langle 110 \rangle$	$\theta = 35°16'$, $g = 46$; $\theta = 90°$, $g = 15$

[a] θ is the angle between a $\langle 111 \rangle$ electron valley responsible for the particular spin-flip scattering and **B**.

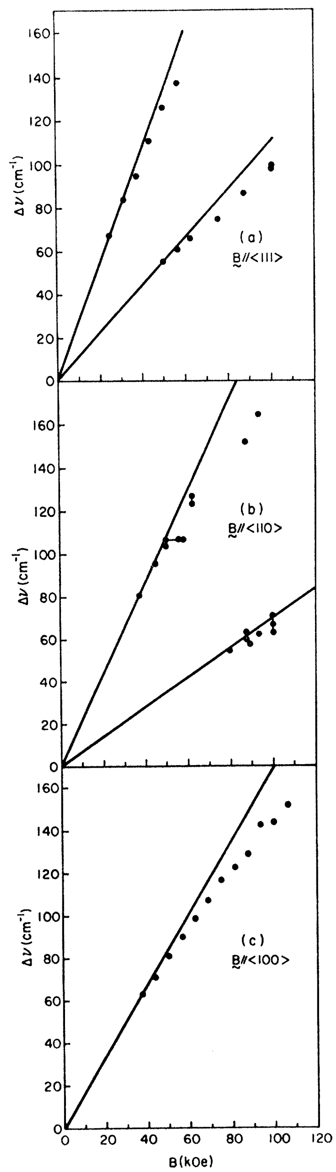

FIG. 1. Frequency shift of spin-flip light in n-PbTe as a function to magnetic field for (a) $\mathbf{B} \| \langle 111 \rangle$, (b) $\mathbf{B} \| \langle 110 \rangle$, and (c) $\mathbf{B} \langle 100 \rangle$.

In previous experiments on isotropic semiconductors[4] we had observed the intensity of the spin-flip transition increasing steadily with the magnetic field, as expected from the field-independent cross section in Eq. (3) and the increasing density of states available. However, in the situation of Fig. 1(a) and (b) where we have two sets of electron valleys at different angles to **B**, an interesting magnetic field dependence was observed for intensities of the two different spin-flip transitions. In both cases, the observed scattered light intensity of the high g-value spin-flip transition decreased gradually and finally disappeared abruptly at $B \approx 60$ kOe for $\mathbf{B} \| \langle 111 \rangle$, and at $B \approx 90$ kOe for $\mathbf{B} \| \langle 110 \rangle$. On the other hand the low g-value line intensity became stronger, and was the strongest at the highest magnetic field with a sudden increase in intensity concurrent with the disappearance of the high g-value spin-flip transition. This intensity dependence may be explained in terms of shifting of electrons from valleys at small angles to $\mathbf{B}$ to the valleys at large angles to $\mathbf{B}$. This phenomenon is expected to arise when the energy separation between the lowest Landau sublevels for the two valleys becomes larger than or comparable to E_F, i.e., when magnetic field is such that

$$\tfrac{1}{2}[(\hbar\omega_c(\theta_1) - g_{\theta_1}\mu B) - (\hbar\omega_c(\theta_2) - g_{\theta_2}\mu B)] \gtrsim E_F(B), \quad (4)$$

where $\omega_c(\theta_1)$ is the cyclotron frequency of electrons in θ_1 valley, g_{θ_1} is the g value of electrons in θ_1 valley, and the subscript 2 applies to the second valley, with $\theta_2 > \theta_1$. The field dependence of E_F at the quantum limit can be neglected in first order. For $\mathbf{B} \| \langle 111 \rangle$, $\theta_1 = 0$, and $\theta_2 = 70°32'$ and with $n_e \approx 10^{17}$ cm^{-3}, the inequality in Eq. (4) is satisfied for $B \gtrsim 50$ kOe, which agrees with experimentally observed magnetic field at which the high g-value transitions disappears. For $\mathbf{B} \| \langle 110 \rangle$, Eq. (4) is satisfied when $B \gtrsim 90$ kOe, which also agrees with the experimental observation of disappearance of the high g-value line for this orientation. Thus we believe the magnetic field dependence of the relative intensities of different g-value transitions shows the intervalley shifting of electrons in PbTe very clearly.

The measured linewidth of the spin-flip scattered light was $\lesssim 2$ cm^{-1} and was limited by the spectrometer resolution. Contributions to the width from nonparabolic variation of the g values and Doppler broadening of scattered radiation account for at least a ~ 2 cm^{-1} linewidth. The $\Delta l = 1$ and $\Delta l = 2$ transitions are also expected to have scattering cross sections comparable to the spin-flip transition; however, these could not be observed in any of the present experiments. Large electron-collision broadening, broadening due to variation of m^* in the nonparabolic band,[4] and broadening due to polaron interaction,[10] may account for the absence of Landau Raman scattering. In addition, Raman-scattering from optic phonons in PbTe at $\Delta\nu = 30$ and 100 cm^{-1} could not be observed which allows us to put an upper limit of $\sim 10^{-12}$ for the Raman scattering efficiency by optic phonons. The ω_0^4 dependence for optic-phonon Raman scattering accounts for these low cross sections.[11] No spin-phonon interaction was observed.

These results should remove the confusion between previous measurements of g values in PbTe. The discrepancy between our measurements and theory indicates a need for further theoretical investigations. Improvement in detection sensitivity and spectral resolution closer to the laser frequency may reveal other interesting details of electron-gas modes.

We wish to thank P. A. Wolff for helpful suggestions, P. H. Schmidt for PbTe samples, Miss L. Rhodes for polishing and orienting the samples, and R. J. Kerl for assistance in taking data.

[10] C. J. Summers, P. G. Harper, and S. D. Smith, Solid State Commun. 5, 615 (1967).

[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), p. 368.