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# Spin-flip acceptor scattering in ZnTe

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Two transitions have been observed in ZnTe:As and in ZnTe:P. These are interpreted as the $-3/2 \rightarrow -1/2$ and $-3/2 \rightarrow +1/2$ transitions of holes bound to the shallow arsenic and phosphorous acceptors. The deduced bound-hole gyromagnetic ratio is similar in each case: $g_{1/2} = 0.61 \pm 0.04$; $g_{3/2} = 0.63 \pm 0.04$ for ZnTe:P and $g_{1/2} = 0.37 \pm 0.04$ and $g_{3/2} = 0.39 \pm 0.04$ for ZnTe:As. These ZnTe:P values are in excellent agreement with the shallow acceptor $g$ value $g_h = 0.59 \pm 0.05$ obtained by Dean *et al.* from luminescence Zeeman studies, but both As and P values are significantly smaller than the values for free holes obtained from theory ($0.92 \pm 0.15$, Hollis) and experiment (0.9–1.1, Hollis and Scott, spin-flip scattering; $0.89 \pm 0.10$, Venghaus *et al.*, magnetoreflectivity). The difference between free- and bound-hole $g$ values is interpreted in terms of Hollis's valence-band theory for ZnTe, which shows that $g_h$ decreases with increasing wave vector near the Brillouin-zone center.

## I. INTRODUCTION

Since the original study of impurity electronic Raman scattering in semiconductors was made by Henry *et al.*[1] in 1966, this technique has been applied to silicon,[2,3] GaAs,[4] GaP,[5] and Ge.[6] Raman studies of semiconductor transitions in which the impurity-spin state changes have been, however, relatively rare. The first impurity spin-flip scattering experiment was done on CdS by Thomas and Hopfield,[7,8] who examined both donor and acceptor transitions. Subsequent spin-flip experiments on CdS have dealt exclusively with donors.[9-17] Acceptor spin-flip scattering has been reported in several papers on ZnTe,[18-21] however, these have emphasized free-hole spin flip. Very recently a preliminary report of acceptor spin flip in ZnTe:P was published[22] and a detailed analysis of acceptor spin-flip scattering in GaP:Zn by Chase *et al.*[23]

## II. ZnTe STUDIES

In the present work we extend our earlier spin-flip studies[18-21] of nominally pure ZnTe to well characterized samples of ZnTe:As and ZnTe:P. These materials have been previously studied by Raman spectroscopy in zero applied field.[24,25] The principal result from the present work is the hole $g$ value. Our spin-flip values for both free holes ($g_{hh} \sim 0.9-1.0$) and shallow bound holes ($g_h = 0.62 \pm 0.04$) agree extremely well with very recent results of Dean *et al.*[26] ($g_h = 0.59 \pm 0.05$) and Venghaus *et al.*[27] ($g_{hh} = 0.89 \pm 0.10$).

### A. Experimental

Samples were cut from large boules of ZnTe grown for earlier experiments[24,25] having (0.01–0.05)% As or P by weight. Specimens were ~1×5×5 mm. They were red and transparent. Excitation was ~40 mW at 520.8 nm from a Kr-ion laser. Samples were immersed in liquid He below the λ point, at 1.6–1.8 K. Right-angle scattering geometries were employed. Other experimental details are in Ref. 21.

Spectra were obtained with a 0.85-m focal length double grating monochromator operating with 20-$\mu$m-slit widths and ~0.6-cm$^{-1}$ spectral resolution. About $3 \times 10^5$ counts/sec were obtained for the $g = 0.40$ line of ZnTe:As under these conditions.

### B. Theory: $g$ values

The valence band in zinc-blende structures such as ZnTe is fourfold degenerate at the Brillouin-zone center, approximating an atomic $p_{3/2}$ wave function. Consequently, the free-hole spin levels will be quantized into $M = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$ states by an external magnetic field. The energies of these spin states are given by the spin Hamiltonian

$$\mathcal{H} = \mu_B g (J_x H_x + J_y H_y + J_z H_z) + \mu_B g' (J_x^3 H_x + J_y^3 H_y + J_z^3 H_z) \quad (1)$$

The $J_i^3$ terms produce unequal splittings between states; i.e., the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ energy spacing is not equal to the $+\frac{1}{2} \leftrightarrow +\frac{3}{2}$ or $-\frac{1}{2} \leftrightarrow -\frac{3}{2}$ transition. Some authors have described this effect by using two different gyromagnetic ratios, denoted $g_{1/2}$ and $g_{3/2}$ and given by

$$g_{1/2} = g + \tfrac{1}{4} g' , \quad (2)$$

$$g_{3/2} = g + \tfrac{9}{4} g' . \quad (3)$$

The effect of these considerations upon EPR spec-

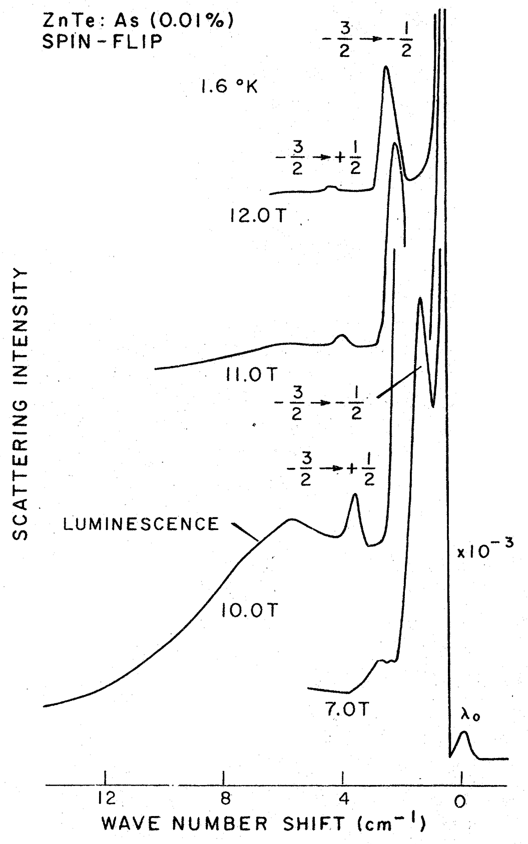

FIG. 1. Spin-flip scattering in ZnTe:As at various fields. The transitions at $h\,\Delta\omega/\mu_B H \approx 0.40$ and 0.77 are $-\frac{3}{2}\rightarrow-\frac{1}{2}$ and $-\frac{3}{2}\rightarrow+\frac{1}{2}$, respectively; 40 mW at 520.8 nm; $T=1.8$ K; 30$\mu$m slits; $10^6$ counts/sec; full scale.

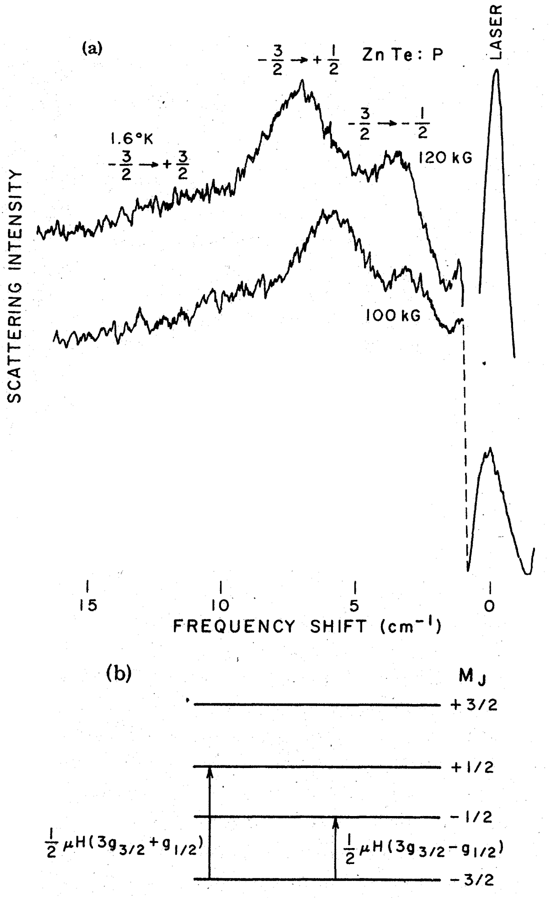

FIG. 2. (a) Spin-flip scattering in ZnTe:P from Ref. 22. The transition at $h\,\Delta\omega/\mu_B H = 0.64$ is $-\frac{3}{2}\rightarrow-\frac{1}{2}$ and at $h\,\Delta\omega/\mu_B H = 1.25$ is $-\frac{3}{2}\rightarrow+\frac{1}{2}$. In Ref. 22 the latter was erroneously assigned as $-\frac{1}{2}\rightarrow+\frac{1}{2}$. (b) Energy-level diagram for spin-$\frac{3}{2}$ system.

tra is well known: two strong nearly degenerate transitions are observed near $\hbar\omega = \mu g H$ [to be precise, at $\hbar\omega = \mu H(\frac{3}{2}g_{3/2} - \frac{1}{2}g_{1/2})$ and $\hbar\omega = \mu H g_{1/2}$] and a very weak transition at $\hbar\omega = 3g_{3/2}\mu H$. The Raman transitions are different, however: $\Delta M = 0, \pm 1, \pm 2$ are all allowed.

At the temperatures of our experiments (~1.6 K), the $-\frac{3}{2}$-spin level will be preferentially populated. (No experiments were performed above 2.1 K because of liquid-helium bubbling.) Consequently, only the $-\frac{3}{2}\rightarrow-\frac{1}{2}$ and $-\frac{3}{2}\rightarrow+\frac{1}{2}$ transitions are expected to be measureable. The data are in accord with this hypothesis.

Figure 1 illustrates representative ZnTe:As data at fields up to 12 T, and Fig. 2(a) shows earlier data on ZnTe:P. We do not resolve in Fig. 1 the splitting of the $-\frac{3}{2}\rightarrow-\frac{1}{2}$ and $-\frac{1}{2}\rightarrow+\frac{1}{2}$ transitions

TABLE I. Gyromagnetic ratios for shallow bound holes in ZnTe.

| $g$ Value[a] | Technique | Ref. |
|---|---|---|
| $g_{1/2}=0.37\pm0.04$<br>$g_{3/2}=0.39\pm0.04$ | ZnTe:As spin-flip | Present work |
| $g_{1/2}=0.61\pm0.04$<br>$g_{3/2}=0.63\pm0.04$ | ZnTe:P spin-flip | Present work |
| $g=0.59\pm0.05$ | Zeeman luminescence | 26 |

[a] These $g$ values are not in good agreement with the free- (heavy-) hole values known from other work for the shallowest Landau level. The free-hole $g$ values are summarized in Table II.

TABLE II. Gyromagnetic ratios for free heavy holes (shallowest Landau level, $K = 0$).

| $g$-values | Technique | Ref. |
|---|---|---|
| $g_{hh} = 0.92 \pm 0.15$ | Kohn-Luttinger theory | 20 |
| $g_{hh} = 0.9 - 1.1$ | Spin-flip experiments | 21 |
| $g_{hh} = 0.89 \pm 0.10$ | Free-exciton magnetoreflectivity | 27 |

(nearly degenerate). These data yield $g$ values summarized in Table I. Figure 2(b) shows schematically the effect of the $g'$ term in Eq. (1).

The sign of $g_{3/2} - g_{1/2}$ is definitely positive and yields $g' = +0.01$ in Eq. (1). This is the same sign and magnitude found for shallow acceptors in Si.[22]

We believe that the difference between the value $g_{hh} \approx 0.9$ in Table II and $g_h \approx 0.6$ in Table I can be explained using the Hollis valence-band calculation, reproduced in Fig. 3. This figure shows that the spin splitting of the uppermost Landau level decreases from $g_{hh} \sim 1$ at $k_H = 0$ to zero at $k_H \sim 5 \times 10^5$ cm$^{-1}$, at which point it changes sign. The bound excitons studied in ZnTe have diameters of order 30 Å. Consequently, the wave functions for holes in these localized states will be derived from free-hole wave functions from $k = 0$ to $k \sim \frac{1}{30}$ Å $\sim 3 \times 10^6$ cm$^{-1}$. The average $g$ value over this region of the Brillouin zone is much less than the $k \approx 0$ value of 0.9–1.0. The binding energies of P and As are different (~60 and 74 meV) and consequently different $g$ values are predicted from this argument, with the shallower P having $g$ nearer the free-hole value.

### C. Cross sections

Both ZnTe:P and ZnTe:As samples were grown with (0.01–0.05)% dopant by weight. If we assume that each of the impurities has a bound hole at 1.6 K, the measured ZnTe:As intensities yield a cross section of ~$1.5 \times 10^{-21}$ cm$^2$/sr spin, by comparison with intensities for $Ba_2NaNb_5O_{15}$, for which the absolute cross section is known. It is comparable to the value per spin obtained by Fleury and Scott,[9] and by Romestain and Geschwind[28] for CdS near resonance. The large cross sections in ZnTe:As make this a good candidate for a spin-flip laser,[10] or for Raman spin-echo experiment.[14]

### D. Spin temperatures

For ZnTe:As with an As concentration of 0.05% by weight and 520.8-nm excitation (at resonance), we find spin temperatures from Stokes to anti-Stokes ratios to be ≥130 K at lattice temperatures of 1.6–1.8 K. Farther off resonance we obtain spin temperatures comparable to the lattice temperature. Similar results were described in Ref. 21.

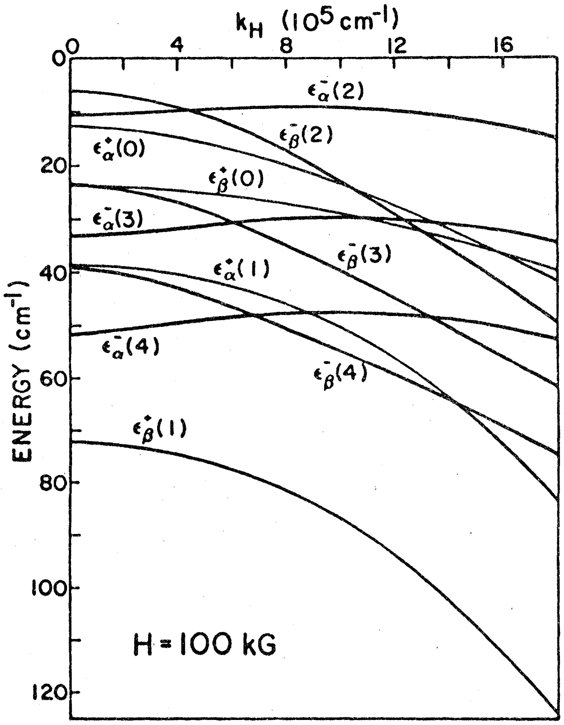

FIG. 3. ZnTe valence bands at $H = 10$ T, from Ref. 20.

## III. SUMMARY

The gyromagnetic ratios for holes bound to the shallow acceptor P in ZnTe are found to be 0.61–0.63 (±0.04), in excellent agreement with the value $0.59 \pm 0.05$ from luminescence[26] for an unknown acceptor at 149-meV binding energy. These values are ~30% less than those for free holes, known to be $g_{hh} \sim 0.9$ from spin-flip scattering,[21] theoretical calculations,[20] and free exciton magnetoreflectivity.[27] ZnTe:As exhibits smaller $g$ values, comparable to the 0.4 value for conduction electrons in ZnTe calculated by Cardona.[29] We do not believe that the $g \sim 0.4$ line in ZnTe:As is due to photoexcited free electrons, because no likely excitation mechanism would yield electron spin-flip intensities much larger than hole spin-flip intensities in this material.

## ACKNOWLEDGMENTS

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