PHYSICAL REVIEW B VOLUME 19, NUMBER 6 15 MARCH 1979

Magnetic field dependence of electronic Raman scattering from ZnTe:Li and ZnTe:As

J. F. Scott, F. Habbal,* J. H. Nicola,† and D. J. Toms
Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado 80309

S. Nakashima
Department of Applied Physics, Faculty of Engineering, University of Osaka, Osaka, Japan

(Received 19 October 1978)

The field dependence of Raman scattering from $1S \rightarrow 2S$, $1S \rightarrow 3S$, and $1S \rightarrow 2P$ transitions of arsenic and lithium acceptors in zinc telluride has been measured at magnetic fields up to 14 T. Eight electronic and two impurity vibrational transitions are identified in ZnTe:As. Seven of the electronic transitions originate in the $1S_{3/2}$ ground state. The eighth originates from the photoexcited level $2P_{5/2}(\Gamma_7^-)$ and terminates on the vibronic state $2S_{3/2}$ + LO.

INTRODUCTION

Several recent papers[1-3] have analyzed the electronic Raman spectra of shallow acceptors in ZnTe. Typically, the spectra are characterized by three intense transitions at 59, 65, and 85 meV, which are assigned, respectively, as the $1S_{3/2} \rightarrow 2S_{3/2}$, $1S_{3/2} \rightarrow 3S_{3/2}$, and $1S_{3/2} \rightarrow 2S_{3/2} +$ LO transitions of the acceptors, e.g., As, Li, P, or Na. Here LO designates the longitudinal-optical phonon energy for long wavelengths ($k \cong 0$). Other weaker features are observed for which the assignments are less certain.

In the present work we report the Raman spectra of such shallow impurity transitions as functions of applied magnetic fields, for fields from zero to 14 T. Frequency shifts up to 13 cm^{-1} are observed. The transitions include $1S \rightarrow 2S$ and $1S \rightarrow 2P$. Very recently, Patel and Yafet have proposed[4] that Raman scattering from such shallow impurity electronic transitions with a 151-μm-wavelength NH$_3$ laser as pump could produce a tunable Raman laser for wavelengths 325–625 μm (i.e., a 15-cm^{-1} shift from 16.0 to 30.7 cm^{-1}—the same magnitude we observe). In addition to the importance as a potential device of this sort, the magnetic field dependence of electronic Raman spectra of shallow acceptors in ZnTe gives considerable information about the nature of the transitions, as we shall show. In particular, we find that the $H = 0$ features at 20.9 and 32.2 meV assigned previously[2] as impurity-induced vibrations (either resonance modes or defect-allowed density-of-states peaks) cannot be vibrational in nature; their strong field dependences identify them as electronic.

EXPERIMENTAL

The data reported here were obtained from samples of ZnTe grown with 0.05% As or 0.01% Li by weight. These are samples from the same boules used earlier[1-3] for work in zero field. They were illuminated with about 200 mW of yellow 568-nm light from a krypton ion laser. Samples were immersed in liquid helium at 1.6–1.8 K. A right-angle geometry was employed with field H perpendicular to the scattering plane. Data were collected at fields up to 14 T. Detection was by means of a 0.85-m double spectrometer (Spex 1401), cooled RCA 31034*A* phototube, and ratemeter.

Typical data for ZnTe:Li are shown in Figs. 1

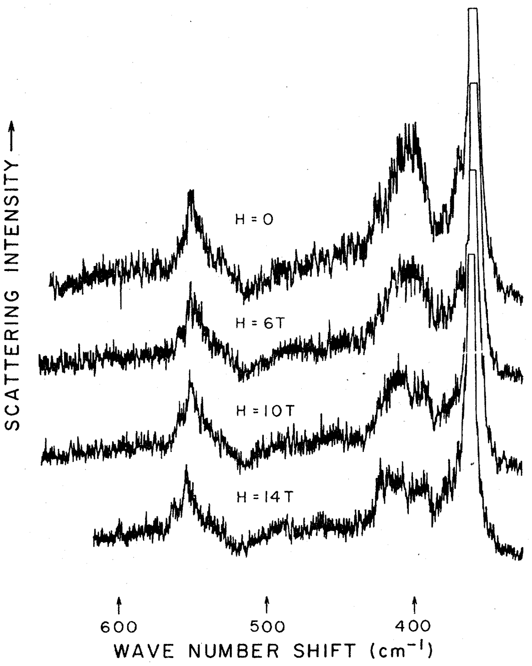

FIG. 1. ZnTe:Li Raman data for the region 320–600 cm^{-1} at H = 0, 6, 10, and 14 T.

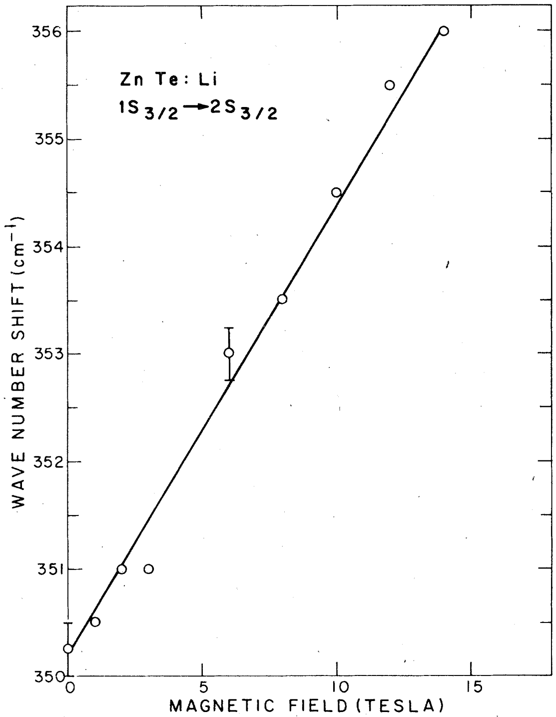

FIG. 2. Field dependence of the $1S_{3/2} \rightarrow 2S_{3/2}$ transition of Li in ZnTe. The slope corresponds to a "g" value of 0.84.

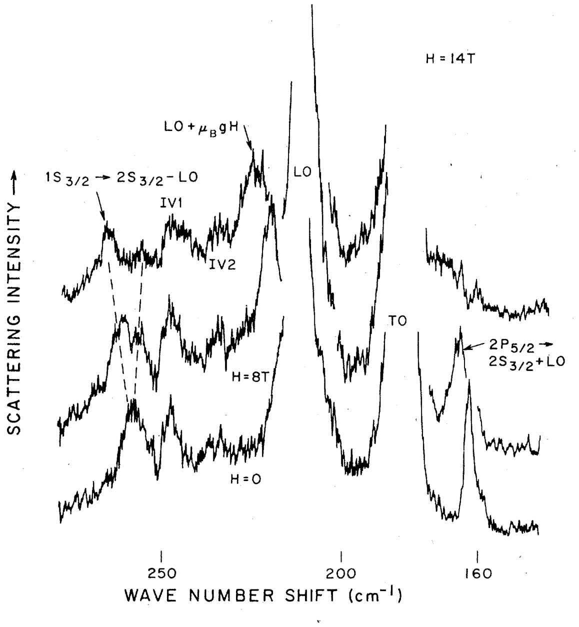

FIG. 3. ZnTe:As Raman data for the region 150–270 cm^{-1} at H = 0, 8, and 14 T.

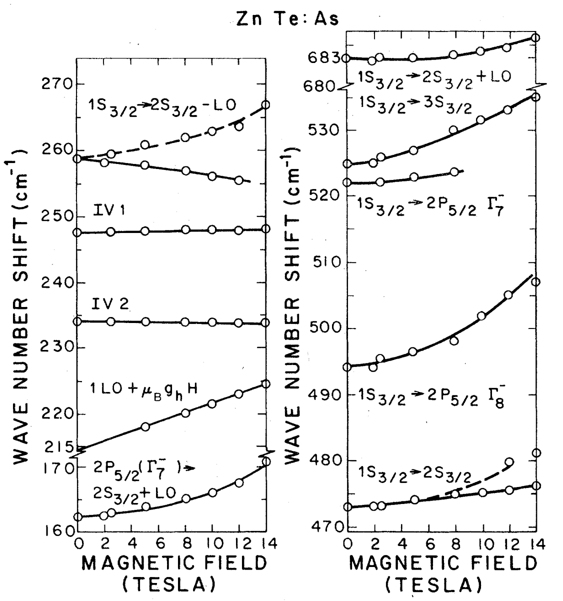

FIG. 4. Graphs of As electronic transition energies in ZnTe vs applied magnetic field.

and 2, for ZnTe:As in Fig. 3. Because of the broader linewidths in our ZnTe:Li samples, quantitative measurements of field dependence were accurate for only the $1S_{3/2} \rightarrow 2S_{3/2}$ transition. A linear field dependence was observed with a slope "g" $= \hbar\omega/\mu_B H = 0.84$, as shown in Fig. 2. This value is comparable to that known for free ($k \cong 0$) heavy holes[5,6] or for holes bound to lithium acceptors.[7,8]

The data for ZnTe:As are much more complete and are summarized in Fig. 4.

ANALYSIS

The magnetic field dependence of donor and acceptor levels in semiconductors is an old and complicated problem. Both infrared[9–11] and luminescence techniques[12,13] have been employed experimentally. The diamagnetic contributions to the $1S \rightarrow 2S$ and $1S \rightarrow 2P_{\pm}$ transitions are quadratic in magnetic field strength H and are expected[12] to be of nearly the same magnitude. The electronic transitions can be readily identified, however, from their zero-field energies and the calculations of Baldereschi and Lipari.[14] We identify the following transitions unambiguously: $1S \rightarrow 2S$, $1S \rightarrow 3S$, $1S \rightarrow 2P$, with LO phonon sidebands. A summary is given in Table I. The transitions at 259 cm^{-1} ($1S_{3/2} \rightarrow 2S_{3/2} - \mathrm{LO}$) and at 162 cm^{-1} ($2P_{5/2} \rightarrow 2S_{3/2} + \mathrm{LO}$) had been misassigned as vibrational in the earlier zero-field study.[2]

The lines at 247.5 and 234 cm^{-1} are field inde-

TABLE I. Transition energies for As in ZnTe.

Assignment	Measured energy (cm^{-1}) (present work) $H=0$	Measured energy (Ref. 2)	Theory (Ref. 14)
$1S_{3/2} \rightarrow 2S_{3/2}+\mathrm{LO}$ (1LO = 213 cm^{-1})	683 ± 1	684 ± 2	
$1S_{3/2} \rightarrow 3S_{3/2}$	525 ± 1	528 ± 2	...
$1S_{3/2} \rightarrow 2P_{5/2}(\Gamma_7^-)$	522 ± 1	522 ± 1 (infrared)	504
$1S_{3/2} \rightarrow 2P_{5/2}(\Gamma_8^-)$	494 ± 1	494 ± 1 (infrared)	448
$1S_{3/2} \rightarrow 2S_{3/2}$	473 ± 1	474 ± 1	442
$1S_{3/2} \rightarrow 2S_{3/2}-\mathrm{LO}$	259 ± 1	260 ± 2	...
$\mathrm{LO}+\mu_B gH$	214 ± 1	...	...
$2P_{5/2}(\Gamma_7^-) \rightarrow 2S_{3/2}+\mathrm{LO}$	162 ± 1	169 ± ?	

pendent. We believe that they are both impurity local vibrations (IV). The line at 247.5 cm^{-1} (IV 1) is probably the local vibration of As impurities at Te sites. The mode at 234 cm^{-1} is also thought to be the localized vibration of a lighter ion at a Te site; it could be Sn, since our spectrochemical analysis of the sample[15] revealed 0.04-wt% Sn as an unintentional dopant.

The remaining spectral feature has a zero-field energy at ~213 cm^{-1} and is indistinguishable from the LO phonon at small fields. It increases in energy very linearly to 225 cm^{-1} at $H = 14$ T. It is identified as the LO phonon plus hole spin-flip. This process was first reported in Ref. 16. The g value deduced is simply the slope of the ω vs H curve in Fig. 4 and is approximately 1.8. This is significantly greater than that of the electrons[17,18] in ZnTe ($g \approx 0.39$) or the shallow holes[18,19] ($g \approx 0.62$). However, g values for unidentified traps of $g = 2.12$ and 1.74 were measured in earlier work in this laboratory[20] on relatively impure ZnTe samples. We do not therefore believe that it is likely that this transition involves holes bound to As acceptors. Transitions involving $1\mathrm{LO}+\mu_B gH$ with $g \approx 0.6$ for holes bound to shallow acceptors would not be observable in our data, due to the much greater intensity of the LO phonon peak nearby.

The last and lowest transition lies at 162 ± 1 cm^{-1} at $H = 0$. Earlier measurement[2] of this unassigned feature yielded a value of 169 cm^{-1} for this line under worse resolution and signal-to-noise ratio. It was suggested[2] that it might be a vibrational "gap" mode. The field dependence measured in the present work shows that its origin is electronic. Its energy is too low for it to be due to $1S_{3/2} \rightarrow 2P_{3/2}-\mathrm{LO}$, which is calculated as 173 cm^{-1}, using the infrared value[2] of 386 ± 1 cm^{-1} for $1S_{3/2} \rightarrow 2P_{3/2}$.

We believe that a plausible assignment for this line is $2P_{5/2}(\Gamma_7^-) \rightarrow 2S_{3/2}+\mathrm{LO}$. The energy for this transition is calculated from $1S \rightarrow 2S_{3/2} = 473$ cm^{-1} and $1S_{3/2} \rightarrow 2P_{5/2}(\Gamma_7^-) = 522$ cm^{-1} to be 164 ± 2 cm^{-1}. Although the $2P_{5/2}$ level at 522 cm^{-1} is not thermally excited at 1.8 K, it is strongly photoexcited. ($1S \rightarrow 2P$ has the largest dipole moment of any of the infrared transitions.) Thus under the conditions of our experiment, $(2P_{5/2} \rightarrow 1S_{3/2}+\mathrm{LO})$ should be observable at 162 – 164 cm^{-1}.

ACKNOWLEDGMENT

This work was supported by NSF Grant No. DMR-78-02552.

---

*Present address: Division of Applied Sciences, Harvard Univ. Cambridge, Mass. 02138.

†Present address: Institute Gleb Wataghin, University of Campinas, Campinas, S. P. Brazil.

[1] S. Nakashima, H. Kojima, and T. Hattori, Solid State Commun. 15, 1699 (1974).

[2] S. Nakashima, H. Kojima, and T. Hattori, Solid State Commun. 17, 689 (1975).

[3] S. Nakashima, T. Hattori, P. E. Simmonds, and E. Amzallag (unpublished).

[4] C. K. N. Patel and Y. Yafet (unpublished).
[5] R. L. Hollis, Phys. Rev. B 15, 932 (1977).
[6] R. L. Hollis and J. F. Scott, Phys. Rev. B 15, 942 (1977).
[7] P. J. Dean, H. Venghaus, J. C. Pfister, B. Schaub, and J. Morine, J. Lumin. 16, 363 (1978).
[8] D. J. Toms, C. A. Helms, J. F. Scott, and S. Nakashima, Phys. Rev. B 18, 871 (1978).
[9] G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, Solid State Commun. 7, 921 (1969).
[10] E. M. Gershenzon, G. N. Gol'tsman, and A. I. Elant'ev, Sov. Phys. JETP 45, 555 (1977).
[11] E. M. Gershenzon, G. N. Gol'tsman, and M. L. Kagane, Sov. Phys. JETP 45, 769 (1977).
[12] J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961).
[13] E. F. Gross, B. P. Zakharchenya, and B. S. Razbirin, Sov. Phys. Solid State 3, 2243 (1962).
[14] A. Baldereschi and N. O. Lipari, Phys. Rev. B 8, 2697 (1973); 9, 1525 (1974).
[15] Analysis by Eagle Picher Co., Miami, Oklahoma.
[16] R. L. Hollis, J. F. Ryan, and J. F. Scott, Phys. Rev. Lett. 34, 209 (1975).
[17] P. J. Dean, H. Venghaus, J. C. Pfister, B. Schaub, and J. Marine, J. Lumin. 16, 363 (1978).
[18] D. J. Toms, J. F. Scott, and S. Nakashima, Phys. Rev. B 19, 928 (1979).
[19] D. J. Toms, C. A. Helms, J. F. Scott, and S. Nakashima, Phys. Rev. B 18, 871 (1978).
[20] R. L. Hollis, J. F. Ryan, D. J. Toms, and J. F. Scott, Phys. Rev. Lett. 31, 1004 (1973).