ELECTRONIC RAMAN SCATTERING BY ACCEPTORS IN GaP

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We have measured electronic Raman scattering by the neutral acceptors Zn and Mg in GaP and have observed transitions between the degenerate orbitals of the ground state, transitions to higher bound states, and transitions to the valence band. We also observe a phonon wing accompanying the lowest electronic transition.

For more than a decade, infrared spectroscopy has been used to study the electronic levels of donors and acceptors.[1] Another method for studying electronic transitions occurring at infrared energies is Raman scattering. Up to now, electronic Raman scattering has been observed only in the study of pure rare-earth crystals containing rare-earth atoms.[2-4] In this Letter, we report the observation of electronic Raman scattering transitions by the neutral acceptors Zn and Mg in GaP. The neutral acceptor consists of a hole trapped on a group II impurity. We observe transitions of the hole from its ground-state orbital to another orbital of the degenerate ground state, to higher states, and to the valence band.

The Raman spectra were recorded photographically using a two-meter Bausch and Lomb $F/18$ spectrograph. Spectra were taken with both the 6328-Å (50 mW) and the 6118-Å (2 mW) lines of a He-Ne gas laser as the light source. Exposure times ranged from a few minutes to several hours. By using two laser lines we were able to distinguish between Raman scattering and luminescence. The spectra were recorded at 20°K by immersing the samples in a stream of cold He gas.

The chief experimental difficulty was that the doped gallium phosphide samples used in these experiments were strongly luminescent when excited with the laser light at low temperatures, even though the energy of the laser light was less than the band-gap energy. The luminescence often completely masked the Raman spectrum. The strength and wavelength dependence of the luminescence depended upon the impurity content of the sample. Thus far, by sample selection, we have observed a luminescence-free Raman spectrum only for the acceptors Zn and Mg. The Mg-doped samples were grown by the floating-zone method, while the Zn-doped samples were grown by the water-vapor growth method.[5]

Figure 1 is an energy-level diagram showing the various acceptor transitions labeled A, B, C, and D. The Raman scattering spectra are shown in Figs. 2(a)-2(d). According to the effective-mass theory of acceptor states, the acceptor ground state is four-fold degenerate with symmetry Γ_8, the symmetry of the valence band. Transition A is a zero-energy transition between the degenerate ground-state orbitals of the acceptor. It is observable because the ground-state levels are broadened

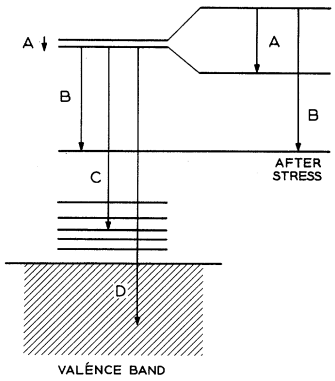

FIG. 1. An energy-level diagram showing transitions of the hole from its ground state orbital to: A, another orbital of the degenerate ground state; B, the first excited state; C, the higher bound excited states; and D, the valence band.

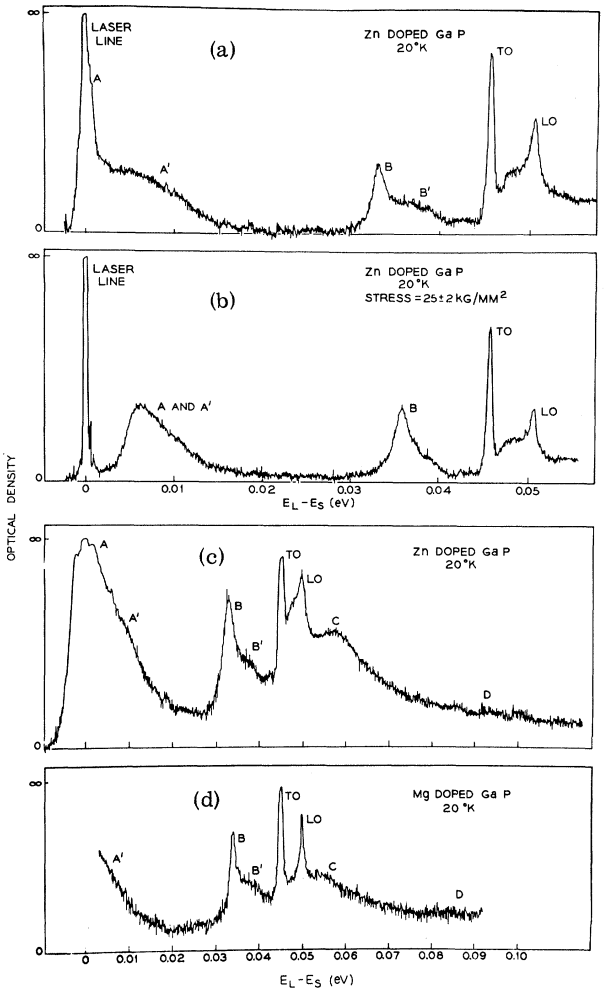

FIG. 2. (a) The low-energy portion of the Zn-acceptor spectrum; (b) the same spectrum as (a) but with a uniaxial stress applied to the crystal; (c) the entire Zn-acceptor spectrum; (d) the entire Mg-acceptor spectrum. These spectra were taken using a He-Ne 6328 Å laser beam. $E_L = 1.959$ eV. In a pure crystal, only the first-order Raman scattering lines, labeled LO and TO, would appear.

by strain with a width of about 1 meV. This transition is clearly observed in Fig. 2(a). (A pure crystal would show only the first-order lattice Raman scattering lines, labeled LO and TO. The second-order Raman scattering spectrum is too weak to be observed in the data in Fig. 2.) Spectrum 2(a) was taken using a sample of high optical quality. Because the quality was so high in this case, there was very little scattered light at the laser frequency, which typically hinders the recording of Raman spectra at energies near the energy of the laser line.

By stressing the sample one can split the ground state into two Kramers doublets. As shown in Fig. 1, this causes transition A to shift away from the laser line by the energy of the ground-state splitting. Figure 2(b) shows a Raman spectrum of the Zn acceptor with a stress of 25 ± 2 kg/mm^2 applied in the 111 direction. Transition A shifts away from the laser line by about 6 meV.

Associated with the electronic transition A is an acoustic phonon wing A'. Phonon wings may accompany electronic Raman scattering transitions just as they accompany many electronic transitions in absorption and emission spectra. This transition is most clearly seen in Fig. 2(a). The intensity of the phonon wing drops to half its maximum value at about 12 meV. It is known that the acoustic phonon branches extend to much higher energies. For example, Dean and Thomas[6] found the energy of the longitudinal acoustic branch at point X of the Brillouin-zone edge to be 31.3 ± 0.05 meV. The cutoff of the one-phonon acoustic phonon wing occurs because only long-wavelength phonons can affect the acceptor. The acceptor ground state is spread over many primitive cells. The acceptor will not be greatly affected by lattice waves with wavelengths small compared with the dimensions of the acceptor ground-state wave function. Therefore, the high-energy zone-edge acoustic phonons do not contribute to the one-phonon wing.

When the sample is stressed, the zone phonon transition A and the phonon wing A' are no longer resolved. See Fig. 2(b). We believe this results from lifetime broadening of transition A. The final state of transition A may decay by emitting a phonon at the stress splitting energy. The rate of this decay will increase as the square of the stress splitting energy, since the acoustic phonon density of states is proportional to the square of the phonon energy.

Transition B to the first excited state of the acceptor is clearly shown in all figures. Its energy was 33.1 meV for Zn and 34.4 meV for Mg. These energies are probably in the gap between the acoustic and optical phonon branches. This may account for the narrow width of this level. The transition labeled B' may be an acoustic phonon wing accompanying B. Transition B did not split under stress. For small stresses, transition B shifted by about one-half the shift of transition A. The shape change of tran-

sition A made measurement of these shifts imprecise. One consistent interpretation of this is that energy level B is a Kramers doublet (Γ_6 or Γ_7) and does not shift with stress. As shown in Fig. 1, this would give a shift of transition B that is just one half the shift of transition A.

Transitions C, to the higher bound states, and transitions D, to the valence-band continuum, are shown in Figs. 2(c) and 2(d). Transition C shows little resolved structure. The lack of structure could be due to these transitions having phonon wings. It may also result from concentration broadening of these levels. We estimate from resistivity measurements that the acceptor concentrations are about 4×10^{18} cm^{-3}. Newman[7] has found that acceptor transitions in Si begin to broaden for concentrations above 10^{16} cm^{-3} and most of the line structure is destroyed for concentrations of 10^{18} cm^{-3}. Samples with lower concentrations of Zn have been investigated, but strong fluorescence masked the Raman lines.

The peak labeled C ends at about 71 meV for Mg and 76 meV for Zn. This peak is followed by a broad transition which we interpret as transition D to the valence band. It is impossible from these data to know precisely the energy at which the valence-band transitions begin. Dean, Cuthbert, Thomas, and Lynch[8] have recently made an accurate determination of the binding energy of the S donor by studying the decay of an exciton bound to this donor. This enabled them to estimate the binding energy of the Zn acceptor, since the sum of the S-donor and Zn-acceptor binding energies is known.[6] They found the binding energy for Zn to be 62 $\pm$ 4 meV. This value is compatible with our interpretation of the Raman spectrum for Zn, since peak C, identified as bound transitions, peaks below 62 meV while the flat spectrum D, identified as transitions to the continuum, occurs above 62 meV.

Finally, it should be noted that the 33.1-meV energy of transition B is only about $\frac{1}{2}$ the acceptor binding energy. This transition energy is low compared with infrared acceptor transitions found in Si and Ge, which generally start at about $\frac{3}{4}$ of the binding energy. Whether the low-lying level associated with transition B is analogous to acceptor levels observed in Si and Ge or is of a different nature remains to be determined.

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VIRTUAL TRANSITIONS TO THE CONTINUUM IN O^{16}†

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In a shell-model calculation, one mixes the simplest configurations by a two-body interaction, thus obtaining energy levels. The wave functions are then used to calculate gamma-transition probabilities and cross sections for various nuclear reactions. The interaction strength and exchange mixture parameters are adjusted to agree with some experimental observation, e.g., the level energies. In certain instances it is necessary to introduce admixtures of more complex configurations. The effect of the high-momentum components of the repulsive hard core are usually included in the energy-independent two-body interaction. Seldom considered, however, are the virtual transitions to low-lying continuum states. As a test case, the shifts of the negative-parity levels of O^{16} due to these low-momentum, off-the-energy-shell transitions of both neutrons and protons have been calculated. Their contributions are found to be significantly large.

The shifts are calculated using the theory