table and in which there is at least one heavy element. Perhaps the most surprising value of φ_{Bp} is that for InAs where there is not only an inversion layer on the p-type material but the Fermi level at the interface is actually above the conduction band edge. A striking confirmation of this result is seen in the I - V characteristic (Fig. 1) of a unit prepared on degenerate p-type InAs. The negative resistance region can only occur if the Fermi level is in the conduction band at the surface. Energy values determined from peak and valley voltages agree with those obtained from capacitance data.

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EVIDENCE FOR THE ROLE OF DONOR STATES IN GaAs ELECTROLUMINESCENCE

F. L. Galeener
National Magnet Laboratory,* Massachusetts Institute of Technology, Cambridge, Massachusetts

and

G. B. Wright, W. E. Krag, T. M. Quist, and H. J. Zeiger
Lincoln Laboratory,† Massachusetts Institute of Technology, Lexington, Massachusetts

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The mechanism of the transition responsible for maser action in GaAs diodes has been the subject of lively interest since the first report of very efficient radiation from GaAs diodes.[1] We wish to report some observations on the effect of a high magnetic field on this emission, which may give some clue to the nature of the transition involved. It will be shown that the observed shift of emission energy with magnetic field can be approximately described by assuming that the transition proceeds through the ground states of donors in GaAs.

The experiments were performed on maser diodes and incoherent diodes at liquid helium temperatures and on incoherent diodes at liquid nitrogen temperatures. These diodes were zinc-diffused GaAs maser diodes[2] whose net n-type impurity concentration was typically $(2-5)\times10^{17}$ cm^{-3}. They were oriented with the magnetic field in the plane of the junction. The incoherent diodes were pulsed at 13 cps with a peak current of 80 mA, while the maser diodes were pulsed at 300 cps with a peak current of 2.75 A. The field was supplied by a Bitter-type solenoid which gave 90 kG at 10 kiloamperes. A typical recorder trace for a maser diode is shown in Fig. 1. As the field is increased, the emission energy shifts, new peaks appear, and others disappear.[3]

The spacing of electromagnetic modes of the

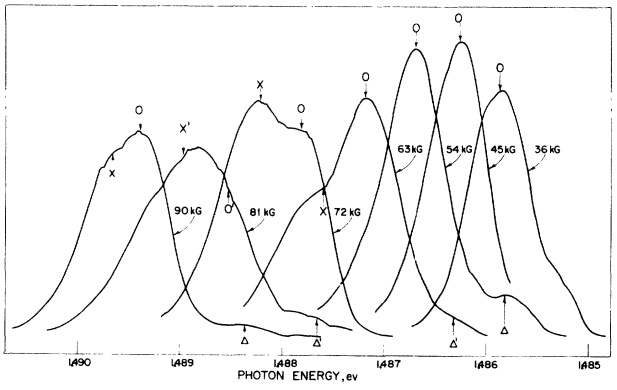

FIG. 1. Recorder trace of GaAs maser emission. Symbols identify the three different series observed. Primed symbols indicate the position of series peaks calculated from the quadratic field dependence.

GaAs diode structure is $\sim 2\times 10^{-4}$ eV. This is considerably smaller than the instrumental resolution used. As the entire spontaneous emission line shifts with field, maser emission takes place in the modes closest to the point of lowest threshold on the spontaneous line. The point on the spontaneous line with the lowest threshold may also change with field, causing a new stimulated emission peak to become prominent.

In Fig. 2(a), we have plotted the energy shift of the points labeled with arrows in Fig. 1, where peaks identified with a given series are indicated by the same symbol. The energy shift of the emission of a given series is quadratic with magnetic field, within experimental error. The shift of peak emission energy with magnetic field for incoherent diodes is shown in Fig. 2(b), where the scatter is greater because of the difficulty of accurately locating the peak of the broad spontaneous emission.

It is interesting to compare the observed quadratic shift with the quadratic shift of a hydrogenic donor in a small magnetic field. This is

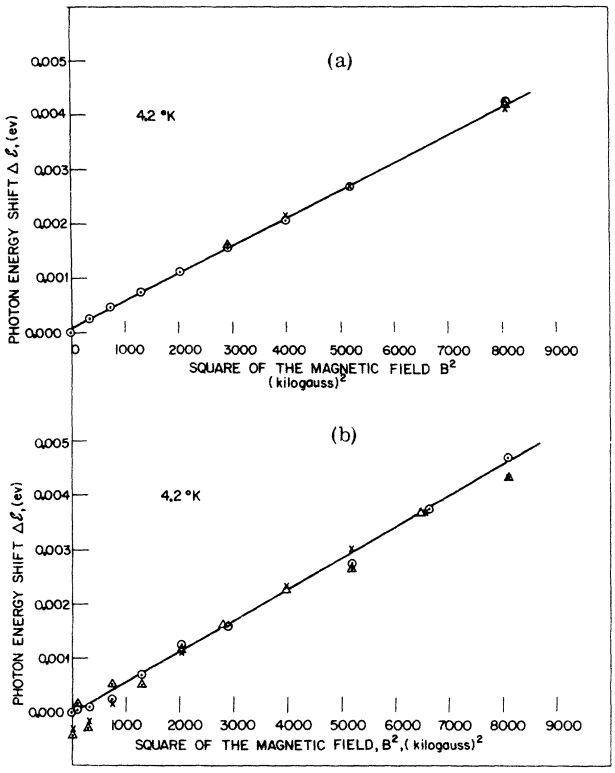

FIG. 2. Shift of emission energy of GaAs diodes with magnetic field: (a) maser diode (triangles, crosses, and circles identify different series); (b) incoherent diodes.

given by

$$\Delta\epsilon = \left(\frac{\hbar^2 e^2/m^2}{13.6}\right)\frac{\kappa^2}{(m^*/m)^3}\frac{B^2}{8},$$

in the effective-mass approximation. When we take the dielectric constant $\kappa = 12.9$,[4] the line for the maser data corresponds to $(m^*/m) = 0.074$, while for the spontaneous emission $(m^*/m) = 0.071$. These values are very close to the accepted conduction electron mass.[5]

This good quantitative fit is a bit puzzling since a hydrogenic impurity in GaAs at 90 kG would experience a magnetic energy shift comparable to the binding energy. The variational calculation of Yafet, Keyes, and Adams[6] indicates that the hydrogenic donor shift on a B^2 plot would deviate quite markedly from a straight line. However, a variational calculation based on a wave function more nearly correct at low magnetic fields[7] gives a shift on a B^2 plot which is more nearly linear, but with a slope reduced by nearly 30%. This would reduce the calculated electron effective mass by approximately 10%, spoiling the apparent close fit. It is nevertheless interesting to speculate that the observed transitions occur from the ground state of a slightly perturbed hydrogenic donor to an acceptor state.

The donor g factor should have a very small effect on the observed emission in a magnetic field. Based on the gap, spin-orbit splitting, and conduction electron mass in GaAs, the conduction electron g factor is $\sim +0.5$,[8] which would give a splitting too small to observe in the present experiment. The ground state of an acceptor is likely to be characterized, loosely speaking, by an effective mass considerably larger than 0.07, giving a much smaller diamagnetic shift than a donor. As shown by Title,[9] the acceptor ground state has a value of $g_\perp$ between ~ 6.7 and 8.1, but the splitting of the acceptor level in a field would be smeared out by the effects of local strain in the lattice. Furthermore, the acceptor binding energy could account for the major part of the shift (~ 0.04 eV) between the gap energy as measured by Sturge,[10] and the radiation observed in GaAs diodes.

Radiative recombination of an exciton bound to a moderately deep donor or acceptor cannot be excluded. Such structures are known to exist,[11] but it is not clear whether their diamagnetic properties can quantitatively explain the observed quadratic shifts.

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OBSERVATION OF REFLECTED LIGHT HARMONICS AT THE BOUNDARY OF PIEZOELECTRIC CRYSTALS*

J. Ducuing and N. Bloembergen

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

(Received 2 May 1963)

The existence of harmonic light waves at the boundary of a nonlinear dielectric medium was predicted by Bloembergen and Pershan,[1] who have given a complete theoretical description for the case of cubic media. In this Letter the experimental verification of some aspects of this theory is reported. The experiments were carried out with materials which absorb both the fundamental and the second harmonic frequencies. The harmonic production was observed in reflection, created by the nonlinear polarization in the absorption depth of both frequencies. This layer is sufficiently thick—of the order of one-sixth optical wavelength—so that the observed effects have the full symmetry of the crystal lattice. They have no relation to surface effects previously reported.[2] The latter are smaller by several orders of magnitude in our case. This is evident from the fact that piezoelectric materials such as tellurium, GaAs, and InSb give signals which are at least two or three orders of magnitude larger than germanium. The signal from the latter crystal, which has bulk inversion symmetry, is not distinguishable from our experimental noise background.

The pulsed, unfocused beam of a ruby laser, Q-switched by a nitrobenzene Kerr cell, passed through an interference filter and was split by a glass plate. The intensity of the small split-off fraction was monitored by the second harmonic intensity it produced in a potassium dihydrogen phosphate crystal, which was not near the condition for phase matching. This method of calibration should give accurate relative values of nonlinearity, since uncertainties in the spatial and temporal distribution due to the multimode nature of the fundamental field are eliminated.[3] The main part of the unfocused laser beam was incident at 45° on the polished plane surface of a GaAs crystal, which could be rotated about its normal, as shown in Fig. 1. The second harmonic intensity was observed perpendicular to the fundamental beam. A Glan-Thomson prism served as an analyzer for the polarization. A diaphragm determined an aperture of about three degrees. The reflection law was accurately obeyed within this instrumental width. An interference filter centered

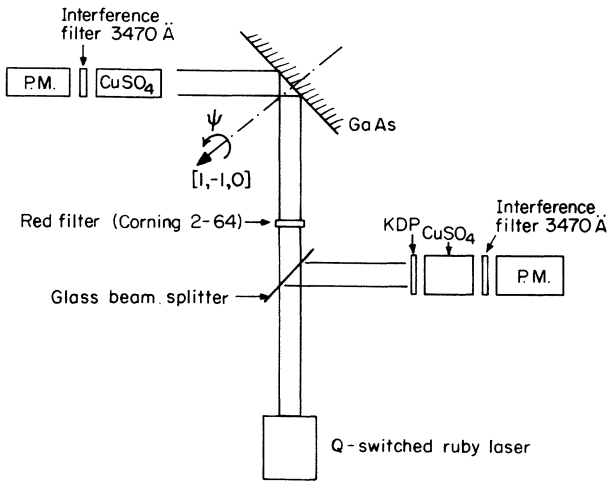

FIG. 1. Diagram of the experimental arrangement.