"Mass Anomaly" in the Zeeman Effect of GaAs Donor 2*p* Levels*

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(Received 28 July 1971)

The value for the GaAs electron effective mass *as deduced from Zeeman splittings of the 2p donor levels* is strongly field dependent for weak magnetic fields. This behavior can be understood quantitatively as a consequence of the Stark perturbation of these levels due to random static electric fields present throughout the semiconductor. From the magnetic field dependence of the Zeeman effective mass we estimate the electric field strength in the sample.

Cyclotron-resonance measurements have given the value $m_0^* = (0.066\,50 \pm 0.000\,07)m$ for the GaAs effective mass at the bottom of the conduction band.[1,2] In order to obtain an independent determination of the effective mass in GaAs, we have studied the Zeeman splitting of donor $2p$ levels in magnetic fields weak enough that the nonparabolic band effects important in the cyclotron-resonance measurements are negligible. (The Zeeman measurements reported here were made with much higher resolution and more accurate magnetic field determinations[3] and on higher purity samples[4] than those previously reported for GaAs.) The results of this study indicate that at low magnetic fields the donor $2p_{\pm 1}$ levels are perturbed by the internal electric fields in the sample which result from ionized donors and acceptors. This perturbation produces an *apparent* variation with magnetic field of the GaAs effective mass as determined in the usual way from the Zeeman splitting of the donor $2p_{\pm 1}$ levels, although the actual electron effective mass is essentially constant. It is well known that in simple parabolic bands the $2p$ level of a hydrogenic donor splits in the presence of an applied magnetic field H into three components characterized by quantum numbers $M_L = -1, 0, +1$. We can define a Zeeman effective mass in terms of the energy difference between the $M_L = -1$ and $M_L = +1$ levels as

$$m_z^* \equiv \frac{\hbar e H}{c[E(2p_{+1}) - E(2p_{-1})]} \equiv \frac{\hbar e H}{c\Delta E_{+1,-1}}. \qquad (1)$$

In the absence of a perturbing electric field, $\Delta E_{+1,-1} = \hbar\omega_c$, where $\omega_c = eH/m_0^* c$ is the cyclotron frequency. Thus, the Zeeman splitting of the $2p_{\pm 1}$ levels defines a "Zeeman mass" m_z^* and this mass should be equal to the cyclotron mass m_0^* if no perturbations are present.

In GaAs, however, not only do we find $m_z^* \neq m_0^*$ at low magnetic fields, but m_z^* is also strongly field dependent for magnetic fields less than about 10 kG. Deviations of m_z^* from m_0^* for magnetic fields from about 1 to 12 kG as determined from high-resolution (~0.07-cm^{-1}) photoconductivity spectra are shown in Fig. 1. The experimental points in this figure were calculated using (1) and the expeximental energy difference $\Delta E_{+1,-1}$ determined from the energy of the peaks of the $1s$-$2p_{-1}$ and $1s$-$2p_{+1}$ donor transition lines. As the magnetic field is decreased in this low magnetic field range, the $2p_{-1}$ and $2p_{+1}$ lines become broader and more asymmetric, with long tails to lower and higher energy, respectively. This effect is shown in Fig. 2 where spectra at $H = 5.105$ and 2.019 kG are compared.

The decrease in Zeeman mass and the asymmetric shape of the lines at low magnetic fields can be explained by the Stark effect on the shallow donor states of the internal electric field due to ionized impurities. In a partially compensated n-type semiconductor at low temperature, neutral and positively charged donors as well as negatively charged acceptors coexist. If the mean spacing between electrically active centers, $\vec{r}_0$, is large compared to the hydrogenic Bohr radius of the donors, $a_{\rm H}$, interactions between neutral

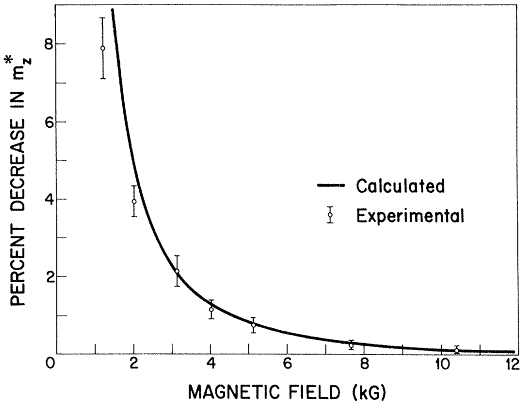

FIG. 1. Percent deviation of the Zeeman mass from the cyclotron effective mass, $[(m_0^* - m_z^*)/m_0^*] \times 100$, as a function of magnetic field, for a GaAs sample with a total electrically active donor concentration $N_D = 5.2 \times 10^{13}$ cm^{-3} and acceptor concentration $N_A = 2.2 \times 10^{13}$ cm^{-3}.

donors will be negligibly weak compared to Coulomb interactions between charged centers (ionized donors and acceptors) and electrons bound to neutral donors. For the GaAs samples studied here, $\vec{r}_0 = (N_{D_0} + N_{D+} + N_{A-})^{-1/3} \cong 2400$ Å, where N_{D_0}, N_{D+}, and N_{A-} are the concentrations of neutral and charged donors and charged acceptors, respectively, whereas $a_{\rm H} \cong 100$ Å. Since $\vec{r}_0$ is large relative to $a_{\rm H}$, it is reasonable to treat the electric field experienced by a neutral donor as fixed in magnitude over the region of space occupied by the donor $2p$ states.[5] Thus, we picture the neutral donors as experiencing a Stark field which is uniform in the vicinity of each donor but varies from donor to donor as a result of the more or less random arrangements of charged centers relative to the donor position.

Treating the electric field at the donor as a perturbation on the donor magnetic eigenstates and setting up the appropriate secular determinant for the hydrogenic $N=2$ levels in a uniform electric field of strength $\mathcal{E}$, we find, with the magnetic field in the z direction, that

$$\Delta E_{+1,-1} = \hbar\omega_c\{1 + |\mathfrak{M}|^2/[E(2p_{+1}) - E(2s)][E(2s) - E(2p_{-1})]\} + O(|\mathfrak{M}|^4) \tag{2}$$

with

$$\mathfrak{M} = e\langle\varphi_{2s}|(\mathcal{E}_x x + \mathcal{E}_y y)|\varphi_{2p\pm1}\rangle,$$

where $\mathcal{E}_i$ is the ith component of the electric field at the donor in question and φ_{2s} and $\varphi_{2p_{\pm1}}$ are donor eigenfunctions in the magnetic field. (The hydrogenic designations $2s$ and $2p_{\pm1}$ merely indicate the zero-magnetic-field states from which the labeled states evolve as the magnetic field is adiabatically turned on when no electric field is present.) Qualitatively, (2) indicates that in the presence of an electric field perpendicular to the applied magnetic field the $2s$ state is coupled to the $2p_{\pm1}$ states. This coupling, in a manner of speaking, causes the $2s$ energy to repel the energy of the $2p_{+1}$ and $2p_{-1}$ states. Since these states lie higher and lower, respectively, than the $2s$ states, they are pushed apart, resulting in an increased value of ΔE and a lowered value of m_z^*. The strength of the repulsion varies inversely with the energy denominator $[\sim(\hbar\omega_c)^2/4]$ in (2) and directly with $|\mathfrak{M}|^2$, which is weakly magnetic field dependent and proportional to $\mathcal{E}_x^2 + \mathcal{E}_y^2$. The wave functions used for calculating $\mathfrak{M}$ in (2) as a function of magnetic field are determined variationally. Trial functions for $|\varphi_{2s}\rangle$ are of the form

$$|\varphi_{2s}\rangle = (2 - \epsilon r_v)\exp(-\rho^2/8a^2)\exp(-\mathcal{K}r_c) + C|\varphi_{1s}\rangle,$$

where $r_v = (\rho^2 + \delta z^2)^{1/2}$, $r_c = (\rho^2 + \alpha z^2 + \beta^2)^{1/2}$, $\rho^2 = x^2 + y^2$, and α, β, δ, ϵ, $\mathcal{K}$, and a^2 are parameters which are varied to produce minimum energy subject to the constraint that $|\varphi_{2s}\rangle$ remain always orthogonal to $|\varphi_{1s}\rangle$. This constraint is satisfied by adjusting C to guarantee orthogonality for each trial set of parameters. The calculations for $|\varphi_{2p_{\pm1}}\rangle$ and $|\varphi_{1s}\rangle$ have already been described.[6]

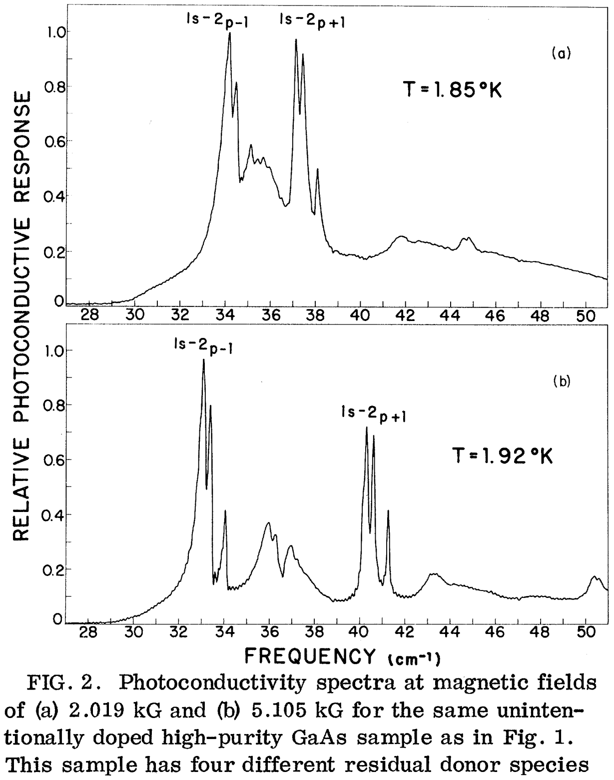

FIG. 2. Photoconductivity spectra at magnetic fields of (a) 2.019 kG and (b) 5.105 kG for the same unintentionally doped high-purity GaAs sample as in Fig. 1. This sample has four different residual donor species with slightly different ground state energies, but only transitions from the ground states of three of the species are well resolved in these spectra. The calculated resolution for these spectra was 0.076 cm^{-1}.

For those neutral donors which happen to be very close to one or more charged impurities, Eq. (2) of course will be inadequate. The actual situation for these cases is much more complicated and will not be discussed here. Equation (2) fails again in very small magnetic fields, but the energy splitting can be determined by an exact solution of the 3×3 secular determinant. [At $H = 1.3$ kG, Eq. (2) gives a correction to $\hbar\omega_c$ which is approximately 7% too large.]

The solid curve in Fig. 1 is computed from Eq. (2) (with appropriate corrections at small fields) using the single adjustable parameter $\mathcal{E}_\perp^2$. In this model $\mathcal{E}_\perp^2$ is the most probable value of the statistical distribution of the quantity $\mathcal{E}_x^2+\mathcal{E}_y^2$ at neutral donor sites in the crystal. We find from the experimental fit

$$\mathcal{E}_\perp^2 = 195 \pm 40 \text{ V}^2\text{ cm}^{-2} \tag{3}$$

which is to be compared with a typical squared nearest-neighbor field of

$$\mathcal{E}_{NN}^2 = |e/\epsilon_0 r_0|^2 = 205 \text{ V}^2\text{ cm}^{-2}, \tag{4}$$

where $r_0=(N_{D+}+N_{A-})^{-1/3}=(2N_{D+})^{-1/3}=2700$ Å. Comparison of (3) and (4) suggests that (3) is not unreasonable.

Pulling of the $2p_{-1}$ and $2p_{+1}$ peaks by relatively strong structure lying between them tends to give measured values of $\Delta E_{+1,-1}$ for $H \lesssim 3.0$ kG that are too small. In the absence of measurements employing polarized infrared radiation it is very difficult to correct accurately for this effect. We have not attempted to do so: The error bars in Fig. 3 reflect only uncertainty in field and peak-energy measurements. Except for this pulling effect at our lowest fields the agreement between theory and experiment appears to be very satisfactory and indicates that the Zeeman effect measurements should enable us to obtain information on the internal electric fields in paritally compensated semiconductors. We expect that Monte Carlo calculations of the electric field distribution now in progress will enable us to make a detailed theoretical study of the line shapes of Fig. 2 and perhaps to determine to what extent charged donors and acceptors are randomly distributed in the semiconductor. (Photoluminescence spectra indicate that at least some ionized donors and acceptors occur as closely spaced pairs.[7])

The presence of internal electric fields in GaAs should couple $|\varphi_{2s}\rangle$ most strongly to $|\varphi_{2p_0}\rangle$, which lies relatively close in energy for $H \gtrsim 5$ kG. This coupling mixes some $|\varphi_{2p_0}\rangle$ into $|\varphi_{2s}\rangle$ and thereby permits some electric dipole oscillator strength in the resulting mixed 2s state. We have observed a weak photoconductivity peak, shown in the spectrum of Fig. 3 for a magnetic field of 10.400 kG, which we identify as the transition from the 1s to the mixed 2s state. This peak grows weaker relative to the $2p_0$ photoconductivity line with increasing magnetic field and falls within about 0.1 cm^{-1} of the energy predicted by variational calculations for the 2s peak using the value[8] 46.1 cm^{-1} for the GaAs Rydberg. In Fig. 3(a) we plot the observed and calculated $E(2s)$-$E(2p_0)$ energy separation as a function of magnetic field. (The solid line is the result of the variational calculation.) We believe that this is the first observation of a 1s-2s transition for a hydrogenic donor.[9,10]

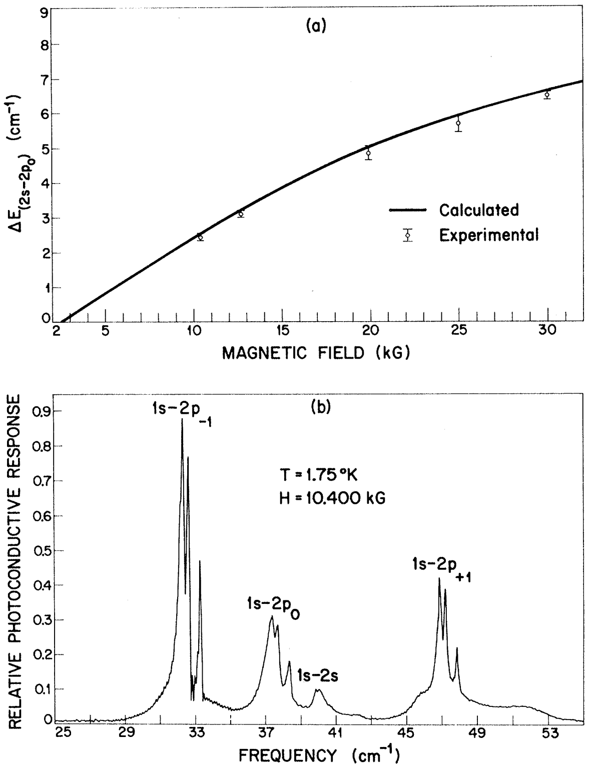

FIG. 3. (a) Variation of the $2s$-$2p_0$ energy separation with magnetic field and (b) typical photoconductivity spectrum showing the peak(s) identified as 1s-2s transitions, for the same sample as in Fig. 1 and 2.

From calculations of $|\varphi_{2s}(r=0)|^2$ and the size of the central-cell corrections for the 1s donor state,[1,8] we estimate that the 2s central-cell correction should be ~0.1 cm^{-1} over the range of fields in Fig. 3. This correction would bring theory and experiment for the 1s-2s transition energy into even better agreement.

Although the decrease in intensity with magnetic field of the 2s peaks relative to the $2p_0$ peaks appears roughly consistent with the Stark coupling model, the ratio of predicted mixed 2s-state oscillator strength to $2p_0$ oscillator strength is much smaller than the observed ratio of photoconductivity associated with the peaks. This suggests that the probability of an electron in the 2s state finding its way into the conduction band before falling back into the 1s state is considerably greater than that for an electron initially in the $2p_0$ state.

Finally, since *all* semiconductor materials are compensated to some extent (especially semiconductors of sufficient purity to observe isolated donor transitions), one can expect to find mass variations of the type reported here in the Zeeman spectra of other semiconductors. Thus, caution must be exercised in deducing accurate conduction-band masses from Zeeman splittings of donors in weak magnetic fields.

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*Work sponsored by the Department of the U. S. Air Force.

[1] H. R. Fetterman, D. M. Larsen, G. E. Stillman, P. E. Tannenwald, and J. Waldman, Phys. Rev. Lett. 26, 975 (1971).

[2] The value $m_0^* = (0.0667 \pm 0.0003)m_0$ has been measured by Chamberlain et al. on a slightly less pure sample. [J. M. Chamberlain, P. E. Simmons, R. A. Stradling, and C. C. Bradley, J. Phys. C: Proc. Phys. Soc., London 4, L38 (1971)].

[3] G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, Solid State Commun. 7, 921 (1969).

[4] R. Kaplan, M. A. Kinch, and W. C. Scott, Solid State Commun. 7, 883 (1969).

[5] We are actually expanding the potential due to charged impurities in a Taylor series about the neutral donor position and keeping only the first term which has a nonvanishing effect on the relative spacings of the donor levels. This is the Stark term. (An additional term of the same order of magnitude as the Stark term but arising from second derivatives of the potential is present and gives rise primarily to broadening. This term will be discussed more fully in a future publication.)

[6] D. M. Larsen, J. Phys. Chem. Solids 29, 271 (1968).

[7] J. A. Rossi, C. M. Wolfe, and J. O. Dimmock, Phys. Rev. Lett. 25, 1614 (1970).

[8] G. E. Stillman, D. M. Larsen, C. M. Wolfe, and R. C. Brandt, to be published.

[9] Transitions *involving* the 2*s* state of a hydrogenic donor have been observed previously [J. A. Rossi, C. M. Wolfe, G. E. Stillman, and J. O. Dommock, Solid State Commun. 8, 2021 (1970)]. In this work, luminescence due to bound exciton recombination at a neutral donor was observed in which the electron bound to the neutral donor was left in the 2*s* excited state and the exciton luminescence peak was shifted by the 1*s*-2*s* energy difference.

[10] We thank Professor W. H. Kleiner for pointing out to us that he has suggested that internal electric fields due to ionized impurity centers may be responsible for the presence of parity forbidden transitions in Si [W. H. Kleiner and W. E. Krag, Phys. Rev. Lett. 25, 1490 (1970)].

Surface Molecular-Orbital Excitations in Electron Energy-Loss Spectra

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(Received 26 July 1971)

We have observed electronic transitions characteristic of molecules at a Ni(110) surface in the energy-loss spectra of 60- to 80-eV primary electrons. We present spectra of a clean Ni(110) surface, an unordered adlayer of nitrogen on Ni(110), and an ordered adlayer of sulfur in the Ni(110)-$c(2\times2)$S surface structure. These spectra derive from a two-step electron backscattering process involving an inelastic loss and an elastic scattering event at the crystal surface. The loss spectra of an ordered surface differ from those of a disordered surface in their sensitivity to primary-beam energy.

Several techniques have been used to study electronic energy levels of bonding electrons in impurities chemisorbed on a metal surface. Hagstrum and Becker[1] have developed the technique of ion neutralization spectroscopy (INS) with which they determined energy levels of chalcogenides on nickel surfaces. Eastman[2] and Waclawski and Plummer[3] reported photoemission spectra of impurities chemisorbed on different transition metals. Plummer and Young[4] determined energy spectra of alkaline-earth atoms adsorbed on tungsten surfaces by measuring the energy distribution of field-emitted electrons, and the authors of Ref. 3 used this last method to determine energy spectra of oxygen on tungsten.

In this paper, we report on the first observation of electronic energy levels of nitrogen and sulfur chemisorbed on a Ni(110) surface by the technique of electron energy-loss spectroscopy. In this spectroscopy, electrons undergo both an inelastic and an elastic scattering process at the crystal surface. Disordered adlayers produce diffuse elastic backscattering which changes weakly in intensity with primary energy [e.g., N on Ni(110)], whereas ordered adlayers produce diffractive elastic scattering which varies strongly with energy [e.g., $c(2\times2)$S on Ni(110)]. The energy dependence of the elastic scattering pro-