Strongly quenched deformation potentials of the Mn acceptor in GaAs

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We have measured the luminescence spectrum of Mn-doped GaAs at liquid-He temperatures with and without an applied uniaxial stress. At zero stress we found clearly resolved donor-acceptor (DA) and band-acceptor recombination bands involving Mn. From these measurements we get a precise acceptor binding energy of 113 ± 0.5 meV. The stress dependence of the peak energy and of the polarization of the DA recombination spectrum was used to derive the following deformation potentials of the acceptor: $a' = -9.1$ eV, $b' = -0.35$ eV, and $d' = -0.8$ eV. The potentials b' and d' are only 18% and 15%, respectively, of the corresponding shear-strain-deformation potentials of the valence band. We attribute this reduction principally to the localization of the bound hole with an additional contribution from a dynamic Jahn-Teller effect.

I. INTRODUCTION

Deep levels in semiconductors are not nearly as well understood[1] as the shallow centers explained by effective-mass theory. Therefore, it seems to be important at present to gain further insight into the properties of deep impurity states by experiment. Two deep Cu acceptors in GaAs[2] have recently been shown to be formed by complexes of lower than lattice symmetry. Shallow acceptors, however, are presumably point defects, as may be concluded, for example, from the shift of the emission from such an acceptor under uniaxial strain. This shift, as measured by Bhargava and Nathan[3] (BN), is similar to the shift of the band-to-band emission only with somewhat reduced deformation potentials. We have performed luminescence experiments on the Mn acceptor in GaAs with zero and nonzero uniaxial stress in order to answer three questions. First, what is the nature of the observed low-temperature emission, is it band-acceptor (BA) or donor-acceptor (DA) recombination? Second, is the Mn acceptor formed by a complex like other deep levels, and third, if it is not, what are the deformation potentials of this acceptor?

II. EXPERIMENTAL

The luminescence spectra were recorded by conventional lock-in techniques. A set of neutral density filters was used to vary the intensity of the exciting He-Ne laser radiation, and a photomultiplier with InGaAs cathode facilitated the detection of low-level signals. Measurements between 4 and 300 K were possible by using a He gas-flow Dewar. The uniaxial stress apparatus was similar to the one described by Pollak and Cardona[4] with appropriate modifications for low-temperature applications.

Manganese-doped GaAs samples were grown by liquid-phase epitaxy. At higher doping levels (5 mg of Mn per 25 g of Ga melt) the samples became p type in our epitaxy furnace, at low doping levels (0.5 mg of Mn per 25 g of Ga melt), however, they remained n type like undoped samples. An n-type sample with electron concentration $n = 1.27 \times 10^{15}$ cm^{-3} and mobility $\mu = 23\,640$ cm^2/V sec at 77 K was chosen for our measurements because low doping levels are favorable for narrow linewidths.

Slabs, parallel to the three principal crystallographic directions, were cut from an epitaxial layer on an (110)-oriented substrate. The substrate plus film thickness was about 1.3 mm, and typical sample dimensions were $1.3 \times 1.2 \times 7$ mm. The uniaxial stress was applied parallel to the long side of the slab. The cross section perpendicular to the stress direction was nearly square to minimize uncertainties in the stress magnitude due to a possible bending of the compressed sample.

III. ZERO STRESS

We intended to clarify at first the nature of the Mn emission at low temperatures without stress. As is well known from the luminescence spectra of shallow acceptors[5] DA and BA recombination bands are clearly resolved at low doping levels. We show for the first time that this is true also for deep acceptors like Mn. Figure 1 exhibits five spectra of Mn-doped GaAs at various temperatures. At 4 K essentially all excess electrons recombine from the donor ground state, and only DA emission is seen. At 9.5 K and higher-temperatures excess electrons are also found in the conduction band, and BA recombination becomes increasingly important. At 28 K, DA recombination is seen only as a weak shoulder.

The circles in Fig. 1 are theoretical points, as discussed below, and the solid lines are experimental results. The line shape of the BA recombination is well described by Eagles's formula.[6] There are minor discrepancies between the measured temperature of the sample holder (given in Fig. 1) and the temperature used in Eagles's formula (given in the legend of Fig. 1), which are deemed insignificant, however, because there might be small deviations of the true sample temperature from our measured temperature. We emphasize, however, two points. First, it is absolutely necessary to use extremely low excitation intensities in order to avoid heating of the conduction electron system. Our excitation intensity I_0 was only about 10 μW mm^{-2}. Second, the fit with Eagles's formula is satisfactory although Mn is a rather deep acceptor, while the formula is derived for effective mass acceptors. This result is to be expected, because only the absorption line shape is sensitive to the acceptor wave function, whereas the emission line shape at low temperature is given mainly by the electron distribution in the conduction band. From the fit we obtain $E_g - E_a = 1.406 \pm 0.0005$ eV. With the gap energy $E_g = 1.519$ eV,[7] we get the acceptor energy

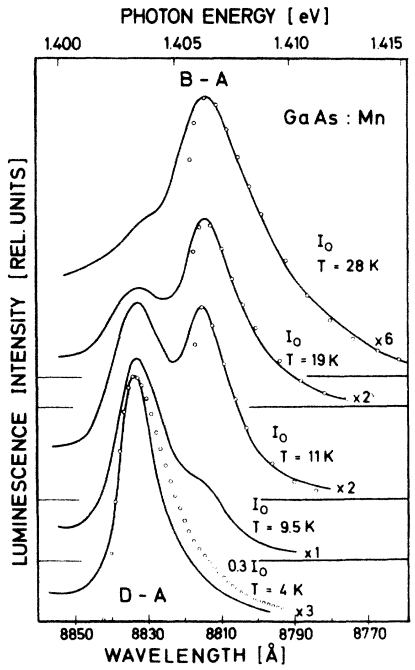

FIG. 1. Photoluminescence spectra of the Mn acceptor in GaAs at five different temperatures and at low-excitation intensity $I_0 \sim 10$ μW mm^{-2}. The phonon replicas on the low-energy side are not shown. In the case of the band-acceptor (BA) recombination band the circles are obtained by Eagles's formula (Ref. 6) with $T = 13$, $T = 17$, and $T = 25$ K. In the case of the donor-acceptor (DA) recombination band the circles correspond to Eq. (1).

$$E_a = 113 \pm 0.5 \text{ meV}.$$

This result is in reasonable agreement with earlier measurements,[8] which gave $E_g - E_a = 1.4089 \pm 0.0003$ eV, leading to $E_a = 110$ meV.

The DA recombination line shape for distant pairs has been calculated by Lorenz *et al.*[9] In the low-excitation limit the line shape is given by

$$g(x) \propto x^{-4} \exp(-4\pi N_d e^6 / 3\epsilon^2 x^3), \qquad (1)$$
$$x = \hbar\omega - E_g + E_a + E_d,$$

and the photon energy of the emission peak is

$$\hbar\omega_{\max} = E_g - E_a - E_d + e^2(\pi N_d)^{1/3}/\epsilon. \qquad (2)$$

All symbols have their usual meaning (see Ref. 9). Because the dielectric constant ϵ and the donor energy E_d are known in GaAs, and $E_g - E_a$ is obtained by the fit of the BA recombination band, the only undetermined parameter is the donor concentration N_d. Increasing donor concentration shifts the emission maximum to higher energies and broadens the emission band. Therefore, one particular N_d chosen to give the emission maximum correctly also determines the halfwidth of the band. The circles on the DA recombination band in Fig. 1 are obtained with $N_d = 9.0 \times 10^{15}$ cm^{-3}, using the accepted values $E_d = 5.8$ meV,[10] and $\epsilon = 12.56$.[10] The halfwidth of the theoretical band shape is seen to be too broad. However, at lower doping levels good agreement has formerly been obtained with shallow levels.[11] At our donor concentration the higher-excited donor states already form a continuum which effectively lowers the conduction band minimum and therefore the effective donor energy could be reduced. If we assume the value $E_d = 5.2$ meV, then $N_d = 5 \times 10^{15}$ cm^{-3} gives very good agreement between theory and experiment. In Fig. 1, however, we did not fit N_d *and* E_d because we have no independent test for the reduction of the effective donor energy. The obtained donor concentration indicates (see the measured electron concentration n) strong compensation caused by the Mn-acceptor doping.

Higher excitation intensities than those of Fig. 1 broaden the DA emission band and shift it to higher energies because of saturation of the transitions between distant pairs. Therefore, already at an excitation intensity of about 2 mW/mm^2 the DA and BA emission bands merge and are no longer resolved into two separate bands.

To conclude our remarks on zero stress results, we note that no Mn-bound exciton could be observed. The absence of the exciton is a rather surprising fact, because all other neutral acceptors studied in GaAs, including the deep acceptors Cu[2] and Sn,[12] are known to bind excitons.

IV. STRESS RESULTS

Figure 2 shows the shift of the Mn DA emission peak as a function of the applied uniaxial stress. If we were to assume a complex center of lower than lattice symmetry we should expect a removal of the orientational degeneracy[13] of differently orientated centers by strain. In this case of lifted orientational degeneracy the strain split levels are not on the same center, but on the contrary different centers, separated in space, assume different energies. At low and moderate doping levels the tightly bound hole cannot penetrate the potential wall separating different centers, therefore thermalization is not possible and at least in some strain directions two or more emission components would be expected. Because we observe only one component at each of the three chosen directions of the strain, we conclude, as shown below in detail, that the Mn acceptor in GaAs has lattice symmetry and is presumably a point defect substituted for a Ga atom.

The strain splitting of point defect acceptors has been considered by Bir *et al.*[14] BN^3 added to the valence band splitting into two bands with quantum numbers $|m_J| = \frac{3}{2}$ and $|m_J| = \frac{1}{2}$ a term quadratic in the stress χ. The splitting and shift of the BA emission energy is given by their formulas

$$\Delta E|_{m_J|=3/2} = [a'(s_{11}+2s_{12}) + \tfrac{1}{2}S]\,\chi\,, \tag{3}$$

$$\Delta E|_{m_J|=1/2} = [a'(s_{11}+2s_{12}) - \tfrac{1}{2}S]\,\chi - q\chi^2\,, \tag{4}$$

where

$$(S)_{100} = 2b'(s_{11}-s_{12})\,, \tag{5a}$$

$$(S)_{111} = d's_{44}/\sqrt{3}\,, \tag{5b}$$

$$(S)_{110} = [b'^2(s_{11}-s_{12})^2 + \tfrac{1}{4}d'^2s_{44}^2]^{1/2}\,, \tag{5c}$$

a', b', and d' are the deformation potentials of the acceptor level, the s_{ij} are elastic compliance constants, χ is the uniaxial stress, $S\chi$ is the linear splitting energy, and q is a constant describing the quadratic part of the energy shift. The donor level is expected to follow the conduction band,[14] therefore, Eqs. (3) and (4) should also describe DA emission bands. In our experiments we observed only one emission component of the DA transition because the halfwidth of the emission is larger than kT. Therefore, the higher-energy $m_j = \pm\frac{3}{2}$ level is already completely depopulated when the stress splitting becomes larger than the zero-stress halfwidth.[15] With the elastic constants for GaAs[16] we obtain by a fit of theory to experiment nevertheless all three deformation potentials a', b', and d' and the quadratic coefficient q.

Even though the splitting of the acceptor levels is not observed directly, it manifests itself as polarization of the emitted radiation. We calculated the polarization of the observed emission assuming a spherical model for the Mn center, and unresolved transitions to its strain-split levels. The parallel and perpendicular polarized intensities $I(\pi)$ and $I(\sigma)$ of a $|m_J| = \frac{1}{2}$ to $|m_J| = \frac{1}{2}$ transition are $I(\pi) = 4$ and $I(\sigma) = 1$ and of a $|m_J| = \frac{1}{2}$ to $|m_J| = \frac{3}{2}$ transition $I(\pi) = 0$ and $I(\sigma) = 3$.[17] With these intensities we obtain for the observed degree of polarization at a given temperature T taking into account the thermal population of the upper level

$$I(\pi)/I(\sigma) = 4/(1+3\,e^{-S\chi/kT}) \tag{6}$$

or with another definition of the degree of polarization

$$\frac{[I(\pi)-I(\sigma)]}{[I(\pi)+I(\sigma)]} = \frac{1-e^{-S\chi/kT}}{(\frac{5}{3}+e^{-S\chi/kT})}\,, \tag{7}$$

where $S\chi$ is the splitting energy of the strain split levels as given in Eq. (5). Here the $|m_J| = \frac{1}{2}$ level has been assumed to move up under a compressive strain in accordance with the valence-band splitting of GaAs.[18]

In principle, we have now two independent

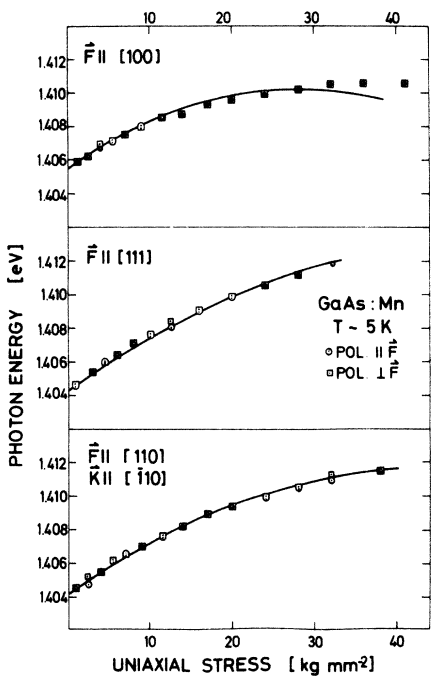

FIG. 2. Shift of the Mn emission (DA) as a function of uniaxial stress in the three principal crystallographic directions. The solid lines are obtained by Eq. (4) with the deformation potentials and quadratic coefficients given in Table I. The circles and squares are experimental data.

methods to obtain the shear strain deformation potentials b' and d'. First we may use Eq. (4) in order to extract them from the shift of the emission peak (see Fig. 2) and second, we may fit Eq. (7) to the observed polarization data. The first method is not very accurate because of two reasons. The acceptor splitting is not observed directly and therefore the constants b' and d' are obtained as relatively small differences between large numbers. In addition a change of b' and d' can be compensated within certain limits by an appropriate change in the quadratic constant q. The second method yields rather accurate values of b'/kT and d'/kT. However, one does not know whether the holes on the split acceptor levels are completely thermalized, therefore only the ratio b'/d' is obtained accurately.[19]

In Fig. 3 the experimentally observed polarization is depicted (circles), as well as the theoretical result of Eq. (7) fitted with the shear strain potentials given in Table I and an effective hole temperature $T = 15$ K. The fit of the experimental data is satisfactory, especially the limiting value of the degree of parallel polarization at large strains is correctly given (60%). In applying Eq. (7) it was not necessary to include a quadratic term in the splitting energy $S\chi$ of the acceptor levels.

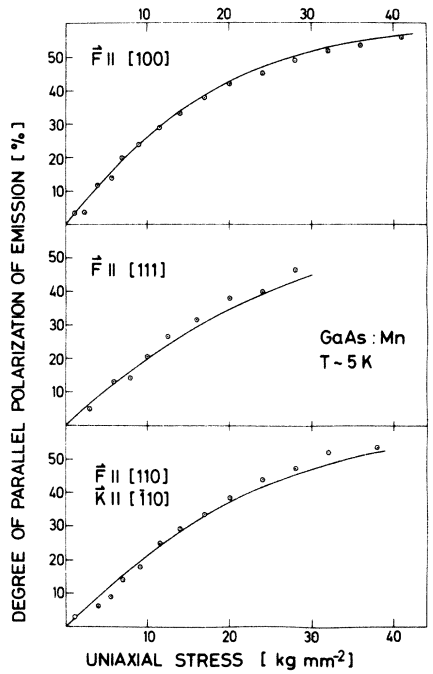

FIG. 3. Degree of parallel polarization of the Mn emission (DA) as a function of uniaxial stress in the three principal crystallographic directions. The degree of polarization is defined as $(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. The solid lines correspond to Eq. (7) with the shear-strain deformation potentials b' and d' given in Table I and an effective temperature $T = 15$ K.

The observed polarization, as well as the agreement between theory and experiment, lends further support to the exclusion of a complex center. For in the case of nonresolved transitions to complex centers of stress-shifted energies (where thermalization is not possible) no polarization would occur. Even assuming possible thermalization between different centers there would be no symmetry of a complex center which would yield us the same limiting value of the polarization for all directions of stress.[13]

In Fig. 2 the circles and squares are again experimental data and the solid lines correspond to Eq. (4) with the deformation potentials and quadratic constants given in Table I. Again the fit of the experimental data is satisfactory. We note, that the quadratic shift, necessary to describe the emission peak shift (Fig. 2), has to be a center of gravity shift rather than a partly quadratic strain splitting of the two acceptor levels (see the polarization results). The deformation potentials of the Mn acceptor are compared in Table I with those of the valence band[3] and the theoretical potentials for effective mass acceptors in Si and Ge.[14]

According to effective-mass theory the hydrostatic deformation potentials a' of a shallow acceptor is equal to the valence-band deformation potential a.[14] Our results indicate that this is true even for the relatively deep acceptor Mn, for our a' is in close agreement with BN's valence-band deformation potential $a = -8.9$ eV. However, the shear strain deformation potentials b' and d' are surprisingly small compared with those both for the valence band and the shallow acceptor mea-

TABLE I. Deformation potentials of the Mn acceptor in GaAs and some related constants.

GaAs:Mn	a' (eV)	b' (eV)	d' (eV)
	-9.15 ± 0.4	-0.35 ± 0.1	-0.8 ± 0.15
	$(q)_{100}\left(\text{eV}\frac{\text{mm}^4}{\text{kg}^2}\right)$	$(q)_{111}\left(\text{eV}\frac{\text{mm}^4}{\text{kg}^2}\right)$	$(q)_{110}\left(\text{eV}\frac{\text{mm}^4}{\text{kg}^2}\right)$
	$(6 \pm 1) \times 10^{-3}$	$(3.5 \pm 0.5) \times 10^{-3}$	$(4 \pm 0.5) \times 10^{-3}$
GaAs:Mn including Ref. a	a'/a	b'/b	d'/d
	1.0 ± 0.05	0.18 ± 0.05	0.15 ± 0.03
Shallow acceptor GaAs[a]	1.0	0.56	0.88
Theory Si[b]	1.0	0.77	0.82
Theory Ge[b]	1.0	0.56	0.61

[a] R. N. Bhargava and M. I. Nathan, Ref. 3.
[b] G. L. Bir, E. I. Burikov, and G. E. Pikus, Ref. 14.

sured by BN. Our error limits given in Table I are not independent. They should be understood in the sense that a change of one constant may be compensated by appropriate changes of other constants within the indicated limits.

There are three effects which may reduce the deformation potentials. The first two are due to the localization of the hole at the acceptor and the third is the dynamic Jahn-Teller effect. The wave function of the bound hole may contain an appreciable admixture of d functions from the Mn core, which are relatively insensitive to strains in the surrounding crystal. This effect is estimated to be unimportant for a state whose binding energy is only about 100 meV. Further, the wave function of a strongly localized hole is much more extended in k space than the wave function of a hole bound at a shallow center. Therefore, the tightly bound hole is sensitive to the properties of the valence band in a larger region of k space surrounding the valence-band maximum and exhibits a correspondingly smaller strain-induced splitting. This effect was found by Pikus and Bir[14,20] to produce a reduction in the deformation potentials for shallow acceptors in Si and Ge as shown in Table I. For a deep acceptor, however, the effect is expected to be larger. A calculation of this effect for a hole bound to a highly localized potential has been made by Morgan[21] and will be published separately. It shows that the deformation potentials are independent of the depth of the bound state and, in GaAs, are about 50% of the band-edge values. The additional reduction by a factor of about 2.5 observed in the experiments would, hence, appear to require the cooperation of a dynamic Jahn-Teller effect. An isotropic coupling of medium strength to e and t modes[22] would be sufficient to explain the smallness of the experimentally observed deformation potentials.

V. CONCLUSIONS

In conclusion, it has been shown that the Mn acceptor, like shallow acceptors, exhibits clearly resolved DA and BA emission bands. Unlike shallower and deeper acceptors, however, the Mn center shows no bound excition emission. The latter observation needs still theoretical interpretation. We give a set of deformation potentials and quadratic shift constants, which explain the shift of the emission peak, as well as its polarization under uniaxial stress. The shear strain deformation potentials b' and d' are found to be much smaller than the corresponding valence-band deformation potentials. This reduction is attributed partly to the localization of the Mn-bound hole with an additional contribution from a dynamic Jahn-Teller effect. The possibility of a complex Mn center has been excluded.

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