

Excited states of DX in $Ga_{1-x}Al_xAs$

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The photoexcited neutral states of the Sn donors in $Ga_{1-x}Al_xAs$ alloys are studied both experimentally and theoretically. Two types of donor states are evidenced: a deep strongly localized one, D^0 , as well as a delocalized effective-mass state d^0 . Both belong to the principal donor Sn_{Ga} , as confirmed by EPR measurements on ^{119}Sn -enriched samples. The D^0 state is consistently modeled as the $A_1(ab)$ antibonding donor state. Theory predicts the coexistence of both states D^0, d^0 in an intermediate alloy-composition range. This level scheme also explains the results of the Si and Te donor reported previously.

I. INTRODUCTION

Magnetic-resonance techniques have been widely applied in the past to determine the basic properties of the single donors in $Ga_{1-x}Al_xAs$ alloys.¹⁻¹² A first essential result is that the DX ground state is apparently diamagnetic. However, different paramagnetic donor states have been observed after optical excitation. Most of the results have been reported for the Si donors in indirect-gap $Ga_{1-x}Al_xAs$ ($x > 0.37$) (Refs. 1-4, 7, 8, and 12). They have been convincingly interpreted in the model of the delocalized $T_2(X)$ effective-mass (EM) state derived from the X minima of the lower conduction band.⁸⁻¹² On the other hand, for the Sn donor in direct-gap materials, two different donor-related EPR spectra have been observed⁵ the dominant one of which, due to its strong central hyperfine interaction,^{10,11} has the characteristics of a strongly localized deep state.

The aim of this work is to provide a coherent picture of these apparently conflicting results. For this we report detailed electron-paramagnetic-resonance (EPR) data for the Sn donor on isotopically enriched ^{119}Sn -doped layers as well as on thick Sn-doped layers in both the direct- and indirect-gap composition range. The spin concentration, which in general cannot be obtained from optically detected magnetic-resonance techniques, has been systematically determined in order to check that the EPR spectrum belongs to the principal substitutional tin donor Sn_{Ga} . We have further determined the alloy dependence of the g factor and the hyperfine constant. The results are compared to the level structure that can be predicted for the neutral donor states. It is characterized by the coexistence of both a deep donor level D^0 , attributed to the $A_1(ab)$ antibonding state, and a shallow EM state d^0 for intermediate alloy-composition ranges $0.3 < x < 0.6$. We show that this model also accounts fully for the experimental situation encountered for the other group-IV donor Si as well as the group-VI donors.

II. EXPERIMENTAL RESULTS

We present EPR results for the Sn donor in $Ga_{1-x}Al_xAs$ epitaxial layers grown by metalorganic vapor phase epitaxy on (001)-oriented semi-insulating GaAs substrates. The alloy composition was varied between $0.30 < x < 0.6$. Typical doping concentrations are $\sim 10^{18} \text{ cm}^{-3}$. Some of the samples were doped with ^{119}Sn enriched to 75%. EPR measurements were done with an X -band spectrometer in the 4 to 100 K temperature range. The samples were photoexcited *in situ* with monochromatic light from a tungsten halogen lamp.

In agreement with previous results on the Sn donor⁵ no EPR spectrum related to the donor DX ground state was observed in any of the samples when it had been cooled down to 4 K in the dark. Optical excitation with a threshold of 0.8 eV (Ref. 5) generates the EPR spectra shown in Fig. 1, curves *A* and *B*. For $0.3 < x < 0.5$ the EPR spectrum is dominated by one isotropic line at $1.9 < g_{iso}(x) < 2.0$ with a peak-to-peak linewidth of ~ 400 G. On thick samples a strongly asymmetrical low-intensity doublet structure at ~ 500 and 4600 G is superposed corresponding to the hyperfine interaction with the ^{119}Sn and ^{117}Sn isotopes, which both have a nuclear spin $I = \frac{1}{2}$ and a natural abundance of 7.8% and 8.6%, respectively. The observation of the low field line in the nonenriched samples is masked by a strong optically induced base-line variation in this magnetic-field range. The EPR spectra obtained on isotopically enriched Sn donor samples unambiguously confirm the hyperfine character of this doublet. In the case of exceptionally highly doped samples ($[Sn] > 5 \times 10^{18} \text{ cm}^{-3}$), an additional sharper line could be observed in direct-gap material.⁵ The spin concentration of the broad line determined by comparison with a NBS spin standard is in all cases within a factor of 2 identical to the nominal donor doping concentration. The spectra were analyzed with the spin Hamiltonian for an electron spin $S = \frac{1}{2}$ nuclear spin $I = \frac{1}{2}$ system

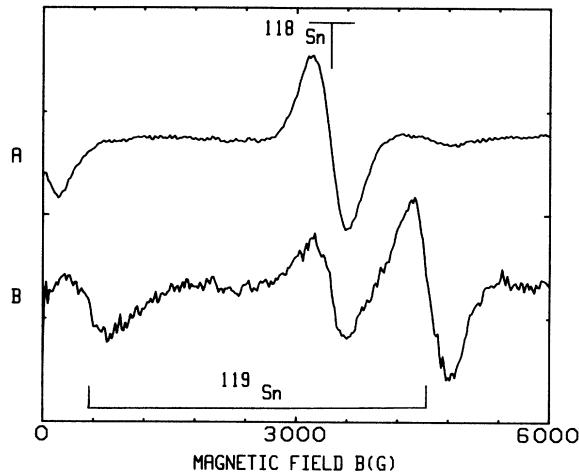


FIG. 1. EPR spectra of tin-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ layers: A, $x=0.35$; B, $x=0.35$; isotopically enriched ^{119}Sn 75%.

$$\mathcal{H} = g\mu_B \mathbf{B} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S}$$

for which closed eigenvalue solutions exist.¹³ The results for g_{iso} are summarized in Fig. 2.

In the case of $x=0.43$ we obtain for example $g_{\text{iso}} = (1.974 \pm 0.010)$ and $A_{\text{iso}}(^{119}\text{Sn}) = 0.33 \pm 0.01$ in good agreement with Refs. 11 and 12. From the central hyperfine interaction constant the electron localization on the $5s$ donor orbital can be deduced, by comparison with the free atom value of $A_{\text{free}}(^{119}\text{Sn}) = -1.465 \text{ cm}^{-1}$,¹⁴ we obtain a localization of 23%. Such a high value is incompatible with an effective-mass state $T_2(X)$. Indeed as shown by Morgan in the analogous case of group-IV donors in GaP the $T_2(X)$ state is characterized by a weak central cell effect and no “ s ” density at the donor nucleus.¹⁵ Even for A_1 EM states such as the ground state of the group-IV donors in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ the localization on the donor S orbital is inferior to 1%. On the contrary, the experimental value is typical for deep A_1 donor states such as the double donor Sn in 2-6 compounds¹⁶ or the anion antisites in 3-5 compounds.¹⁷ Thus the question arises, what is the origin of this deep donor

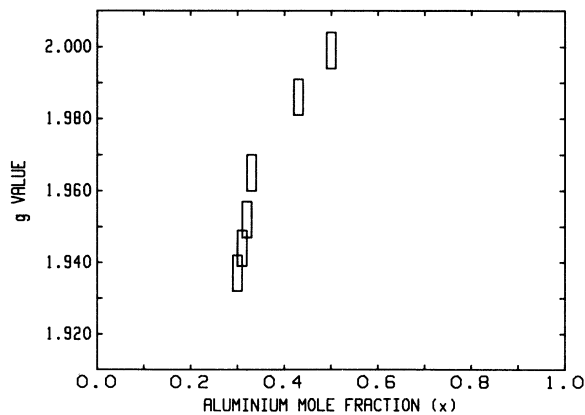


FIG. 2. Alloy variations of the g value of the D^0 state in $\text{Ga}_{1-x}\text{Al}_x\text{As}:\text{Sn}$.

state, which, from its photoexcitation process, its electron spin $S = \frac{1}{2}$, and total concentration, must be identified with the neutral donor state D^0 .

III. THEORETICAL PREDICTIONS

Donor impurities in semiconductors can be investigated from two different points of view: localized descriptions and effective-mass theory (EMT). In the localized descriptions it is known¹⁸ that for single donors in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ the basic states of interest are mainly built from antibonding combinations of the orbitals belonging to the donor and its first neighbors. This leads to two characteristic states: a symmetric nondegenerate one $A_1(ab)$ and an excited triply degenerate one $T_2(ab)$. All calculations, either tight binding (TB) (Refs. 18 and 19) or local density (LDA),^{20,21} tend to show that the $A_1(ab)$ state always falls close to the bottom of the conduction band while $T_2(ab)$ is always about 1 eV higher, i.e., is resonant with the conduction band. The composition dependence of $A_1(ab)$ is difficult to predict with the required accuracy (much better than 100 meV). For instance, the LDA calculations of Refs. 20 and 21, respectively, predict this level to be at $E_c + 160 \text{ meV}$ and $E_c + 260 \text{ meV}$ in GaAs. To be more quantitative we have thus preferred to start from independent experimental information, in the manner of Ref. 22 where the measured position of $A_1(ab)$ in GaAs under pressure has been extrapolated to zero pressure. For Si and Ge this leads to $E_c + 260 \text{ meV}$ and $E_c + 50 \text{ meV}$, respectively. Then it was noticed that the composition dependence of the D_4 level observed in Ref. 23 also extrapolates to the Ge value in pure GaAs, showing that it is probably due to residual Ge donors. To obtain the composition dependence of $A_1(ab)$ for the Si donor we have thus drawn, in Fig. 3, a line parallel to the D_4 level, as all deep donors are likely to exhibit the same composition dependence. Finally, to obtain the curve corresponding to Sn in Fig. 3 we have

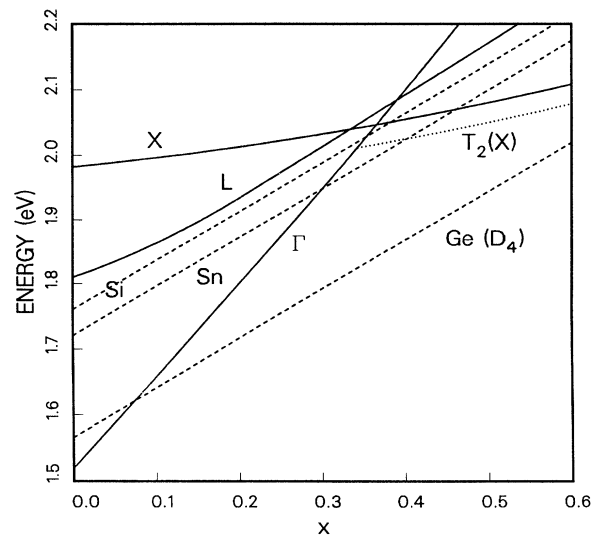


FIG. 3. Conduction-band structure of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ at 2 K (Ref. 25). Alloy variation of the $A_1(ab)$ states of Si, Sn, Ge, and the shallow effective-mass states.

simply taken the chemical shifts measured for the Γ effective-mass states in Ref. 24 and scaled them to produce the correct Si-Ge difference for the $A_1(ab)$ state. From this the Sn level is ~ 40 meV lower than the Si value, instead of 10 meV for the value calculated in Ref. 20. Note also that this level corresponds to an average value since alloy disorder will give rise to a distribution of $A_1(ab)$ levels.

The opposite view corresponds to EMT. For direct-gap materials, the Γ conduction band is lowest with an effective mass $m_\Gamma = 0.065$, so that the binding energy of the lowest $1s$ hydrogenic state is $E_{B\Gamma} = 5.7$ meV. In indirect-gap materials, the X conduction band is lowest, with $m_l = 1.9$ and $m_t = 0.19$.²⁵ Treating each minimum independently the binding energy of the $1s$ state can be obtained from Ref. 26 as $E_{BX} \sim 30$ meV. For group-IV donors on the atom III site there is no intervalley coupling¹⁵ which results in a triply degenerate $T_2(X)$ state at this energy. In the case of group-IV donors on site V the intervalley coupling splits the three one-valley states into an A_1 and an E component. We concentrate in the following on the group-IV donors and have thus drawn in Fig. 3 the $T_2(X)$ state which follows the X conduction band at about 30 meV.

The obvious conclusion of Fig. 3 is that the $A_1(ab)$ state for Sn becomes localized in the gap for $x > 0.3$ and is the stable state up to $x \simeq 0.4$ beyond which $T_2(X)$ becomes lowest. This explains quite naturally the magnetic-resonance results for the deep donor state of Sn in direct-gap materials characterized by an isotropic g value and a hyperfine constant indicative of an “ s ” electron density of about 20%. Indeed we have shown previously that the properties of the $A_1(ab)$ state are well described by self-consistent TB Green’s-functions calculations.¹⁸ We have first performed such calculations for the arsenic antisite As_{Ga} in GaAs. For the paramagnetic state As_{Ga}^+ we predict a value of 17% for the unpaired “ s ” electron population at the arsenic nucleus, just the value deduced from the experimental hyperfine constant. We also find that the localization of $A_1(ab)$ practically does not vary when the level position moves across the gap. The same order of magnitude is then obtained for single donors which is in agreement with the experimental value observed for Sn.

It now becomes clear that Fig. 3 provides a simple explanation of the apparently conflicting EPR results reported for the Sn and Si donors. For Sn in direct-gap materials the ground state is $A_1(ab)$ so that the spectrum is isotropic with strong central cell interaction. On the other hand, for Si in indirect-gap materials the ground state becomes $T_2(X)$, characterized by an anisotropic g tensor and no central cell hyperfine interaction. For very high doping concentrations, allowing a shift of the quasi-Fermi level after low-temperature photoexcitation to $E_c + 100$ meV the resonant $T_2(X)$ state will equally become observable for compositions $0.3 < x < 0.37$.⁵ An interesting problem arises in the intermediate region $x \sim 0.35 - 0.4$ where the crossing of the two states occurs. This region is likely to be broad in view of the distribution of the $A_1(ab)$ states in energy caused by al-

loy disorder. In the absence of symmetry-lowering distortions, the two states should not interact in view of their different symmetry (only weak coupling could be induced via local fluctuations in Al distribution). Thus this region should correspond to a range where the two spectra coexist independently. This is confirmed by our measurement of Sn for $x = 0.48$ where we find, as in the exceptionally highly doped sample ($x = 0.31$), two spectra: one at $g \sim 2$ corresponding to $A_1(ab)$, the other one at $g \sim 1.95$ with unresolved anisotropy which corresponds to the limiting situation of $T_2(X)$.

Finer details of the experimental trends can also be understood in this description. The strong decrease $g(x)$ at low x shown in Fig. 2 can be attributed to increased LS mixing with the conduction band. Although such mixing strictly vanishes by symmetry at the Γ point it becomes nonzero away from this point and its overall strength increases when the distance in energy between $A_1(ab)$ and the band decreases. A second point concerns the decrease in anisotropy observed for Si when x decreases. This can possibly be attributed to a reduction in the strain splitting of the $T_2(X)$ states since the lattice mismatch decreases, as well as to the coupling between the $T_2(X)$ and $A_1(ab)$ states which, even if weak, might mix the two states and reduce the anisotropy further. A final interesting point concerns the central hyperfine interaction. It should stay roughly constant for Sn for those states which keep $A_1(ab)$ behavior but decrease in the overlap region for states with increasing $T_2(X)$ behavior. The reverse should be true for the EM state when decreasing the concentration from $x = 1$. Such behavior seems to be qualitatively obeyed by the few preliminary measurements performed in the crossing region.

Finally, the present conclusions are strengthened by the comparison with GaP where all donors exhibit X EMT character except Ge for which the possibility of an A_1 deep state has been proposed.²⁷ This corresponds to Fig. 3 for indirect-gap materials, confirming the plausibility of this interpretation.

IV. CONCLUSION

We have shown in this work that the use of ^{119}Sn -enriched samples allows one to prove unambiguously by EPR that the neutral state D^0 of the Sn donor exhibits an isotropic spectrum with strong central cell interaction. This behavior is only consistent with a deep state with strong “ s ” character on the donor. We have then considered the theoretical predictions for such single donors and concluded that the neutral donor ground state is the $A_1(ab)$ deep state for $0.3 < x < 0.4$ and the $T_2(X)$ effective-mass one for $x > 0.4$. This is found to describe coherently the experimental situation not only for the Sn donor but also for Si and the group-VI donors. The observability of the deep donor state D^0 will depend strongly on its level position relative to the EM states and thus be influenced by chemical shifts of D^0 . We have seen that for Si the observation of the D^0 state of the Si donor is equally expected in the $x \simeq 0.35$ alloy-composition range. However, in the case of Te, which has the shallowest D^0 state, it may stay resonant with the conduction band over the whole composition range.

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