

Electron-paramagnetic-resonance study of Se-doped AlSb: Evidence for negative U of the DX center

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A metastable electron-paramagnetic-resonance (EPR) signal is observed in Se-doped AlSb. When cooled in the dark, the sample is nonparamagnetic. After illumination with white light from a tungsten source a strong, persistent EPR signal with an isotropic g factor of 1.949 is observed. The metastability of the signal is consistent with earlier work done on DX -like centers. The absence of any EPR when cooled in the dark is direct evidence for the negative- U model. The EPR arises from the effective-mass state of the defect, which is not filled at thermal equilibrium. A detailed analysis of the line shape reveals that the linewidth is determined by hyperfine interactions. The extent of the wave function is found to be comparable to the predicted value of the effective-mass state.

Following the original observation of DX centers by Lang and Logan,¹ it has become apparent that this center is omnipresent in many compound semiconductors and their alloys.²⁻⁴ The most noticeable feature of the DX defect is the structural metastability. This is also accompanied by the metastability of the properties of the material such as persistent photoconductivity and persistent photo-EPR (where EPR is electron paramagnetic resonance). The earlier models assumed that the DX center was a complex of the donor (D) with an unknown intrinsic defect (X), presumably the anion vacancy. Later models propose a simpler structure with only the donor atom. This is mainly based on the fact that the concentration of the defect seemed to be independent of the growth conditions, but always linearly proportional and close to the donor concentration. The structural metastability consists of the two stable positions of the donor atom; it either resides on the substitutional lattice position (T_d) where it acts as a hydrogenic donor atom, or the atom and/or surrounding host lattice relaxes, and thus forms a new (C_{3v} symmetry) ground state.

Several different microscopic models for the lattice relaxation have been proposed⁵ for the DX center. Theoretical calculations performed for GaAs (Ref. 6) have shown that group-IV and group-VI donors undergo different types of structural relaxation upon electron capture. In the case of group-IV donors substituting Ga atoms, the donor breaks the bond with one of the nearest-neighbor As atoms and is itself

displaced from the donor site in the $\langle 111 \rangle$ direction. On the other hand, for group-VI donors, the formation of the DX center is associated with a bond-breaking dislodgement of one of the four Ga atoms surrounding the donor site. It is important to note that in both cases a vacant Ga site is formed. A principal conclusion of this model is that the localized DX state exhibits an effective negative electron correlation energy (negative U) resulting in a diamagnetic ground state with paired-off spins.

In the negative- U model paramagnetic, neutral centers d^0 never exist, since they are spontaneously transformed into the nonparamagnetic configurations d^+ and DX^- in the exothermic reaction⁶



In this case the negatively charged DX^- relaxes to a C_{3v} symmetry. In a positive- U model, however, the d^0 state of the hydrogenic donor can always be realized by a suitable adjustment of the Fermi level. Thus, the absence of an EPR signal in an n -type semiconductor after freezing out of the carriers is direct evidence for a negative- U situation.

For most of the binary III-V semiconductors, the DX level is resonant with the conduction band. This makes it very hard to measure. The solution is to apply hydrostatic pressure,⁷ or, equivalently, use ternary compounds, e.g., replace some of the gallium atoms with aluminum in GaAs.

Both methods shift the DX level into the band gap, where they can serve as efficient electron traps. For GaAs this occurs at pressures above 20 kbar or for more than 22 at. % Al content. Both methods are cumbersome and results of various experiments are often inconclusive or contradictory.

Apart from the deep DX level, the donor forms the usual shallow, effective-mass level⁷ connected to the minimum of the conduction band. The position of this level depends on the type of material and the valley to which it is connected, but for direct band-gap semiconductors it is of the order of 10 meV. Because they are so shallow, they will be emptied into the conduction band for most temperatures. This warrants the use of AlSb for studying DX ; it is an easy-to-grow bulk binary III-V semiconductor with the DX level in the band gap. In addition, the effective-mass level is very deep (100 meV), mainly because of the high effective mass ($m^* = m_e$). The result is that the system is always in well-defined states in which the electrons are localized in either the hydrogenic donor, or the DX state.

An earlier EPR study of a DX center in AlSb by Jost *et al.* indeed showed some metastability.⁸ Unfortunately, their choice of the donor (Te) resulted in the presence of EPR signal before illumination. Moreover, after illumination, the EPR changed not only intensity, but also position and linewidth. Therefore, it cannot be excluded that the first signal was caused by DX and the second by the shallow effective-mass level. Consequently, no conclusion about the sign of the electron correlation energy (U) can be drawn from those results. As we will show, the selenium donor does not have this drawback.

Previous work showed that the selenium donor shows metastable behavior as expected for DX . Becla *et al.* observed photoinduced persistent optical absorption in this system.⁹ The current paper describes an EPR study on similar material, Se-doped AlSb.

The sample used in this study is a Czochralski-grown AlSb sample with a high concentration of selenium doping ($2 \times 10^{17} \text{ cm}^{-3}$).⁹ This resulted in n -type AlSb with a high free-electron concentration at room temperature. The EPR spectrometer used in the experiments is a Bruker ER 200D X-band (9.43 GHz) spectrometer tuned for absorption with a TE₁₀₂ rectangular cavity with $Q=3000$. The sample was cooled to low temperatures in an Oxford ESR 900 He-gas-flow cryostat, operating at temperatures from 3.9 to 300 K. The illumination was from a tungsten lamp.

When the temperature is lowered in the dark the sample becomes highly resistive as evidenced by the high Q factor of the EPR spectrometer, which shows no significant deviation from the value of the empty cavity. This proves that the carriers freeze out. This has been confirmed by resistivity measurements that indicate freeze-out on a deep level—presumably DX —with a binding energy of 180 meV. Under these conditions the sample is nonparamagnetic; no signal could be detected above the noise level up to 0.8 T. During illumination a strong signal arises around $g=1.949$, see Fig. 1. After switching off the light, this signal increases in intensity. This increase can be explained by the trapping of the free carriers in the d^0 state when the light is switched off. These free carriers cause conduction in the sample, which reduces the Q factor and screens the interior of the sample from the resonating microwaves. These effects reduce the

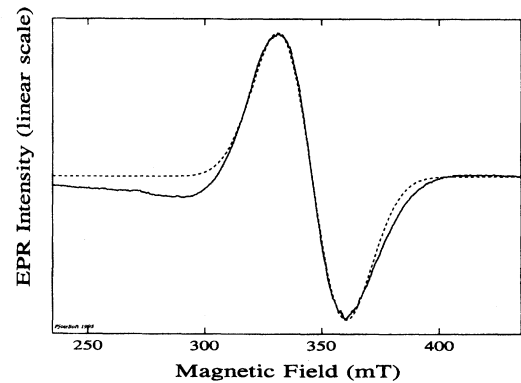


FIG. 1. Isotropic EPR spectrum of AlSb:Se after illumination. This signal persists, with no noticeable changes in intensity for at least several hours in the dark. The dashed line is a simulation with $g=1.949$ and includes hyperfine interactions with a shell of 12 Sb atoms.

absorbed energy, i.e., lower the signal originating from the effective mass states d^0 . Figure 1 illustrates this signal after illumination. After switching off the light, the Q factor is restored to its preillumination value, and the signal persists undiminished for at least several hours.

It is known that the DX center can thermally relax to the ground state at temperatures higher than ca. 100–120 K. Figure 2 shows the thermal quenching behavior of the EPR signal. To obtain an experimental point on this graph, the following procedure was followed: first the temperature was raised from 14 K to the indicated temperature, then the sample was kept at this point for about 5 min, after which the temperature was restored to 14 K, and the EPR signal intensity was measured. This procedure was used in order to avoid secondary effects, such as temperature dependencies of the Q factor, paramagnetic relaxation times T_1 and T_2 , and Boltzmann distribution over the magnetic sublevels since they can affect the signal dramatically. In this way the signal is proportional to the concentration of the paramagnetic cen-

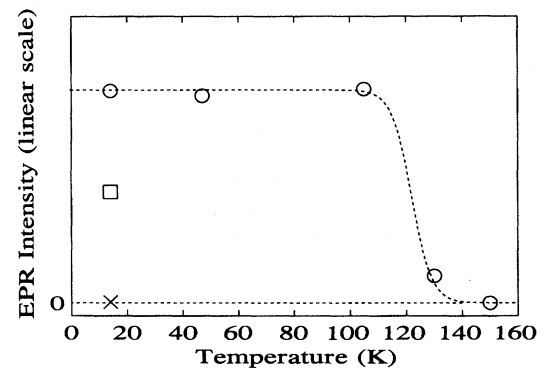


FIG. 2. Thermal quenching of the illumination-induced EPR spectrum in AlSb:Se measured at 14 K. The figure shows the EPR intensity for cooling in the dark (\times), during illumination (\square), and after switching off the light (\circ). To return the sample to the nonparamagnetic state it has to be heated to a temperature above 115–130 K.

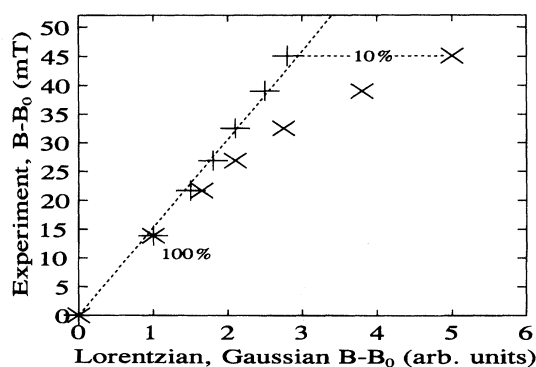


FIG. 3. Line-shape analysis of the EPR line. Experimental values of the magnetic field where the line reaches 100%, 80%, 60%, 40%, 20%, and 10% of the maximum are plotted vs the theoretical values for Gaussian (+) and Lorentzian (x) line shapes.

ters. It is clear from Fig. 2 that at temperatures below 115 K no relaxation occurs. At 115–130 K the signal drops, and the original state of absence of paramagnetism is recovered.

The observed thermal quenching of the persistent EPR signal is very similar to the thermal quenching of the persistent photoconductivity in $Al_xGa_{1-x}As$.¹⁰ In the latter case the persistent photoconductivity was due to optical excitation of electrons from the deep DX level to the metastable shallow hydrogenic level. Thermal ionization of this level produces the persistent photoconductivity. The important difference between $Al_xGa_{1-x}As$ and $AlSb$ is that in $AlSb$ the energy levels corresponding to both DX and hydrogenic donor configurations produce relatively deeper levels. The fact that no EPR signal is observed in this case supports the negative- U model. The illumination transfers the systems to the hydrogenic donors, which are paramagnetic as each of the donors can accommodate only one electron.

The signal is isotropic with a g value of 1.949. In order to analyze the line shape, the magnetic fields relative to the center of the line where the intensity reaches certain fractions of the maximum are plotted versus the theoretical positions for Gaussian and Lorentzian line shapes¹¹ (see Fig. 3). The points corresponding to a Gaussian line shape turn out to be on a straight line, proving that this is the actual line shape. The Gaussian line shape excludes the possibility that the line

broadening is dominated by lifetime effects, which would result in a Lorentzian line shape. von Bardeleben observed a Lorentzian line broadening of the EPR signal from the hydrogenic state of the DX -type donors for high concentrations of the defect.¹² This high concentration can shorten the lifetime and broaden the line. The effective-mass state in $AlSb$ is more localized, so that there is less overlap of the wave functions, even for very high concentrations, and the range of lifetime broadening is not yet reached in the sample used here.

The EPR line in Fig. 1 is very broad, 29 mT peak-to-peak. This is not uncommon in III-V semiconductors, and is in most cases due to the fact that all stable isotopes of group-III and group-V elements have nuclear spin interacting with the paramagnetic electron, and broadening of the line. In the framework of the theory of linear combination of atomic orbitals the hyperfine interaction is linearly proportional to the amount of the paramagnetic wave function at the site of the nucleus in question, and the element-specific interaction constant.¹³ We can easily calculate the density of the wave function on the various shells of atoms. As discussed above, the paramagnetic state is an effective-mass-like state around the selenium atom substituting for an antimony cation. The binding energy of this state can be calculated from the effective mass (m^*) and the dielectric constant (ϵ) of $AlSb$ (Ref. 14) and is approximately 100 meV. From this, the Bohr radius can be derived: $a_1 = 5.6 \text{ \AA}$. To find the amount of electron on each atom the square of the effective-mass wave function

$$\Psi_s(r) = \sqrt{1/\pi a_1^3} e^{-r/a_1} \quad (2)$$

is evaluated at the position of the nucleus and then multiplied by the volume per atom. $AlSb$ crystallizes in the zinc-blende structure with a lattice constant of 6.1355 \AA .¹⁵ Therefore, when ignoring possible lattice relaxations, this volume is 19.3 \AA^3 .

The largest amount of electron can then be found on the selenium donor (3.5%), but because nearly all selenium has $I=0$, there is no resulting resolvable hyperfine interaction. The next shell has four aluminum atoms, and on each atom resides 1.35% of the electron. As can be seen in Table I, the largest hyperfine interaction is not from this shell, but from the next, containing twelve antimony atoms. Based on this, a

TABLE I. Local electron densities (Ψ_s^2) of the effective-mass wave function on the specified core, total amount of the paramagnetic electron (α), and resulting hyperfine interactions (A) for the first shells of atoms around the Se donor. n represents the number of atoms in the shell, r is the distance to the central Se atom, and I the nuclear spin.

Shell	Element	n	r (\AA)	Ψ_s^2 (\AA^{-3})	α	I (abundance)	$2AI$ (mT)
0	Se	1	0	18.1×10^{-4}	3.5%	0 (92.4%)	0
						1 (7.60%)	21.8
1	Al	4	2.66	7.01×10^{-4}	1.35%	(100%)	9.34
2	Sb	12	4.34	3.84×10^{-4}	0.74%	(57.3%)	30.6
						(42.7%)	23.2
3	Al	12	5.09	2.94×10^{-4}	0.57%	(100%)	3.95
4	Sb	6	6.14	2.02×10^{-4}	0.39%	(57.3%)	16.1
						(42.7%)	12.2
5	Al	12	6.69	1.66×10^{-4}	0.32%	(100%)	2.22

simulation was made with densities on the first four shells as indicated in Table I. The resulting linewidth was 73 mT. This is a factor 2.5 higher than the experimentally observed value. Figure 1 shows a simulation with only hyperfine interactions with the 12 Sb nuclei. In order to get a good fit, the density had to be taken as 0.33% on each atom. This is an upper limit, since further hyperfine interactions will only broaden the line. Therefore, it is clear that the value of 0.73% for the effective-mass state of Table I is too high; the actual amounts are a factor 2.2–2.5 lower.

The linewidth, as caused by the hyperfine interactions with the surrounding nuclei is smaller than can be expected for the theoretical effective-mass state. There may be several reasons for this.

(1) Not all of the paramagnetic electron is in atomic orbitals, but resides partly in the voids of the crystal. In that case, the simple calculation presented above will yield too high a local density.

(2) Even if all of the electron is in atomic orbitals, it is not necessarily in s orbitals. The higher orbitals cause less hyperfine interaction, and are completely ignored in this paper.

(3) Central-core corrections can make the wave function deviate significantly from the spherical effective-mass shape. This is very likely, since the effective mass electron is so localized in AISb (viz., $a_1 = 5.6$ Å, comparable with the lattice constant) that the host lattice does not behave as an isotropic dielectric medium, but rather has structure.

(4) The effective-mass state is shallower, because m^* is smaller. In view of this, the observed linewidth is comparable to the simulated linewidth based on an effective-mass wave function.

In conclusion, these results show that the Se donor in AISb shows metastable behavior and is in agreement with the optical absorption experiments⁹ and is similar to EPR experiments on DX centers in other III-V semiconductors. The absence of any EPR when the sample is cooled in the dark and the carriers freeze out on the DX level is direct evidence for the negative- U model.

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