Stability of D^- centers in GaAs

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Some of the reasons for the lack of stability of the D^- centers in bulk GaAs are considered using the idea of screening. Screening due to other impurity electrons tends to reduce the binding energy of D^- centers much faster than that of neutral donor centers. Estimates of optical-matrix elements and the order of temperatures needed for the dissociation of the D^- ion show why it is difficult to observe D^- centers in bulk GaAs.

I. INTRODUCTION

In many semiconductors when a neutral donor captures an extra electron, a negative-donor center (D^-) is formed. As the shallow donors are regarded as "hydrogenlike," D^- centers are analogous to H^- ions. Lampert[1] predicted the binding energy of the extra electron of the D^- ion as 0.055 Ry*. The direct observation of the D^- centers in Si was reported by Gershenzon, Ladyzhenskii, and Melnikov,[2] who determined the binding energy of the D^- centers directly from the long-wavelength photoconductivity band at low temperatures. Since then many experiments have been performed to explore the D^- ions in bulk semiconductors. Natori and Kamimura[3] have calculated the energy-level structures of the D^- ion in many-valley semiconductors in the high stress and stress-free cases, neglecting valley-orbit interaction. Larsen[4] has also reported the stress-dependence of the D^- binding energy. The binding energy of D^- center in Si as a function of uniaxial compressive stress including Valley-orbit corrections has been reported by Oliveira and Falicov.[5] Chandramohan, Balasubramanian, and Tomak[6] have calculated the binding energy of D^- centers in GaAs. Recently D^- centers have been identified in III-V compounds by far-infrared spectroscopic experiments by Najda *et al.*[7] These experiments show that it is difficult to observe D^- states in these bulk semiconductors without applying stress or magnetic fields.

Experiments by Huant, Najda, and Etienne[8] on D^- centers in GaAs-$Ga_{1-x}Al_xAs$ quantum wells reveal stabilization of these centers in confined systems. Since the binding energy of the second electron in bulk GaAs is so small (0.35 meV) for convenience of experimental observations of these centers, one enhances the binding energy by magnetic-field localization, by pressure-induced localization, or by confinement. Theoretical studies on D^- centers in a quantum well also show enhancement of binding energy[9,10] due to confinement. Even though the second electron binding energy in a 3d crystal of GaAs is very small compared to the binding energy of a neutral donor (~6 meV), the former is well above the experimental accuracy possible. Hence the question arises as to why it becomes hard to observe a D^- state in the bulk GaAs without a localizing magnetic field or other means for enhancing the binding energy.

We try to examine in the present work some possible reasons for the above by considering the screening due to other impurity electrons. It is well known[11-13] that the binding energy of a neutral donor decreases with increase of impurity concentration and eventually becomes zero at a critical concentration. Phelps and Bajaj[14] attempted some years ago to find the effect of screening on the binding energy of a D^- ion using Thomas-Fermi potentials. The same screening function is used for both the electron-nucleus and electron-electron interactions. Their estimates show that the binding energy goes to zero at electron concentrations which are one order of magnitude smaller than the critical concentration at which the D^0 binding energy goes to zero. It is known that the Thomas-Fermi screening is not adequate to give the correct critical concentration. In the present work we give our results of calculations of the D^- center binding energies in GaAs. We consider the Coulomb interaction between the electron and nucleus screened by an effective static dielectric function valid for all wave numbers. We also give estimates of the temperature range over which the D^- ion can be stable. We have also calculated the optical-matrix elements to see the stability of D^- against ionization.

II. EFFECT OF SCREENING

The Hamiltonian for a D^- center with screened impurity potential is

$$H=-\nabla_1^2-\nabla_2^2+V(\mathbf{r}_1)+V(\mathbf{r}_2)+\frac{2}{r_{12}}\ , \tag{1}$$

where we have used the effective Bohr radius $a_B^*=\hbar^2k_0/m^*e^2$ as the unit of length and the effective Rydberg $\text{Ry}^*=m^*e^4/2k_0^2\hbar^2$ as the unit of energy. For GaAs one has $a_B^*=102.57$ Å, $\text{Ry}^*=5.32$ meV with the static dielectric constant $k_0=13.2$ and $m^*=0.0681m_0, m_0$ being free-electron mass.

We choose the Chandrasekhar-type trial function including the electron correlation,

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=N[e^{-ar_1-br_2}+e^{-br_1-ar_2}](1+cr_{12})$$

where a, b, c, are variational parameters.

$V(\mathbf{r})$ in Eq. (1) is given by

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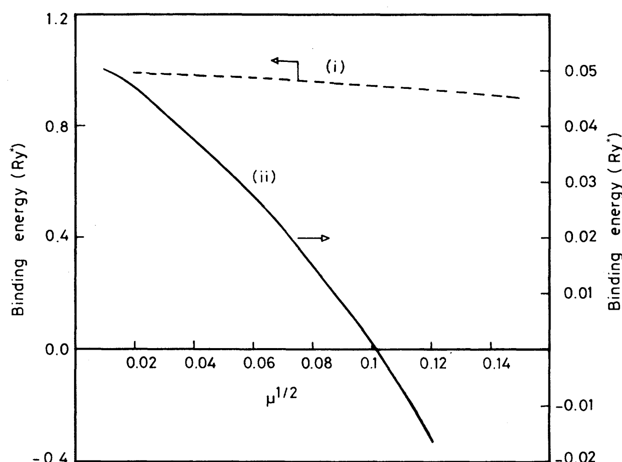

FIG. 1. (i) D^0 binding energy as a function of $\mu^{1/2}$. (ii) D^- binding energy as a function of $\mu^{1/2}$. (See also Table I).

$$V(\mathbf{r})=n_{\mathrm{FT}}\left[-\frac{4\pi e^2}{q^2\epsilon_{\mathrm{eff}}(\mathbf{q})}\right], \tag{2}$$

where n_{FT} stands for the "Fourier transform of" and the effective dielectric function $\epsilon_{\mathrm{eff}}(\mathbf{q})$ is

$$\epsilon_{\mathrm{eff}}(\mathbf{q})=\left[\frac{q^4+cq^2+D}{q^4+Aq^2+B}\right]+\frac{4\pi}{q^2}\left[\frac{3N}{2E_F}\right] \times\left[\frac{1}{2}+\frac{4k_F^2-q^2}{8k_Fq}\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right]. \tag{3}$$

A, B, C, and D are constants obtained by Richardson and Vinsome.[15] The first term is the dielectric function for the host part and the second term is that for the impurity electrons (with density N) treated as an electron gas with Fermi energy E_F, and wave number k_F. For the electron-electron repulsion term in Eq. (1), we have assumed that the screening is by the static dielectric constant (k_0) alone. In terms of dimensionless quantities $x(=q/2k_F)$, $\mu(=a_B^*k_F)$, $A_1[=A(k_0/m^*)^2]$, $B_1[=B(k_0/m^*)^4]$, $C_1[=C(k_0/m^*)^2]$, $D_1[=D(k_0/m^*)^4]$, we have

TABLE I. Numerical equivalence of $\mu^{1/2}$ and the concentration N in cm^{-3}.

$\mu^{1/2}$	N
0.01	3.1298×10^4
0.02	2.0031×10^6
0.03	2.2816×10^7
0.04	1.2820×10^8
0.05	4.8903×10^8
0.06	1.4602×10^9
0.07	3.6822×10^9
0.08	8.2046×10^9
0.09	1.6633×10^{10}
0.10	3.1298×10^{10}
0.11	5.5446×10^{10}
0.12	9.3455×10^{10}

TABLE II. D^- binding energy and the maximum temperature.

$\mu^{1/2}$	Extra electron binding energy (Ry)*	$T_{\max}$ (K)
0.01	0.0500	3.08
0.02	0.0470	2.90
0.03	0.0432	2.67
0.04	0.0386	2.38
0.05	0.0334	2.06
0.06	0.0277	1.71
0.07	0.0215	1.33
0.08	0.0147	0.91
0.09	0.0076	0.47
0.10	0.0024	0.15

$$\epsilon_{\mathrm{eff}}(x)=\frac{16\mu^4x^4+4C_1\mu^2x^2+D_1}{16\mu^4x^4+4A_1\mu^2x^2+B_1}+\frac{k_0}{\pi\mu x^2}L(x)$$

where

$$L(x)=\left[\frac{1}{2}+\frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|\right].$$

While the expectation values of the kinetic energy and the electron-electron repulsion terms are evaluated using the Hylleraas coordinates,[16] the expectation value of the potential energy involves numerical integration.

By varying the parameters a, b, and c, the $\langle H\rangle_{\min}$ is found as a function of μ. The extra electron binding energy is obtained by subtracting $\langle H\rangle_{\min}$ from the neutral donor binding energy. The results are given in Fig. 1. It shows that the D^- binding energy goes to zero much faster than the D^0 binding energy. This seems to suggest that screening by a small number of electrons (even those from native impurities) can reduce the binding substantially, making these D^- centers quite unstable.

III. ESTIMATES OF TEMPERATURE RANGE AND OPTICAL-MATRIX ELEMENTS

We make simple estimates of the temperature by just equating appropriate binding energies to thermal energies. The results are given in Table II. The results show that D^- is ionized even at extremely low temperatures.

TABLE III. Modulus square of the dipole matrix elements as a function of $\mu^{1/2}$.

	$\lvert\langle i\lvert eZ\rvert f\rangle\rvert^2$ (cgs units),	
$\mu^{1/2}$	for D^0 ($\times10^{-47}$)	for D^- ($\times10^{-44}$)
0.01	1.3165	1.1181
0.02	1.3241	1.1693
0.03	1.3345	1.2097
0.04	1.3465	1.1978
0.05	1.3605	1.0301
0.06	1.3764	0.4672

Since the D^- binding energy approaches zero quite fast as the impurity electron concentration increases, the maximum temperature above which D^- is ionized becomes very small.

For estimating the optical-matrix elements we take the initial state and the final state as

$$|i\rangle = N[e^{-ar_1-br_2}+e^{-br_1-ar_2}] \,, \tag{4}$$

$$|f\rangle = \left[\frac{b'^3}{\pi V}\right]^{1/2} e^{-b'r_2} e^{i\mathbf{k}\cdot\mathbf{r}_1} \,.$$

N is the normalization constant and b' is the inverse Bohr parameter obtained for D^0 (for simplicity we have dropped the r_{12} term in the Chandrasekhar-type function). The optical transition probability is proportional to the modulus square of the dipole matrix element,

$$\begin{aligned} -\langle i|eZ_1|f\rangle &= -Ne\left[\frac{b'^3}{\pi V}\right]^{1/2} \int [e^{-ar_1-br_2}+e^{-br_1-ar_2}] r_1 \cos\theta_1 e^{-b'r_2} e^{i\mathbf{k}\cdot\mathbf{r}_1} d^3r_1 d^3r_2 \\ &= -i256\pi^2 NKe\left[\frac{b'^3}{\pi V}\right]^{1/2} \left\{ \frac{a}{(b+b')^3(a^2+k^2)^3} + \frac{b}{(a+b')^3(b^2+k^2)^3} \right\} . \end{aligned} \tag{5}$$

The transition probability is proportional to

$$|\langle i|eZ_1|f\rangle|^2 = \left[\frac{(256\pi^2 NKe)^2 b'^3}{\pi V}\right] \left\{ \frac{a}{(b+b')^3(a^2+k^2)^3} + \frac{b}{(a+b')^3(b^2+k^2)^3} \right\}^2 . \tag{6}$$

A similar calculation is done for the dipole matrix elements in the case of a neutral donor D^0.

For the D^0, the optical-matrix element between the states $|i\rangle = b'^3/\pi V)^{1/2} e^{-b'r}$ and $|f\rangle = (1/\sqrt{V}) e^{i\mathbf{k}'\cdot\mathbf{r}}$ works out to be

$$-\langle i|eZ|f\rangle = \frac{-i32\pi b' e k'}{(b'^2+k'^2)^3} \left[\frac{b'^3}{\pi V}\right]^{1/2} . \tag{7}$$

Typical values of the modulus square of the dipole matrix elements are presented in Table III.

The results show that the optical-matrix elements for D^- are an order of magnitude larger than for D^0. This shows that the ionization probability for D^- is much higher than that for D^0.

In summary, we find that the D^- binding energy goes to zero much more rapidly with an increase of impurity concentration than with the D^0 binding energy. Even native impurities can thus destabilize a D^- center in GaAs. The range of temperature in which a D^- center could be stable is extremely small. The magnitudes of optical-matrix elements show that the dissociation of D^- is more favorable than the ionization of D^0.

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