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Ge DONORS IN GaP AND THE ROLE OF HIGHER BAND MINIMA IN IMPURITY THEORY

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It is shown that the anomalously deep and non-degenerate ground state of Ge donors in GaP is better described as a deep state attached to higher X-minima of the conduction band than as a shallow one attached to the absolute minima. This is because of a very strong intervalley interaction between the higher minima at X for point-charge impurities located at the cation site.

I. Introduction

As a cation-substitutional donor in GaP, Ge has a behavior quite different from the other group-IV elements. Its binding energy (201.5 meV, [1]) is much larger than that of Si (85.3 meV, [2]) or Sn (69 meV, [1]). Moreover, its symmetry character appears to be anomalous. Because of the symmetry of the band minima [3], there is no valley-orbit interaction for cation-site donors for the X_1 conduction band valleys (we neglect the camel's back structure of the band minima [4]), so that a 3-fold degenerate Γ_{25} (p-like) ground state is expected. For anion-site, group VI donors, on the other hand, the triplet is valley-orbit split into a lower Γ_1 singlet and an upper Γ_{12} doublet. The EPR spectrum of Si and Sn under stress confirms that their ground state is a triplet, whereas the Ge EPR spectrum, similar to that of group VI donors, indicates an s-like ground state [5,6].

Furthermore, consider the binding energies of the Ge and S donors. Both have the same core as the atoms they replace (Ga and P respectively) and should be well described by the same point-charge bare potential. The ground state of S is pushed down by the valley-orbit interaction, and would be expected to be deeper. Experiment, however, shows that Ge is much deeper than S (201.5 meV for Ge [1], 108 meV for S [2]).

In this work, the puzzling properties of the Ge donor in GaP are explained by considering the higher X_3 minima, which lie about .4 eV [4,7] above the X_1 ones. Their symmetry allows a valley-orbit split Γ_1 ground state for cation-substitutional donors, and an analysis of the Bloch functions shows that the valley-orbit interaction is so strongly attractive for a point-charge donor to compensate for the higher band energy.

II. Results and Discussion

Recent advances in the theory of donors in many-valley semicon-

ductors [8-11] have shown that intervalley interactions can be strong enough to produce deep levels, and that their strength depends on the detailed structure of the Bloch functions. In the empirical pseudopotential formalism, we obtain the pseudo-Bloch functions by a standard calculation with 92 plane waves [12], and describe the GaP : Ge and GaP : S impurity potential $V(\vec{q})$ in two alternative ways: (a) as a point charge screened by the momentum dependent diagonal dielectric function $\varepsilon(\vec{q})$ of GaP [13,14]; (b) by the same screened potential as in (a), but truncated in momentum space i.e. with $V(\vec{q}) = 0$ for $q > (2\pi/a)\sqrt{11}$, where a is the GaP lattice constant and the cut-off in $\vec{q}$ is the same as that of the empirical form factors. This twofold choice is a check on the consistency of the calculation, because, as we shall see, results for either the (a) or the (b) potential are qualitatively similar, irrespective of the non-uniqueness of the impurity pseudopotential.

We define, for a pair of minima k_{oi} and k_{oj} a dimensionless parameter λ_{ij}, given by:

$$\langle \vec{k}_{oi} | V | \vec{k}_{oj} \rangle = -\lambda_{ij} \frac{4\pi e^2}{\varepsilon(\Delta k_{ij})\ \Delta k_{ij}^2} \qquad (1)$$

where $\Delta k_{ij} = |\vec{k}_{oi} - \vec{k}_{oj}|$. For the three X-minima of GaP, the result is independent of i and j, and is described by one parameter λ. In Table I (top line), we report the values of λ computed according to the procedure described above and in [10], for the lower X_1 valleys, for cation and anion substitutional donors. As expected from symmetry arguments [3], λ vanishes on the cation site.

On the anion site, a substantial reduction from unity is found, i.e. a sizeable suppression of the strength of intervalley interactions by umklapp effects. For a binding energy calculation, we need the effective-mass values m_t and m_l. While $m_t = 0.25$ is determined by cyclotron resonance [15], the determination of m_l is not as straightforward because of the camel's back. Raman measurements [2] indicate however a binding energy of ~55 meV for the Γ_{12} component of the S ground state multiplet, and this suggests an "effective" m_l/m_t ratio of order ~5-6. We therefore set $m_l = 1.25$, and obtain the results shown in Table I (first and third columns).

Table I. Intervalley interaction parameter λ and binding energies

	(a)		(b)	
	Anion	Cation	Anion	Cation
$\lambda(X_1)$	0.53	0.00	0.39	0.00
$\lambda(X_3)$	0.00	1.11	0.00	1.25
Γ_1 B.E.(meV)	153	deep	94	deep
Γ_{12} B.E.(meV)	50	38	55	38

The theoretical binding energies for the (a) and (b) potential encompass the experimental values 108 meV [2] for Γ_1, and 54.8 meV for Γ_{12} [2].

The corresponding result for Ge, for which the X_1-valley λ vanishes, would be 55 meV, rather than the experimental 201 meV. We are therefore led to consider the upper X_3 valleys (second line of Table

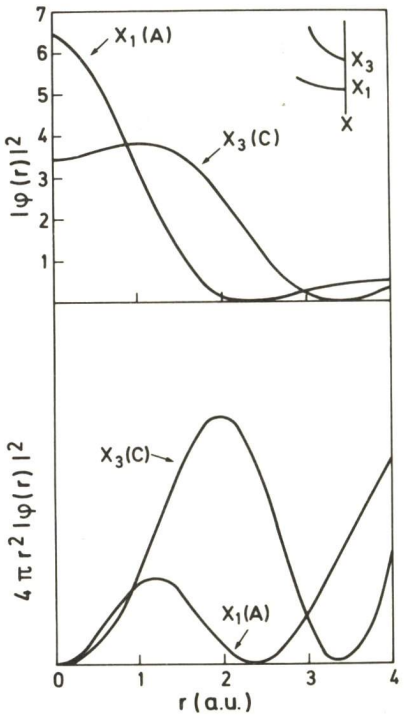

Fig. 1. Spherical average of charge density (top) and radial charge density (bottom) for Γ_1 combination of X_1 Bloch waves about the anion site, and of X_3 waves about the cation site

I). From pseudopotential calculations we estimate for these valleys $m_t = 0.23$ and $m_l = 0.76$. The value of λ vanishes for the anion-substitutional case, but is very large, in excess of 1, for cation-substitutional impurities. These large values are so big to trigger the formation of a deep state. The complete breakdown of our approximations prevents a binding energy calculation in this case.

To understand the origin of such large matrix elements, we consider the charge distribution $|\rho(r)|^2$ of the Γ_1-symmetric combination, of the X_1 Bloch functions about the anion site, and of the X_3 about the cation, respectively. The spherical average of such quantities is shown in the top panel of Fig. 1, while the lower panel shows the same quantities weighted by the volume element $4\pi r^2$, to give the radial charge distribution function. It is apparent that the X_3 wavefunctions are much more effective in piling up charge within a 3-4 a.u. range from the impurity, where the potential is very strong, and screening is ineffective. The resulting gain in potential energy more than compensates the 0.4 eV kinetic energy of the X_3 minima.

In conclusion we have shown that the anomalous properties of the Ge donor in GaP are explained in term of the very strong intervalley interaction of the X_3 wavefunctions. In analogy to the case of muonium in Ge [16], it confirms that shallow-deep instabilities can be triggered by secondary extrema of the band structure.

References

1) A.T. Vink, R.L.A. Van der Heyden and J.A.W. Van der Does de Bye: J. Luminesc. 8 (1973) 105.
2) A.C. Carter, P.J. Dean, M.S. Skolnick and R.A. Stradling: J. Phys. C 10 (1977) 5111.
3) T.N. Morgan: Phys. Rev. Lett. 21 (1968) 819.
4) P. Lawaetz: Solid State Commun. 16 (1975) 65.
5) F. Mehran, T.N. Morgan, R.S. Title and S.E. Blum: Phys. Rev. B 6 (1972) 3917.
6) F. Mehran, T.N. Morgan, R.S. Title and S.E. Blum: Solid State Commun. 11 (1972) 661.
7) D.S. Kyser and V. Rehn: Phys. Rev. Lett. 40 (1978) 1038.
8) K. Shindo and H. Nara: J. Phys. Soc. Japan 40 (1976) 1640.
9) R. Resta: J. Phys. C 10 (1977) L 179.

10) M. Altarelli, W.Y. Hsu and R.A. Sabatini: J. Phys. C 10 (1977) L 605.
11) D.C. Herbert and J. Inkson: J. Phys. C 10 (1977) L 695.
12) M.L. Cohen and T.K. Bergstresser: Phys. Rev. 141 (1966) 789.
13) P.K.W. Vinsome and D. Richardson: J. Phys. C 4 (1971) 2650.
14) J. Bernholc and S.T. Pantelides: Phys. Rev. B 15 (1977) 4935.
15) K. Suzuki and N. Miura: Solid State Commun. 18 (1976) 233.
16) M. Altarelli and W.Y. Hsu: Phys. Rev. Lett. 43 (1979) 1346.