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ANOMALOUS BEHAVIOR OF SHALLOW DONOR GROUND STATE LEVELS IN Ge UNDER PRESSURE

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The crossing between absolute (L_1) and secondary (Δ_1) minima which occurs in Ge under the application of a hydrostatic pressure has been found to evidence the strong multi-valley interactions responsible of an anomalous pressure dependence of the A_1 level. Two alternative experimental investigations are suggested to evidence these expectations.

WE PRESENT in this paper a detailed analysis of the ground state levels of shallow donors in Ge when pluri-minima effects are considered. The valley-orbit and subsidiary minima interactions have been here accounted for the first time in the configuration of the conduction band structure of Ge which, under hydrostatic pressure, assumes the typical features of the GeSi alloys.[1] Our results evidence important effects when the four L_1 minima and the six Δ_1 minima (Si-like) lie at about the same energy a configuration in which the multi-valley interactions play a dominant role. The non crossing rule (among states of the same symmetry) is here clearly evidenced and an anomalous pressure dependence of the binding energy of the A_1 level is predicted for the first time. These results could suggest new experimental investigations to evidence the strong interactions arising from pluri-minima configurations, here theoretically predicted.

At atmospheric pressure in Ge the shallow donors ground states is split into two levels of degenerancies 1 and 3 whose symmetries are A_1 and T_1 respectively, and for the Si-like minima into three levels of degeneracies 1, 2 and 3 whose symmetries are A_1, E and T_1 respectively. All these levels are here computed taking into account the valley-orbit[2,3] and subsidiary minima[4] interactions. Central cell corrections[5] were not included, since the exact location in energy of the A_1 level[2] is not the aim of the present study.

Following[6] the complete formal treatment of Bassani, Iadonisi and Preziosi[7] we have started with the conduction band structure of Ge at atmospheric pressure and separated the k-space in the extended zone scheme into ten subzones Ω ($i \equiv 1, 10$). Every subzone contains a minimum located at $\underline{k}_{0i}$, four for the absolute L_1 minima, and six for the Δ_1 subsidiary minima (Si-like),[8] which are about 0.18 eV above, located at $k_0 = 2\pi/a_0(0.82, 0{,}00)$, being a_0 the lattice parameter. The eigenvalues E of the impurity states are so obtained from the solution of the secular determinant[7]

$$\mathrm{Det}\ |\ (E_i^0 - E)\ \delta_{ij} + U_{ij}(1 - \delta_{ij})\ | = 0 \quad (1)$$

where U_{ij} is defined by:

$$U_{ij} = \int_{\Omega_i} \mathrm{d}\underline{k} \int_{\Omega_j} \mathrm{d}\underline{k}'\ \phi_i^{0*}(\underline{k})\, U_{ij}(\underline{k}, \underline{k}')\, \phi_j^0(\underline{k}') \quad (2)$$

being $U_{ij}(\underline{k}, \underline{k}')$ the Bloch matrix elements connecting states of different subzones through the impurity potential $U(r) = -e^2/r\epsilon$. $\phi_i^0(\underline{k})$ and E_i^0 are the eigenfunction and eigenvalue respectively of the zero order solution for the ground state calculated for each minimum i (considered as independent) in the EMA.[9] The q-dependence of the

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Table 1.

Quantity	Value	Units
$\epsilon_{12}(L_1 - L_1)$	2.2*	–
$\epsilon_{13}(\Delta_1 - \Delta_1)_{//}$	1.6*	–
$\epsilon_{14}(\Delta_1 - \Delta_1)_{\perp}$	2.3*	–
$\epsilon_{15}(L_1 - \Delta_1)$	2.2*	–
U_{12}	$-0.184^{\dagger}$	meV
U_{13}	$-0.512^{\dagger}$	meV
U_{14}	$-0.713^{\dagger}$	meV
U_{15}	$-0.472^{\dagger}$	meV
$[E(T_1) - E(A_1)]\, L_1$	$0.77^{\dagger}$	meV
$[E(T_1) - E(A_1)]\, \Delta_1$	$3.86^{\dagger}$	meV
$[E(E) - E(T_1)]\, \Delta_1$	$0.40^{\dagger}$	meV

* These values are deduced from Fig. 3 of Walter and Cohen.[10]

† Present work.

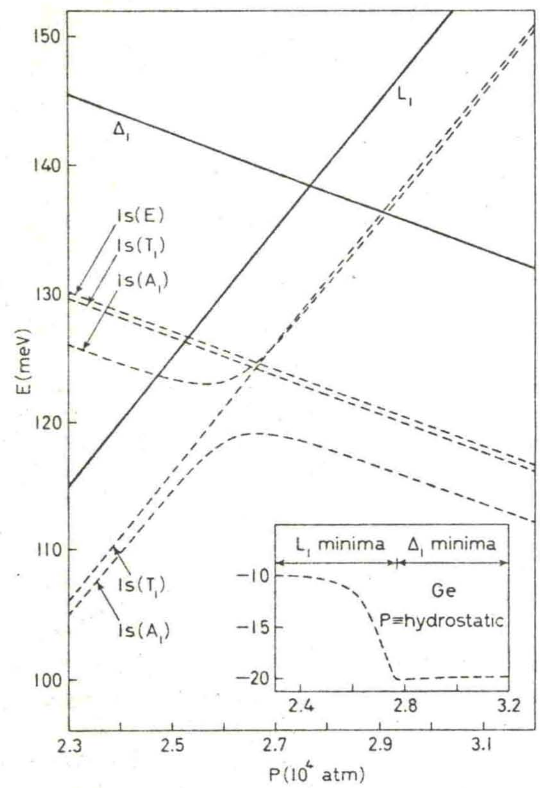

FIG. 1. Pressure dependence of the ground state levels for shallow donors in Ge (broken lines). Full lines exhibit the pressure dependence of the L_1 and Δ_1 minima. The energy is measured from the conduction band edge at atmospheric pressure. The insert evidences the anomalous pressure dependence of the binding energy of the $1s\,(A_1)$ level in the crossing region between L_1 and Δ_1 minima. The binding energy is measured from the conduction band edge at the given pressure.

dielectric constant $\epsilon = \epsilon\,(\underline{k}_{0i} - \underline{k}_{0j} = \underline{q})$ has been taken into account following the results of Walter and Cohen.[10] The ellipsoidal shape of the equienergetic surfaces about the minima have been taken into account through an appropriate average of the longitudinal and transverse effective Bohr radii.[9] The Bloch functions have been replaced with plane wave functions, a reasonable approximation for a slowly varying potential. The integration method was carried on with a delta function, as discussed by Callaway.[11] The values so obtained for U_{ij} are reported in Table 1 with the proper dielectric constant values used for calculations. The U_{ij} listed refer to the following interactions: U_{12} to $L_1 - L_1$, U_{13} to $\Delta_1 - \Delta_1$ (parallel valleys), U_{14} to $\Delta_1 - \Delta_1$ (perpendicular valleys), and U_{15} to $L_1 - \Delta_1$. The calculated values for the energy splittings between the T_1 and A_1 levels associated with the L_1 minima, and the T_1 and A_1, and E and T_1 levels associated with the Δ_1 minima for Ge at atmospheric pressure are also reported in Table 1.

The effect of an applied hydrostatic pressure P was then included assuming a rigid shift in energy of the L_1 and Δ_1 minima with P,[12] and a dielectric constant ϵ pressure independent. Using the pressure coefficients (respect to the valence band) $dE(L_1)/dP = 5\ 10^{-6}$ eV/atm, and $dE(\Delta_1)/dP = -1.5\ 10^{-6}$ eV/atm[12] the new energy locations of L_1 and Δ_1 minima have been calculated. Accordingly the new solutions of the secular determinant (1) have been carried on.

Results are reported in Fig. 1, where the strong interaction between the two A_1 levels associated with the L_1 and Δ_1 minima respectively is evidenced, in accord with the non crossing rule.[13] This effect is maximum when the L_1 and Δ_1 minima are approaching the same energy and causes the binding energy of the A_1 level to exhibit the anomalous behaviour evidenced in the insert. On the contrary the T_1 and E levels follow with pressure the behaviour of the minima they belong to, as expected. The conduction band structure of the GeSi alloys varies with composition[1] in a manner similar to the variation of the Ge conduction band under hydrostatic pressure; at $P = 28\ 10^3$ atm and $Ge_{1-x}Si$ with $x = 15\%$ the ten $L_1 + \Delta_1$ minima lie in the crossing region. Consequently let us emphasize the following facts. (i) Two alternative experimental techniques, hydrostatic pressure and/or GeSi alloys, may be devised to evidence the theoretical predictions; (ii) the possibility of controlling to some extent the binding energy of a shallow donor is *a priori* feasible.

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On évidence les fortes interactiones 'multi-valley' responsable d'une dépendance anomale de la pression du niveau d'impurité A parmi le croisement entre les minimes absolu (L_1) et secondaire (Δ_1) dans le Ge sous pression hydrostatiques. On suggér deux investigations expérimentales en alternative pour donner évidence aux prévisions théoriques.