CHINESE PHYS. LETT.
Vol.4, No.9(1987)

CHINESE PHYSICS LETTERS
Science Press, Beijing
Springer-Verlag

DEEP GROUND STATES RELATED TO Fe IN $GaAs_{1-x}P_x$ ALLOY SYSTEM

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(Received 17 January 1987; version received 19 May 1987)

A theory suggested by Vogl et al. is extended to the iron-doped $GaAs_{1-x}P_x$ alloy system. The deep ground states (including acceptor (Fe^0/Fe^-) levels, donor (Fe^+/Fe^0) levels, local charges and spin densities) are predicted for different composition χ. The calculated results show good agreement with the relevant experimental data and reveal their variation trends.

Recently, Vogl and Baranowski[1,2] developed a simplified but global theory for the substitutional 3d-transition-metal impurities in compound semiconductors. The theory provides for the first time an explanation for both the spin-related ESR data and the optical data for a variety of impurity-host systems and predicts their major chemical trends. In this letter, we shall prove that this theory can be extended to the iron-doped $GaAs_{1-x}P_x$ alloy system, and the variation trends of ground deep-level energies, local charges and spin densities for an extended composition range are also obtained.

Owing to the limitation of space, we can only list some major points of the theory as follows: 1. The atomic multiplet structure of free iron atom is calculated in terms of spin-unrestricted Hartree-Fock model based on the Anderson-Parmenter Hamiltonian[3], including 3d- and 4s-shells. 2. A sp^3s^* ten-state linear combination of atomic orbitals (LCAO) model[4], which is modified to include next nearest neighbours, is used for host. LCAO parameters are obtained from fitting the experimental results[5] for different compositions. 3. With a Green's function method, the Schrodinger equation of the perturbed crystal is solved. The crucial defect matrix is constructed by assuming that (i) it is of short range, (ii) the off-site matrix elements are universal functions of bond length, (iii) the on-site matrix elements are proportional to atomic energy difference and depend linearly on the spin orbital occupation probabilities. 4. Different charge state effects are included in a self-consistent manner[6]. 5. The deep donor energy E(D) associated with an iron atom is the energy required to move a bound electron from the neutral iron atom into the bottom of the conduction band $E_{cond.}$ and thus can be determined by the total Hartree-Fock energy differences, Hence one may write:

$$E(D) = \Delta E_{tot}(+) + E_{cond.} - \Delta E_{tot}(0) ,$$

where $\Delta E_{tot}(0)$ and $\Delta E_{tot}(+)$ represent the differences of the total energy of the $GaAs_{1-x}P_x$ alloy with a neutral substitutional iron atom and an ionized one, respectively, from that of the corresponding non-doped alloy. The acceptor energy can be written analogously.

In our calculation, the cubic symmetry of the host semiconductors is always assumed for different compositions. Under the cubic symmetry, the fivefold degenerate 3d-orbital of iron atom is splitted into an e-symmetric ($d_{x^2-y^2}$-like) doublet and a t_2-symmetric (d_{xy}-like) triplet. The four sp^3 dangling bonds of the nearest neighbours, which are pointing toward the impurity atoms, can form one fully symmetric a_1(s-like) state and three t_2-symmetric (p-like) states in terms of linear combinations. The calculations show that the iron 4s level and the fully symmetric a_1 (s-like) state of the neighbouring hybrids form a doubly occupied (a_1^-) bonding state deep in the valence band and antibonding state high up in the conduction band. Therefore, the s-type level simply takes up two electrons. By means of a defect molecule which models $GaAs_{1-x}P_x$: $\mathring{Fe}$, a qualitative electronic configuration of substitutional neutral iron in $GaAs_{1-x}P_x$ is presented in fig.1 (not including a_1 state). After crystal-field splitting and exchange splitting, the $t_2\uparrow$ and $t_2^*\downarrow$ states of iron will most effectively couple to the $t_2^*\uparrow$ and $t_2^*\downarrow$ of the neighbouring dangling bonds, which lie energetically in the uppermost portion of the valence band. Because no (σ-bonding) states of e-symmetry can be formed in the tetrahedral semiconductors[7], the $e\uparrow$ and $e\downarrow$ states remain no-bonding and maintain their atomic-like characters. The occupation of states is shown clearly in the fig.1, where 11 electrons come from the neutral iron (6 d-electrons) and the dangling bonds (5 electrons). From fig.1, we know that the e-symmetric ground acceptor state corresponds to configuration transition from $e^2\uparrow t_2^3\uparrow t_2^{*3}\downarrow t_2^{*3}\downarrow e^0\downarrow t_2^0\downarrow$ to $e^2\uparrow t^3\uparrow t_2^{*3}\downarrow t_2^{*3}\uparrow e^1\downarrow t_2^0\downarrow$. Figure 2 shows our calculated results together with the recent optical data[8] of the atomic-like e-symmetric ground acceptor levels with different compositions of the iron-doped $GaAs_{1-x}P_x$. From fig.2, we can see that the theory shows satisfactory overall agreement with the experimental data and reveals their chemical trends. An approximation of the theoretical expression for the ground acceptor levels as a function of composition x can be written as

$$E(x) = E(0) + \alpha x \ , \qquad \alpha \doteq 0.5 \ , \qquad E(0) = 0.43$$

We have found the high-spin solution to be the ground state for all compositions, which is in agreement with the experiments. A host-like t_2-symmetric donor level ($\mathring{Fe}/\mathring{Fe}^+$) curve is depicted by the theory but it remains to be proved by experiment.

Reference 8 attempted to use the vacuum referred bind energy (VRBE) hypothesis[9] to explain their optical data. We think that their explana-

tion is not reasonable, because the VRBE hypothesis is based on the antibonding nature of the deep gap-level with respect to the impurity atom-host orbital combination. As is shown before, the e-level is non-bonding, atomic-like state, hence the VRBE hypothesis cannot be used here. We believe that the variation trend of the acceptor levels of fig.2 is a consequence of the atomic-like feature of the e-symmetric state. Although the VRBE hypothesis may have a similar conclusion, its physical mechanism is quite different from ours. The similar cases will occur when we deal with the impurities Ti, Co in III-V compounds or alloys, because their acceptor levels are predicted to be similar to Fe.

Figure 3 and 4 show that the local charge $\langle n_d \rangle_{imp.}$ and the spin density $\langle s \rangle_{imp.}$ almost do not vary with the compositions for both $GaAs_{1-x}P_x$: $\mathring{Fe}$ and $GaAs_{1-x}P_x$: $\bar{Fe}$. The reason why the difference of $\langle n_d \rangle_{imp.}$ is so small between the neutral and the negative charge impurity's states in $GaAs_{1-x}P_x$ can be explained in terms of a self-regulating neutrality effect[2,3]. The total spin of the impurity-host system, which is measured in ESR-experiments, is observed to arise only partly from the impurity; the rest comes mainly from the induced spin-polarization of the neighbouring atoms.

We would like to thank Prof. P. Vogl for his kindly help.

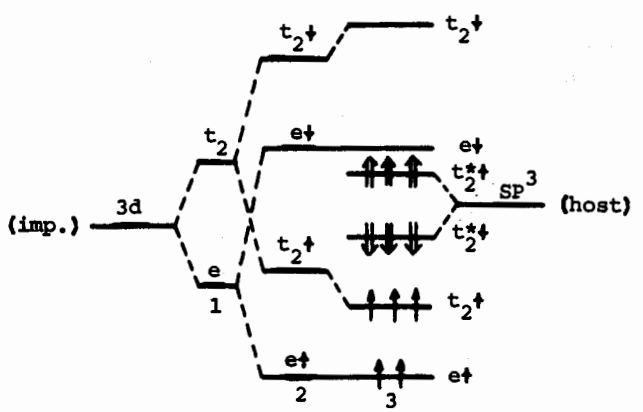

Fig.1 A defect molecule model exhibited the qualitative electronic configuration of $GaAs_{1-x}P_x$:$\mathring{Fe}$. For d states, the crystal-field splitting, exchange splitting and coupling with the neighbouring hybrids are indicated by 1, 2 and 3, respectively.
↑ host-like electron
↑ impurity-like electron

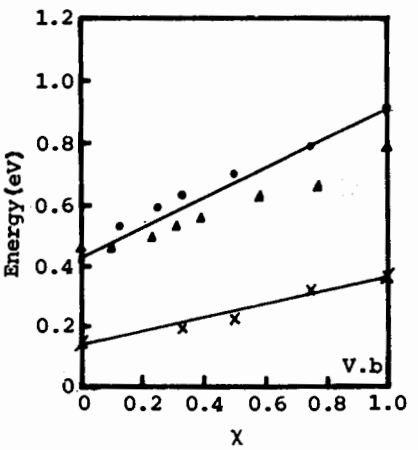

Fig.2 Predicted e-symmetric ground acceptor levels (·) and t_2-symmetric ground donor levels (X) of the iron doped $GaAs_{1-x}P_x$ system versus composition x, compared with the experimental data (▲). The valence band edge is denoted by V.b..

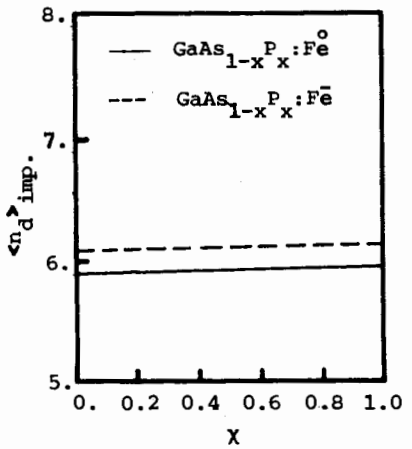

Fig.3 Predicted local charge $\langle n_d \rangle_{imp.}$ of $GaAs_{1-x}P_x:Fe^{\circ}$ and $GaAs_{1-x}P_x:Fe^{-}$ versus composition x.

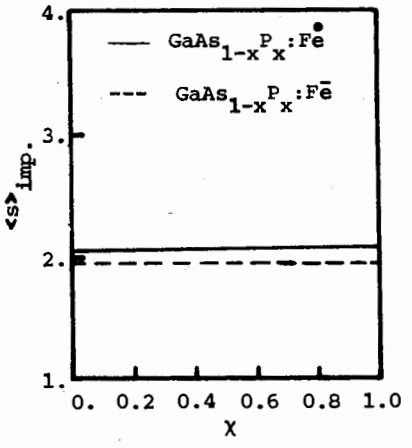

Fig.4 Predicted spin density $\langle s \rangle_{imp.}$ of $GaAs_{1-x}P_x:Fe^{\bullet}$ and $GaAs_{1-x}P_x:Fe^{-}$ versus composition x.

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