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Acceptor and Donor Levels of 3d Impurities at Interstitial Sites in GaAs

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Abstract We present results for the electronic structure of 3d transition-metal interstitial impurities in GaAs. Both anion and cation interstitial defect sites of high-symmetry are considered. The existence of acceptor and donor states in the gap for impurities at the anion interstitial site is investigated, including many-electron corrections to the one-electron energy levels. Our results show that the trend for the 3d-induced e and t_2 states is very similar in both tetrahedral interstitial sites. We find that Co, Fe, Mn and Cr could present donor levels in the gap. Acceptor levels are predicted to occur in the gap only for interstitial Co and Mn.

1. INTRODUCTION

Among the impurity systems in III-V semiconducturs, transition metals (TM) constitute a class by themselves, intensively studied in the past years from both experimental and theoretical points of view [1,2]. The technological relevance of such systems comes mostly from the growth of semi-insulating substrate materials.

One of the more intriguing properties of TM impurity systenis is their ability to introduce several energy leveis related to different charge states in the gap region. The explanation of this phenomenon was proposed by Haldane and Anderson[3]: a strong hybridization between the metal d-orbital and ligand p-orbital is involved, such as to reduce the value of the Mott-Hubbard energy.

It is well established that the TM atoms enter the III-V semiconductor lattice preferentially in a cation-substitutional position; however there are some experimental evidences[4,5] that suggests the presente of TM impurities at interstitial sites in III-V compounds. We investigated recently[6] the behavior of 3d TM elements (Cu to Mn) orcupying the tetrahedral As interstitial site in GaAs, focusing on acceptor levels, (-/0). The results showed that only Mn and Co introduce acceptor states in the gap which are related to the 3d orbital.

In this work, our aim is to analyse the behavior of TMs from Cu up to Cr, as isolated impurities placed at the high-symmetry *anion* and *cation* interstitial lattice sites, for *acceptor* and *donor* states. The one-electron energy levels are obtained through the multiple-scattering X_α molecular cluster model (MS-X_α) which has been successfully applied to investigate deep-level impurities in IV and III-V[7-10] semiconductors. To investigate the existence of acceptor and donor states in the gap we have included many-electron multiplet corrections[11] to the one-electron ionization energies.

2. THEORETICAL MODEL

The results presented in this work were obtained through hydrogen -terminated 27-atom clusters centered at both high-symmetry anion (T_A) and cation (T_C) tetrahedral interstitial sites, where the impurity is placed. For the impurities at the T_A site we adopted the cluster (1T4As6Ga16H) and for the impurities at the T_C site the cluster adopted was (1T4Ga6As 16H). The perfect crystal comprises a first shell of 4As (4Ga) anda second shell of 6Ga (6As) depending on whether the cluster is centered at the T_A (or T_C) sites respectively, and 16 hydrogen atoms (distributed in two shells with four and twelve atoms respectively) are used as boundary condition. According to the covalent crystal cluster model, the *internal bonds* of the cluster are occupied by 56 valence electrons in the case of the perfect crystal simulation, so that 2 electronic charges (positive for the T_A cluster and negative for the T_C cluster) have to be added to the Watson sphere to keep charge neutrality. This hydrogen-saturation model has already been used to study substitutional[12] and interstitial[13] 3d TM impurities in Si, and also 3d atoms replacing Ga in GaAs[14].

The calsulations carried out here were performed by assuming cluster models where the hydrogen saturators are placed closertothe host atoms than the Ga-As bond distance, at a position for which the crystal band gap, 1.5eV, is reproduced. The calculated values for the valence band widths are - 11.0eV which are in fairly good agreernent with the experimental results[15]. A detailed description of the cluster models used can be found in ref.6.

3. RESULTS AND DISCUSSION

3.1 - One-electron energy level results

In fig.1 we present the results for neutral impurities, from Cu up to Cr, at the T_A interstitial site together with the referencecluster simulating the GaAs perfect crystal. For the impurity systems, besides the occupied orbitals appearing in the gap, only e and t_2 resonances with significant d-character are emphasized. In the cases of Mn and Cr the spectra shown in the figure correspond to the high-spin configurations, e.g. $t_2^5e^2$ and $t_2^4e^2$ respectively.

We start the analysis of the spectra with interstitial Cu in GaAs, which introduced into the gap a fully occupied e-symmetry level and ana, level occupied by one electron. This a, level is rather delocalized and has a dominant conduction band character. As we proceed to Ni, the uppermost occupied state is now the e-symmetry gap orbital, fully occupied which appears close to the top of the valence band but energetically lower than the Cu e-gap level. This is a consequence of the decrease in electron repulsion energy caused by the lack of the a, electron, present for Cu; this effect overcomes the decrease in nuclear charge. We point out that in either case, Cu or Ni, these gap states have a lowpercentage of d-charge. For tiie Co impurity a t_2-symmetry state penetrates the gap region and is found fully occupied below the already partially occupied e-gap level. In going from Co to Cr, these e and t_2-gap states rise in energy and becomemore localized. It is worth pointing out that in the case of interstitial Cr the d-derived e orbital is already found in the conduction band.

In table 1, we exhibit the percentage of d-charge insidethe metal sphere for the e and t_2-gap orbitals obtained for the impurities at the T_A site, the one-electron configurations $t_2^m e^n$ used and the obtained effective crystal-field splittings (e-t, splittings), Δ_{eff}. We should mention that the chemical trend found in the one-electron energy levels for the impurities at the T_C site is very similar to that seen for the impurities at the T_A site. In fig. 2 the behavior of the impurity gap levels is depicted for both T_A and T_C sites with decreasing impurity atomic number Z. As wemay observe, the crystal-field splittings are slightly

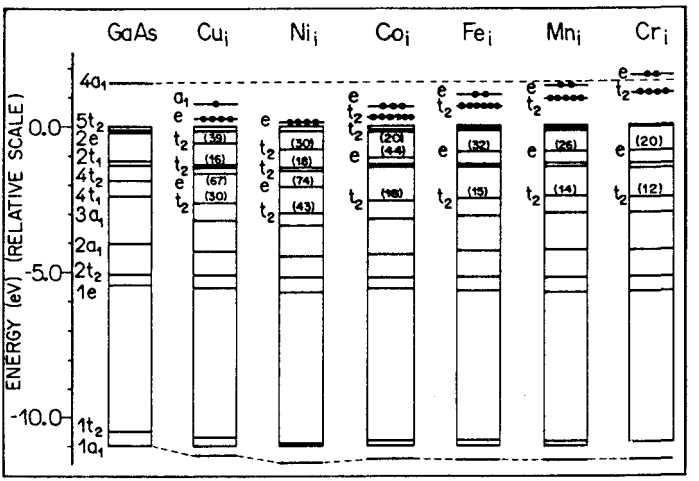

Fig.1 - One electron energy levels for 3d neutral impurities, TM_i, at the anion interstitial (T_A) site in GaAs. The spectrum for the GaAs perfect crystal is also shown. In the valence band only e and t_2 orbitals with significant d-character are emphasized (their *d*-contribution, in percents, is indicated in parenthesis). All the occupied levels appearing in the gap are shown.

Table 1 - Percentage of *d*-charge in the metal muffin-tin sphere for the t_2 and e-gap levels, the one-electron configurations ($t_2^m e^n$) used in the calculations and the crystal-field splittings for the 3d TM impurities at the anion interstitial site.

	$Q(t_2)$	$Q(e)$	$t_2^m e^n$	Δ_{eff}(eV)
Cu	-	0.25	$t_2^6 e^4 a^1$	-
Ni	-	0.18	$t_2^6 e^4$	-
Co	0.44	0.47	$t_2^6 e^3$	0.40
Fe	0.57	0.57	$t_2^6 e^2$	0.40
Mn	0.57	0.62	$t_2^5 e^2$	0.45
Cr	0.55	0.64	$t_2^4 e^2$	0.55

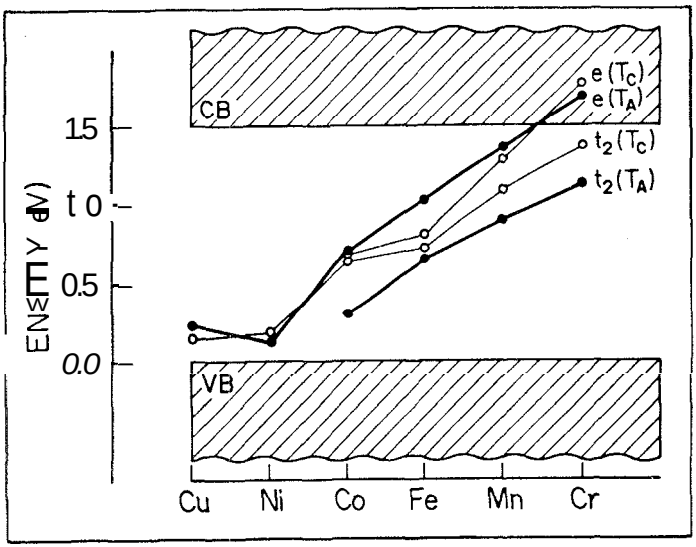

Fig.2 - Behavior of the impurity gap levels for 3d TM impurities at the anion interstitial (T_A) site (heavy solid line) and at the cation interstitial (T_C) site (thin solid line) with decreasing impurity atomic number.

larger when the irnpurities enter the T_A site, thereby indicating that the crystal-field effect is somewhat weaker over the impurities at the T_C site. The overall analysis of our calculations yields the conclusion that the trends displayed by the interstitial impurity levels are quite similar to those inferred for the 3d TM impurities replacing the cation in GaAs[14] (substitutional impurities). It is worth noting, however, that the interstitial irnpurities place the t_2-gap level below the e-gap level (as has already been observed for interstitial 3d atorns in Si[13]); in contrast, for substitutional irnpurities the order is reversed. We note further that the effective crystal-field splittings are smaller for interstitial than for substitutional impurities. In what concerns the optical properties of such systems this feature is of fundamental irnportance.

3.2 - Acceptor and Donor Levels

We estimated the position of the first acceptor and donor levels in the gap for Co, Fe and Mn at the T_A interstitial site by including the many-electron correction energies to the one-electron energies, through the approach proposed by Fazzio, Caldas and Zunger[11] (FCZ). For interstitial Cr only the donor level was investigated since the one-electron energy level is already found in the conduction band. We will omit here the description of the (FCZ) method which can be found in detail elsewhere[11]. We just point out that interaction energies are expressed in terms of three quantities: the hybridization parameters λ_e and λ_t accounting for the reduction of electron repulsion energies within the d-shell of the impurity, and A_{eff} which amounts to the difference in total energies between configurations. These three quantities are directly extracted from our calculations instead of being obtained from a fit to the experimental data on optical transitions, as in earlier works[10,11].

In fig.3 we show the calculated donor (0/+) and acceptor (-/0) levels for Co, Fe, Mn and Cr at the T_A site. The obtained ground-state symmetries are also shown. As we note, interstitial Co and Mn could present first acceptor states in the gap, while for interstitial Fe the acceptor levels will lie in the conduction band. We mention that if acceptor levels exist for the interstitial Ni and Cu impurities, they will not be related to d-character states, as the 3d-induced e and t_2 levels are fully occupied. It is further worth mentioning that the single-donor level (0/+) trend is quite similar to that obtained for interstitial 3d impurities in silicon[16]. Our results indicate that all the interstitial impurities studied present high-spin ground states.

Considering the acceptor and donor energies associated to each impurity, we can extract the Mott-Hubbard correlation energy U which amounts to the difference in energies between the acceptor and donor levels. We find U values of 0.17 eV, 1.13 eV and 0.47 eV for Co, Fe and Mn respectively. It is interesting to note that these values are rather large compared to those predicted for impurities such as interstitials in Si[16] (with exception of Co). We should say that these findings may be

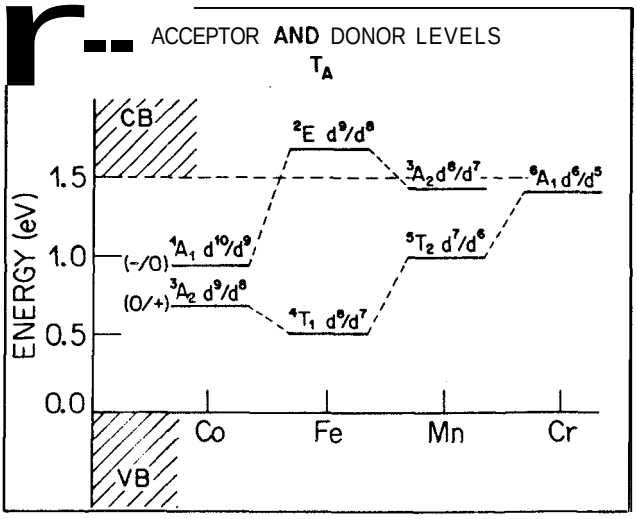

Fig.3 - Calculated donor (0/+) and acceptor (-/0) levels for 3d TM impurities at the anion interstitial (T_A) site. The obtained final ground-state symmetries are shown.

closely related to the strong *d-character* of the levels involved in the transitions, an effect which induces rernarkably high values for the Mott-Hubbard correlation energies.

As another interesting feature, we mention that the multiple-charge-state character generally observed for TM centers in semiconductors[1,2] is also obtained here for the 3d atoms as interstitials in GaAs. For interstitial 3d TM impurities in III-V compounds there are no established experimental level position. We hope that our theoretically predicted donor-and acceptor energies can be of help in future experimental investigations, as for example, in diffusion processes of these impurities in serniconductor materials.

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Resumo

Apresentamos os resultados para a estrutura eletrônica de impurezas intersticiais de metal de transição 3d em GaAs. Ambos os sítios intersticiais de mais alta simetria são considerados. Investigamos, para as impurezas no sítio intersticial do ânion, a existência de estados aceitadores e doadores no gap, através da inclusão de correções de muitos elétrons aos níveis de energia de um-elétron. Nossos resultados mostram que a tendência na posição dos níveis de impureza, e e t_2, é muito similar em ambos os interstícios tetraédricos. Obtemos que as impurezas Co, Fe e Mn podem apresentar estados doadores no gap. Níveis aceitadores são preditos ocorrer no gap somente para as impurezas intersticiais de Co e Mn.