Electronic States of Copper-Related Impurities in Germanium

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We report on results for the electronic states of the isolated substitutional and interstitial copper impurities as well as of the interstitial-substitutional copper pair complex in germanium. The self-consistent-field calculations were performed by using the multiple- scattering $X\alpha$ theory within the framework of the Watson-sphere-terminated molecular-cluster method. The calculations have been carried out by taking into account the spin-polarization effects. The Slater transition procedure has been used to evaluate the total energy differences between the electronic configurations in order to obtain the donor and acceptor energies associated with the impurities. Our results for the electronic states confirm the experimental interpretations and allow us to propose a microscopic model to describe the formation of the impurity levels of the $Cu_i - Cu_s$ pair complex from the molecular orbitals of the isolated Cu_s and Cu_i impurities.

I. Introduction

Among the impurities related to deep levels in germanium, copper is probably the most investigated under an experimental point of view due to its unavoidable diffusion into most of samples during heat treatments. It has been known that electronic states have been introduced into the forbidden band of originally-pure germanium when this material is quenched from high temperature. When the quenched temperature is above 600°C there are deep levels arising from copper-related defects[1-4]. It has been agreed, since the work of Woodbury and Tyler[5], that substitutional copper (Cu_s) introduces three deep acceptor levels in the band gap of germanium placed at $E_v + 0.04$ eV, $E_v + 0.32$ eV, and $E_c - 0.26$ eV. In addition to that, it has been agreed that impurity rapid diffusion is due to singly ionized interstitial copper[6,7]. Recently, it has been observed through deep level transient spectroscopy (DLTS) and Hall measurements[4] two hole trap levels in heat-treated germanium. The energy level placed at $E_v + 0.23$ eV has been suggested to have donor character, and to be related to interstitial copper impurity (Cu_i). It has also been assigned the level placed at $E_v + 0.09$ eV to be related to $Cu_i - Cu_s$ pair acceptor state. It has been proposed that this level could be due to the double acceptor state of Cu_s impurity perturbed by the adjacent Cu_i^+ ion, and so to be related to the transition $(Cu_i^+ Cu_s^{2-})^- / (Cu_i^+ Cu_s^-)^0$. The theoretical tool which has been used to explain the pair impurity system is the so-called ionic model[8].

Despite the experimental data available for copper in germanium, there has been little theoretical work on defects properties in germanium. As the purity germanium single crystal, with well controlled and ultra-low impurity content, has became available, it is important to know whether the same impurities have analogous properties related to different semiconductors.

The aim of this work is to report on rigorous self-consistent calculations performed on the Cu_s, Cu_i, and Cu_s-Cu_i impurities in germanium by using the multiple-scattering $X\alpha$ theory[9,10] within the framework of the Watson-sphere-terminated molecular-cluster method[11]. We simulate the Cu_s impurity through a 17-atom cluster and the Cu_i and Cu_i-Cu_s

impurities through a 27-atom cluster. The calculations are carried out to the self-consistent-field limit by including all electrons and spin-polarization effects. The sites of the impurities, which determine the geometry configurations of the systems, were chosen by taking in consideration the experimental suggestions. On the other hand, our calculations were performed, for the first time, to support or not the proposed microscopic models for the centers. The paper is organized as follows: In Sec. II we describe the theoretical model used by us to simulate the impurities. In Sec. III the results of our calculations are discussed and some models are proposed to explain the main features obtained for the electronic structure for the centers. A summary as well as our main conclusions are presented in Sec. IV.

II. Theoretical model

Since that the calculations carried out in the present investigation are performed within the framework of the molecular cluster model, the electronic properties of a point defect or impurity in the lattice are determined from the electronic structure of a selected cluster of atoms surrounding the impurity. However, as we must be able to locate the impurity levels relative to the band edges of the material, the bulk solid is simulated by a cluster of host atoms that will be referred to hereafter as *"perfect cluster"*. A defect in the lattice is then simulated by a *"defect cluster"* which is constructed by modifications on the *"perfect cluster"*.

The one-electron Schrödinger equation is solved for the molecular cluster by using the multiple-scattering theory developed by Johnson and Slater[9,10]. The molecular self-consistent potential is obtained by using the local density functional theory according to the exchange-correlation $X\alpha$ approximation[10]. The undesirable dangling-bond effects at the cluster surface are avoided by adopting the Fazzio et al. solution for the boundary condition problem[11]. According to this model, the effects of the dangling bonds are neutralized by transferring the filling electrons in these broken bonds to a sphere surrounding the cluster (Watson sphere).

The so called Watson-sphere-terminated molecular-cluster model has been used to investigated several complex defects in silicon[12–18] and the C-H impurity pair in germanium[19].

The clusters utilized in our studies of the impurities are schematically shown in Fig. 1 and 2. The *"perfect cluster"* in Td symmetry illustrated in Fig. 1 is used to study the isolated substitutional copper impurity in germanium. It comprises three shells of equivalent atoms. The central atom is surrounded by sixteen Ge atoms (four first neighbors and twelve second neighbors) in a tetrahedral configuration. The 17Ge-atom cluster is adopted with the purpose of defining the band edges of the *"perfect cluster"* which simulates the perfect germanium crystal. The *"defect cluster"* is built replacing the Ge central atom by the Cu atom.

The cluster illustrated in Fig. 2 is used to study the isolated interstitial copper impurity as well as the interstitial-substitutional copper pair in germanium. We adopted initially a 26Ge-atom centered at the tetrahedral interstitial site (T) which comprises four shells of equivalent atoms. The first, second, third, and fourth shells have four, six, four, and twelve germanium atoms, respectively. A copper atom is placed at the center of the cluster (T-site) in order to simulate the interstitial impurity. In this case, the atoms in the cluster are classified according to four shells in Td symmetry indicated by the numbers 1, 2, 3, and 4 in Fig. 2. In order to simulate the Cu_i-Cu_s complex a copper atom is placed at the center of the cluster and another copper atom replaces a nearest-neighbor germanium atom. When a Ge atom is replaced by a copper impurity, the symmetry of the cluster is lowered to C_{3V} and each one of the shells are further divided in classes of equivalence denoted by a, b, and c in Fig. 2.

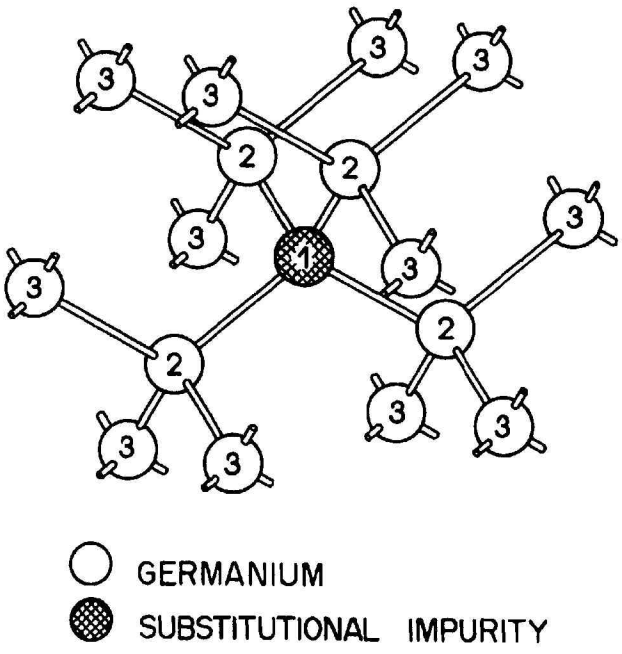

Figure 1: Schematic representation of the 16Ge + Cu_s cluster simulating the substitutional copper impurity in germanium. It comprises one central copper atom and two shells of germanium atoms, numbered from 1 to 3, in Td symmetry.

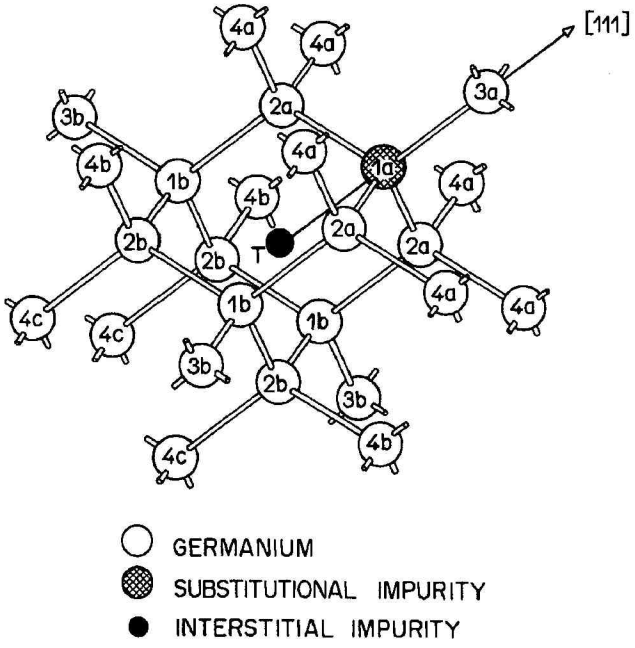

Figure 2: Schematic representation of the 26Ge + Cu_i and 25Ge + Cu_iCu_s clusters simulating the interstitial copper impurity and the interstitial-substitutional copper pair in germanium, respectively. As a T-centered cluster it comprises one central copper atom and four shells of germanium atoms, numbered from 1 to 4, in Td symmetry. By replacing a nearest-neighbor germanium atom by copper the symmetry is lowered to C_{3v}. The atoms in this symmetry belong to classes of equivalence which are indicated by the labels a, b, and c.

III. Results

We first start by analysing the results for the 17Ge and 26Ge clusters which simulate the perfect Ge crystal. Although the relativistic effects have been neglected in our calculations, we conclude that the energy spectra of the *"perfect clusters"* provide a fairly consistent description of the crystal band edges. The comparison between theory and experiment is made in Fig. 3. The values 1.37 eV and 0.82 eV obtained for the crystal band gap as well as the values 10.43 eV and 11.18 eV obtained for the valence band width for the 17Ge and 26Ge, respectively, are in good agreement with the experimental results reported by McLean[20] and Grobman et al.[21] It is worth mentioning that these *"perfect clusters"* have been used before to study complex and isolated impurities in germanium.[19,22]

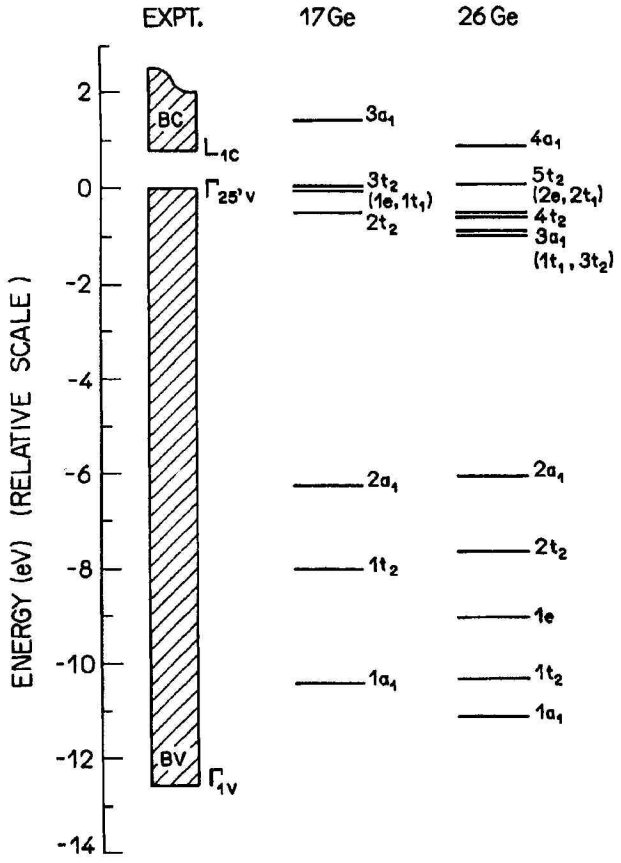

Figure 3: One-electron self-consistent energy spectra of the 17Ge and 26Ge clusters simulating the electronic structure of the germanium crystal. The experimental values for the germanium valence-band width and band gap are also shown. The zero of energy is placed at the top of the valence band.

A. Substitutional copper impurity in germanium

In order to analyse the results for the substitutional copper impurity in germanium, we have first calculated the electronic structure of the germanium vacancy which is simulated by removing the central atom from the 17Ge cluster. This is made because it is always instructive to picture a substitutional impurity as an atom captured by a single vacancy. The energy spectrum of the 16Ge + V cluster, simulating the electronic structure of the germanium vacancy, is shown in Fig. 4. According to the results, the main effects are the introduction of a t_2 deep level into the band gap, occupied by two electrons, and a strong dislocation of the a_1 levels. The a_1^* level lies close to the top of the valence band. The aforementioned levels are originated from the broken sp^3 bonds between the central atom and the four Ge nearest-neighbors. The t_2 gap level is quite delocalized, with 2%, 18%, and 61% of charge inside the empty sphere, first, and second shell of Ge neighbors, respectively. Our results are very similar to those obtained for the silicon vacancy[23,24].

The one-electron energy spectrum of the $16Ge+Cu_s$ cluster, simulating the substitutional copper impurity in germanium, is also displayed in Fig. 4. According to the results the t_2 gap level, occupied by three electrons, is highly delocalized showing a dangling-bond-like character since there is 5%, 23%, and 51% of charge inside the copper impurity sphere, first, and second shell of germanium neighbors, respectively. Therefore, the t_2 gap level remains almost unchanged when a copper atom is placed at the vacancy site. We can also observe that the copper $3d$ atomic orbitals give rise to two resonances which are labelled e(d) and $t_2(d)$ in Fig. 4 and are placed at $E_v - 6.30$ eV and $E_v - 6.15$ eV, respectively. Finally, we can notice that the a_1^* level, placed at $E_v - 1.56$ eV, has 37% of its charge inside the copper sphere.

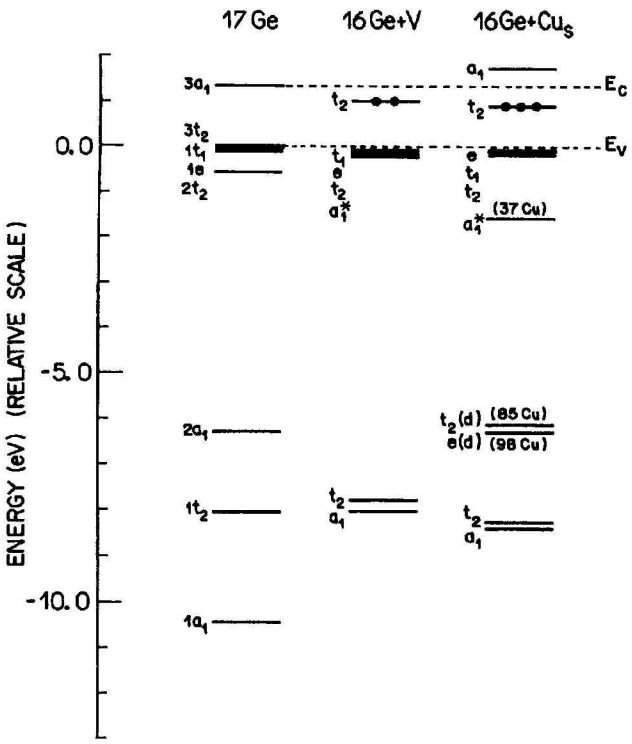

Figure 4: Self-consistent one-electron energy spectra of the 16Ge + V and 16Ge + Cu_s clusters simulating the electronic structure of the germanium vacancy and substitutional copper impurity in germanium, respectively. The solid circles indicate the occupancy of the levels in the spectra. The values in parenthesis give the percentage of charge, normalized to one electron, within the copper sphere. The results for the 17Ge cluster are also shown.

In Fig. 5 it is shown the model which is proposed by us to explain the main features obtained for the electronic states of the $Ge : Cu_s$ system: the copper $3d$ states interact very weakly with the lattice, and they keep having atomic characters playing a small role in altering the electronic structure of the vacancy into which the impurity is placed. This behavior is similar to that predicted by the calculations of Cartling[25] for zinc in silicon, by Hemstreet[26] for copper in silicon, by Alves and Leite[27] for gold and platinum in silicon, and by Fazzio et al.[28] for gold, silver, and copper in silicon. On the other hand, the copper 4s atomic states seem to interact with the a_1^* vacancy state, pushing the bonding molecular orbital into the valence band, and the antibonding molecular orbital into the conduction band. This latter provides the extra electron which is accommodated by the dangling-bond-like t_2 level in the gap.

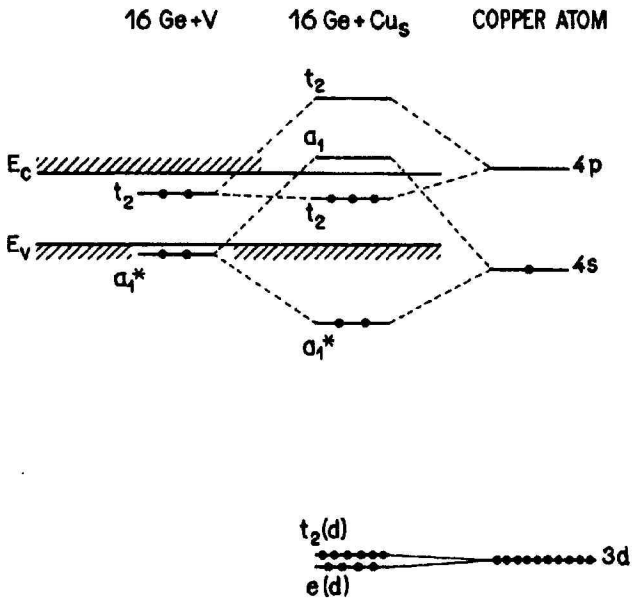

Figure 5: Schematic representation of the impurity levels of the 16Ge + Cu_s cluster as originated from the interaction between molecular orbitals of the germanium vacancy (16Ge + V) and the atomic copper states. The band edges are indicated and the full circles represent the occupancy of the levels.

The interaction between the copper 4s orbitals and the a_1^* vacancy states neither rebuilds the crystal orbitals nor stays vacancy-like level. This result permits to apply the *"vacancy"* model proposed by Watkins[29] to describe the substitutional copper impurity in germanium since this center basically behaves as *"perturbed"* germanium vacancy.

We proceed our calculations to take into account the spin-polarization effects so as to verify the effective spin of the center. It is obtained that the center is described by an $^4A_2$ orbital singlet, implying that the values L = 0 and S = 3/2 are ascribed to the angular momentum and spin values of the Cu_s impurity in germanium, respectively. Since three paired electrons are occupying a t_2 dangling-bond-like level and the angular momentum of the center has the value L = 0, we believe that instabilities are not expect to occur. Therefore, the substitutional copper impurity in germanium is stable with respect to Jahn-Teller (JT) distortions.

The first, second, and third acceptor transitions correspond to the capture of one, two, and three electrons in the t_2 gap level, respectively. These charge states are simulated by adding electrons in the electronic states of the $16Ge + Cu_s$ cluster. The results of the simulation show that simply, doubly, and triply ionized global states are described by a $^3T_1$ orbital triplet, by a $^2T_1$ orbital triplet, and by an $^1A_1$ orbital singlet, respectively. Although these results indicate that the impurity is an active JT center when in its single or double charge states, we conclude that distortions are expect to be small or absent due to the delocalized character of the t_2 dangling-bond-like state.

We evaluate the transition states by using the Slater procedure. As we do not have an absolute reference to compare the ionized clusters, the neutral cluster is used to evaluate the first donor and acceptor transitions. The singly ionized cluster is used to obtain the first and second acceptor transitions, and the doubly ionized cluster is used to evaluate the second and third transitions. The results obtained by applying this scheme show that the donor state is placed into the valence band and three acceptor states are placed into the forbidden band. Accordingly, we can conclude that the triple acceptor character of the substitutional copper in germanium is verified even though distortions are not taking into consideration.

Besides the fact that we are not able to place the three acceptor levels together into the band gap, we can conclude that our results confirm the experimental investigations[1-7] and give strong support to say that substitutional copper impurity in germanium gives rise to three acceptor levels, and that the different levels are not associated with copper atoms at different types of sites.

B. Tetrahedral interstitial copper impurity in germanium

The self-consistent energy spectrum of the $26Ge + Cu_i$ cluster, simulating the neutral tetrahedral

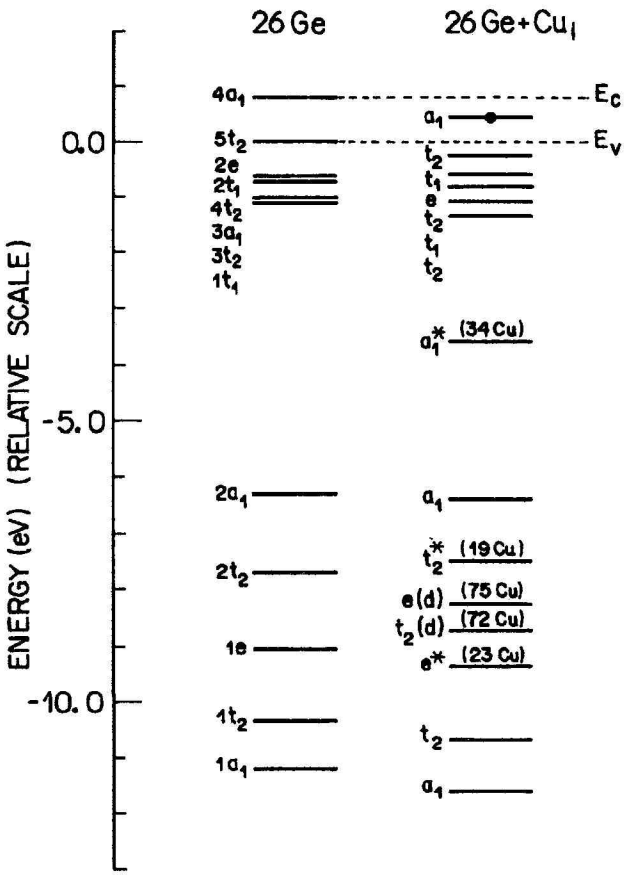

Figure 6: Self-consistent one-electron energy spectrum of 26Ge+Cu_i cluster simulating the tetrahedral interstitial copper impurity in germanium. The full circle indicates the occupancy of the level in the spectrum. The numbers within parenthesis denote the percentage of charge, normalized to one electron, within the copper impurity sphere. The results for the 26Ge cluster are also shown.

interstitial copper impurity in germanium, is shown in Fig. 6. We are also including in the figure the spectrum of the 26Ge cluster. According to the results, the copper interstitial impurity gives rise to two resonances labelled $e(d)$ and $t_2(d)$ which result from the crystal-field splitting of the copper $3d$ orbitals. These levels are placed at $E_v - 8.27$ eV and $E_v - 8.72$ eV, and they are strongly localized states with 75% and 72% of charge within the impurity sphere, respectively. Another important result of the calculations is that Cu_i introduces an a_1 energy level within the band gap occupied by one electron. This level has a delocalized character, and it is derived from the bottom of the conduction band. We can also see that the levels labelled e^*, t_2^* and a_1^* have a significant percentage of charge within the impurity sphere. The a_1^* level can be identified as an interaction between the copper 4s orbital and the *"perfect cluster"* $3a_1$ level, and the e^* and t_2^* orbitals as $1e$ and $2t_2$ crystal levels which are perturbed by $3d$ atomic-like levels. The above explanation for the impurity molecular orbitals can be visualized in Fig. 7.

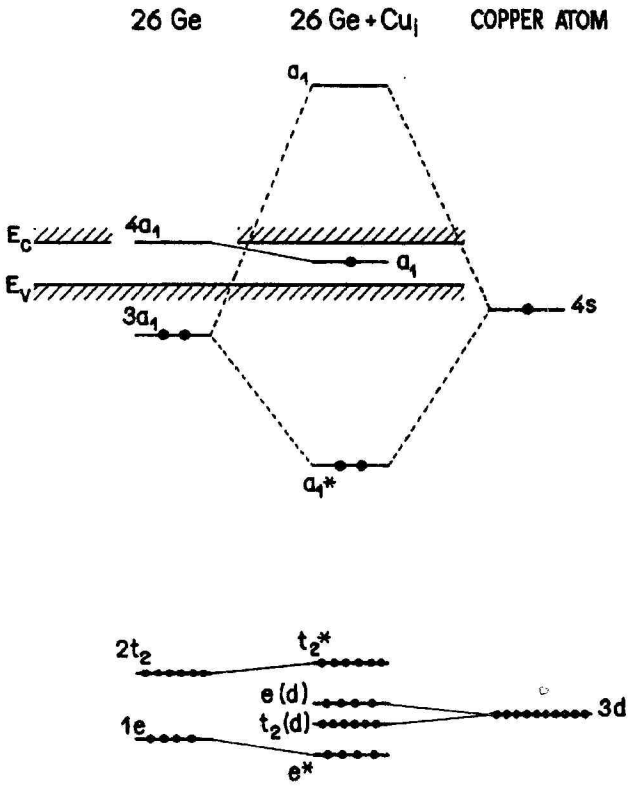

Figure 7: Schematic representation of the impurity levels of the 26Ge + Cu_i cluster as originated from the interaction between molecular orbitals of the germanium crystal (26Ge) and the atomic copper states. The band edges are indicated and the full circles represent the occupancy of the levels.

Spin-polarization effects and Slater transition-state concept are used in order to obtain the effective spin and acceptor and donor energies of the center. According to the results, we conclude that the interstitial copper impurity in germanium is stable in this structural configuration with respect to JT distortions. The ground state is an $^2A_1$ orbital singlet, implying that the values L = 0 and S = 1/2 are ascribed to the angular momentum and spin eigenvalues, respectively. We obtain the donor transition (0/+) placed at $E_v + 0.12$ eV and the acceptor transition (-/0) into the conduction

band. Our results are consistent with those observed by Kamiura and Hashimoto[4]. Therefore, it is possible to infer that their analysis about the observed trap with a donor character at $E_v + 0.23$ eV as arising from Cu_i is reinforced by our results.

C. Interstitial-substitutional copper pair impurities in germanium

The energy spectrum of the $25Ge + Cu_iCu_s$ cluster, simulating the interstitial-substitutional copper pair impurities in germanium, is displayed in Fig. 8. Included in this figure are only, the states derived from copper $3d$ atomic orbitals as well as the gap and the a_1^* levels. The results shown in Fig. 8 indicate that the overall features of the isolated substitutional and interstitial copper impurity states are not strongly changed by the interaction with each other. The energy levels result from the crystal-field splitting when the symmetry is lowered from Td to C_{3v} for the $Cu_i - Cu_s$ complex. The gap levels, which appear according to the $5e^2 5a_1^1 6a_1^1$ electronic configuration, are derived from the substitutional copper dangling-bond-like t_2 level, which splits into e and a_1 levels when the symmetry is lowered to C_{3v} and from the interstitial copper a_1 gap level. An important information that can be taken from the calculations is that the highest gap level ($6a_1$) is dangling-bond-like.

The analysis of our results leads to the conclusion that the properties of the $Cu_i - Cu_s$ pair can be described by bearing in mind that the complex impurity levels arise from the interaction between the molecular orbitals of the isolated impurities. We may conclude that there is no clear indication from the calculations that some charge is transferred between the impurities.

Spin-polarized calculations are carried out with the purpose of determining the effective spin of the center, and the obtained results for the gap levels are shown in Fig. 9. According to the calculations we can described the ground state of the center by an $^5A_1$ orbital singlet, implying that the values L = 0 and S = 2 are ascribed to the angular momentum and spin values of the $Cu_i - Cu_s$ complex in germanium, respectively. Furthermore, we conclude that the pair is stable with respect to JT distortions.

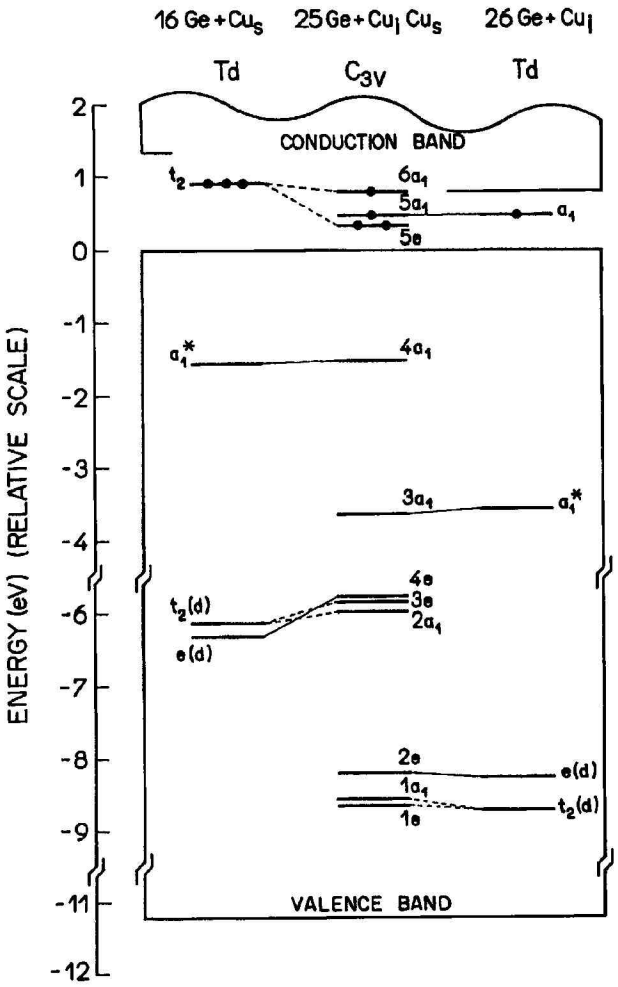

Figure 8: Impurity levels, relative to the band edges, induced by the pair complex $Cu_i - Cu_s$ (25Ge + Cu_iCu_s) in germanium as derived from the interaction between the molecular orbitals of the substitutional copper (16Ge + Cu_s) and the interstitial copper (26Ge + Cu_i) impurities. The full circles indicate the occupancy of the gap levels. Besides the gap levels only the copper 3d, 4s-derived energy levels identified in the energy espectra of the 25Ge + Cu_iCu_s, 26Ge + Cu_i, and 16Ge + Cu_s clusters are shown.

The donor and acceptor transitions are calculated by using the same procedure previously described. The first acceptor transition (-/0) of the pair is found at E_v + 0.30 eV and the first donor (0/+) transition is placed into the valence band. These results are also consistent with those observed by Kamiura and Hashimoto[4]. Nevertheless, it is worth mentioning here that the final negative state, when the (-/0) transition

is taken into consideration, is unstable with respect to JT distortions. Despite the fact that distortions are not taken into account, we can conclude that the $Cu_i - Cu_s$ pair investigated in this work is responsible for the trap with acceptor character observed by DLTS and Hall measurements[4], since the final state of the acceptor transition is quite delocalized and distortions are expected to be small or absent.

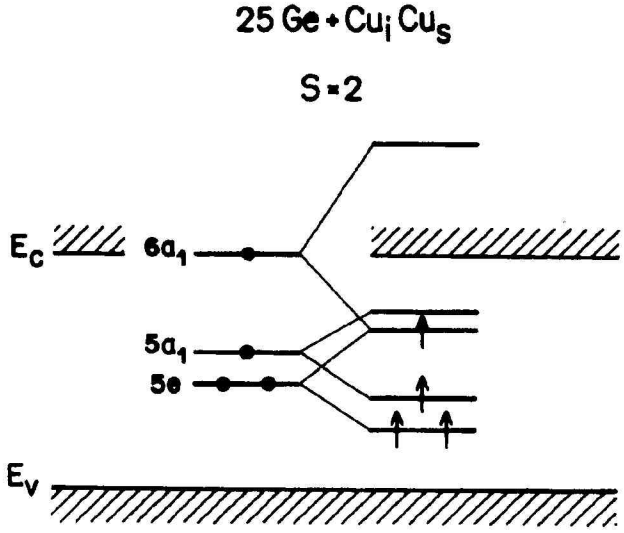

Figure 9: Energy gap levels for the 25Ge + Cu_iCu_s cluster simulating the Cu_iCu_s pair complex in germanium according to spin-polarized calculations. The arrows indicate the occupancy of the levels with up (↑) and down (↓) spins. The total spin S for the center is also given.

IV. Summary and conclusions

Based on the results obtained in this work we propose microscopic models to describe the electronic structures of the Cu_s, Cu_i, and $Cu_i - Cu_s$ impurities in germanium. The models provide a good explanation for the DLTS and Hall measurements[1-8] taken on copper-related centers in germanium and they are based on the fact that the copper 3d-derived states play a minor role in determining the electrical, optical, and magnetic properties of all impurities investigated here.

For the Cu_s impurity it is obtained that the gap level, which is associated with the relevant properties of the center, is dangling-bond-like. Therefore, the substitutional copper impurity in germanium gives rise to a deep state in the gap which is due to the broken bonds on the germanium neighbors. In other words, it is vacancy-like state. Also, it is obtained that this center is described by an $^4A_2$ orbital singlet and is responsible for introducing three acceptor levels into the band gap.

The Cu_i impurity introduces a delocalized energy level into the band gap which is derived from the bottom of the conduction band. This level has a donor character confirming that the interstitial copper impurity in germanium gives rise to a deep state in the material gap.

For the $Cu_i - Cu_s$ complex pair in germanium a model is built based upon the demonstration that the electrical, optical, and magnetic properties of the pair are related to delocalized states. It is found that the neutral complex ground state $^5A_1$ has an effective spin S = 2 which is related to a molecular orbital spread out over the entire cluster rather than related to the Coulomb interaction between two ionic charges as was proposed[4]. The analysis of our results leads to the conclusion that the properties of the $Cu_i - Cu_s$ pair can be described by bearing in mind that the complex impurity levels arise from the interaction between the molecular orbitals of the isolated impurities. Although our results do not support that some ionic character can be ascribed to the stabilized pair, it is verified that the pair is responsible for the acceptor transition state observed by the experimental results[4].

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