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Trends in the electronic properties of substitutional 3*d* transition-metal impurities in GaAs

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The $X\alpha$ scattered-wave method, in its spin-restricted version, has been used to calculate the electronic states associated with an ideal gallium vacancy as well as with the following substitutional transition-metal impurities in gallium arsenide: chromium, manganese, iron, cobalt, nickel, and copper. The gallium vacancy is found to behave as a simple acceptor with an ionization energy of approximately 0.50 eV. In addition, a level of a_1 symmetry with considerable amplitude in the vacancy sphere is found at an energy of approximately 0.75 eV *below* the valence edge. The transition-metal impurities can be broken up into two categories, depending on whether or not the 3*d* states of the transition metal play an active role in determining the active electronic states of the defect. Those impurities to the left of (and including) cobalt are found to behave in the "standard" way, as the active impurity states in the gap have substantial *d* character and there is clear evidence of bond formation involving the impurity and the neighboring host ligands. By contrast, nickel and copper appear to behave as simple acceptors in the sense that the active defect levels have little *d* character and are rather more characteristic of the broken bonds at the impurity site. The *d* states of this latter group appear as "resonances" in the host valence band and play little direct role in determining the electronic properties of the material. The paper concludes with a discussion of these results and possible factors that might affect their validity.

I. INTRODUCTION

Transition-metal impurities in semiconductors have been the objects of a great deal of study in recent years because they so often appear as common contaminants or as deliberately introduced dopants in these materials. In either case they tend to behave as deep centers and can significantly affect the electronic properties of the material involved. While considerable effort has gone into characterizing the properties of these deep impurities, the experimental results usually have proved difficult to interpret because of the uncertainty involved in assigning the observed behavior to a specific defect center. This is particularly true in the case of inherently macroscopic electrical measurements such as capacitance, photoconductivity, or Hall effect. The analysis is further complicated by the fact that no unified theory of such deep centers currently exists. As a result, the microscopic properties of this particular class of defects, with few exceptions, are still not well understood.

In an effort to provide some basic theoretical information which might prove helpful in classifying and interpreting some of the available data, a series of cluster calculations of the electronic states associated with a well-defined set of deep defects, viz., neutral, substitutional transition-metal impurities from the 3*d* transition series, have been carried out[1-3] for selected semiconductor hosts. The results of such calculations for deep centers in silicon have been discussed previously,[1] and in this paper we concentrate on the behavior of the neutral 3*d* transition-metal impurities chromium, manganese, iron, cobalt, nickel, and copper in gallium arsenide. The general aim of this work is to give an overview of the qualitative trends in behavior exhibited by this particular group of impurities, and a more detailed discussion of the individual electronic states will be presented elsewhere.

The results of the present study are similar to those obtained for silicon, and many of the conclusions reached then are applicable to the present case as well. In particular, it is again found that the customary crystal-field picture, in which the active impurity levels are *assumed* to be modified transition-metal *d* states, is only approximately valid in those cases where there is a reasonably good energy match between the impurity *d* states and the *s*- and *p*-like valence levels of the host. Such is not the case for those impurities such as nickel, copper, and zinc near the end of the 3*d* transition series, and these centers are more appropriately viewed as simple acceptors in the sense that their active defect states are more characteristic of the broken bonds at the impurity site. The *d* states occur as fairly sharp "resonances" in the host valence band and play no significant role in determining the electronic properties of such defects.

The plan of this paper is as follows. A brief outline of some of the calculational details is given in Sec. II. The results of the various cluster calculations carried out in this investigation are presented in Sec. III, while Sec. IV concludes the paper with a discussion of the results and possible factors that might affect their validity.

II. CALCULATIONAL PROCEDURE

The cluster approach utilizes the strongly localized nature of the deep-defect perturbation potential and focuses attention on a "molecule" composed of the defect in question plus those neighboring host atoms within the range of the defect potential. In the present work the electronic states of such a cluster are calculated using the scattered-wave formalism of Johnson *et al.*,[4,5] coupled with the local $X\alpha$ exchange approximation,[5] and the defect states are obtained directly by means of comparison to analogous calculations on an "ideal" cluster without the defect. A major advantage of the $X\alpha$ scattered-wave formalism is that the calculations can be carried to self-consistency, thereby allowing for the very important effects of electronic relaxation in the presence of the impurity. Furthermore, no semiempirical parameters are required, and the results are essentially "exact" within the constraints of the muffin-tin and local $X\alpha$ exchange approximations.

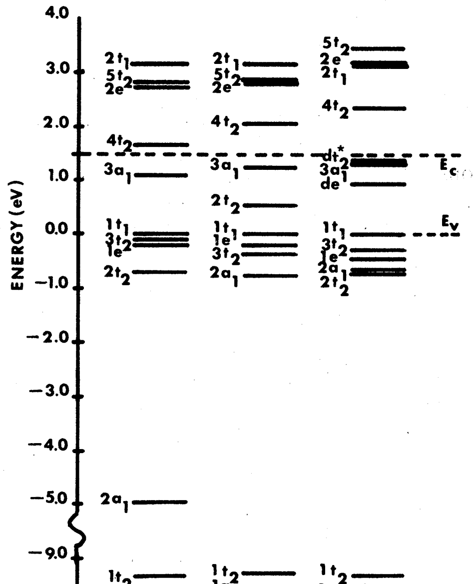

FIG. 1. Energy-level spectra of the (a) ideal gallium arsenide cluster and the defect clusters containing (b) a gallium vacancy and (c) a substitutional chromium impurity. All energies are in eV (see Ref. 7) and are measured with respect to the cluster valence edge as defined in the text.

The actual calculational procedure is essentially the same as that used previously.[1-3] Since available experimental data all indicate that the transition-metal impurities are incorporated substitutionally into the gallium arsenide lattice at the gallium site, the simplest ideal cluster of any use is formed by surrounding a central gallium atom by four arsenic nearest neighbors and twelve hydrogenlike saturators at the positions of the twelve next-nearest-neighbor gallium sites (to saturate the arsenic "dangling" bonds). The various defect clusters are obtained by replacing the central gallium atom by the appropriate point defect. In all cases the clusters are surrounded by an outer Watson sphere with a charge of $-3e$, where e is the magnitude of the electronic charge, in order to ensure overall charge neutrality of the cluster as a whole as well as to account for, in a rough way, the Madelung contribution to the cluster potential due to external host atoms not explicity considered. For simplicity, all muffin-tin radii are taken to be equal to one-half the nearest-neighbor distance in bulk GaAs (2.31 bohr), and the same value of α, 0.706, is used everywhere[6] except within the various transition-metal impurity spheres. In the latter cases the appropriate values of α have been taken from the tables of Schwarz.[6]

III. RESULTS

The calculated energy-level spectrum of the ideal gallium arsenide cluster is shown in Fig. 1(a) and consists of a set of occupied valence states separated from the empty conduction levels by a gap of approximately 1.10 eV.[7] The states are labeled according to the irreducible representations of the tetrahedral point group, and the "zero" of energy is taken to be the uppermost occupied valence state, labeled $1t_1$ in Fig. 1(a). Since this state is clearly a bulk state and appears virtually unchanged in all of the clusters considered in the present investigation, it will be taken as a reference to define the "valence-band edge" of the gallium arsenide cluster. When comparing energy spectra for different defects in gallium arsenide, the corresponding $1t_1$ cluster levels will be aligned with that of the ideal cluster, and all energies will then be measured with respect to this reference.

When discussing the electronic states of impurities in semiconductors, it is often useful to think of impurity formation as a two-step procedure: creation of a host vacancy, followed by placement of the impurity atom at the vacancy site. In the present case the appropriate first step of this procedure would correspond to the removal of the central gallium atom from the ideal cluster, and the energy-level spectrum associated with the resulting vacancy cluster is shown in Fig. 1(b).

The main qualitative difference between the spectra of Figs. 1(a) and 1(b) is the strong upward shift in energy of the $2a_1$ and $2t_2$ levels that occurs with the removal of the central gallium atom. In the ideal case these states are associated with bonds formed between the central gallium atoms and its four arsenic neighbors, but they become nonbonding in character as these bonds are broken during the creation of the vacancy. The fully occupied $2a_1$ level of Fig. 1(b), which lies approximately 0.75 eV below the valence edge, has a significant amount (30%) of s-like charge localized within the vacancy muffin-tin sphere and can be interpreted as a resonance in the host valence band. The $2t_2$ level is pushed up out of the cluster valence band all the way into the band gap, approximately 0.50 eV above the valence edge, and can be thought of as a simple acceptor level associated with the broken bonds at the vacancy site. Since three electrons must be subtracted from the cluster because of the removal of the neutral gallium atom, this state is only partially occupied with three electrons in Fig. 1(b), and one might expect a Jahn-Teller distortion to occur. Such a possibility is neglected in the present work, as there are no detailed experimental data available which might allow one to form a microscopic model for the relaxation. Nevertheless, the calculated position of the $2t_2$ level is in reasonably good agreement with those data which do exist,[8] indicating that any such Jahn-Teller effects are probably small. The present calculated energy level of the gallium vacancy is also in good agreement with the recent theoretical calculations of Daw and Smith,[9] who used the Green's-function method of Koster and Slater.[10,11]

The next step in the procedure corresponds to placing a neutral transition-metal impurity at the vacancy site in the center of the cluster and repeating the calculation. This step has been applied separately to each of the following impurities from the $3d$ transition series: chromium, manganese, iron, cobalt, nickel, and copper. In each case one finds that additional states with substantial d character and either e or t_2 symmetry are introduced into the cluster spectrum. These additional states are related to the atomic d states of the transition-metal impurity which have been split by the tetrahedral field of the neighboring host atoms. The extent to which these crystal-field-split d states interact with the neighboring ligands varies as one goes along the $3d$ row from chromium and copper, and this variation is found to have a profound effect on the nature of the active impurity states that are associated with these deep centers.

Consider first the case of a neutral chromium impurity in gallium arsenide. Although this example has already been discussed elsewhere,[2,3] many of the qualitative features of the problem are typical of those found for other members of the $3d$ transition series, and a summary of some of the more pertinent results will be presented here so that they may be used as a guide in the following discussions.

The energy-level spectrum of the chromium cluster is shown in Fig. 1(c). Comparison to Fig. 1(b) indicates that the $2t_2$ acceptor level associated with the broken bonds is no longer present in the gap but has been pushed back down among the valence states of the cluster, as in the ideal case. Furthermore, one observes additional levels of e and t_2 symmetry [labeled de and dt_2^* in Fig. 1(c)] within the host band gap. Inspection of the charge distributions of the individual cluster states shows that the de level, which is only partially occupied (with three electrons) in the case of a neutral chromium impurity, is largely chromium d-like and can be associated with the e-symmetric component of the crystal-field-split atomic d states of chromium. The dt_2^* and $2t_2$ levels of Fig. 1(c) also show a significant admixture of chromium d character (25–30%), while the $2a_1$ level has a substantial amount of chromium s character.

A logical interpretation of these results is that the $4s$ and t_2 symmetric component of the $3d$ states of chromium interact with the neighboring arsenic ligands to reform the broken bonds at the impurity site, and the $2t_2$ and dt_2^* states of Fig. 1(c) represent the bonding and antibonding combinations, respectively, that result from the interactions between the t_2 symmetric states of the impurity and the arsenic ligands. Three of the six chromium electrons are involved in the bond formation, and the remaining three go into a strongly d-like impurity level [de in Fig. 1(c)] in the gap, located approximately 0.95 eV above the cluster valence edge. This description is very close to the standard model of a substitutional transition-metal impurity in a semiconductor put forth by Ludwig and Woodbury[12] based on their electron paramagnetic resonance (EPR) studies of such defects in silicon.

If chromium is now replaced by other members of the $3d$ transition series, the schematic results shown in Fig. 2 are obtained. For clarity, the uninteresting "bulk" levels of the various defect clusters (which do not vary significantly as one changes impurities) have been omitted, and only those states which have more than 10% d character or which reside within the cluster band gap (i.e., between the $1t_1$ and $3a_1$ levels) are shown explicit-

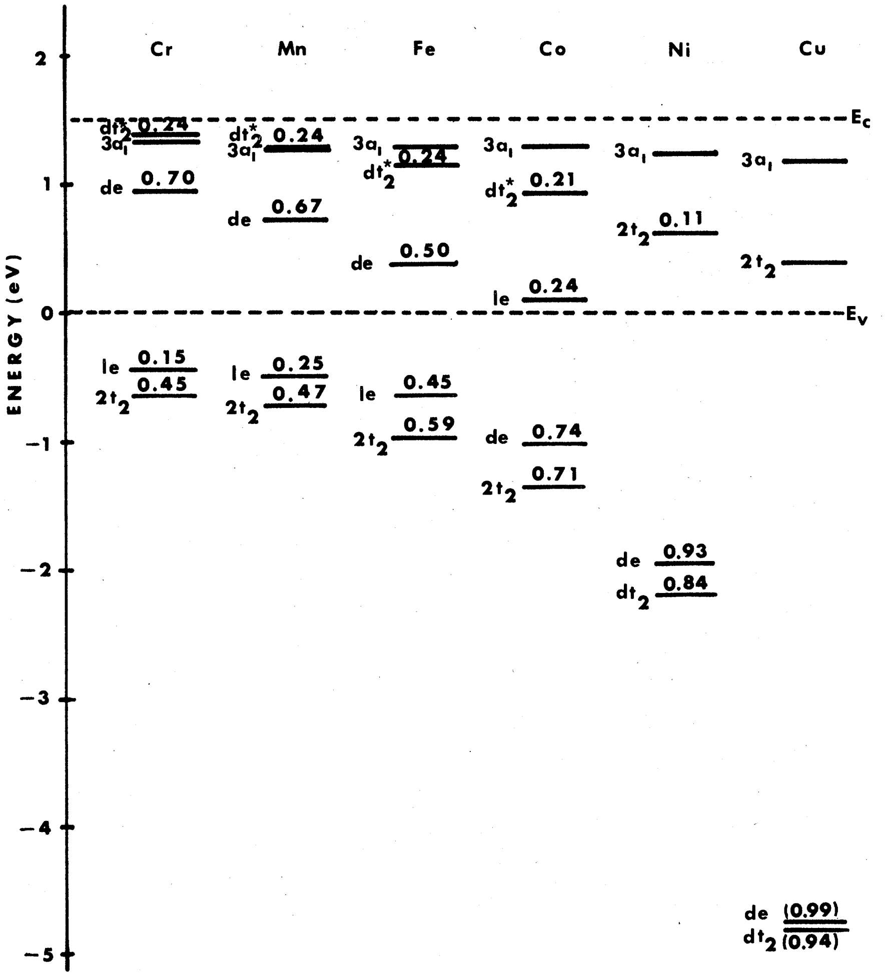

FIG. 2. Impurity-related energy levels calculated for the various neutral transition-metal impurities considered in this work. All energies are in eV (see Ref. 7) and are measured from the cluster valence edge, denoted by E_v in the figure (see text). Those states associated with the impurity d states have the fraction of such character shown adjacent to the corresponding level.

ly. In the former case the fraction of d character of each such state, obtained by performing a partial-wave analysis of the corresponding orbital charge distribution, is shown adjacent to the level, while Table I contains a listing of the energies (and occupancies) of those states within the band gap. As before, all energies are measured with respect to the cluster valence edge defined previously.

Also shown in Table I is a representative sampling of the experimentally observed energy levels[13-21] associated with samples of gallium arsenide containing these $3d$ impurities. One should be cautioned that the quoted results are generally "extracted" from electrical measurements and that the microscopic nature of the associated defect is often unknown. Therefore, it is not always appropriate to compare directly the theoretical and experimental values shown in Table I. Nevertheless, they are both listed for completeness as well as for use in later discussion.

As one proceeds across the $3d$ row of the Periodic Table from chromium toward copper, the transition-metal d states move down in energy with respect to the s-p bands of the host, and this behavior is reflected in the spectra of Fig. 2. The d-like de state found in the host band gap in the case of chromium, for example, becomes fully occupied and moves down through the gap and into the valence levels of the host as one goes from manganese to copper in the $3d$ series. As this state approaches the valence band the fraction of d character decreases while the amount of d admixture in the e-like valence level [corresponding to the $1e$ level of Fig. 1(a)] increases, indicating an increasingly stronger interaction between the

TABLE I. Summary of active defect levels. Symmetries and energies of the defect levels associated with the various deep centers considered in this work. All energies are expressed in eV and are measured from the cluster valence edge (see text).

Defect	State	Calculated energy (eV)	Expt. energy (eV)	Reference
Cr	de	0.95	0.80, 0.90	13,14,22
Mn	de	0.72	0.09, 0.11	15,16,19,29
	dt_2^*	1.29		
Fe	de	0.37	0.52	13,14
	dt_2^*	1.14		
Co	dt_2^*	0.94	0.16, 0.56	14–16,18,19,21
Ni	$2t_2$	0.68	0.21, 0.43, 0.53	13–16,19,20
Cu	$2t_2$	0.38	0.15, 0.44	14,17
V_{Ga}	$2t_2$	0.50	0.35, 0.50	8

impurity and the π states of the neighboring host ligands.

Once this state is within the valence band, the pattern reverses and the fraction of d character increases strongly as the impurity level moves down deeper into the valence states and away from the bulk $1e$ level. At the same time the d admixture of the bulk level decreases. When the impurity de state is more than about 2 eV or so below the valence-band edge, as in the case of nickel and copper, the bulk $1e$ level has little or no d character and the lower-lying impurity-related de state is almost purely d-like. This latter state then has the character of an atomic d-like resonance among the s–p valence states of the host.

A similar pattern is observed in the case of the t_2-symmetric impurity-related states. As one proceeds from manganese to cobalt, the admixture of d character into the $2t_2$ level increases while the dt_2^* state becomes occupied and is pulled down deeper into the host band gap. However, as the barycenter of the transition-metal d states moves down into the valence band, as in the examples of the nickel and copper defect clusters, the interaction with the neighboring ligands decreases sharply. The d admixture in the $2t_2$ level becomes negligible, and this state is pushed up in energy into the gap. At the same time, the dt_2^* level disappears and one finds a strongly d-like dt_2 state among the occupied bulk states of the cluster. In fact, the defect spectra of both the nickel and copper clusters are very similar to the vacancy spectrum of Fig. 1(c), except for the addition of the pair of d-like de and dt_2 levels within the occupied valence states of the cluster spectrum. The t_2-symmetric defect level within the cluster band gap has little or no d character, and the nickel and copper d states appear as d-like resonances among the bulk valence levels.

This behavior contrasts sharply with that obtained for the standard transition-metal impurity, using chromium as a typical example, and does not fit the usual Ludwig and Woodbury model[2] at all. A more logical interpretation of the present results is the picture of an isolated (or weakly interacting) impurity atom at a gallium vacancy site in the lattice, with the active defect levels in the host band gap being associated with the broken bonds at the impurity site rather than with the impurity atom itself.

IV. DISCUSSION AND CONCLUSIONS

It has customarily been assumed that the active impurity states of all transition-metal impurities in semiconductors such as gallium arsenide are essentially atomiclike d states that have been modified somewhat, due to interactions with the neighboring host atoms. The present investigations indicate that this picture is not quite universal, and one should be able to observe at least two different types of limiting behavior depending on whether or not the $3d$ states of the transition metal play an active role in determining the nature of the electronic states in the host band gap.

Those transition-metal impurities to the left of cobalt in the $3d$ row of the Periodic Table do appear to behave qualitatively in the standard way, using chromium in gallium arsenide as a typical example. The cluster states show clear evidence of bond formation involving the transition-metal impurity and the host ligands, and the active impurity states are characterized by substantial d character, which decreases with increasing Z from chromium to cobalt.

This picture begins to break down for cobalt, and by the time one reaches nickel and copper one observes that the active impurity levels exhibit little or no d character and there is no evidence of any significant σ bonding involving the impurity and host. Instead, the transition-metal d states show up as resonances in the cluster valence band and play no crucial role in determining the electronic properties of the defect. The latter are determined rather by the broken bonds at the impurity site, much as in the case of a gallium vacancy.

Impurities of the first type are usually labeled as "complex" because their electronic properties are often dominated by multielectron effects[21-26] which cannot be described correctly within the one-electron approximation.[2,3] Their luminescence and optical spectra, for example, generally are dominated by sharp structure which can be associated with *d–d* intracenter transitions, and they invariably exhibit a "Hund-rule" ground state with a maximum number of unpaired spins. Because of the localized nature of the *d*-like impurity states, intracenter electron-electron interactions involving the impurity electrons become important, and the one-electron defect spectrum must be replaced by a multielectron multiplet spectrum, as in the case of a free atom or ion. Such multiplet states are clearly outside the domain of validity of the spin-restricted, one-electron formalism employed here, and it is for this reason that little emphasis has been placed on the numerical details of the one-electron defect levels so calculated. Such multielectron effects are particularly important in the cases of those impurities, such as Mn^{2+}, which have the $3d^5$ configuration, corresponding to a half-filled shell. The multielectron interactions in such cases are so dominant as to make conclusions based on a one-electron calculation virtually meaningless.

Crystal-field theory,[27] which *assumes* that the defect states are basically atomic *d* multiplets which have been split by electrostatic interactions with the surrounding host atoms, has traditionally been used[12,21-28] to describe the electronic spectra of such complex impurities. The present results suggest that any such attempt must take into account the strong covalent bonding between the impurity and the host in order to prove effective. This is generally done by fitting several lower-lying multiplet states to available experimental data,[21,27,28] thereby implicitly including such covalent effects in the values of the crystal-field parameters so derived. In the case of the $3d$ transition-metal impurities in gallium arsenide, however, sufficient data for this purpose are almost never available and the crystal-field approach has been useful mainly for attaching labels to empirical energy levels which have been proposed to interpret some of the existing data.

Another method, which can be used to calculate a defect multiplet spectrum analogous to that obtained from crystal-field theory without the need of such experimental information, has been proposed elsewhere[2,3] and tested on chromium in gallium arsenide, again chosen as a prototype example of the standard complex type of impurity. This approach uses the results of spin-restricted one-electron cluster calculations such as those reported here to calculate explicitly the necessary covalent corrections to the atomic crystal-field parameters and was found (in the case of chromium) to give a satisfactory description of both the correct multielectron ground state and the sharp structure observed in the luminescence and optical spectra. Neither of these features is correctly described by the one-electron cluster calculations presented in this paper. As there is nothing special about the choice of chromium for this application, it is expected that the approach should be applicable to the other complex impurities as well.

Manganese is an extreme example of the importance of such multielectron interactions within this complex group of impurities. The experimentally observed behavior of manganese in gallium arsenide[29] would appear to contradict the qualitative trend reported here. Its luminescence spectrum shows no sharp structure associated with *d–d* transitions, and EPR measurements indicate an isolated point defect on a gallium site in the lattice. Moreover, the associated acceptor level is relatively shallow, being located only about 0.11 eV above the valence-band edge. This behavior is quite different from that observed for chromium and iron, which bracket manganese in the Periodic Table, and would not be expected on the basis of the calculations of the previous section.

This discrepancy between the observed and the predicted behavior of manganese can be attributed to the lack of a proper treatment of the especially strong intracenter electron-electron interactions associated with the $3d^5$ configuration of Mn. If one uses the method of Refs. 2 and 3 to incorporate such interactions, one finds that the ground-state multiplet of manganese is the $^6A_1$ level, a result which is in excellent agreement with the EPR data. Further, one would not expect to observe prominent *d–d* transitions in the luminescence spectrum because there are no spin-allowed transitions from this $^6A_1$ ground state to any other multiplet levels of the $3d^5$ configuration. Finally, the energy of the $^6A_1$ ground state can be as much as an electron volt lower in energy than the average energy of the $(de)^4 dt_2^*$ configuration. This implies that the hole ionization energy of the manganese acceptor would be correspondingly less than one would estimate by taking merely the energy separation of the dt_2 level from the valence edge, thereby reducing the calculated value of the ionization energy of manganese from something in excess of one eV to just a few tenths of an eV, in qualitative agreement with the observed trend.

By contrast, the active defect levels of nickel and copper (and presumably zinc) show little or no *d* character, and these impurities can be expected to behave as simple acceptors in the sense that multielectron effects should not be too important. The acceptor level calculated for copper, for example, appears to be in good agreement with available photoconductivity data,[17] and its optical and luminescence spectra show little evidence of the sharp structure associated with *d–d* intracenter transitions. The seemingly anomalous behavior of copper compared to other standard transition-metal impurities such as chromium and iron in gallium arsenide has long been a source of puzzlement to workers in the field, but it appears that this behavior is simply a result of the fact that the copper *d* levels lie too low in energy, with respect to the *sp* states of the host, to make bonding between the two energetically advantageous. The defect states are not associated with the copper *d* levels and, therefore, simply cannot be described within the context of crystal-field theory. Similar simple behavior should also be observed in the cases of nickel and zinc.

The behavior of the substitutional 3*d* transition-metal impurities in gallium arsenide described here is similar to the pattern observed previously in silicon, and the controlling reasons appear to be the same in both cases. Since the argument is simply one of the energy match (or mismatch) between the transition-metal *d* states and the *sp* valence states of the host, it should be applicable to the 3*d* transition-metal impurities in other semiconductor hosts such as gallium phosphide and indium phosphide as well, and similar patterns of behavior would be expected.

Before closing it should be noted that several major approximations have been made in performing the one-electron calculations described here, and their possible effects on the conclusions reached will now be briefly discussed. First of all, lattice relation of the neighboring host atoms about the various defects has been neglected in these investigations. Such distortions undoubtedly occur in many of the cases considered here, but only rarely[23, 24] are there enough data available to provide a microscopic model of the relaxation. While the neglect of such effects might have a significant impact on the quantitative details of the electronic properties calculated for the unrelaxed case, they are not expected to alter the major qualitative features or trends discussed in this work. At any rate, treatment of such effects must await either better and more detailed experimental data or an effective theoretical program for calculating accurate distortion geometries.

The use of a muffin-tin approximation to the cluster potential can be another source of error in the present calculations. The replacement of the correct potential by a constant value (its volume average) in the interstitial region would appear to be a rather severe approximation in the case of open tetrahedral systems with directional bonding and can indeed lead to significant errors in the band structure of the *host* material, especially in the case of the more extended conduction states. However, localized defect states have only a relatively small probability of being in the interstitial region, and one might expect that their energy levels should not be greatly affected by such an approximation.

Detailed calculations have shown that the muffin-tin errors arise primarily from that part of the interstitial region which lies immediately outside the atomic spheres, and that considerable improvement in results can be obtained by using the method of overlapping spheres.[30] In this approach one increases the muffin-tin radii slightly, thereby overlapping the spheres and reducing the effective volume of the interstitial region. This not only places more of the charge in physically realistic regions, but it also removes that part of the interstitial region which contributes most of the error. This approach has been applied with great success to such large, open, and loosely coordinated systems as tetracyanoquinodimethane (TCNQ), where the intersphere volume is almost thirty times as large as the sum of the atomic sphere volumes, and so it should be applicable to the present case as well, where this ratio is close to 4 : 1.

Consequently, cluster calculations using overlapping spheres have been carried out for the ideal gallium arsenide cluster as well as for defect clusters containing substitutional nickel and copper impurities. No attempt has been made to choose optimal values of the overlapping sphere radii, but rather each nonoverlapping radius has been increased until the volume of the corresponding sphere is doubled. This corresponds to a radial increase of approximately 25% over the nonoverlapping value, and it is a general rule of thumb that such an increase usually tends to give most of the correction that is to be obtained from this approach.

The resulting energy spectra for the ideal cluster and the defect cluster containing a substitutional nickel impurity are both shown in Fig. 3, along with the corresponding spectra obtained using nonoverlapping spheres. Again, all $1t_1$ cluster levels are aligned for comparison, and all energies are measured with respect to this reference.

Comparison of the cluster charge distributions with and without overlap shows that almost 90% of

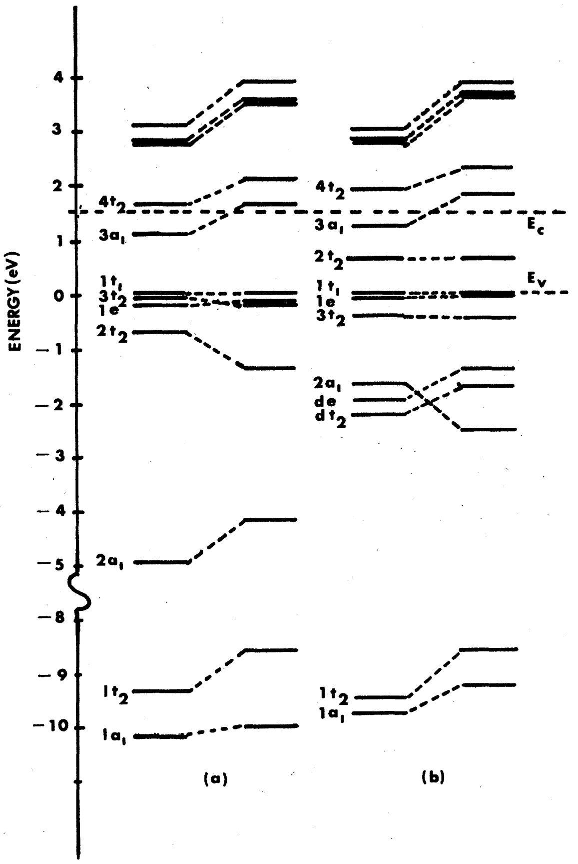

FIG. 3. Comparison of the energy spectra obtained using both overlapping and nonoverlapping spheres for (a) the ideal gallium arsenide cluster and (b) the defect cluster containing a substitutional nickel impurity. All energies are in eV (see Ref. 7) and are measured from the cluster valence edge, denoted by E_v in the figure (see text).

the interstitial charge is removed when the atomic sphere volumes are doubled. Since doubling the size of each individual sphere only decreases the intersphere volume from 78 to 64% of the total cluster volume, this drastic reduction in the interstitial charge clearly indicates that most of the charge was concentrated immediately outside the atomic sphere regions in the nonoverlapping case, particularly along the bonding directions.

Inspection of the energy spectra shown in Fig. 3 indicates that both the d-like states and those host levels associated with σ bonding (and antibonding) between the central atom and its four nearest neighbors are strongly affected by the overlap. The energy gap of the ideal cluster increases from 1.1 to 1.7 eV as the sphere radii are increased by approximately 25%, and the d-like de and dt_2 levels of nickel are pushed up by a similar amount. The position of the $2t_2$-like acceptor level associated with the nickel impurity, however, remains virtually unchanged, varying only from $E_v + 0.68$ eV to $E_v + 0.67$ eV. Because of the upward shift of the nickel d states with respect to the s- and p-like bulk states, the percentage of d character of the $2t_2$ level does increase from 11% to almost 30%, indicating a somewhat stronger interaction between the impurity and the host lattice, but this state is still primarily nonbonding in character and there is little evidence of actual σ-bond formation involving the nickel d states.

A similar result is obtained for copper: the position of the $2t_2$ acceptor level varies from 0.38 to 0.44 eV above the cluster valence edge as the volume of the muffin-tin spheres is doubled. The d states of copper are pushed up by over 2 eV higher into the valence band, resulting in an increase of d character in the $2t_2$ level from almost zero to approximately 18%, but again there is little evidence of actual bond formation. One would still expect nickel and copper to behave primarily as simple acceptors, and the relatively small shifts in the energies of the acceptor levels indicate that the muffin-tin approximation gives an adequate qualitative description of the rather localized defect states.

Similar considerations apply to questions of cluster size and/or choice of boundary conditions. While such factors may strongly affect the host spectrum, the short-ranged impurity-host interactions are only weakly influenced by such changes at the cluster periphery, and such perturbations should result in only modest shifts in the calculated positions of the defect levels. For example, unpublished calculations by the present author show that the value of the t_2-like acceptor level associated with a silicon vacancy[1] varies by less than 0.10 eV as one increases the size of the defect cluster from seventeen to seventy-two atoms, and similar results can be expected for gallium arsenide.

Corrections of roughly the same magnitude can also be associated with changes in cluster boundary conditions, as evidenced by the very recent investigations of Fazzio, Leite, and De Siqueira,[31] who have used the $X\alpha$ scattered-wave cluster method to investigate the properties of lattice vacancies and copper and selenium impurities in gallium arsenide. They, too, use a seventeen-atom cluster to represent the defect-host system, but they leave the host gallium atoms at the twelve next-nearest-neighbor sites instead of replacing them by hydrogenlike saturators. This procedure introduces dangling bond states associated with the gallium atoms at the cluster surface, but these states are not occupied as the calculations are carried to self-consistency. Instead, the associated electrons are placed at the surface of the

Watson sphere, resulting in a charge of $-27e$ on the Watson sphere. While the cluster calculations of Fazzio *et al.* show significant differences in the host spectrum when compared to the present studies (the ideal energy gap is calculated to be 1.92 eV instead of 1.10 eV, for example), the qualitative features of the defect states of both the gallium vacancy and the substitutional copper impurity are very similar to those obtained here, and the positions of the corresponding acceptor levels are in excellent agreement in both cases (again differing by less than 0.10 eV).

A potentially more serious approximation is the use of a local density formalism (LDF) for exchange and correlation (the $X\alpha$ exchange approximation) in the present calculations. While the LDF has been applied to a wide variety of molecules and solids and seems to yield excellent results for ground-state properties such as cohesive energies, equilibrium lattice spacing, and/or bond lengths, etc., generally one cannot identify the associated one-electron eigenvalues with the actual elementary excitations of the system, even though this is commonly done. Even when appropriate transition-state procedures are followed, one often finds, for example, that atomic eigenvalues may be in error by as much as 15–25% as compared to observed ionization photoelectron spectra,[32-35] and band gaps in semiconductors and insulators are often calculated to be too small[36] by 25–40%. Of particular consequence in the context of the present calculations is the tendency of the LDF to *underestimate* the $s-d$ transfer energies in atoms of the $3d$ transition series and to position the d states incorrectly with respect to the s- and p-like conduction-band states of bulk transition metals.

The major source of these difficulties seems to be the noncancellation of the Coulomb and exchange self-interaction (SI) terms in the LDF.[33-35] While such unphysical interactions are explicitly canceled in the Hartree-Fock approximation, such is not the case when one uses a local density approximation for exchange. The spurious SI terms are different for each single-particle orbital involved in the LDF, and their importance varies roughly with the localization of the state involved, being negligible for very diffuse states and rather substantial for more localized states such as the d states of the transition metals. The overall effect of including such SI terms in the LDF is to underestimate the exchange contribution to the potential for those states which show some degree of localization,[33,34] thus leading to higher one-electron eigenvalues for such states.

In atoms, such SI errors are found to be particularly large for the $3d$ states of the transition metals from the $3d$ row of the Periodic Table.[34] In the context of the present cluster calculations this suggests that the eigenvalues of the localized d-like states associated with the transition-metal impurities are probably placed too high in energy with respect to the s- and p-like states of the host, although it is impossible to guess at the magnitude of the errors involved without doing a careful calculation. Nevertheless, such errors should not affect the trends described earlier, as they would imply an even greater mismatch between the d states of nickel and copper, for example, and the broken bond levels associated with nonbonding combinations of the neighboring arsenic $4s$ and $4p$ states. Moreover, one could speculate that self-interaction corrections would tend to shift all of the active transition-metal defect levels down in energy with respect to the valence edge, which would be more in agreement with experimental trends (see Table I). Much detailed analysis remains to be carried out before such conjecture can be taken seriously, however.

In conclusion, the purpose of these studies has been to present a systematic overview of the electronic properties of a well-defined class of deep centers: substitutional $3d$ transition-metal impurities in ideal gallium arsenide. The advantage of such theoretical investigations is that there is no uncertainty in the nature of the particular defects involved, and hence no difficulty in relating the calculated properties to a particular microscopic state of the impurity. Despite the various approximations made in these calculations, it is expected that the qualitative conclusions obtained will remain valid as long as the single-electron approximation itself holds up, and it is hoped that these qualitative features will prove to be of some help to those workers attempting to unravel the many and varied experimental data currently available.

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[1] L. A. Hemstreet, Phys. Rev. B 15, 834 (1977).

[2] L. A. Hemstreet and J. O. Dimmock, Phys. Rev. B 20, 1527 (1977).

[3] L. A. Hemstreet and J. O. Dimmock, Solid State Commun. 31, 461 (1979).

[4] K. H. Johnson and F. C. Smith, Jr., Phys. Rev. B 5, 831 (1972).

[5] J. C. Slater, *The Self-Consistent Field for Molecules and Solids* (McGraw-Hill, New York, 1974).

[6] K. Schwarz, Phys. Rev. B 5, 2466 (1972).

[7] All energies quoted in the text represent the "unrelaxed" eigenvalues (or differences in such eigenvalues) actually calculated using the $X\alpha$ scattered-wave method. Transition-state procedures (see Ref. 5) have not been employed except in selected test cases and, even then, only the unrelaxed results are quoted for uniformity of presentation and ease of comparison. Such tests indicate that orbital relaxation typically increases the quoted eigenvalue differences by less than 0.10 eV.

[8] D. Bois, J. Phys. (Paris) 35, C3, 241 (1974).

[9] M. S. Daw and D. L. Smith, Phys. Rev. B 20, 5150 (1979).

[10] G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1956).

[11] J. Bernholc and S. T. Pantiledes, Phys. Rev. B 18, 1780 (1978).

[12] G. W. Ludwig and H. H. Woodbury, Phys. Rev. Lett. 5, 98 (1960).

[13] G. A. Allen, J. Phys. D 1, 593 (1968).

[14] V. K. Bazhenov and N. N. Solov'ev, Fiz. Tekh. Poluprovodn. 5, 1828 (1971) [Sov. Phys.—Semicond. 5, 1589 (1972)].

[15] W. J. Brown, Jr., and J. S. Blakemore, J. Appl. Phys. 43, 2242 (1972).

[16] R. W. Haisty and G. R. Cronin, in *Physics of Semiconductors, Proceedings of the 7th International Conference, Paris, 1964,* edited by M. Hulin (Academic, New York, 1964), p. 1161.

[17] A. V. Lyubchenko, M. K. Sheinkman, V. A. Brodovi, and N. M. Krolevets, Fiz. Tekh. Poluprovodn. 2, 492 (1968) [Sov. Phys.—Semicond. 2, 406 (1968)].

[18] M. F. Bekmuratov and V. I. Murygin, Fiz. Tekh. Poluprovodn. 7, 83 (1973) [Sov. Phys.—Semicond. 7, 55 (1973)].

[19] Sh. M. Gasanli, O. V. Emel'yanenko, D. N. Nasledov, and G. N. Talalakin, Fiz. Tekh. Pduprovodn. 6, 2053 (1972) [Sov. Phys.—Semicond. 6, 1747 (1973)].

[20] V. I. Fistul' and A. M. Agaev, Fiz. Tverd. Tela (Leningrad) 7, 3681 (1965) [Sov. Phys.—Solid State 7, 2975 (1966)].

[21] J. M. Baranowski, M. Grynberg, and E. M. Magerromov, Phys. Status Solidi B 50, 544 (1972).

[22] W. H. Koshel, S. G. Bishop, and B. D. McCombe, Solid State Commun. 19, 521 (1976).

[23] U. Kaufmann and J. Schneider, Solid State Commun. 25, 1113 (1978).

[24] J. J. Krebs and G. H. Strauss, Phys. Rev. B 15, 17 (1977); 16, 971 (1977).

[25] T. Instone and L. Eaves, J. Phys. C 11, L771 (1978).

[26] U. Kaufmann and W. H. Koschel, Phys. Rev. B 17, 2081 (1978).

[27] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University, Cambridge, 1961).

[28] J. W. Allen, in *Physics of Semiconductors, Proceedings of the 7th International Conference, Paris, 1964,* edited by M. Hulin (Academic, New York, 1964), p. 781.

[29] M. Illegems, R. Dingle, and L. W. Rupp, Jr., J. Appl. Phys. 46, 3059 (1975).

[30] F. Herman, A. R. Williams, and K. H. Johnson, J. Chem. Phys. 61, 3508 (1974).

[31] A. Fazzio, J. R. Leite, and M. L. De Siqueira, J. Phys. C 12, 3469 (1979).

[32] B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966).

[33] M. S. Gopinathan, Phys. Rev. A 15, 2135 (1977).

[34] A. Zunger, J. P. Perdew, and G. L. Oliver (unpublished).

[35] A. Zunger and M. L. Cohen, Phys. Rev. B 18, 5449 (1978).

[36] A. Zunger and A. J. Freeman, Phys. Rev. B 16, 2901 (1977).