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Cluster calculations of rare-earth ions in semiconductors

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Electronic structures of $4f$ electrons of the rare-earth ions Er^{3+} and Yb^{3+} in the semiconductors InP, GaP, and GaAs are calculated on the basis of a self-consistent, local-density-functional DV-$X\alpha$ cluster calculation. The calculated results show that one-electron-energy states of the $4f$ electrons of Er^{3+} and Yb^{3+} ions appear in the energy gap of the semiconductors. Using the self-consistent wave functions of $4f$ electrons, we estimate the spin-orbit interaction of the multiplet of $4f$ electrons of rare-earth ions.

I. INTRODUCTION

Rare-earth (RE) impurities in III-V semiconductors have been arousing a keen interest in optoelectronics and device applications since some of the sharp luminescence spectra due to $4f$-$4f$ intra-atom transitions are observed in the infrared region.[1] Since $4f$ electrons occupy imperfectly the $4f$ orbitals of a rare-earth atom, we have a multiplet energy structure of $4f$ electrons due to electron-electron and spin-orbit interactions.[2] In spite of the complex multiplet structure, the multielectronic states of a rare-earth atom can be explained by a small number of parameters which are adjustable to the experimental photoluminescence (PL) spectra.[3,4] The reason why the calculation of the multiplet structure agrees successfully with experiments is that the $4f$ electrons are screened by the outer electrons and that the multiplet structure in the host materials can be treated as that of an atom to a good approximation.

Experimentally the sharp photoluminescence peak of Yb at 0.99 μm has been investigated most extensively since the luminescence of Yb is intense compared with other RE ions and the multiplet structure is simple.[5–10] In the PL experiments, the $4f$ electrons are excited by photoexcited electron-hole pairs which are delocalized in the semiconductors. The energy transfer from the electron-hole pairs to the $4f$ electrons might be due to nonradiative electron-electron interaction such as an Auger or impact excitation mechanism.[11,12] The quantum efficiency of the PL is small, however, since the energy transfer from the electron-hole recombination to the $4f$ electrons is ineffective and is strongly quenched at high temperatures.[9,13,14]

Recently, the electroluminescence (EL) of Er ions in InP has been observed by one of the authors, in which hot carriers injected in the conduction band hit Er ions to excite the ground state of the multiplet structure to the excited one.[9] The EL and cathodoluminescence (CL) (Ref. 15) are advantageous from the point of view of the quantum efficiency as the kinetic energy of free electrons is directly transferred to the $4f$ electrons of RE ions. This transfer is due to inelastic electron-electron scattering between $4f$ electrons and hot electrons, and thus no recombination process of electron-hole pairs is involved in the luminescence of the rare-earth ions. In fact the EL intensity is much less dependent on temperature than that of PL.[9] Since both excitation mechanisms are related to the energy loss of the delocalized one-electron energy states and the energy gain of the multiplet structure, some theoretical analysis for the electronic states of $4f$ electrons doped in semiconductors will contribute greatly to the understanding of the energy-transfer mechanism.

Theoretically the atomic spectra of a trivalent rare-earth ion is well explained as mentioned above. The electron-electron interaction between $4f$ electrons has to be the largest (~ 10 eV) in order to form the multiplet structure, ${}^{2S+1}L$. Next comes the spin-orbit interaction, (~ 1 eV) and then the effect of the ligand field (~ 0.1 eV). This energy scheme is different from the multiplet structure of the transition metals in which the ligand field of d electrons is as large as the electron-electron interaction, and the spin-orbit interaction is negligibly small.[16] This difference is due to the fact that the $4f$ orbitals are more localized in the atom compared with the $3d$ orbitals. The hierarchic nature of the interaction energy gave success to the perturbation theory of the multiplet structure in the early 1960s.

As regards the electronic structure of the rare-earth atoms in semiconductors, Hemstreet has calculated the cluster of Yb in InP by the relativistic $X\alpha$-scattered-wave cluster method to obtain the one-electron energy state of $4f$ electrons.[17] However, his cluster consists of one Yb, four P, and twelve H atoms for the boundary treatment and thus we do not know the effect of the bonding of III-V semiconductors from his calculation.

In the present paper, we show the results of the DV-$X\alpha$ cluster calculations of the electronic structure of $4f$ electrons of the RE ions, Er and Yb, in the minimum clusters of InP, GaP, and GaAs and discuss the coupling of the inner $4f$-electron orbitals to the valence electron orbitals of semiconductors. Further, based on the calculated, self-consistent wave functions of $4f$ electrons we estimate the energy of the spin-orbit interaction and ligand field of surrounded semiconductor atoms to discuss the multiplet structure. We do not calculate directly the multiplet structures split by spin-orbit interaction and ligand field but instead make rough estimates of them using the equivalent operator method and the calculated self-consistent wave functions of $4f$ electrons.

In the next section we explain the method of the cluster calculation. In Sec. III we present the calculated results and discuss the energy position of $4f$ levels. In Sec. IV we calculate the spin-orbit interaction and the ligand field interaction from the wave functions obtained by the present calculation. The conclusion is given in Sec. V.

II. METHOD

Our cluster model consists of one rare-earth trivalent ion at the center, four nearest-neighbor group-V atoms, and twelve next-nearest-neighbor group-III atoms of III-V semiconductors. As a result, there are 17 atoms in the cluster as shown in Fig. 1. We have adopted GaAs, GaP, and InP as host semiconductors. For rare-earth ions, we have adopted Er^{3+} and Yb^{3+} which are assumed to be located substitutionally on Ga or In sites of the host materials. As a result, the following six clusters are considered: $ErGa_{12}As_4$, $YbGa_{12}As_4$, $ErGa_{12}P_4$, $YbGa_{12}P_4$, $ErIn_{12}P_4$, and $YbIn_{12}P_4$. We consider only the substitutional site for the rare-earth ions in the present paper for simplicity, though studies of PL spectra, x-ray diffraction, and Rutherford backscattering have shown that not only substitutional sites but also interstitial sites are possible for rare-earth ions.[5,9] The lattice constants of the clusters are taken to be the same as those of the pure crystals: 6.095, 5.451, and 5.869 Å for GaAs, GaP, and InP, respectively.

The method we have used is the self-consistent, numerical basis set, DV-$X\alpha$ cluster calculation in which the atomic basis functions are numerically obtained by solving the self-consistent atomic $X\alpha$ Schrödinger equation at each iteration.[18] Atomic basis functions are taken up from the $1s$ orbital to $6s, 5d$ for Er and Yb, $5p$ for In, $4p$ for Ga and As, and $3p$ for P, respectively. The value of α for the exchange and correlation potential is taken as 0.7 within the local-density approximation.[19] Rare-earth ions as trivalent ions donate three electrons, $6s^2$ and $5d^1$ to the conduction band, the wave functions of which are delocalized for group-IV and III-V semiconductors. However, since the Coulomb interaction of free electrons in the conduction band with the trivalent RE ions is screened in semiconductors, the donated electrons are not strongly bound at the site of the RE ion. In fact a rare-earth atom in a molecule or solid generally exists as a trivalent ion. Further if we put the three donated electrons in the present cluster, the excess charge of these electrons appears on the surface of the cluster. Thus we eliminate these three electrons in the calculation as our cluster size is too small to calculate the electronic states of these electrons correctly. The exclusion of these electrons reflects well the situation of EL (and PL) experiments for lightly RE-doped semiconductors, in which most carriers are in the conduction band.

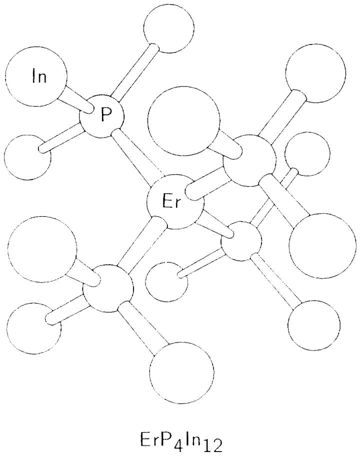

FIG. 1. A cluster used in the present calculation. Rare-earth ion (Er or Yb) at the center, 4 group-V atoms (P,As), and 12 group-III atoms (Ga,In).

In the cluster calculation the boundary condition is important. Hemstreet put hydrogen atoms at the boundary.[17] Gemma removed the dangling-bond orbitals from the basis set of the calculation.[20] However, we found that these boundary conditions made the convergence of the present calculation very difficult. Without the dangling-bond states in the basis set, a small oscillation in the charge of rare-earth ions which appeared during the iteration procedure caused a large oscillation in the energy position of $4f$ levels. To avoid the convergence problem, the dangling-bond states are artificially introduced. As the oscillation in the dangling-bond states is out of phase of the oscillation in the other states, the oscillation in the $4f$ levels is found to be greatly reduced. The dangling charge does not affect the $4f$ states. This is because the localized $4f$ wave function is only sensitive to the self-consistent charge of the $4f$ electrons themselves, but not very sensitive to the delocalized charge of the surrounding atoms. Actually the present results of the position of $4f$ levels are similar to that given by Hemstreet.[17]

Because of the sensitivity of the $4f$ energy-level position to the charge of $4f$ orbitals, it is difficult to find the self-consistency from an arbitrary initial condition of the charge. To avoid the divergent oscillation of the charge, the mixing ratio of the output charge to the input charge for making the new input charge in the next iteration is set to be very small and is changed as a function of the difference between the output and input charges for each iteration. Actually this mixing ratio of the output charge is changed from 0.05 to 0.001. Even though we take such a small mixing ratio, we observe that the $4f$ charge shows some small oscillation during the iteration while the other charge of the semiconductor atoms goes monotonically and very slowly to the self-consistent values. Small out-of-phase oscillation is observed in the dangling-bond charge which has played an important role for reducing the amplitude of the oscillation of $4f$ levels discussed above.

III. CALCULATED RESULTS OF ONE-ELECTRON ENERGY STATES

In Fig. 2 we show the one-electron energy states of the clusters of Er:InP, Yb:InP, Er:GaP, Yb:GaP, Er:GaAs, and Yb:GaAs, where E_F is the Fermi level of the cluster. Each group of the energy levels designated with A to E for Er:InP in Fig. 2 shows In $4d$ levels, P $3s$, P $3p$ + In $5s$ (valence band), Er $4f$ related level, and P $3p$ + In $5s$ (conduction band), respectively. The dangling-bond states of In $5p$ (and $5s$) which appear in the energy gap region because of the boundary treatment will not be considered in the following discussion.

When we compare the results of Er:InP and Yb:InP, the energy levels are almost the same except for some levels near the Fermi level. The atomic characters of the levels near the Fermi level consist of Er (or Yb) $4f$, P $3p$, In $5s$, and In $5p$. This result shows that only the $4f$ atomic wave function of RE ions can be coupled to the valence orbitals of P and In atoms, and the contribution from the other atomic wave functions such as $5d$, $6s$ of Er is small.

Let us consider the $4f$-related levels of Er^{3+} and Yb^{3+} in InP. In the tetrahedral symmetry of the cluster, the $4f$ atomic orbitals ($\ell = 3$) split into the irreducible representation of the point group, T_d, to form molecular orbitals (MO's) with other atomic orbitals:

$$4f(\ell = 3) = \Gamma_2 + \Gamma_4 + \Gamma_5, \qquad (1)$$

where Γ_2, Γ_4, and Γ_5 are irreducible representations of the point group of T_d as shown in Table I, which are denoted in another form as A_2, T_1, and T_2, respectively.[16] In Table II we show the symmetry of the MO's, Γ_j, and the atomic charge obtained by Mulliken's analysis for five $4f$-related levels of Yb:InP near the Fermi level. We also list the one-electron energy, the degeneracy of the level without spin degeneracy, g, and the number of occupied electrons, n, in Table II. Four of the five levels have large amplitudes of the $4f$ atomic character. These states appear just above the top of the valence-band levels, which have the same symmetry of $4f$ electrons as shown in Eq. (1). The energy level of Γ_3 does not couple with $4f$ orbitals since $4f$ orbitals do not have Γ_3 symmetry as shown in Eq. (1). In Table I we show the reducible character for molecular orbitals, χ^s_{nn}, χ^p_{nn}, χ^s_{nnn}, and χ^p_{nnn} for s, p orbitals at the nearest- and next-nearest-neighbor sites of a RE ion, respectively, and their decomposition into the irreducible representation of the T_d point group. Since the nearest-neighbor P $3p$ orbitals and the next-nearest-neighbor In $5s$ do not have the symmetry of Γ_2 as shown in Table I, the Mulliken charges of these orbitals in the Γ_2 $4f$ level are almost zero (Table II) within numerical accuracy. The reason why P $3s$ does not appear in MO's is not explained by the group theory but by the fact the MO near the top of the valence band does not have s components. Thus the $4f$ states may be acceptor-like levels of semiconductors in the sense that they couple with the valence-band orbitals.

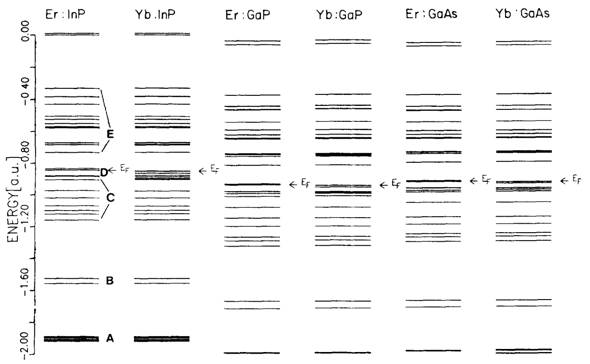

FIG. 2. One-electron energy levels of the clusters; Er:InP, Yb:InP, Er:GaP, Yb:GaP, Er:GaAs, and Yb:GaAs. See the text for the mark from A to E.

Let us explain the reason why the $4f$ levels appear just above the valence band. As mentioned in Sec. II, the energy position for $4f$ orbitals is very sensitive to the self-consistent charge of the $4f$ electrons themselves. Even if we added an electron in $4f$ orbitals of an atom, all $4f$-related energy levels would be located far above the bottom of the conduction band and thus all electrons

TABLE I. The character table of the point group T_d and the reducible character for s and p orbitals for nearest- and next-nearest-neighbor sites.

T_d	E	$6S_4$	$3C_2$	$6\sigma_d$	$8C_3$	
Γ_1	1	1	1	1	1	
Γ_2	1	-1	1	-1	1	
Γ_3	2	0	2	0	-1	
Γ_4	2	1	-1	-1	0	
Γ_5	3	-1	-1	1	0	x, y, z
χ^s_{nn}	4	0	0	2	1	$\Gamma_1 + \Gamma_5$
χ^p_{nn}	12	0	0	2	0	$\Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$
χ^s_{nnn}	12	0	0	2	0	$\Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$
χ^p_{nnn}	36	0	0	2	0	$3\Gamma_1 + \Gamma_2 + 4\Gamma_3 + 5\Gamma_3 + 7\Gamma_5$

TABLE II. One-electron energy states near $4f$ levels for YbInP: g and n are the degeneracy of the level without spin and the number of the occupied electrons, respectively. We also list the self-consistent atomic charge within Mulliken's analysis.

Energy [a.u.]	g	n	Symmetry	Yb $4f$	P $3p$	In $5s$	In $5p$
−0.85039	3	2	Γ_5	0.1065	0.3664	0.2408	0.2854
−0.85151	1	2	Γ_2	0.9824	0.0040	0.0017	0.0120
−0.86440	3	6	Γ_4	0.7550	0.1528	0.0211	0.0608
−0.87723	2	4	Γ_3	0.0	0.3363	0.4078	0.4337
−0.88695	3	6	Γ_4	0.1723	0.4253	0.1739	0.1990

would be removed as an output charge. Similarly if we subtract an electron from $4f$ orbitals, $4f$ levels would appear then far below the top of the valence band, so that all $4f$ levels would be fully occupied in the next iteration. In this way the large change of the occupation number of $4f$ orbitals gives divergent oscillation of the charge. Thus only small changes of $4f$ electrons are possible and all $4f$ levels in the cluster should be at least in the energy gap region. The small change of the $4f$ charge for self-consistency is possible only by changing the coupling with the valence bands. When the energy of $4f$-related levels increases from the top of the valence band, the coupling coefficient of the valence orbitals in the unoccupied $4f$ levels decreases. Then the $4f$ component of the unoccupied level increases, and the $4f$ charge decreases monotonically. Thus the detailed valence of the energy position of the $4f$ levels is obtained by energy gain (decrease) of electron-electron interaction and the energy loss caused by the decoupling with the valence band when the energy $4f$ levels increase. That is a possible physical explanation for why the $4f$ levels appear just above the top of the valence bands, which generally occurs in the present cases.

Since the $4f$ level position is sensitive to the charge, the value of α in the $X\alpha$ potential is important. The energy position of $4f$ levels may change if α is changed. However, it is not simple to make a model for determining the energy position since the coupling constant of $4f$ electrons with the valence band depends on α, too. This is because the atomic wave function is the solution of the $X\alpha$ Schrödinger equation, which is consistent with the $X\alpha$ cluster calculation. For a reasonable region of α (at least $\alpha = 0.7 \pm 0.1$), the above discussion will be valid since the coupling will not become zero for the $4f$ levels up to the center of the energy gap.

The above discussion is consistent with the chemical trend of two rare-earth ions of Er and Yb and three host materials. As shown in Fig. 2, the energy position of $4f$ levels of Yb appears nearer to the top of the valence band than that of Er for the same host semiconductors. Assuming that there is no large difference of the derivative of the electron-electron interaction for large electron density, the covalent bonding of Yb $4f$ orbitals with the valence bands is smaller than that of Er $4f$ orbitals since the $4f$ orbital of Yb is more localized. Thus a smaller increase in the number of electrons is sufficient for Yb appearing above the top of the valence band. In fact, the Mulliken charges of Er and Yb are $11.58 \sim 11.68$ and $13.1 \sim 13.2$, respectively, which does not change for three host semiconductors while neutral Er and Yb atoms have 11 and 13 $4f$ electrons, respectively.

It should be mentioned that if there is an electron trapped by a shallow-donor state, the above discussion is not valid, since the $4f$ level can be coupled with the conduction band, too. In this case the $4f$ states will appear near the donor level. Though the present cluster size is too small to show this situation, such a possible shift (or change of symmetry) of the $4f$ occupied levels might be an origin of the excitation mechanism of the multiplet of the $4f$ electrons appearing in PL and EL experiments.

IV. SPIN-ORBIT INTERACTION

Using the self-consistent atomic basis functions of $4f$ orbitals and the potential, we have estimated the spin-orbit interaction, H_{so}, which is given by

$$H_{\mathrm{so}} = \sum_i \frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{du(r)}{dr}\ell_i s_i \equiv \sum_i \xi(r)\ell_i s_i, \qquad (2)$$

where $u(r)$ is the spherically symmetrized atomic potential, and the summation is taken over $4f$ electrons. In the many-electron system, we can use the equivalent operator method to calculate the spin-orbit interaction of the multiplet structure, ${}^{2S+1}L$ (Refs. 22 and 16),

$$H_{\mathrm{so}} = \lambda \mathbf{S}\cdot\mathbf{L}, \qquad (3)$$

where $\mathbf{S}$ and $\mathbf{L}$ are the total spin and total angular momentum, respectively, and λ is a coupling constant which depends on the number of f electrons, $\mathbf{S}$ and $\mathbf{L}$.

Let us consider the ground state of the multiplet of Er:InP. The ground state of $4f^{11}$ is ${}^4I$. In this case, we can easily show the following, according to the general procedure:[16]

$$\lambda = -\frac{\zeta_{4f}}{3} \quad \text{for } {}^4I \text{ of } 4f^{11}, \qquad (4)$$

where

$$\zeta_{4f} = \int_0^\infty \xi(r)\{R_{4f}(r)\}^2 r^2 dr, \qquad (5)$$

and $R_{4f}(r)$ is the radial distribution function of $4f$

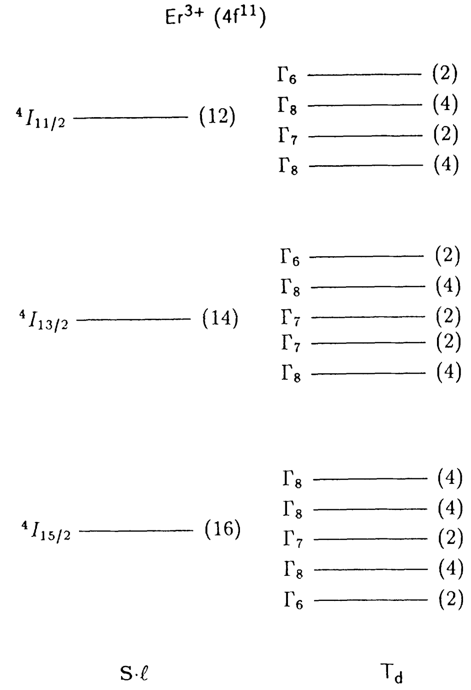

FIG. 3. The schematic energy levels of the multiplet structure of Er^{3+}.

atomic orbitals. Thus the energy difference ΔE between the ground state $({}^4I_{15/2})$ and the first excited state $({}^4I_{13/2})$ is expressed as follows:

$$\Delta E = E({}^4I_{13/2}) - E({}^4I_{15/2}) = -\tfrac{15}{2}\lambda = \tfrac{5}{2}\zeta_{4f}. \qquad (6)$$

Similarly for Yb^{3+} : $4f^{13}$, the ground state is ${}^2F$ and

$$\lambda = -\zeta_{4f} \quad \text{for } {}^2F \text{ of } 4f^{13}. \qquad (7)$$

Thus the energy difference ΔE becomes

$$\Delta E = E({}^2F_{5/2}) - E({}^2F_{7/2}) = -\tfrac{7}{2}\lambda = \tfrac{7}{2}\zeta_{4f}. \qquad (8)$$

The calculated results of ΔE are 0.90 and 1.52 eV for Er:InP and Yb:InP, respectively. The PL experiments show that the corresponding energy differences are near 0.8 and 1.2 eV. In spite of the estimates without the intermediate interaction,[3] agreement between the present results and the experiments is satisfactory.

Finally we briefly mention the effect of ligand field for multiplet structure. Using the chart of the splitting of the multiplets by Lea, Leask, and Wolf,[21] the parameter of ligand field x after their notation is near -1.0 for III-V compounds. Using $x = -1.0$, the multiplets of ${}^4I_{15/2}$, ${}^4I_{13/2}$, and ${}^4I_{11/2}$ split into the irreducible representations of the point group T_d as shown qualitatively in Fig. 3. In the figure the degeneracy of the irreducible representations is shown.

In PL spectra of Er, the transitions from the first excited states of the ${}^4I_{13/2}$ to the ground states of ${}^4I_{15/2}$ are observed in which these multiplets are split by ligand field. In fact, the fine structure of PL experiments shows five peaks for Er:Si,[23] in which Er is considered to have a tetrahedral symmetry, and eight peaks at the C_{2v} symmetry site for Er:GaAs.[24] Detailed spectra should be explained by calculating the matrix element of the transition probability of the irreducible representations.

V. CONCLUSION

In conclusion we have performed a DV-$X\alpha$ cluster calculation for rare-earth ions of Er and Yb in III-V semiconductors. The calculated results show that the one-electron energy levels of the $4f$ orbitals of trivalent rare-earth ions appear just above the top of the valence-band-like acceptor levels. These energy levels always appear for Er and Yb ions in InP, GaP, and GaAs host semiconductors. Using the self-consistent atomic basis wave functions of $4f$ orbitals and the atomic potential, the spin-orbit interaction for Er:InP and Yb:InP is calculated. In spite of neglecting the intermediate interaction, the spin-orbit interaction between the ground state and the first excited one shows good agreement with experiments. The splitting of the multiplet structure by the ligand field is shown, with use of the given chart by Lea, Leask, and Wolf.

It is desirable that the multiplet structure be calculated by the usual quantum chemical configuration-interaction method. Further, the matrix elements of the transition between the multiplet structure split by the spin-orbit interaction and the ligand field should be calculated from first principles.

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