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The strong correlation of the 4f electrons of erbium in silicon

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Abstract

The local spin density approximation (LSDA) with the Hubbard model correction is adopted to describe the electronic structures of O-codoped Er–Si systems. The electrons in the 4f orbitals of Er atoms are taken as localized electrons in the framework of an all-electron treatment. The total density of states (DOS) and the partial densities of states for Si(3s, 3p), Er(4f), Er(5d), Er(6s), O(2s), and O(2p) in this ErSiO system are calculated. It is found that the inclusion of the Hubbard U greatly influences the partial DOS of the Er 4f electrons. The separation between the spin-up and the spin-down states of the highly localized 4f orbitals is larger than that of the LSDA results obtained without considering the Hubbard U -parameter. The calculation results provide possible explanations of the experimentally observed erbium-induced impurity energy levels in Si detected by deep-level transient spectroscopy.

1. Introduction

In recent years, the optical properties of Er-doped Si have received a great deal of attention because of the possibility of realizing Si-based efficient light-emitting devices [1]. The luminescence of Si:Er is suggested to be arising from the transitions from $^4I_{13/2}$ to $^4I_{15/2}$ levels of 4f electrons in Er³⁺ ions, which are forbidden for free atoms and only allowed when the crystal field of the host breaks the inversion symmetry and mixes states of opposite parities [2–4]. Earlier theoretical studies on the Si:Er system treated the Er 4f electrons as core electrons screened by the 5s, 5p filled shells and 6s, 5d valence orbitals [5–7]. This ‘frozen 4f’ approximation seems not to be infallible, since photoemission measurements verified experimentally that the 4f orbitals of rare-earth elements would hybridize with the Si valence band [8]. Later, Gan *et al* [9] and Wan *et al* [10] treated the Er 4f orbitals as valence states in order to describe the electronic structures of such systems by taking into account the interactions between the impurity and host Si. In the work of Wan *et al* [10], an *ab*

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initio method—based on the local density approximation (LDA) architecture—was employed. However, the strong localization of the 4f electrons of the Er cannot be clearly described in the mean-field approximation. As a result, when considering the system as a whole, this treatment may lead to the miscalculation of the Hamiltonian matrix which represents the interaction of itinerant electrons. The density of states (DOS) for Er 4f electrons in the Wan *et al* calculation may deviate significantly from the real one, since the on-site Coulomb interaction for a strongly correlated electron system has not been considered. Recently, the Hubbard U -model has been added to the framework of the local spin density approximation (LSDA). Harmon *et al* [11] used the LSDA + U method to calculate the properties of metal Gd. The results for the 4f electrons of Gd were found to agree well with the x-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromatic spectra of the excited states. Huang *et al* [12] also applied this method to study the electronic structures of Er atoms doped into C_{82} , and illustrated the applicability of the LSDA + U method to large clusters. In this work, we present a LSDA + U calculation considering the strongly correlated 4f electrons and itinerant s, p, d electrons as a whole system. The full features of the electronic structures of the Si:Er(O) system are obtained.

2. Method and model

In the case of Er codoped with O in a silicon host, the most favourable structure configuration has been proved to be an Er atom in the hexagon interstitial (H_i) position surrounded by six O nearest neighbours [2, 10, 13]. To simulate this $H_i + O$ configuration, the cluster model used in the Wan *et al* work is employed, so it is easy to explore the change of electronic structures resulting from the inclusion of the Hubbard U . Figure 1 shows schematically the cluster $ErSi_{38}O_6$. All the dangling bonds of the outer shell Si atoms are saturated by hydrogen atoms (not shown in the figure). The relaxation due to the embedded impurity has been taken into consideration. The shifts of the O atoms and the Si atoms nearest to the Er have been determined by the previous LDA calculation and are checked again by the LSDA + U method here. The distances from the Er to the nearest O and Si are 0.218 and 0.260 nm, respectively. Although the size of the cluster is rather small, it can still govern the basic features of the Er 4f electrons. Since the Er 4f electrons are relatively localized, including more Si atoms in the outer shell of the cluster does not change the DOS for Er 4f substantially. In order to identify the energy levels with respect to the Si bands, the electronic structure of a similar cluster of Si without Er and O atoms and thus with no relaxation of Si atoms is calculated, to represent the band structure of bulk Si.

The discrete variational self-consistent method (DV-SCM) takes a set of sample points in the calculation of certain physical quantities. Thus the overlap and Hamiltonian matrices, the wavefunctions, and the densities of the charges obtained are all expressed in numerical values. The von Barth–Hedin exchange–correlation potentials [14] are adopted. The symmetry of the system is C_{3v} , as can be clearly elicited from figure 1. Atomic basis functions are symmetrized according to such symmetry and used as basis functions. Consequently the matrix of secular equations can be divided into four blocks, belonging to different group representations, i.e. A_1 , A_2 , and two E blocks. Here A_1 , A_2 , and E are the three representations of the group C_{3v} . The initial valence electron configuration for the Er atom is taken as $4f^{11}5d^16s^2$. In the LSDA + U method postulated by [15], the total energy can be expressed as

$$E = E^{LSDA} + \frac{1}{2} \sum_{m,m',\sigma} U(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0) + \frac{1}{2} \sum_{\substack{m,m',\sigma \\ (m \neq m')}} (U - J)(n_{im\sigma} - n^0)(n_{im'\sigma} - n^0), \quad (1)$$

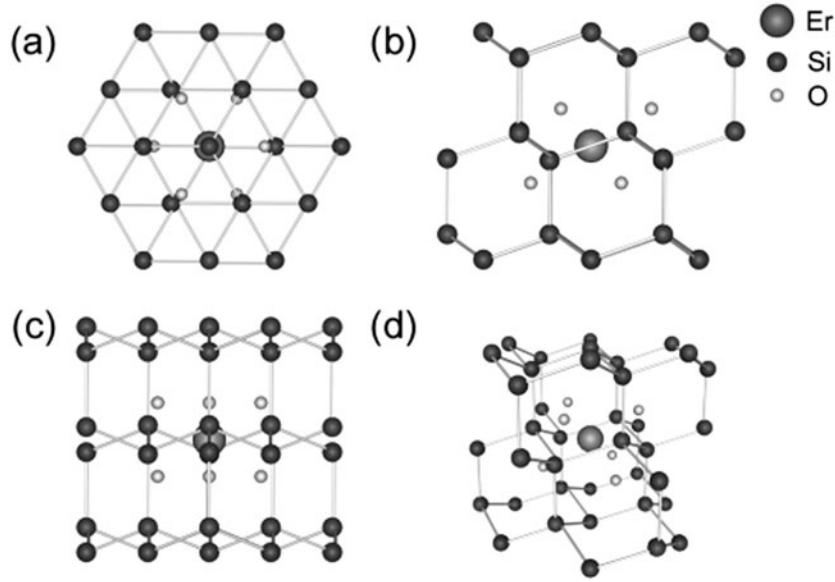


Figure 1. The cluster model used to simulate the electronic structure of the ErSiO system. The Er atom is placed in the H_3 position. (a) Top view, (b) front view, (c) left side view, (d) perspective view. The 44 H atoms used to saturate the dangling bonds of the outer shell Si atoms are not shown here.

where E^{LSDA} is the conventional LSDA total energy, U and J are the on-site Coulomb parameter and the exchange parameter, respectively, m and m' are the localized molecular orbitals, and $n_{m,\sigma}$ is the occupancy of the localized molecular orbital m with spin σ . For simplicity, the approximation that U and J are independent of the orbital parameter m is made. Here the average occupation of localized orbitals is approximated as n^0 and can be calculated using the following equation:

$$n^0 = \sum_{m,0} n_{m,0} / k \quad (2)$$

where k is the total number of localized molecular orbitals. Similarly to the formulation of the conventional LSDA, the single-particle potential can be derived from the total energy equation (1) in the following form:

$$V_{m\sigma} = U \sum_{m'} (n_{m'\sigma} - n^0) + (U - J) \sum_{m' (\neq m)} (n_{m'\sigma} - n^0) + V^{LSDA}, \quad (3)$$

where V^{LSDA} is calculated from the charge density of the system. The second term on the right-hand side of the equation is what we need to take into account for the calculation of the interaction among the localized electrons. The parameters U and J of Er atoms are chosen to be 6.50 and 0.70 eV according to [12], in which these values were derived from the values of U_{eff} and J given by Anisimov *et al* [16], and their validity has been shown there. Although the method that we used in this work is still a one-electron method with a single Slater determinant as a trial function, and the above treatment is still a mean-field approximation, such a separation treatment has been proved to be effective in many cases for the strongly correlated d and f electron systems by previous authors [11, 12].

In the DV-SCM program, well converged results from the LSDA ($n_{m\sigma}$, n^0 , V^{LSDA} , etc) are taken as the starting configuration for calculating the correction $V_{m\sigma}$ in equation (3), which

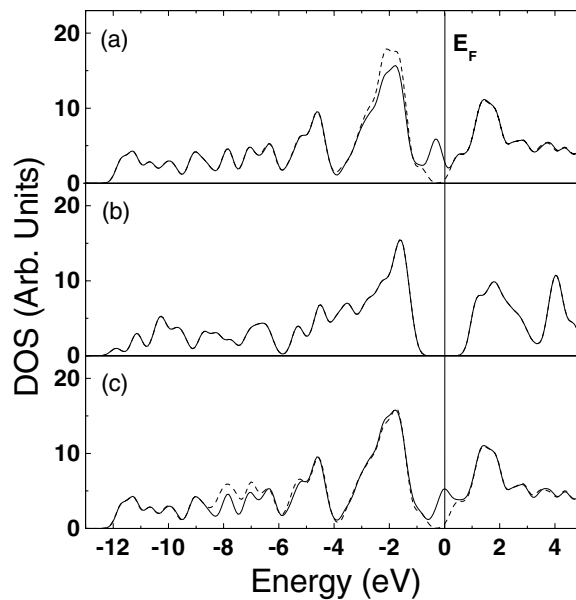


Figure 2. (a) The TDOS of the $\text{ErSi}_{38}\text{O}_6$ cluster calculated using the LSDA, (b) the DOS of a pure Si cluster, and (c) the TDOS of the $\text{ErSi}_{38}\text{O}_6$ cluster calculated by the LSDA + U method. (The solid and dashed curves represent the spin-down and the spin-up states.)

can be used to describe the interactions among all the localized electrons and the itinerant electrons. After solving the corrected Hamiltonian, the electronic structures of the system will be recalculated until the new converged results are achieved.

3. Results and discussion

Firstly, we calculate the DOS of such a system in the LSDA architecture without considering the Hubbard U -correction. The result is shown in part (a) of figure 2. It is about the same as that obtained by Wan *et al*, especially for the spin-up states [10]. The DOS of a pure Si cluster is shown in part (b); it represents the Si bulk band structure. The band gap obtained from it is about 1.1 eV. The Fermi level is located within the band gap at 0.42 eV below the conduction band minimum. Figure 3 shows the PDOSs of the Er 4f, 5d, 6s and O 2s, 2p orbitals. The main features agree basically with the Wan *et al* results [10]. The gap states are found to be mainly 4f characterized, but at the same time hybridized with other orbitals. The valence electron configuration of Er is determined as $4f^{11.29}5d^{1.75}6s^{0.19}$. The ratio of the occupation number of the spin-down state to that of the spin-up state takes the values 0.66, 0.99, and 0.65 for 4f, 5d, and 6s levels, respectively.

Before showing the results from the LSDA+ U method, we would like to recall the criterion mentioned by Anisimov *et al* [16] for correcting the calculation for the localized system with the Hubbard model. The mean-field approximation serves well for the conditions $U \ll W$ and $U \gg W$, where U is the Hubbard parameter and W is the bandwidth. In figure 2(a), it is apparent that the Hubbard U -parameter (6.5 eV) is larger but not much larger than the bandwidth. Thus the correction with the Hubbard model is adequate.

The calculation results obtained by the LSDA + U method are shown in figures 2(c) and 4. The TDOS shown in part (c) does not change too much as compared with that in part

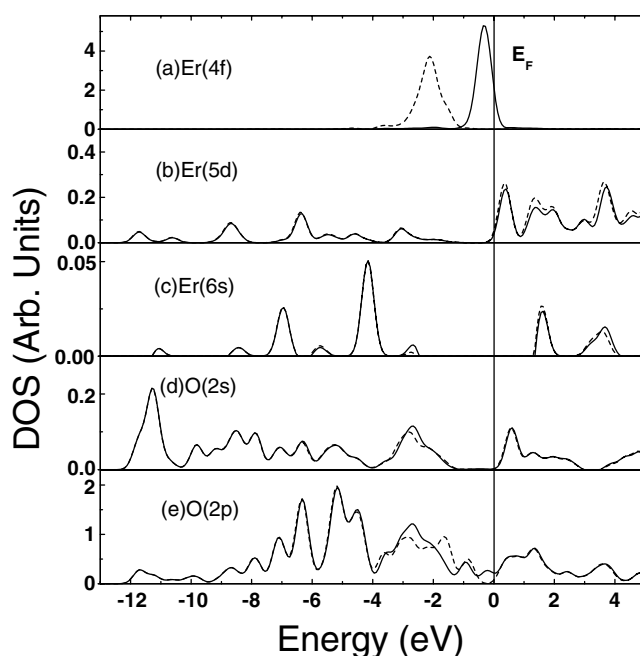


Figure 3. DOSs for Er and O atoms calculated using the LSDA. (a)–(c) PDOSs of Er 4f, 5d, and 6s orbitals; (d), (e) PDOSs of the O atoms. (The solid and dashed curves represent the spin-down and the spin-up states.)

(a), except for those states in the band gap. This is actually the main effect of the strong on-site Coulomb interaction. In figure 4, except for the Er 4f orbitals, all the PDOSs change slightly (around the Fermi level) as compared with figure 3. This is to be expected, since the non-4f electrons do not correlate strongly, and thus are affected only slightly by the Hubbard correction, which plays a significant role for the strongly correlated 4f states. So the replacement of V^{LSDA} with $V_{m\sigma}$ (equation (3)) changes the PDOS of Er 4f orbitals dramatically, resulting in an obvious shifting of energy positions and a splitting into several energy states. They are still highly localized, but hybridized at the same time with other non-4f orbitals. In figure 4(a), the original peak of the spin-down state shifts towards the Fermi level and splits into two peaks with a separation of about 1.2 eV, while the spin-up band shifts downward significantly and separates from the spin-down states by about 6.0 eV. This amount of separation is comparable to the U -parameter chosen for the calculation, just as is predicted from the Hubbard U -model. Now the valence electron configuration is $4f^{11.16}5d^{1.89}6s^{0.17}$. The electrons lost from the 4f orbitals are most likely to occupy the 5d orbitals. Because of the localization of the 4f orbital, the 4f electrons contribute less to the formation of the covalent bond between the Er and other atoms. And since the atomic wavefunctions are used to compose the molecular orbitals, the PDOS of the 4f electrons may keep in the atomic shell shape. The PDOS of Er 4f has also been calculated with the cluster $Si_{44}O_6Er$, which is a little larger than the $Si_{38}O_6Er$ cluster. The result is quite close to that in figure 4(a). This verifies the validity of our cluster model in dealing with the Er 4f features.

In plotting the DOSs of figures 2–4, the discrete energy eigenvalues of secular equations have been broadened with a Gaussian broadening parameter. The broadening function is as

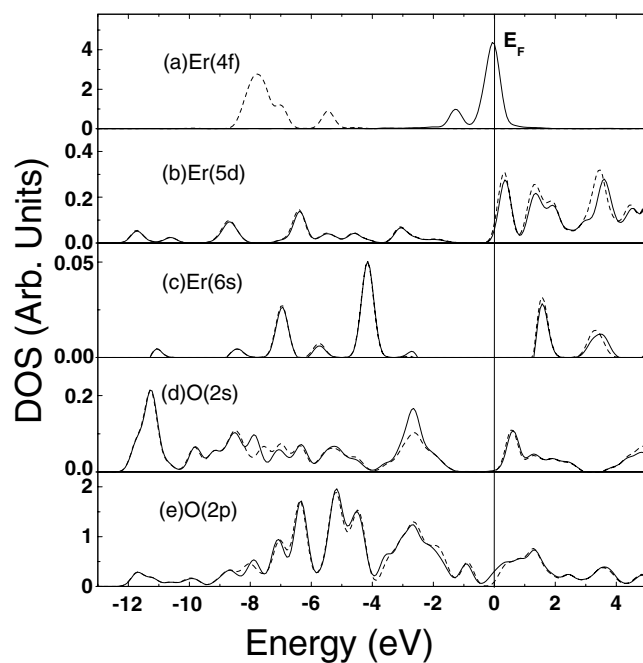


Figure 4. DOSs for Er and O atoms calculated by using the LSDA + U method. (a)–(c) PDOSs of Er 4f, 5d, and 6s orbitals; (d), (e) the PDOS of O atoms. (The solid and dashed curves represent the spin-down and the spin-up states.)

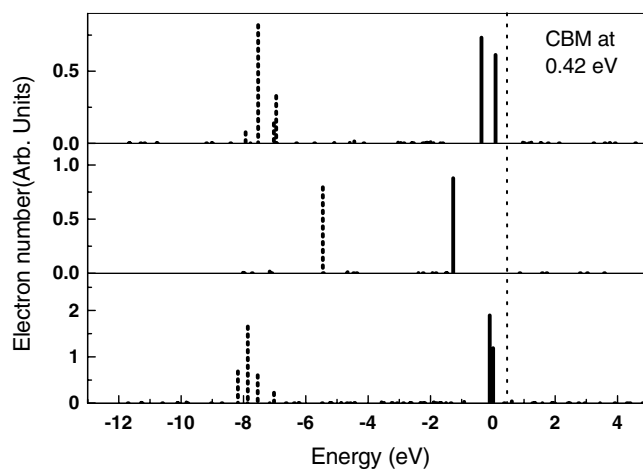


Figure 5. The weight of the Er 4f states in the molecular wavefunctions for different symmetry blocks A_1 , A_2 , and E of the secular equations. (The solid and dashed lines represent the spin-down and the spin-up states.)

follows:

$$\text{DOS}(E) = (2\pi\sigma^2) \sum_I \exp[-(E - E_i)^2/2\sigma^2], \quad (4)$$

where σ is taken to be 0.2 eV. In order to show the occupancies of the Er 4f levels in figure 4(a), the broadening extension is removed from the PDOS of Er 4f. The result is shown in figure 5.

The lines in the figure represent the positions of energy levels, and the height of the line represents the weight of the 4f states, defined as

$$\text{weight of 4f states} = \frac{\sum_k |C_k|^2}{\sum_i |C_i|^2}, \quad (5)$$

where C_i is the coefficient of the i th basis function used to construct the molecular orbitals, and C_k is the coefficient of the 4f orbital-related basis functions. Since the eigenstates of the E representation are twofold degenerate, the weight of the 4f states of each molecular orbital in the E block is doubled. There are seven spin-down eigenstates (two in A_1 , one in A_2 , and four in E). Their weight for the 4f states is close to 1.0. The two states in the E representation are slightly separated near the Fermi level.

Experimentally, the gap states of Er in Si have been studied by several groups using deep-level transient spectroscopy (DLTS) [17–21]. Benton *et al* [17] first reported the observation of nine discrete defect levels in ion-implanted Er-doped Si. However, they could not identify whether these levels are related to Er impurity. Later, Libertino *et al* [18] found in their experiments five impurity levels located at 0.15, 0.20, 0.26, 0.36, and 0.51 eV below the conduction band edge. Among them, the 0.15 eV level seems to be a shallow donor and has been assigned in the Wan *et al* work as a resonant state of the silicon 2p and erbium 5d levels induced by oxygen. This is also verified by the PDOS of Er(5d) in figure 4, where the peak near the conduction band edge is extended into the energy gap. The other four levels were assigned as being induced by the Er–defect complexes. Recently, Cavallini and co-workers [19–21] observed in Er-doped liquid phase epitaxy silicon a series of majority carrier traps and minority carrier traps. They attributed the three energy levels located at 0.20, 0.39, and 0.68 eV below the conduction band edge as being induced by Er. Although there is a lack of consensus regarding how many deep levels are related to Er and where are they located, the unquestionable fact is that Er actually induces multiple deep impurity levels in the Si band gap. In the framework of the LSDA + U treatment, the existence of multiple deep levels in Er-doped Si can be understood. In figure 5, there are four energy states located in the band gap of silicon, at 0.33eV (A_1), 0.43 eV (E), 0.52 eV (E), and 0.79 eV (A_1) below the conduction band edge. Although these values do not coincide exactly with the above experimental data, it still gives a possible explanation of the origin of the Er-related deep energy levels in the DLTS spectra.

4. Conclusions

For weakly correlated systems, the LSDA has been successfully used to describe the electronic states. However, the LSDA is unsuitable for the description of highly correlated cases such as the SiErO system where the 4f electrons are highly localized and thus correlated. The method that we used in this work takes into consideration the strong-correlation Hubbard correction. A spin- and orbital-dependent one-electron potential is added to the conventional LSDA potential, so the itinerant and localized electrons are treated as a whole. The partial densities of states for the valence electrons of Si, O, Er and the localized 4f electrons of Er are obtained. It is found that the spin-up and spin-down electronic states change remarkably when the Hubbard U is included. The spin-down states of the 4f electrons create four discrete energy levels in the Si band gap. They possibly correspond to the Er-induced deep impurity levels observed in the DLTS measurements.

Acknowledgments

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