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Electronic structure and optical properties of europium-activated yttrium oxide phosphor

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The electronic structure and optical properties of a red phosphor, Y_2O_3:Eu, have been studied using the first-principles molecular-orbital and band-structure methods. Using the calculated one-electron energy levels, several properties of the host material and properties of the phosphor based on host-impurity interactions have been explained. However, it has been found that the luminescence properties of Eu^{3+} require the spin-orbit effects to be included in the computational methods.

I. INTRODUCTION

The electronic structures of materials based on *f*- and *d*-electron atoms have long presented a challenge to condensed-matter theories.[1] Most optoelectronic materials contain elements from the transition-metal or the rare-earth series. In order to understand the optoelectronic processes in these materials, a knowledge of their electronic structure is crucial. Recently, it was shown that optical properties of transition-metal ions in oxides and sulfides of zinc can be studied through a complementary use of cluster molecular-orbital and band-structure theories.[2,3] One-electron energy levels calculated within the framework of scattered-wave molecular-orbital[4] and augmented-spherical-wave (ASW) band-structure theories[5] gave a reasonable and consistent explanation of various optical transitions in these materials.

In this paper we have extended this approach to yttria (Y_2O_3) activated by trivalent europium which contains ions both from the transition-metal and the rare-earth series. This material is used as a red phosphor in the lighting industry and also in laser devices. Considerable experimental results exist in the literature on the excited-state properties of this phosphor.[6-9] Traditionally, excitation energies involving a rare-earth ion have been studied within the semiempirical crystal-field theories.[8,10] Such approaches tend to analyze the electronic structure of rare-earth ions independently of the host lattice, with the host-impurity interaction being introduced in a semiempirical manner utilizing local symmetry properties. It is also assumed that the *f* electrons are localized at the impurity site and the covalency effect is insignificant; therefore, the covalency contributions can be incorporated parametrically to explain the observed experimental data. Some recent calculations[11] have indicated that this assumption may not be valid. A significant amount of mixing between the *f* electrons and the extended states of the host lattice have been found with the amount of mixing dependent on the position of a rare-earth ion in the Periodic Table and its valence state. In order to include such covalency effects, the electronic structure of the rare-earth ion together with the host material can be studied by using a cluster approach[12] or supercell band-structure method.[13] Two interesting features of this phosphor which indicate the importance of rigorous treatment of this host-impurity interactions are worth mentioning: the presence of a charge-transfer band[7] and the observation of two-photon transitions near 17.5 eV.[14] The exact nature of the charge-transfer bands is not definitely known although the presence of such a band is obvious from the absorption spectrum of Y_2O_3:Eu.[7] These bands have been used in empirical theories[15] to explain various luminescence processes. Second, multiphoton emission in Y_2O_3:Eu near 17.6 eV indicates production of more than one secondary electron-hole pair in the host lattice which eventually recombine at the europium site. Such a recombination process would require significant host-impurity coupling.

One-electron theories are not free from all conceptual difficulties when extended to the study of problems involving rare-earth ions for which the relativistic effects are very crucial. These effects, particularly those resulting from strong spin-orbit coupling, can and should be handled with relativistic many-body theories or configuration interactions.

In this paper the electronic structure of Y_2O_3 has been investigated by both the cluster and the band-structure methods, while that of the europium ion has been studied by the cluster method only. It will be shown that these one-electron methods provide satisfactory explanations of the host material properties as well as those properties which are dependent on host-impurity interactions. However, the one-electron energy levels fail to explain transitions among the *f* manifold of europium. In order to predict these transitions, one has to include the electron correlation and spin-orbit interaction explicitly, either by a many-body approach or a configuration-interaction method.

II. METHODS AND RESULT

The electronic structure of yttrium oxide has been calculated using the ASW band structure[5] and the scattered-wave cluster molecular-orbital[1,4] methods. The localized energy levels and wave functions of the trivalent europium ion impurities substituting for yttrium have been studied by the cluster approach. These methods have been discussed in detail in the literature and in our earlier publications.[2,3]

The cluster calculations were performed using the metal centered clusters, consisting of the metal ion and its six nearest-neighbor oxygen atoms. Both for the yttrium and the europium centered clusters, the clusters are chosen with D_{3d} symmetry, which corresponds to the site symmetry of the eight metal ions occupying special positions $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.[16] It has been assumed that clusters centered at the low-symmetry site would lead to only minor changes in the relative separation of the energy eigenvalues. In view of the small crystal-field splitting observed for the f-like states, this is a reasonable approximation.

First we will consider the results from the cluster calculation. This calculation was done with a $(YO_6)^{9-}$ cluster enclosed inside a Watson sphere. The exchange parameters α used for yttrium and oxygen atoms are 0.704 65 and 0.744 47, respectively. The $4p$ atomic states of yttrium and the $2p$ and $2s$ atomic states of oxygen are treated as valence orbitals which give rise to three distinct bands of energy levels in the valence band.

The oxygen p-like band consists of two a_{1g}, one a_{1u}, one a_{2g}, two a_{2u}, three e_g, and two e_u molecular orbitals. These molecular orbitals have been labeled using the irreducible representations of the D_{3d} point group. The bandwidth is calculated to be 2.01 eV. The oxygen $2s$-like states lead to one a_{2u}, one e_u, one e_g, and one a_{1g} molecular orbitals, with the width of this band being 0.46 eV. The interband gap between the $2s$- and $2p$-like bands is 12.70 eV. The $4p$-like states of yttrium give rise to one a_{2u} and one e_u molecular orbitals, which appear 4.12 eV below the bottom of the oxygen $2s$-like band.

The d-like states of yttrium lead to two e_g and one a_{1g} molecular orbitals. The crystal-field splitting is found to be 2.25 eV. The d-like states are 5.6 eV (221 nm) above the top of the valence band. This separation compares very well with the observed band gap of yttria (5.6 eV).[17] The d-like states are found to have very little admixture of oxygen states, indicating weak covalency.

In addition to the molecular orbitals, which can be identified with the atomic states, two molecular orbitals in the irreducible representation a_{2u} and a_{1g} are also found inside the gap between the valence and conduction bands. These molecular orbitals are 4.78 and 3.85 eV above the valence band and have significant oxygenlike character. The physical significance of these levels will be discussed later in the text.

The band-structure calculations for yttrium oxide by the ASW method have been done using the structural information from x-ray crystallographic studies.[16] Yttrium oxide has a body-centered-cubic structure conforming to the space group $Ia3$. The lattice constant is 10.604 Å. There are 80 atoms per unit cell: 32 metal atoms and 48 oxygen atoms. Eight of the metal ions occupy the special positions $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, the rest occupying the sites $(u, 0, \frac{1}{4})$. The oxygen atoms are located at general (x,y,z) positions and are arranged in a distorted octahedron around the metal ion. The muffin-tin radii for the atomic spheres for oxygen and yttrium are chosen to be 2.645 67 and 3.183 23 a.u., respectively. The oxygen $1s$ and metal $1s$ through $4p$ levels are treated as core levels. Calculations are also performed using the $4p$ level of yttrium included among valence orbitals. However, the final energy bands are found to be similar in both the calculations. Since the conduction-band state are more crucial to our understanding of the excited-state properties of yttria, we will present results of our calculation which treat the yttrium $4p$-like levels as core states.

The energy bands and density of states are shown in Figs. 1 and 2. In Fig. 1, the energy bands are plotted along the symmetry directions of the Brillouin zone. The Fermi energy is located near 3.0 eV. The oxygen $2s$-like bands are located 12.0 eV below the Fermi energy, which compares very well with 14.7 eV calculated from the cluster method. Both the oxygen $2p$- and yttrium $4d$-like bands are flat, with the exception of one band near the bottom of the conduction band. This band is due to metal s-like states with the energy minimum at the Γ point. The energy separation at this point between the minimum of this band and the top of the valence band is 3.3 eV. However, the minimum due to the metal $3d$-like bands and the top of the valence band is 5.64 eV. This latter gap is in good agreement with the observed band gap for this material[17] and also with the band gap calculated from the cluster calculation, assuming that the optical transitions near the band edge are charge-transfer transitions involving oxygen p-like and yttrium d-like states. However, the band that slopes down from the H point to the Γ point, as well as the cluster state found in

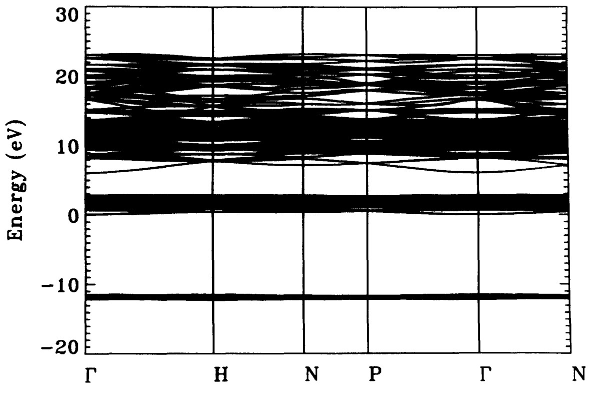

FIG. 1. Energy bands of yttrium oxide based on a calculation by the ASW method. The valence bands mostly due to the oxygen p-like states are between 0.0 and 3.0 eV. Note the energy band at the bottom of the conduction bands which exhibits considerable curvature compared with other energy bands.

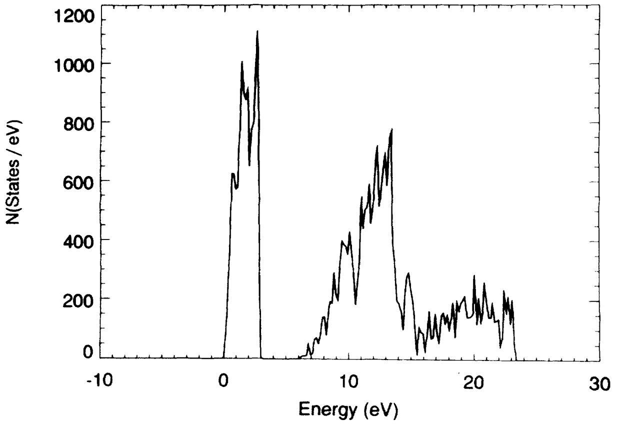

FIG. 2. Density of states calculated for Y_2O_3 per electron volt. The energy scale ranges from oxygen 2*p*-like bands to conduction bands. The minor peaks are not meaningful and should be ignored.

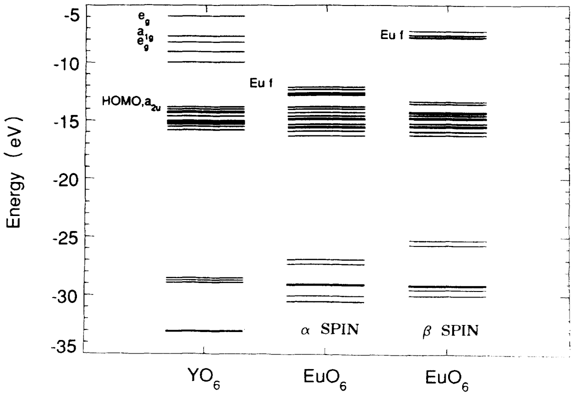

FIG. 3. An energy-level diagram for Y_2O_3:Eu based on the cluster calculations. The energy levels associated with α (up) spins and β (down) spins are shown separately. The *d*-like molecular orbitals due to the Y ion are labeled using the irreducible representations of the D_{3d} point group.

the energy gap, are enigmatic. However, the density-of-states plot (Fig. 2) using all the energy bands shows a very low density between 3.0 and 5.0 eV. Therefore, it is possible that although these bands are actually present, they have a negligible optical absorption., The optical measurements of the band gap do in fact exhibit a very weak tail extending to 3.0 eV.[6] Thermal activation energy measurements also give a small energy gap of 1.46 eV.[18] Thus, the experimental studies of the energy gap for this material are not in conflict with the presence of this band; rather, they seem to indicate the presence of some diffuse bands less than 5.6 eV above the valence-band maximum. The joint-density-of-states (JDOS) calculations also indicate a similar trend. The JDOS increases monotonically from 5.0 to 10.0 eV where one observes a peak due to transitions from the oxygen *p*-like band to yttrium *d*-like states.

Finally, the results from the europium centered cluster will be discussed. This cluster calculation has been performed using the spin-polarized version of the scattered-wave method, including relativistic corrections. The cluster geometry is the same as that of the yttrium centered cluster except for the europium ion substituting for yttrium. The exchange parameter for europium is taken to be 0.695 49.

A trivalent europium ion contains six *f*-like electrons. In D_{3d} symmetry, the sevenfold *f*-like orbitals split into two a_{2u}, two e_u, and one a_{1u} molecular orbitals. These molecular orbitals are further split by an exchange correlation favoring a high spin configuration. The energy levels for europium are shown in Fig. 3 along with those for the yttrium centered cluster for comparison. The one-electron molecular-orbital energy eigenvalues for spinup and spindown states are shown separately.

One of the molecular orbitals, a_{2u}, is empty because of the hole in the *f*-shell in the trivalent europium ion. The energy separation among the molecular orbitals from the *f*-like state is less than 0.7 eV, indicating a weak crystal-field effect. The exchange splitting is found to be 4.48 eV, which compares very well with values calculated by earlier workers.[19]

A weak crystal-field splitting observed experimentally for rare-earth ions has been explained in terms of localization of *f*-like states and weak covalency of the rare-earth ions. Although the present calculation leads to a weak crystal field, the molecular orbitals associated with the europium *f*-like states indicate significant charge transfer to the ligand orbitals. The lower a_{2u}, e_u, and a_{1u} molecular orbitals have 95% to 98% of their total charge mostly localized at europium; the last two orbitals, e_u and a_{2u}, are, however, significantly delocalized, with approximately 28% of their charge being transferred to nearest neighbors. A similar trend is also observed for the unoccupied spindown states.

The lowest-energy *f*-like molecular orbital, a_{2u}, is found to be 0.58 eV above the highest occupied molecular orbitals which are mostly due to the nearest-neighbor oxygen atoms. These valence orbitals are also split due to the exchange-correlation effect. This splitting is less than 0.2 eV. The 5*p*-like levels of europium have been treated as valence orbitals. The molecular orbitals resulting from this state are found to be very delocalized with more than 20% charge transfer to the nearest ligand atoms. The most notable feature of the present investigation is the delocalization of both 4*f*- and 5*p*-like states of europium in an oxygen environment, while the crystal-field effect on these levels is considerably weak. This explains why the charge-transfer bands for trivalent europium are very strong. The significant mixing of the europium *f*-like orbitals and oxygen *p*- orbitals would lead to a high probability for the charge-transfer transitions.

III. DISCUSSION

There were two other motivations behind this work: determination of the origin and nature of the excitation peaks associated with trivalent europium ions, and interpretation of the trends in quantum efficiency of this phosphor as a function of excitation energy.[14]

The emission frequencies for europium are usually explained in terms of electronic transitions among the f-electron manifolds. The main transitions are identified with the ^5D-^7F transition corresponding to a spin-flip transition from the ^5D_J manifold to the ^7F_J manifold due to the six f-like electrons. Our calculations give a value of 4.48 eV for a spin-forbidden transition from the upspin one-electron state e_u to the lowest unoccupied spin-down state a_{2u} originating from the f-like states of europium. This is in good agreement with the exchange splitting calculated for europium ions in europium sulfide.[19] These calculations clearly indicate that the transition frequencies associated with the trivalent europium ion cannot be explained using one-electron molecular-orbital energies, which is in keeping with the strong spin-order interaction for this ion. However, one should use these one-electron states, which describe the covalency effects in a rigorous manner, as the basis functions for configuration interaction or diagrammatic many-body calculations, including the spin-orbit interactions in the perturbation Hamiltonian.

The 254-nm radiation from a mercury discharge is believed to excite electrons into a charge-transfer band. This transition involves either excitation of electrons from oxygenlike levels to europiumlike states or excitation of electrons from the europium f-like levels to the conduction band. In the second case, a tetravalent europium ion would be temporarily formed, which is very unlikely. Since this transition involves the host lattice, this excitation frequency can be calculated from the one-electron energy levels. The present calculation gives a value of 5.6 eV for a transition from the top of the valence band to a spin-down f-like state. There are also a few other levels to which transition can occur at a lower energy of 4.6 eV. It would be interesting to determine exactly how energy transfer occurs from the charge-transfer band to the emitting state of europium. It would involve not only energy transfer but also a spin flip at the europium site.

In a recent paper the quantum efficiency of this phosphor, Q_E or η, in the energy range of 5.0 to 25 eV, was reported.[14] Results from measurements using higher energy excitations are available in the literature.[20] In the energy range 5.0–25.0 eV, a number of interesting structures in the quantum-efficiency plot as a function of excitation energy were observed. The quantum efficiency η of this phosphor increases from 0.6 to 1.0 as excitation energy increases from 5.0 to 6.0 eV and then drops to 0.6 at 8.0 eV. Near 14.0 eV, η becomes 1 again and increases almost linearly to 2.25 near 18.0 eV. The most interesting feature in the variation of η with the exciting energy is that between 14.0 and 18 eV, η increases by 1.25, indicating the occurrence of a two- or three-photon process.

Multiphoton processes in this phosphor can be explained in terms of interband Auger transitions[21] which lead to production of secondary electron-hole pairs from the primary electron-hole pairs generated by the incident photon. It is well known that the threshold energies for multiple photon emission due to an interband Auger process will occur at energy values greater than integral multiples of the band-gap energy. The change in quantum efficiency from 1.0 to 2.25 (± 0.38) indicates the presence at least of two-photon processes.

When the excitation energy is greater than 5.6 eV, the absorption of the exciting radiation is primarily due to the host materials. Electrons in the valence band absorb the incident radiation and make transitions to the conduction-band states, thus creating the primary electron-hole pair. Recombination of these electron-hole pairs at the europium center results in the emission of the optical photons. It is reasonable to assume that the probability of recombination at the europium center is independent of the excitation energy in the energy range dominated by the host absorption process. Absorption in this region depends both on the density of states in the valence-band region and in the conduction-band region. Figure 3 indicates the first density-of-states peak at 6.0 eV relative to the top of the valence band. This coincides satisfactorily with the observed quantum-efficiency peak at 6.5 eV.

The two-photon efficiency was calculated using the formalism outlined in Ref. 22. However, it is obvious from the band structures that the primary excitation process would lead to heavy electrons and holes, thus increasing the direct electron-hole recombination process. The interband Auger process would not occur until the elec-

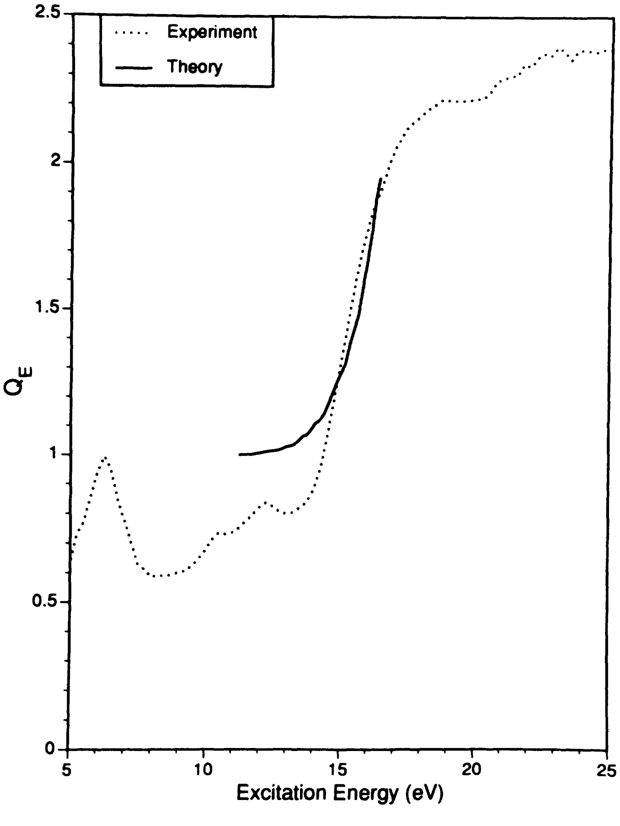

FIG. 4. Experimental and theoretical values of quantum efficiency have been plotted as a function of energy. Calculation has been done only for two-photon transitions with an explicit assumption for quantum efficiency equal to 1 before the onset of two-photon transitions.

trons from the valence band can be excited to the conduction bands due to yttrium 5*s*- and 5*p*-like states. These bands have significant curvature, implying that the electrons would roll down the band faster than the holes, thus reducing the probability of direct electron-hole recombination. Once the electron-electron interaction leads to creation of a secondary-hole pair, quantum efficiency would increase with increasing excitation energy. In our calculation we have chosen arbitrarily the single-photon quantum efficiency to match with observed quantum efficiency and attempted to determine the two-photon threshold frequency from the calculated density of states. The calculated quantum efficiency is plotted against the observed quantum efficiency (Fig. 4). Our results not only explain the threshold for two-photon emission but they also provide a satisfactory explanation of the variations of quantum efficiency beyond the threshold energy.

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