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1989 J. Phys.: Condens. Matter 1 5037

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The electronic structure of a rare-earth luminescent centre in alkaline-earth sulphides

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Received 16 September 1988, in final form 3 January 1989

Abstract. The cluster method is used to investigate the electronic structure of rare-earth Eu^{2+} - and Ce^{3+} -doped SrS and CaS alkaline-earth sulphides in the local-density theory regime. The ground state is obtained self-consistently by the DV- $X\alpha$ method, while the transition state theory is used to calculate the excitation energy of the rare-earth luminescent centre. The calculated excitation energy corresponding to the 4f–5d transition of SrS:Eu is 3.19 eV, which is in agreement with the experimental data at 430 nm for the absorption peak in SrS:Eu. The compositions of the ground state and excited state are also calculated; this can give information about the electroluminescence excitation mechanism.

1. Introduction

Recently, rare-earth-doped alkaline-earth sulphides have been extensively investigated as multi-colouring luminescent devices. In [1, 2] the electroluminescent (EL) phosphor of Ce- and Eu-doped SrS and CaS thin films was studied. It was found that these films show efficiencies as high as Mn^{2+} - and Tb^{3+} -doped ZnS thin films [2] and were revealed as promising materials for white-light EL devices. These new kinds of EL material have the following interesting trend [3]: Mn^{2+} and Tb^{3+} centres seem to be ineffective in CaS and SrS, although they are quite efficient in ZnS. By contrast, Ce^{3+} and Eu^{2+} centres are very efficient in CaS and SrS, but they are inefficient in ZnS. The SrS and CaS crystals have a rocksalt crystal structure, which is different from the zincblende structure of ZnS. An obvious difference between the band structures of these two materials is that ZnS has a direct energy gap, while CaS and SrS have an indirect energy gap. The luminescent centres Ce^{3+} and Eu^{2+} are also different from Mn^{2+} and Tb^{3+} . It is generally accepted that, for ZnS, which has a direct energy gap at the Γ point, the EL mechanism is a direct impact excitation process. For CaS and SrS, a more complicated excitation mechanism has been suggested in [3] to explain the temporal variations in EL intensity experiments for CaS:Eu, SrS:Ce, K and ZnS:Ce.

In [4] the band structure of CaS and SrS was calculated using the LMTO ASA method. The results confirmed the conclusion of an indirect band energy gap with a conduction band minimum at the X point. It is worthwhile investigating the electronic structure of such materials doped with luminescent centres in order to understand the excitation

mechanism which may be useful for the selection of host materials and luminescent centres for high-quality EL devices. The random distribution of rare-earth ions in the host materials is an additional complication in the theoretical study using the usual band theory. In this work, the cluster method is used to obtain an *ab initio* calculation of the electronic structure of the luminescent centre and its interaction with the host crystal.

2. The cluster model and theoretical approach

In this work, the cluster method is used to study Eu- and Ce-doped CaS and SrS. It is well known that these materials have a rocksalt crystal structure and the doped rare-earth ions are sited at the cation position as substitutional impurities. The RS_6M_{12} cluster, which consists of the rare-earth ion R (\equiv Eu or Ce) and its six nearest-neighbour S ions and 12 next-nearest-neighbour alkaline-earth ions (Sr or Ca), is adopted in our calculations.

The electronic structure is obtained by solving the Hartree–Fock–Slater equation self-consistently in the framework of local-density functional theory. The essential point of this method is that the non-local Hartree–Fock exchange operator can be replaced under certain conditions approximately by a potential depending only on the local electron density. The one-electron Hamiltonian can be written as

$$h = T + V_{\text{Coul}}(r) + V_{x-c}(r) \\ = -\frac{1}{2}\nabla^2 - \sum_j \frac{z_j}{|\mathbf{r} - \mathbf{R}_j|} + \int \frac{p(r') dr'}{|\mathbf{r} - \mathbf{r}'|} + V_{x-c}(r) \quad (1)$$

where T , V_{Coul} and V_{x-c} are the kinetic energy, Coulomb and exchange–correlation potential, respectively. The electron–nuclear attraction is $Z_j/|\mathbf{r} - \mathbf{R}_j|$, where \mathbf{R}_j and Z_j are the position and nuclear charge of the j th atom. The third term is electron–electron repulsion at position r . The form in [5] is used in this work for the electron–electron exchange–correlation potential V_{x-c} .

Since we are dealing with one kind of strongly ionic compound which has an ionicity fraction of over 0.785 in its mixed ionic–covalent bonding, the effect of the crystalline field must be taken into account. This effect is considered by using the embedded-cluster method [6] in this calculation, in which the potential generated by the environmental crystal ions around the cluster is also included in the one-electron Hamiltonian, i.e. the sum or integration in equation (1) is not only over all ions in the cluster but also over the ions contained in the environmental crystal. In this work, 324 crystal ions distributed around the cluster are considered and the charge of the total system (the cluster and crystal together) remains neutral.

As in the usual linear combination of atomic orbitals (LCAO) method, the eigenfunctions ψ_i of the cluster are expanded in terms of symmetry orbitals φ_j :

$$\psi_i(r) = \sum_j \varphi_j(r) C_{ji} \quad (2)$$

which are composed as linear combinations, corresponding to the cluster point group symmetry, of numerical atomic orbitals located on different ions in the cluster. The

Table 1. The Mulliken population numbers for CaS:Eu, SrS:Eu and SrS:Ce, K.

Cluster	Orbital	CaS:Eu	SrS:Eu	SrS:Ce, K
Eu (Ce)	4f	6.79	6.78	1.15
Eu (Ce)	5d	0.69	0.75	0.97
Eu (Ce)	6s	0.22	0.26	0.24
Sr (Ca)	4d (3d)	0.09	0.14	0.10
Sr (Ca)	5s (4s)	0.25	0.23	0.17
S	3s	1.94	1.96	1.96
S	3p	5.26	5.21	5.27

expansion coefficients C_{ji} are obtained using a discrete variational method by solving the matrix secular equation

$$(\mathbf{H} - \varepsilon\mathbf{S})\mathbf{C} = 0 \quad (3)$$

where \mathbf{H} , \mathbf{S} and ε are the Hamiltonian matrix, the overlap matrix and the eigenvalue, respectively.

The frozen-core electron approximation is used in this work for simplicity. It implies that only the valence electrons will respond to the variation in environment and that the more tightly bound core electrons of atoms remain their atomic status. In our calculation, the Eu 4f, 5d and 6s, the Ce 4f, 5d and 6s, the Sr 4d and 5s, the Ca 3d and 4s and the S 3s and 3p states are considered as valence orbitals. The number of various valence electron states are obtained by Mulliken population analysis. The density of states (DOS) is obtained from a Lorentz type of broadening:

$$D_j(\varepsilon) = \sum_i f_j(i) \frac{\delta/\pi}{(\varepsilon - \varepsilon_i)^2 + \delta}$$

as described in [7]; here a value of 0.2 eV is adopted for the Lorentzian width parameter δ . The transition state theory [8] is used to obtain the absorption spectrum.

3. Results and discussion

First, we consider the electronic structure of the ground state. The ionic radii of rare-earth ions—1.1 Å for Ce^{3+} and 1.12 Å for Eu^{2+} ions as substitutional ions in alkaline-earth sulphides are very close to those of alkaline-earth cations—1.13 Å for Sr^{2+} and 0.99 Å for Ca^{2+} ions. The 10% difference between the radius of Ca^{2+} and that of the rare-earth ions may cause a small relaxation of the host crystal. In this preliminary work, the effect of relaxation is neglected. For the Ce^{3+} experiments, the same number of K^+ ions as the Ce^{3+} ions was used to dope the SrS (or CaS) simultaneously, in order to compensate the charge of the Ce^{3+} ions. In our calculation, instead of the randomly distributed Ce^{3+} and K^+ , an average charge of environmental anions was used to compensate the charge difference between Ce and alkaline-earth ions.

The Mulliken population numbers of various ionic orbitals are listed in table 1. A small number of electrons occupies the Sr 4d and 5s (or Ca 3d and 4s) states, which indicates hybridisation of Eu(Ce) 5d with Sr 4d and 5s (or Ca 3d and 4s) orbitals. From the Mulliken population numbers of Eu and Ce ions, one can obtain valencies of 1.3 and

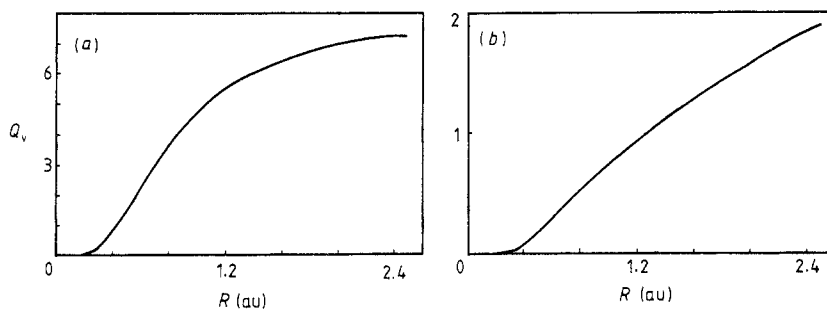


Figure 1. Plots of the number Q_v of valence electrons against the ionic sphere radius: (a) Eu ion ($R_0 = 2.117$ au); (b) Ce ion ($R_0 = 2.098$ au). The valency of the ion is equal to $Z_n - Q_c - Q_v$, where Z_n and Q_c are the nuclear charge and the number of core electrons, respectively. They are $4 - Q_v$ for the Ce ion and $9 - Q_v$ for the Eu ion, respectively.

1.65 for Eu and Ce ions, respectively. Owing to the approximate nature of the Mulliken population analysis, the number of valence electrons of rare-earth ions in clusters is also calculated by integrating in an ionic sphere of radius R_0 around the related ions. The relationship obtained between the number of valence electron and the radius R_0 of the ionic sphere is shown in figures 1(a) and 1(b) for Eu and Ce ions, respectively. The valency of each ion is equal to $Z_n - Q_c - Q_v$, where Z_n , Q_c and Q_v are the nuclear charge, the number of core electrons and the number of valence electrons, respectively. From figure 1, one can see that the valency of Eu in an ionic sphere of radius 1.12 \AA is 1.98, which is close to the purely ionic value of 2. On the contrary, the valency of Ce in an ionic sphere with $R_0 = 1.11 \text{ \AA}$ is 2.35, which is smaller than the purely ionic value of 3. This may indicate that the covalency of Ce is stronger than that of Eu or that the distribution of the valence electrons of Eu is more spread out.

The DOS and the local DOS of various orbitals are shown in figures 2(a) and 2(b) for CaS:Eu and CaS:Ce, K, respectively. The common features of these two cases are that a partially filled 4f band is located across the Fermi energy E_F , the 3s band of S ions is below E_F by about 8–9 eV, and the 3p band of S ions consists of a main peak at 2 eV below E_F with a broad tail of 5 eV width, which is caused by mixing of the rare-earth and alkaline-earth ion orbitals. The Sr 4d and Ca 3d states are also strongly localised with a peak at 5–5.5 eV above E_F . The conduction band consists of Ce (Eu) 5d and Sr 4d5s (Ca 3d4s) states with considerable hybridisation between them. This makes the excited state of the rare-earth ion not a purely ionic band but a hybridisation band.

From the eigen-energy levels of clusters, a T_u symmetry triplet state composed of the 4f orbitals of rare-earth ions can be considered as the ground state of luminescent centres and several T_g symmetry triplet states composed of the 5d orbitals of rare-earth ions, the 4d (3d) and 5s (4s) orbitals of alkaline-earth ions and the 3p orbital of S ions can be identified as the excited states of the luminescent centres. The compositions of the ground state and the excited states for $\text{EuS}_6\text{Ca}_{12}$, $\text{EuS}_6\text{Sr}_{12}$ and $\text{CeS}_6\text{Sr}_{12}$ clusters are listed in tables 2 and 3, respectively. The ground state consists purely of Eu (Ce) 4f, while the excited state is a highly hybridised state composed of Eu (Ce) 5d, Sr 4d and 5s, (Ca 3d and 4s) and S 3p states. The difference between Eu and Ce is that the Eu 5d state is only 24–26% of the total, while the Ce 5d state can be as high as 75%. This may be one of the reasons why Ce ions have a higher luminescent efficiency than do Eu ions.

According to the transition state theory, the excitation energy is equal to the eigen-energy difference between the ground state and the excited state in the transition state

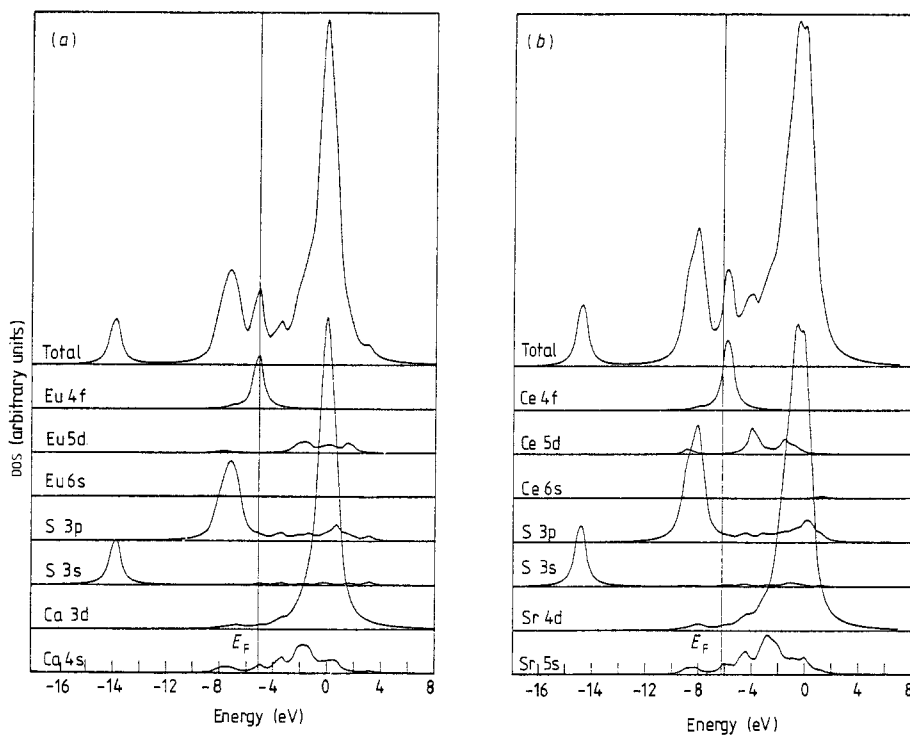


Figure 2. The DOS and local DOS of (a) CaS:Eu and (b) SrS:Ce, K.

Table 2. The compositions of the ground states of the luminescent centres for $\text{EuS}_6\text{Ca}_{12}$, $\text{EuS}_6\text{Sr}_{12}$ and $\text{CeS}_6\text{Sr}_{12}$ clusters.

Cluster	Eu (Ce) 4f	Sr 4d (Ca 3d)	Sr 5s (Ca 4s)	S 3p
$\text{EuS}_6\text{Ca}_{12}$	0.98	0.002	0.002	0.02
$\text{EuS}_6\text{Sr}_{12}$	0.97	—	0.02	0.02
$\text{CeS}_6\text{Sr}_{12}$	0.98	0.002	0.0	0.01

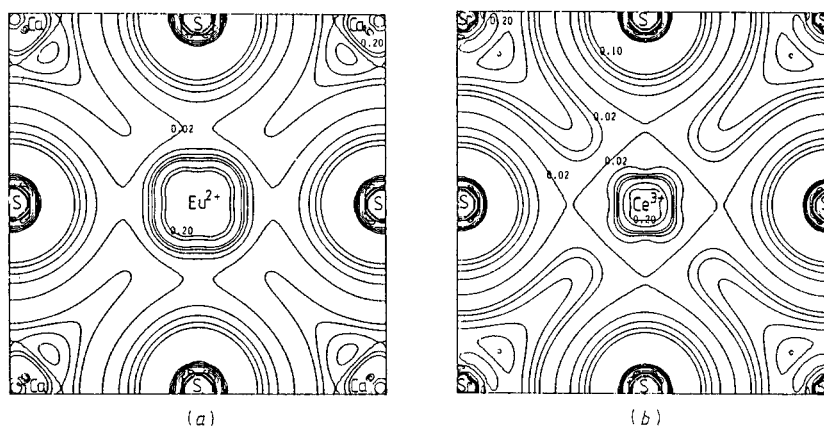
Table 3. The compositions of the excited states of luminescent centres for $\text{EuS}_6\text{Ca}_{12}$, $\text{EuS}_6\text{Sr}_{12}$ and $\text{CeS}_6\text{Sr}_{12}$ clusters.

Cluster	Eu (Ce) 5d	Sr 4d (Ca 3d)	Sr 5s (Ca 4s)	S 3p
$\text{EuS}_6\text{Ca}_{12}$	0.24	0.22	0.42	0.12
$\text{EuS}_6\text{Sr}_{12}$	0.26	0.20	0.42	0.10
$\text{CeS}_6\text{Sr}_{12}$	0.75	0.10	0.10	0.04

calculation. The calculated results are shown in table 4. The value of 3.19 eV for SrS:Eu is in agreement with the experimental data at 430 nm (2.88 eV) and a shift to a longer wavelength for CaS:Eu with respect to those of SrS:Eu is in agreement with the experimental trend of emission spectra in the $\text{Ca}_x\text{Sr}_{1-x}\text{S}:\text{Eu}$ system [1].

Table 4. The transition-state-calculated ground-state and excited-state energy of luminescent centres for $\text{EuS}_6\text{Ca}_{12}$, $\text{EuS}_6\text{Sr}_{12}$ and $\text{CeS}_6\text{Sr}_{12}$ clusters.

Cluster	Energy (eV)		ΔE (eV)
	Ground state T_u	Excited state T_g	
$\text{EuS}_6\text{Ca}_{12}$	-5.30	-2.36	2.94
$\text{EuS}_6\text{Sr}_{12}$	-4.08	-0.89	3.19
$\text{CeS}_6\text{Sr}_{12}$	-6.24	-3.90	2.34

**Figure 3.** The electron density distributions in the (010) plane for (a) $\text{EuS}_6\text{Ca}_{12}$ and (b) $\text{CeS}_6\text{Sr}_{12}$ clusters.

As the rare-earth ions have unfilled 4f orbitals, spin-polarised calculations were also carried out for $\text{EuS}_6\text{Ca}_{12}$ and $\text{EuS}_6\text{Sr}_{12}$ clusters. Essentially the same results as for absorption energy are obtained. The reason is that the randomly distributed rare-earth ions act only as paramagnetic ions and are spin degenerate in a zero external magnetic field.

The charge density maps in the (010) plane are shown in the figures 3(a) and 3(b) for $\text{CaS}:\text{Eu}$ and $\text{SrS}:\text{Ce}$, respectively. There is no explicit difference between these two cases. In figure 4 the ground-state orbital and excited-state orbital are plotted in the (010) plane for $\text{EuS}_6\text{Ca}_{12}$ and $\text{CeS}_6\text{Sr}_{12}$ clusters. The ground state is an f-type state, while the excited states show some hybridisation between the rare-earth ion, the sulphur ions and the alkaline-earth ions.

4. Conclusion

The $\text{EuS}_6\text{Ca}_{12}$, $\text{EuS}_6\text{Sr}_{12}$ and $\text{CeS}_6\text{Sr}_{12}$ clusters are used to simulate alkaline-earth sulphides doped with rare-earth luminescent centres. The electronic structure of these systems are investigated by the DV- X_α method. The excitation energy is obtained by the transition state theory. The absorption energy obtained is in agreement with experiment. The ground state is an f-like state, but the excited state is a highly hybridised orbital rather than a 5d-like state. Investigations of the emission spectrum and the relative

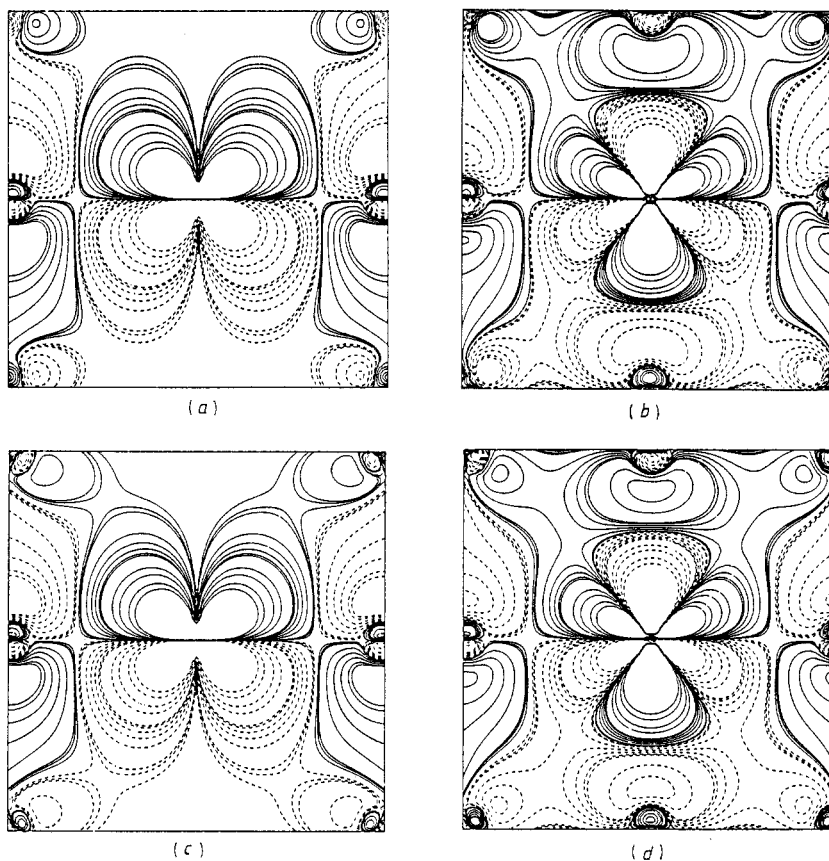


Figure 4. The ground-state orbital in the (010) plane (a) for a $\text{EuS}_6\text{Ca}_{12}$ cluster and (c) for a $\text{CeS}_6\text{Se}_{12}$ cluster and the excited-state orbital in the (010) plane (b) for a $\text{EuS}_6\text{Ca}_{12}$ cluster and (d) for a $\text{CeS}_6\text{Se}_{12}$ cluster: —, positive part of the wavefunction; - - -, negative part of the wavefunction. The atomic positions here are the same as in figure 3.

excitation mechanism are now in progress under the configuration coordinate approximation.

Acknowledgments

This work is supported by the National Science Fund Grant 1870757 and the Science Fund of the Chinese Academy of Sciences.

One of the authors (HMC) would like to thank Dr S Tanaka for providing their new results and preprints. Part of the calculations was performed on the Facom 340 computer at the computing centre of Xiamen University.

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