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The electronic structure of europium chalcogenides and pnictides

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Abstract

The electronic structure of some europium chalcogenides and pnictides is calculated using the *ab initio* self-interaction corrected local-spin-density approximation (SIC-LSD). This approach allows both a localized description of the rare earth f-electrons and an itinerant description of s-, p-, and d-electrons. Localizing different numbers of f-electrons on the rare earth atom corresponds to different nominal valencies, and the total energies can be compared, providing a first-principles description of valency. All the chalcogenides are found to be insulators in the ferromagnetic state and to have a divalent configuration. For the pnictides we find that EuN is half-metallic and the rest are normal metals. However, a valence change occurs as we go down the pnictide column of the periodic table. EuN and EuP are trivalent, EuAs is only just trivalent, and EuSb is found to be divalent. Our results suggest that these materials may find applications in spintronic and spin filtering devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Rare earth compounds attract considerable experimental and theoretical attention due to the intricate electronic properties relating to the highly correlated f-electrons. In the atomic state most rare earth elements are divalent, but in the solid state the majority form trivalent ions. The elemental rare earths all become trivalent, with the exception of Eu and Yb which are divalent. Europium compounds can occur in divalent and trivalent configurations. Europium chalcogenides and most of the pnictides crystallize in the simple NaCl crystal structure, and so form a series that can be studied within first principles theory relatively easily. Recently the

chalcogenides have attracted a lot of attention due to their potential applications in spintronic and spin filtering devices.

In a recent paper, Steeneken *et al* [1] have presented evidence that EuO is a ferromagnetic semiconductor and that the charge carriers in electron-doped EuO will exhibit almost 100% spin-polarization. In this paper we perform self-consistent electronic structure calculations to investigate, and gain more insight into, this claim. The EuS system has recently been used as a spin filter in a hybrid Gd/EuS/Al device which showed a large magnetoresistance [2]. Unfortunately the low T_c of 16.8 K in EuS makes it unsuitable for commercial applications, but nonetheless this does make it worthwhile to study, in a systematic manner, the electronic and magnetic properties of the remaining Eu chalcogenides.

Traditional calculations of the electronic structure of rare earth materials treat the s-, p- and d-electrons as itinerant, while the f-electrons are treated as atomic-like. However, treating electrons within the same material using two different theories is less than satisfactory. Recently, self-interaction corrections (SIC) [3] to the local spin density (LSD) approximation to density functional theory (DFT) [4, 5] have provided us with a successful method of treating all the electrons in rare earth materials on an equal footing. The self-interaction correction represents an f-electron localization energy, and the question of which f^n configuration of the rare earth ion will be the most stable is a competition between this localization energy and the energy which an electron may gain by hybridizing into the conduction band states. This energy balance is a very delicate quantity, and it may be changed easily by altering external parameters.

Rare earth chalcogenides show a wide range of magnetic behaviours at low temperatures. EuO and EuS are both ferromagnetic while EuSe and EuTe are antiferromagnetic. They all undergo magnetic phase transitions at low temperatures [6]. We have performed electronic structure calculations for all these materials in the ferromagnetic state to investigate the trends and possible potential of these materials for applications in spin filtering devices.

In this paper we briefly describe the SIC-LSD formalism in section 2, and go on to discuss our calculation of the electronic structure of the Eu chalcogenides and pnictides in both the divalent and trivalent states in section 3. We conclude the paper in section 4.

2. The SIC-LSD formalism

The standard method for making *ab initio* calculations of the properties of materials is density functional theory with a local approximation for the exchange–correlation energy. A drawback of this approach is that it introduces a spurious self-interaction for each electron. While these are usually negligible they become important when localization phenomena are under investigation [7–10]. The SIC-LSD scheme is a method of improving the LSD approach by subtracting the spurious interaction of each occupied electron with itself from the usual LSD approximation to the total energy. This yields a much-improved description of static Coulomb correlation effects over the conventional LSD approximation. Examples of the benefits of this approach have been demonstrated in many applications, including studies of the Hubbard model [11, 12], the 3d monoxides [9, 10], La_2CuO_4 [13, 14], f-electron systems [15–17], solid hydrogen [18], orbital ordering [19], and metal–insulator transitions [20].

In the SIC-LSD method the total energy is minimized with respect to both the electron density and the number of electrons from which the self-interaction has been subtracted. This leads to a determination of the nominal valence in solids defined as the integer number of electrons available to form energy bands

$$N_v = Z - N_{\text{core}} - N_{\text{SIC}}, \quad (1)$$

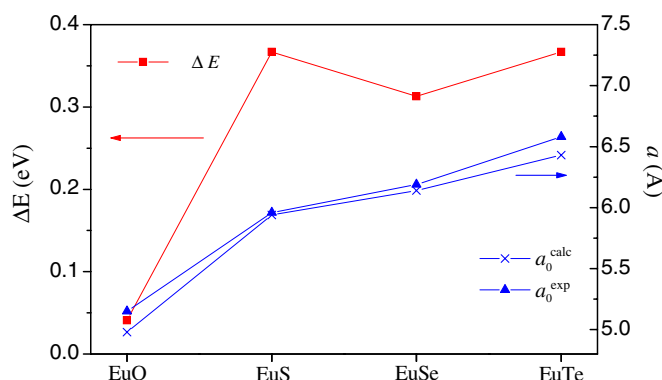


Figure 1. The values of the lattice constant for the europium chalcogenides from experiment [22] (triangles) and this calculation (\times). Also shown is the calculated energy difference between the divalent and trivalent form (squares). A positive value means divalency while a negative value indicates trivalency. For consistency with previous results, the energies here include the 0.58 eV calibration determined for the elemental rare earths and their sulfides by Strange *et al* [15] to yield the observed valence transition pressure in SmS.

where N_{core} is the number of atomic core electrons, Z is the atomic number, and N_{SIC} is the number of states for which the self-interaction correction has been removed. This definition means that N_v is two for systems normally thought of as divalent and three for systems that are trivalent, as one might expect.

3. Results and discussion

Most of the rare earth chalcogenides and pnictides crystallize in the common rocksalt structure. We have performed SIC-LSD calculations for Eu chalcogenides and pnictides using an LMTO method for the band structure [21]. Calculations of the electronic structure have been performed in the ferromagnetic state for all the materials in both the divalent and trivalent state. Whichever of these we find with the lower total energy should be the stable valence. When the energies of two valence states are roughly equal this can indicate a likelihood of intermediate valence.

It is well-known that the LSD approximation to density functional theory does not predict band gaps correctly. The SIC-LSD approach has been shown to improve the calculation of band gaps [10], and we would expect that this method could reproduce trends in band gaps fairly reliably.

3.1. Europium chalcogenides

In figure 1 we show the calculated and experimental lattice constants for all the chalcogenides. We also show the energy differences between the two valence states. It is clear that all the europium chalcogenides are divalent. This is as we would expect on simple shell-filling grounds. We can also see from this figure that the calculated lattice constants are in good agreement with experiment. The energy difference between the two valence states is fairly independent of chalcogenide for S, Se and Te, and we observe that there is a clear correlation between the lattice constant and the difference in energy between the divalent and trivalent states.

In figure 2 we show the density of states for divalent EuO, EuS, EuSe and EuTe. At low energies around -8 to -10 eV are the seven fully occupied f-states (not shown) in the majority

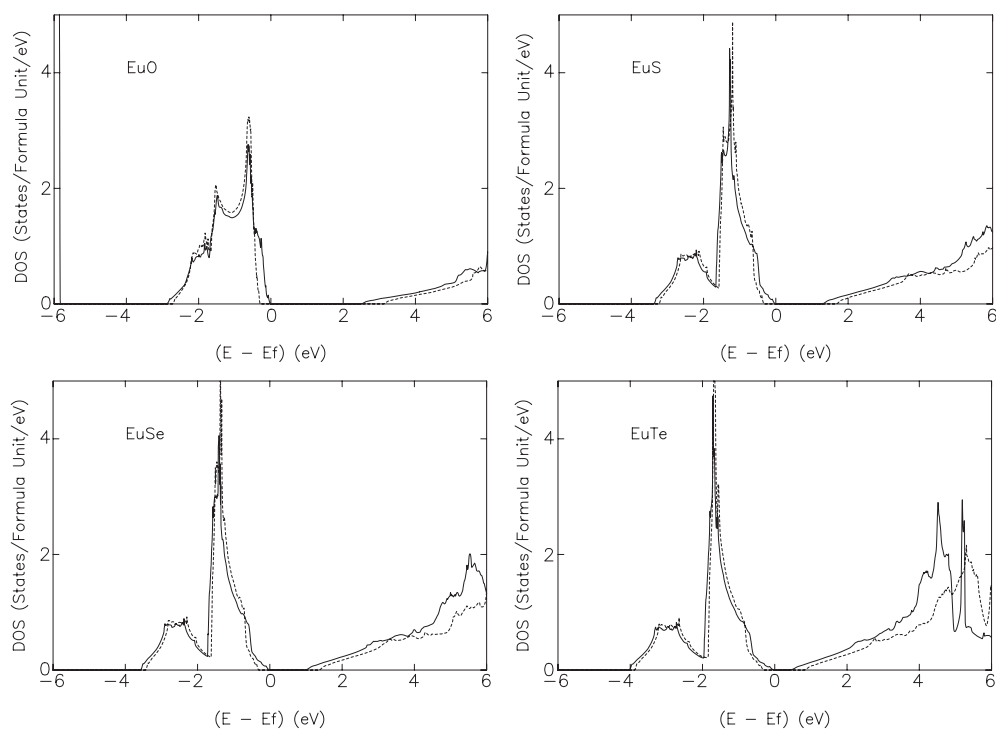


Figure 2. The spin-resolved density of states for the divalent europium chalcogenides (majority spin (full curve) and minority spin (dashed curve)). In EuO the calculated energy gap is 2.5 eV compared with the experimental value of 1.2 eV.

spin channel. Above these is a gap to states which are predominantly chalcogenide p-bands. Then there is a further gap around the Fermi energy. Above E_f are the Eu s-d bands which include some hybridized chalcogenide p-character. The unoccupied f-states are well above the Fermi energy and not many of them can be seen on these figures. There is a large increase in lattice constant as we proceed down the column in the periodic table, with a corresponding sharpening of the features of the density of states. This is particularly clear in the chalcogenide p-states. In figure 2 we have decomposed the density of states by spin. The f-bands define the majority spin of course. However, we can immediately observe that there is interesting behaviour closer to the Fermi energy. The chalcogenide p-states couple antiferromagnetically to the rare earth sites, presumably via a super-exchange mechanism, as can be observed in the magnetic moments. For all the chalcogenides we find that the magnetic moment on the rare earth site is between 7.05 and $7.08 \mu_B$ and the chalcogenide moment is between -0.05 and $-0.08 \mu_B$. The occupied majority spin states extend up to a higher energy than the occupied minority spin states. On the other hand the majority spin conduction band states extend down to a lower energy than the minority spin conduction band states. This means that there is a significantly lower band gap for the majority spin than for the minority spin electrons. In table 1 we show the calculated band gap for all the chalcogenides decomposed by spin and the calculated exchange splitting of the bottom of the conduction band. These results unambiguously confirm the recent experiments by Steeneken *et al* [1], which showed that EuO is a small band gap semiconductor and that in the ferromagnetic state the charge carriers are almost entirely in one spin direction. Our calculations suggest that there may be a range of

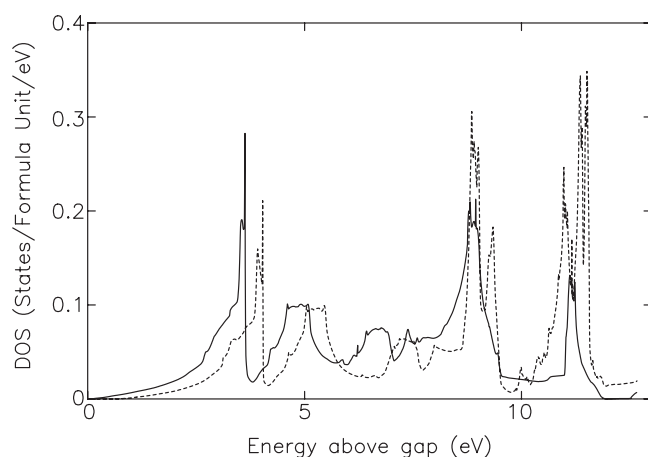


Figure 3. The unoccupied region of the oxygen p-resolved density of states for EuO. The full curve is for majority spin and the dashed curve for minority spin. The conduction band minimum is taken as the zero of energy on this scale. The positions of the peaks compare very favourably with the XAS measurements of Steeneken *et al* [1].

Table 1. The first row is the band gaps for the europium chalcogenides. It is clear that the gap for the majority spin electrons is significantly smaller than the gap for the minority spin electrons. The second row is the spin splitting ΔE_{ex} at the bottom of the conduction band. All energies are in eV.

	EuO		EuS		EuSe		EuTe	
Gap	↑	↓	↑	↓	↑	↓	↑	↓
ΔE_{ex}	2.5	3.4	1.3	2.0	1.0	1.6	0.4	1.1
	0.62		0.39		0.38		0.39	

temperatures for which this is true for all the europium chalcogenides in their ferromagnetic state. Furthermore, these results have a clear implication that the band gaps can be controlled by a judicious choice of material and doping. Steeneken and co-workers estimate the exchange splitting in the conduction band of EuO as 0.6 eV, and again we find excellent agreement with this value.

Steeneken and co-workers have also determined the spin-resolved x-ray absorption spectrum for EuO at the oxygen K-edge. They have shown that it is in good agreement with the density of states calculated with the LDA + U method with $U = 7.0$ eV. In figure 3 we show the spin-resolved unoccupied p-density of states on the oxygen site calculated with the SIC-LSD method, which is completely first principles, and comparison with the XAS spectrum shows that it also exhibits good agreement with the XAS results. Steeneken and co-workers found principal peaks at 532 eV (majority spin) and 532.6 eV (minority spin) in excellent agreement with the lower two peaks of our density of states. There is also a shoulder on this peak in the experiment at 534.5 eV, which corresponds with the smaller peak around 5 eV on our figure. The gap between the peaks around 532 eV and the next principal peaks around 536 eV in the experiment is overestimated by the calculation by about 1 eV. In the experiment there are majority spin peaks at around 536 and 538 eV and the corresponding minority spin peaks at 536.8 and 539 eV. Again these agree well with our spin-split peaks at around 8.8 and 11.2 eV. These latter peaks occur mainly due to hybridization of the oxygen p-bands with the unoccupied europium f-bands.

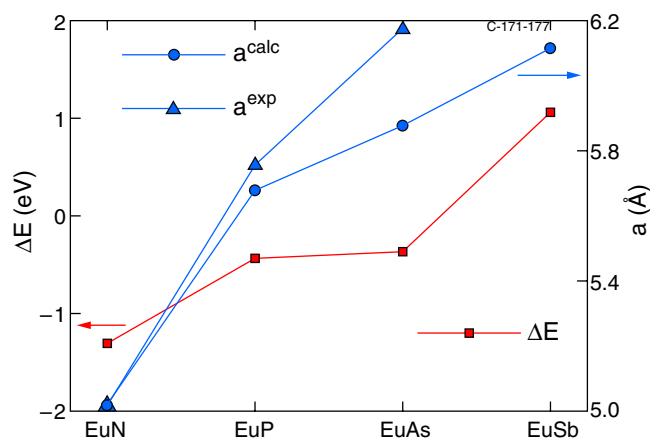


Figure 4. The values of the lattice constant for the europium pnictides in the NaCl structure from the SIC-LSD calculation. The \times symbols represent the calculated values and the triangles are the experimental values [23]. We have been unable to find an experimental value for EuSb. Also shown is the calculated energy difference between the divalent and trivalent forms (squares). For consistency with previous results the energies here again include the 0.58 eV calibration introduced by Strange *et al* [15].

3.2. Europium pnictides

In figure 4 we show the equilibrium lattice constant for the europium pnictides. We also show the energy difference between the divalent and trivalent configurations (a positive value of ΔE indicates divalency). It is clear that EuN and EuP are trivalent and EuSb is divalent. Although the calculation predicts that EuAs is trivalent, the energy difference is small and is within the margin of uncertainty for the calculation, possibly indicating intermediate valence in this compound. The large discrepancy for EuAs is because it is found to be just trivalent in the NaCl structure whereas in the true crystal structure it is divalent (see later). The calculated divalent lattice constant is 6.076 Å in the NaCl structure, which is very close to the experimental value. The experimental value is derived as the same volume per unit cell as in the observed Na₂O₂ structure. For these materials the energy difference between the two valence states is strongly dependent on the pnictide concerned.

These results are in full agreement with the assertion of Hulliger [24], who states that EuN and EuP are known to be trivalent, while EuAs is known to contain some divalent ions. We are not aware of any definitive measurement of the valence state of EuSb, but clearly if the trend continues it will be divalent. In reality EuAs does not have the rocksalt crystal structure and we have been unable to discover the true crystal structure of EuSb. EuAs adopts the Na₂O₂ crystal structure, which is a distortion of the NiAs structure due to the formation of anion–anion pairs [24]. We speculate that the appearance of the divalent ions in the material is responsible for this change in crystal structure. Calculations on the experimentally observed crystal structure support this viewpoint, because we find that the divalent state of EuAs is favoured by about 0.8 eV per formula unit in the Na₂O₂ crystal structure compared with the trivalent state being favoured by 0.2 eV in the NaCl structure. We also note from figure 4 that the correlation between lattice constant and the energy difference between the divalent and trivalent states is less pronounced for the pnictides than for the chalcogenides. This energy difference between divalent and trivalent states varies more in the pnictides than in the chalcogenides. Note that the scales of figures 1 and 4 run over 0.4 and 2.0 eV respectively.

Table 2. The first row is the spin contribution to the magnetic moment for the divalent europium pnictides. The second row is the spin magnetic moment for the trivalent europium pnictides. All magnetic moments are in Bohr units. The magnetic moments are further decomposed by site.

	EuN		EuP		EuAs		EuSb	
Eu(2+)	6.98	-0.98	7.03	-0.13	7.05	-0.04	7.06	-0.05
Eu(3+)	6.29	-0.30	6.48	-0.18	6.54	-0.18	6.67	-0.12

These results are qualitatively similar to those obtained for the ytterbium pnictides [25, 26], where there is also an increasing tendency towards divalency as one goes down the pnictide column of the periodic table. However, in that case the divalent state is not reached, and Yb has a tendency to form highly enhanced heavy fermion systems such as YbBiPt, for example.

In table 2 we show the magnetic moments of the europium pnictides in both the divalent and trivalent forms. In the trivalent form the behaviour is as would be expected. The moments on each site decrease in magnitude as the atoms get closer together. The pnictide moment has the opposite direction to the europium moment. In the divalent state, EuP, EuAs and EuSb all have europium moments close to $7 \mu_B$, and the induced moment on the pnictide site is fairly small. This is not the case for EuN, where the lattice constant is around 15% smaller than in the other pnictides. In EuN there is stronger overlap of the nitrogen p-electrons and the Eu f-electrons, leading to the nitrogen having a magnetic moment close to $1 \mu_B$ in the opposite direction to the Eu moment. Comparison of the electronic structure of the other divalent pnictides with EuN shows that in EuN there has been a transfer of weight of around 0.7 electrons from the rare earth s-d bands to the minority spin nitrogen p-band.

In figure 5 we show the densities of states for the europium pnictides in the trivalent state. These exhibit some similarity to, and some key differences from, the densities of states of divalent chalcogenides. The pnictide semi-core s-bands are above the localized europium 4f levels in the pnictides, while they are below the f-levels in the chalcogenides. However, the dramatic differences occur around the Fermi energy. The pnictides only have three p-electrons and so three electrons from the europium are required to fill this electron shell. This is done by the two 5d-6s electrons and one europium f-electron. Trivalency leads to a single majority spin f-state that is virtually empty sitting very close to the Fermi energy. This is the energetically favoured state certainly for EuN and EuP, and so they are definitely trivalent. As we proceed down the pnictide column of the periodic table this f-level becomes progressively more occupied, signalling the change of valence as discussed by Strange *et al* [15]. In the pnictides the empty minority spin f-states can be seen clearly about 4–5.5 eV above E_f . In all the pnictides the empty majority spin f-state overlaps with the pnictide p-band and pins the Fermi energy. Hence there are some heavy f-electrons at E_f and also a few holes in the pnictide p-band. As we go down the pnictide column the Fermi energy penetrates more and more into the narrow f-peak at E_f (this effect is too small to be clearly visible in figure 5). This means that there are more occupied band-like f-states and according to the suggestion of Strange *et al* [15] this implies a greater tendency to divalency, and this is indeed what we observe in the energy difference between the two valencies. It is also worth noting that the densities of states shown in figure 5 bear a remarkable similarity to those shown by Svane *et al* [26] for the ytterbium pnictides. This is not surprising, given that both classes of materials have a single f-band very close to the Fermi energy. The density of states again yields very interesting behaviour for these materials when we decompose it by spin. For EuN we note from figure 5 that the minority spin density of states is zero at the Fermi energy. The pnictide p-band density of states falls to zero just below the Fermi energy. The empty f-state close to the Fermi energy is a pure majority spin state. It hybridizes with majority spin p-states and draws some pnictide

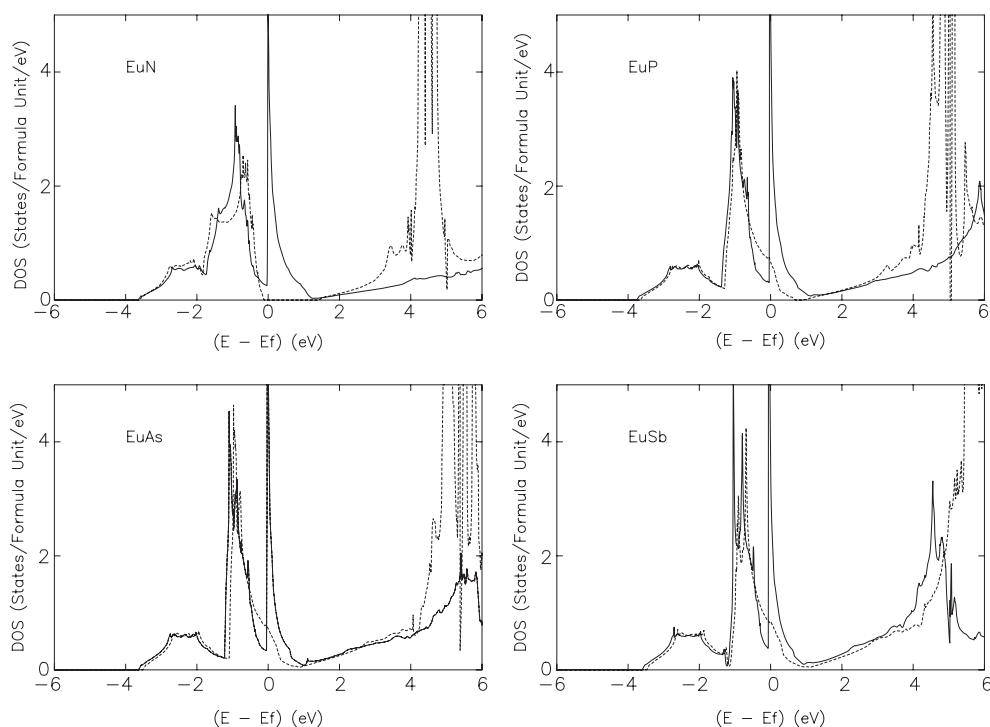


Figure 5. The spin-resolved density of states for europium pnictides, in the trivalent state (majority spin = full curve, minority spin = dashed curve).

majority spin p-character above the Fermi energy. There is no minority spin character at the Fermi energy at all. So the calculation predicts that EuN is a half-metallic ferromagnet with a minority spin band gap of 1.4 eV and a z -component of spin-magnetic moment of $6 \mu_B$. If we include the expected orbital moment according to Hund's rules this would give a total moment of $3 \mu_B$. The gap in the minority spin bands of EuN is subject to the same uncertainty as other gaps calculated using DFT. However, it is very unlikely that calculational uncertainty could change our prediction of half-metallicity in EuN. As we proceed down the pnictide column of the periodic table there is a transfer of around 1.4 electrons from the pnictide p-states to the Eu s-d bands and the f-state which sits close to the Fermi energy. The bulk of this transfer occurs between EuN and EuP, although it continues as we go down the periodic table, and it results in the other europium pnictides being normal metals. To understand the transition from half-metallic to full metallic behaviour we need to make a detailed study of the density of states. As we go from EuN to EuP, the lattice constant increases, and the minority spin bands move slightly up in energy. The minority spin pnictide p-states then become less filled and the majority spin Eu f-band at the Fermi energy and some of the s-d states have a higher occupancy. During this transition the minority spin p-bands actually rise above the Fermi energy and the gap is destroyed in this spin channel. Thus, EuN is a half-metallic metal, while EuP and the other europium pnictides are normal metals. This extreme sensitivity of the bands to changes in the lattice constant also accounts for the strong dependence of the energy difference between the two valence states on the pnictide atom.

In figure 6 we show the density of states for EuSb in the divalent state. This is the calculated ground state. We note that the occupied f-states have risen considerably from their energy in

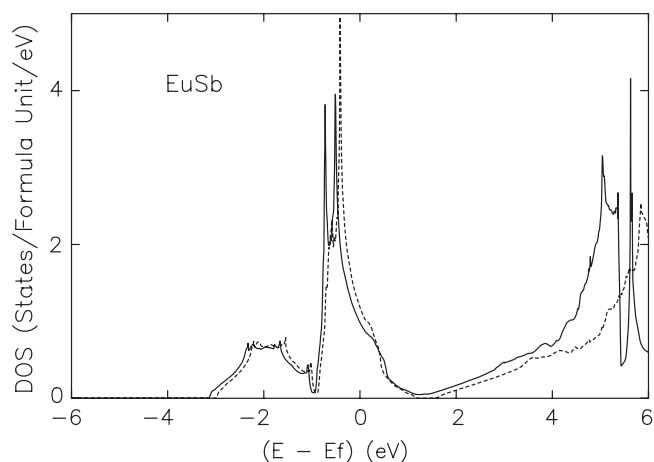


Figure 6. The spin-resolved density of states for europium antimonide in the divalent state (majority spin = full curve, minority spin = dashed curve).

the trivalent state. The results appear similar to those for the europium chalcogenides (although there is one fewer electron in the antimonide than in the telluride). In the divalent state EuSb is clearly a normal metal. About 1 eV above E_f , EuSb just fails to open up a gap which would correspond to the energy gaps in the chalcogenides.

4. Conclusions

In this paper we have reported a series of electronic structure calculations for the europium chalcogenides and pnictides. These calculations tell us several things that are interesting from both a fundamental and applied point of view. Firstly we have shown that the Eu chalcogenides in their ferromagnetic state are semiconductors, and the band gaps for the different spin channels are very different. Therefore we have materials whose carriers will be more or less 100% spin-polarized in the ambient temperature range. We suggest that, by alloying, it should be possible to create materials with a range of differential band gaps for the different spins. Secondly, we have shown that EuN is a half-metallic system with a substantial moment in its ferromagnetic state, while the other europium pnictides are normal metals. Again we might suggest that alloying of the ferromagnetic pnictides would allow us to have a half-metallic system with a range of possible energy gaps in the minority spin channel. Thirdly, our calculations strongly suggest that the position of the occupied f-levels in europium materials is dependent on the valence, but not on the chemical environment, of the europium ion. Finally, we predict a valence transition in the europium pnictides as we proceed down the pnictide column of the periodic table which may account for the observed deviation from the common rocksalt crystal structure expected for EuAs and EuSb. It seems that the europium chalcogenides and pnictides are possible candidates for spintronic and spin filtering applications.

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