The Electronic Structure of Europium Chalcogenides and Pnictides

M. Horne\(^1\), P. Strange\(^1\), W.M. Temmerman\(^2\), Z. Szotek\(^2\), A. Svane\(^3\) and H. Winter\(^4\)

\(^1\)Department of Physics, Keele University, Staffordshire, ST5 5DY, England
\(^2\)Daresbury Laboratory, Warrington WA4 4AD, England
\(^3\)Institute of Physics and Astronomy, University of Aarhus, DK-8000, Aarhus, Denmark.
\(^4\)AIFP, Forschungzentrum Karlsruhe GmbH, Postfach 3640, D-76021, Karlsruhe, Germany

(Dated: October 22, 2018)

The electronic structure of some europium chalcogenides and pnictides is calculated using the \textit{ab-initio} self-interaction corrected local-spin-density approximation (SIC-LSD). This approach allows both a localised description of the rare earth \textit{f}−electrons and an itinerant description of \textit{s}, \textit{p} and \textit{d}−electrons. Localising different numbers of \textit{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 just trivalent and EuSb is found to be divalent. Our results suggest that these materials may find application in spintronic and spin filtering devices.

PACS numbers:

\begin{enumerate}
  \item I. INTRODUCTION
\end{enumerate}

Rare earth compounds attract considerable experimental and theoretical attention due to the intricate electronic properties relating to the highly correlated \textit{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 crystallise 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 \textit{et al.}\(^{1\text{a}}\) have presented evidence that EuO is a ferromagnetic semiconductor where the charge carriers exhibit almost 100\% spin-polarisation. 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\(^{2\text{b}}\). 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 \textit{s}, \textit{p} and \textit{d} electrons as itinerant, while the \textit{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)\(^{3\text{b}}\) to the Local Spin Density (LSD) approximation to Density Functional Theory (DFT)\(^{4\text{b}}\) 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 \textit{f}−electron localization energy, and the question of which \textit{f}\(^\alpha\) 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 may be changed easily by altering external parameters.

In this paper we briefly describe the SIC-LSD formalism in section II 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 III. We conclude the paper in section IV.

\begin{enumerate}
  \item II. THE SIC-LSD FORMALISM
\end{enumerate}

The standard method for making \textit{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 localisation phenomena are under investigation\(^{5\text{e},6\text{e},7\text{e},8\text{e},9\text{e}}\). 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\(^{10\text{e},11\text{e}}\), the 3d monoxides\(^{8\text{e}}\), \textit{La}\(_2\text{CuO}_4\)\(^{12\text{e},13\text{e}}\), \textit{f}−electron systems\(^{14\text{e},15\text{e},16\text{e}}\), solid hydrogen\(^{17\text{e}}\), orbital ordering\(^{18\text{e}}\) and metal-insulator transitions\(^{19\text{e}}\).
In the SIC-LSD method the total energy is minimised 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

\[ N_v = Z - N_{\text{core}} - N_{\text{SIC}}, \]  

where \( N_{\text{core}} \) is the number of atomic core electrons, \( Z \) is the atomic number and \( N_{\text{SIC}} \) is the number of states for which the self-interaction correction has been removed. This definition means that \( N_v \) is 2 for systems normally thought of as divalent and 3 for systems that are trivalent, as one might expect.

III. RESULTS AND DISCUSSION

Most of the rare earth chalcogenides and pnictides crystallise in the common rocksalt structure. We have performed SIC-LSD calculations for Eu chalcogenides and pnictides using an LMTO method for the band structure. 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.

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, and we would expect that this method could reproduce trends in band gaps fairly reliably.

A. 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 the atomic number and the difference in energy between the divalent and trivalent state. The calculated exchange splitting of the bottom of the 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 I 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. 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 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

FIG. 1: The values of the lattice constant for the europium chalcogenides from experimental (triangles) and this calculation (×). 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 43mRy calibration determined for the elemental rare earths and their sulphides by Strange et al.
FIG. 2: The spin-resolved density of states for the divalent europium chalcogenides (majority spin (full line) and minority spin (dashed line)). In EuO the calculated energy gap is 2.5 eV compared with the experimental value of 1.2 eV.

TABLE I: 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 $\Delta E_{ex}$ at the bottom of the conduction band. All energies are in eV.

|        | EuO | EuS  | EuSe | EuTe |
|--------|-----|------|------|------|
| gap    | 2.5 | 3.4  | 1.3  | 2.0  |
| $\Delta E_{ex}$ | 0.62 | 0.39 | 0.38 | 0.39 |

judicious choice of material and doping. Steeneken et al. estimate the exchange splitting in the conduction band of EuO as 0.6 eV, and again we find excellent agreement with this value.

Steeneken et al. have also determined the 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. In

FIG. 3: The unoccupied region of the oxygen $p$-resolved density of states for EuO. The full line is for majority spin and the dashed line for minority spin. The Fermi energy is zero on this scale. The positions of the peaks compare very favourably with the XAS measurements of Steeneken et al.
the experiment the principal peaks occur at 532.5 eV with a shoulder at 534.5 eV and a double peak structure at 536.0 and 538.0 eV. These features match well with our density of states peaks at 0.25 Ry (3.4 eV), 0.37 Ry (5.0 eV), 0.65 Ry (8.8 eV) and 0.82 Ry (11.2 eV).

B. 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 $\Delta E$ 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. For these materials the energy difference between the valence states is strongly dependent on the pnictide concerned.

These results are in full agreement with the assertion of Hulliger who states that the 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.

![Graph showing lattice constant vs. energy difference](image)

**TABLE II:** 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|
| Eu(3+) | 6.29| -0.30| 6.48 | -0.18|

EuAs adopts the Na$_2$O$_2$ crystal structure which is a distortion of the NiAs structure due to the formation of anion-anion pairs. 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 Na$_2$O$_2$ 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 Figs. 4 and 5 run over 0.4 eV and 2.0 eV respectively. These results are qualitatively similar to those obtained for the ytterbium pnictides 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 II 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 Eu 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 pnict-
FIG. 5: The spin-resolved density of states for Europium Pnictides, in the trivalent state (majority spin = full line, minority spin = dashed line).

tide semi-core s-bands are above the localised 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. In the pnictides the empty minority spin f-states can be seen clearly about 0.3-0.4 Rydbergs 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. 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. 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 hybridises with majority spin p-states and draws some pnictide 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
bands to changes in the lattice constant also accounts for

tides are normal metals. This extreme sensitivity of the

metallic metal, while EuP and the other europium pnic-

tionide in the divalent state. Thus, EuN is a half-

- bands actually rise above the Fermi energy and the gap

 occupancy. During this transition the minority spin

- s-states to the Eu - d bands and the f-state which

 sits close to the Fermi energy. The bulk of this trans-

 fer 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 un-

 derstand 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 con-

 stant increases, the minority spin bands move slightly up

 in energy. The minority spin pnictide -states then be-

 come less filled and the majority spin Eu -band at the

 Fermi energy and some of the - d states have a higher

 occupancy. During this transition the minority spin -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 -states have risen considerably

 from their energy in 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 0.1 Rydbergs above , EuSb just

 fails to open up a gap which would correspond to the

 energy gaps in the chalcogenides.

 IV. 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 chalco-

 genides 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-polarised in the ambient tem-

 perature range. We suggest that, by alloying, it should

 be possible to create materials with a range of differen-

tial 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 pnic-

tides would allow us to have a half metallic system with a

 range of possible energy gaps in the minority spin chan-

 nel. Thirdly our calculations strongly suggest that the

 position of the occupied -levels in europium materials

 is dependent on the valence, but not on the chemical en-

 vironment, of the europium ion. Finally we predict a va-

 lence 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.

 1 P.G. Steeneken, L.H. Tjeng, I. Ellimov, G.A. Sawatzky, G. Ghiringhelli, N.B. Brookes and D.-J Huang, Phys. Rev. Letts. 88, 047201-1 – 047201-4, (2002)

 2 P. LeClair, J.K. Ha, H.J.M. Swagten, J.T. Kohlhepp, C.H. van de Vin, and W.J.M. de Jonge, Applied Physics Letters 80, 625 (2002).

 3 J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

 4 P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

 5 W. Kohn and P. Vashishta, in 'Theory of the Inhomogeneous Electron Gas', ed S. Lundqvist and N.H. March (Plenum Press, New York), (1982).

 6 W. M. Temmerman, A. Svane, Z. Szotek and H. Winter, in Electronic Density Functional Theory: Recent Progress and New Directions, Eds J. F. Dobson, G. Vignale and M.P. Das (Plenum, 1997.)

 7 W.M. Temmerman, A. Svane, Z. Szotek, H. Winter and S. Beiden, Lecture Notes in Physics Vol 535, "Electronic Structure and Physical Properties of Solids: The uses of the LMTO method", ed. H. Dreyssé, 296, (Springer-Verlag, 2001)

 8 A. Svane and O. Gunnarsson, Phys. Rev. Lett. 65, 1148
Z. Szotek, W. M. Temmerman and H. Winter, Phys. Rev. B 47, 4029 (1993).

A. Svane and O. Gunnarsson, Phys. Rev. B 37, 9919 (1988); A. Svane and O. Gunnarsson, Europhys. Lett. 7, 171 (1988).

J. Majewski and P. Vogl, Phys. Rev. B 46, 12219; ibid, 12235 (1992).

A. Svane, Phys. Rev. Lett. 68, 1900 (1992).

W. M. Temmerman, Z. Szotek and H. Winter, Phys. Rev. B 47, 11533 (1993).

P. Strange, A. Svane, W.M. Temmerman, Z. Szotek and H. Winter, Nature 399, 756 (1999).

L. Petit, A. Svane, W.M.Temmerman and Z. Szotek, Sol. State. Commun. 116, 379, (2000)

L. Petit, A. Svane, Z. Sotek and W.M. Temmerman, Science, 301, 498, (2003).

A. Svane and O. Gunnarsson, Solid State Commun. 76, 851 (1990).

R. Tyer, W.M. Temmerman, Z. Szotek, G. Banach, A. Svane, L. Petit, and G.A. Gehring, Europhys. Lett., 65, 519, (2004).

W.M. Temmerman, H. Winter, Z. Szotek and A. Svane, Phys. Rev. Lett. 86, 2435, (2001).

O. K. Andersen and O. Jepsen, Phys. Rev. Lett. 53, 2571 (1984); O. K. Andersen, O. Jepsen and O. Götzel, Canonical Description of the Band Structures of Metals, Proc. of Int. School of Physics, Course LXXXIX, Varenna, 1985, ed. by F. Bassani, F. Fumi and M. P. Tosi (North– Holland, Amsterdam, 1985), p. 59.

M. Gasgnier, Handbook on the Physics and Chemistry of Rare Earths, Vol. 5, chapter 41 (1984).

P. Villars and L.D. Calvert, Pearson’s Handbook of Crystallographic Data for Intermetallic Phases, 2. ed., (ASM International, Ohio, 1991).

F. Hulliger, Handbook on the Physics and Chemistry of Rare Earths, Vol. 4, chapter 33, p218 (1984).

W.M. Temmerman, Z. Szotek, A. Svane, P. Strange, H. Winter, A.Delin, B. Johansson, O. Eriksson, L. Fast and J.M. Wills, Phys. Rev. Lett.83, 3900, (1999).

A. Svane, W.M. Temmerman, Z. Szotek, L. Petit, P. Strange and H. Winter, Phys. Rev. B. 62, 13394, (2000).