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An analysis on electronic and structural transformation in divalent rare earth chalcogendie

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Abstract
The electronic structure of the praseodymiummonopnictides and monochalcogenides is studied using the self-interaction corrected (SIC) local spin density (LSD) approximation. This method allows for a description of the Pr ions with some f electrons localized in atomic like orbitals, while other f degrees of freedom are forming hybridized bands. In addition the electronic structure of rare earth monosulfides were studied by Me Clure using a simple model, which correlates the magnetic susceptibility data with the type of electrical conductivity, observed. Theoretical study of pressure induced phase transitions in cerium Chalcogenides were carried out by Svane using the SIC-LSD approximation. Phase transformation studies on samarium monochalcogenides were carried out experimentally up to 55 GPA which reports a high pressure NaCl type to CsCl type phase transition in SmSe and SmTe. Rare earth monochalcogenides including monoxides crystallize in face centered cubic structure of NaCl type. The Chalcogenides of rare earth metals are one such group, which posses a wide range of electrical magnetic and other physiochemical properties. Some of them show valence fluctuations and few others exhibit insulator - metal transition induced either by doping or by high-pressure.

Keywords: structural transformation, pressure, rare earth, chalcogendie, Electronic, Divalent, SIC, LSD, electrons, magnetic, conductivity, high-pressure, metal transition.

1. Introduction
In recent years, the mono-pnictides of rare earths (RE) with NaCl structure have drawn considerable interest of material scientists, because of their diverse structural, transport, magnetic and vibrational properties [1-4]. The partially filled f-electron orbitals of RE atom are in general found to be responsible for the anomalous properties in these compounds. X-ray diffraction technique has been used recently by Shirotani *et al* [5]. to investigate the high-pressure structural properties in these compounds [5-7], and it was observed that many of these compounds undergo a structural phase transition either to CsCl or body centered tetragonal (BCT) structures. High-pressure structural phase transformation of four rare earth pnictides i.e. CeBi, PrBi, UBi and PuBi has been studied theoretically. The mono-bismuth ides contain the pnictogen ion with the highest Z and largest atomic radius that can be studied to investigate the role of p-f mixing on the structural properties in REBi compounds. These also have the p orbitals with the highest quantum numbers of the pnictogen. Therefore, the knowledge of the pressure behaviour of bismuth ides is important in developing, comparing and understanding the systematic of the lanthanide and actinide mono pnictides. Also for a better description, it is necessary to take into account the hybridization of the f and conduction band orbitals, which can be related to the hybridization of the f and porbitals of the metalloids.

Review of Literatures
Several experimental and theoretical studies on the electronic structure and high pressure behaviour of rare-earth monopnictides and monochalcogenides have been published. In the lanthanum monopnictides a pressure induced structural phase transition occurs from the NaCl (B1) structure to a tetragonal structure, which may be viewed as a distorted CsCl (B2) structure. In the lanthanum monochalcogenides similar phase transitions were predicted to occur, however to a pure B2 phase. Recent studies of the electronic structure of the lanthanum monopnictides [5, 6] and monochalcogenides [7], using the self-consistent tight-binding linear muffin-tin orbital (LMTO) method, confirm the observed behaviour of these materials under pressure. From Ce onwards, the presence of localized f electrons makes a similar band structure calculation inadequate, as the LSD approximation does not capture the strong correlation effects. In the LDA + Umethod, the position of the narrow f bands is corrected by explicitly including these correlations. The method has been applied to calculate the electronic structure and optical properties of the Pr pnictides [8]. A second approach treats the f electrons as part of the core, whilst the remaining valence electrons continue to be treated in the LSD approximation. This method was among others applied to RESb compounds [9], and Gd, and Er pnictides [10]. In the present work we will undertake a systematic theoretical investigation of the Pr monopnictides and monochalcogenidesusing an ab initio electronic structure method based on the self-interaction corrected (SIC) local spin density (LSD) approximation [11]. In this scheme the Pr f electrons may be described as either localized or delocalized, and various valencies of Pr can be investigated and the most favourable predicted.

Electronic Structure and Structural Phase
Rare earth monochalcogenides including monoxides crystallize in face centered cubic structure of NaCl type. The Chalcogenides of rare earth metals are one such group, which

posses a wide range of electrical magnetic and other physiochemical properties. Some of them show valence fluctuations and few others exhibit insulator - metal transition induced either by doping or by high-pressure. When the rare earth element is trivalent, the volumes of the corresponding monochalcogenides show the usual lanthanide contraction and the compounds have metallic properties for e.g. LaS, LaSe and LaTe have electrical restivities at room temperature of the order of 250\x Q Cm. When the rare earth element is divalent, the volumes are larger by about 15% and are found to be semiconducting. Under pressure these divalent rare earth monochalcogenides undergoes a semiconductor to metal transition.

The electrical and magnetic properties of rare earth monosulfides were studied by Didchenko and Gortsema in 1963. In addition the electronic structure of rare earth monosulfides were studied by Me Clure using a simple model, which correlates the magnetic susceptibility data with the type of electrical conductivity, observed. Theoretical study of pressure induced phase transitions in cerium chalcogenides were carried out by Svane using the SIC-LSD approximation. Phase transformation studies on samarium monochalcogenides were carried out experimentally by Le Bihan et al. (1995) upto 55 GPa which reports a high pressure NaCl type to CsCl type phase transition in SmSe and SmTe. The trivalent lanthanum monochalcogenides LaX (X = S, Se, Te) are found to be superconductors having transition temperature in the range of 0.8 - 1.5 K. The superconducting transition temperature (Tc) as well as the electronic specific heat coefficient (y) increases from sulphide to telluride. Theoretical calculation of superconducting transition temperature of these compounds at ambient pressure were reported by Sankaralingam et al In 1992. Electronic structure calculations using the local density approximation have been carried out for LaS by Lu et al. in which the structural properties of LaS and SmS were studied. Recent theoretical calculations of LaS surface and LaS/CdS interface by Eriksson et al. 1998 predicted that LaS/CdS geometry should be a good candidate for cold electron emitter devices. The magneto - optical spectroscopy for LaSe has been studied by Pittini et al. in which the magneto optical spectra of LaSe and CeSe demonstrate that magneto-optics is also a valuable tool for studying the /states. Magneto-optics studies on LaX (X = S, Se and Te) were also done by Drioli in 1999, which confirmed that even a non-magnetic or a weakly magnetic material, i.e. one with non-occupied spin-polarised states, can have a strong magneto-optical signal.

SIC-LSD Formalism

The basis of the SIC-LSD formalism is a self-interaction free total energy functional ESIC, obtained by subtracting from the LSD total energy functional ELSD the self-interaction of each occupied electron state ψα [21]:

ESIC = ELSD −occ α δSIC α (1)

Here, the self-interaction correction for the state

ψα is δSIC α = U[nα] + ELSD XC [nα] (2)

with U[nα] being the Hartree energy and ELSD XC [nα] the LSD exchange–correlation energy for the corresponding charge density nα = |ψα| 2.

It is the LSD approximation to the exchange– correlation energy functional which gives rise to the spurious self-interaction. The exact exchange–correlation energy of density functional theory, EXC, has the property that for any single electron spin density, nα it cancels exactly the Hartree energy: U[nα] + EXC[nα] = 0. (3) In the LSD approximation this cancellation is incomplete, and for spatially well localized states ψα the self-interaction δα can be substantial. On the other hand, for extended states in periodic solids the self-interaction vanishes. Hence, in order to gain energy from the self-interaction correction in a periodic solid, the Bloch symmetry of the wavefunction ψα must be broken. This does not conflict with Bloch's theorem, since the Hamiltonian describing the state ψα will no longer be translationally invariant. For a full exploration of the functional in equation (1), various scenarios of localized and delocalized states need to be examined. The LSD minimum remains a local minimum of ESIC, since the scenario with no localized states is a viable option, but other scenarios may result in a lower total energy, as is indeed found in Pr compounds in this work. The localized electrons acquire core like characteristics, and the self-interaction correction plays the role of localization energy which competes with the band formation energy gained by allowing electrons to delocalize. The number of localized f electrons leads to a convenient definition of the valency of the rare-earth ion, given as the number of electrons available for band formation:

Nval = Z − Ncore − NSIC. (4)

Here Z (=59) is the atomic number, Ncore is the number of the atomic core (and semi-core) electrons (=54 for Pr) and NSIC is the number of localized f electrons. Thus, with two localized f electrons (f2) the Pr ion will be trivalent. Similarly, f 1 and f 0 configurations would be referred to as tetravalent and pentavalent configurations. It is important to note that those f degrees of freedom which are not localized are available for band formation. The pentavalent configuration corresponds to the normal LSD picture,i.e. the entire f manifold is treated as band states. The SIC-LSD approach has been implemented with the LMTO method.

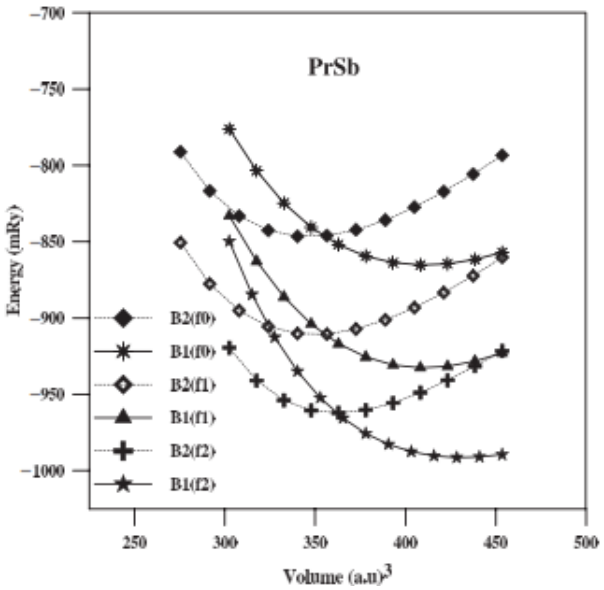

Fig 1: Calculated total energy versus relative volume of PrSb in the B1 and B2 structures with the Pr ions in the trivalent, tetravalent and pentavalent configurations.

Since the ASA is not sufficiently accurate for calculating the energy difference between the NaCl and CsCl structures, we have used the full potential (FP) LMTO method to correct the ASA total energies, i.e. we assume that the LSD total energy correction between the FP and ASA (at a particular lattice constant) can be taken over also to SIC-LSD calculations. The calculations used 525 and 455 k points in the irreducible Brillouin zone of the NaCl and CsCl structures, respectively. The inclusion of Pr 5p states as band states (in a separate semi-core panel) is crucial for getting an accurate evaluation of the total energy. Apart from those f states that remain delocalized, the valence panel contains the Pr 6s and 5d states, as well as the pnictide/chalcogenide s, p and d states.

Conclusion

The atomic sphere approximation (ASA) is used, according to which the polyhedral Wigner–Seitz cell is approximated by slightly overlapping atom centred spheres. The spin–orbit interaction is included explicitly in the Hamiltonian. To improve packing in the NaCl structure, 'empty spheres' have been introduced in the high symmetry interstitial sites. Since the ASA is not sufficiently accurate for calculating the energy difference between the NaCl and CsCl structures, we have used the full potential (FP) LMTO method [26] to correct the ASA total energies, i.e. we assume that the LSD total energy correction between the FP and ASA (at a particular lattice constant) can be taken over also to SIC-LSD calculations. The calculations used 525 and 455 k points in the irreducible Brillouin zone of the NaCl and CsCl structures.

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