

STUDIES IN LANTHANIDE OXIDE FLUORIDES

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EFFECTS OF PRESSURE ON THE ELECTRONIC STRUCTURE
OF THE SAMARIUM MONOCHALCOGENIDES*

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ABSTRACT

A program for the calculation of the electronic band structures of the rare-earth mononictides and monochalcogenides is discussed and reviewed. Explicit calculational results are then presented for SmS and SmTe, both for their normal lattice parameters and for reduced lattice parameters corresponding to experimentally obtainable pressures. These calculations strongly indicate that the mechanism for the recently observed pressure-induced semiconductor-to-metal transition in SmS is 4f electron delocalization, but the mechanism for a like transition in SmTe is a simple band-gap closing with pressure.

I. INTRODUCTION AND GENERAL DISCUSSION

The samarium solid-state compounds SmS, SmSe, and SmTe are of interest not only because of their own unique and specific physical properties, but also due to their belonging to a large general class of solid-state compounds. This class is the NaCl-structured mononictides (N, P, As, Sb, Bi) and monochalcogenides (S, Se, Te) of the rare-earth elements, and contains an exceedingly rich diversity of solid-state properties as one moves his consideration from compound to compound within the class. Generally speaking, all members of the class are refractory; e.g., PrS melts at about 2500°K. At the same time, the class contains individual members representing just about every range of electrical conductivity, from good metals to wide-gap semiconductors. Metallic examples are HoP and DyP,¹ but HoN and DyN are semiconductors with band gaps of about 1 eV.² Diverse magnetic properties also exist as one moves through the class of compounds. TmN does not order magnetically, while GdN is a ferromagnet; but GdP is an antiferromagnet, while other compounds like HoP are ferrimagnetic.³

Of course, the similarities and differences in the physical properties of this class of rare-earth compounds are directly related to the electronic structures of the individual compounds; i.e., they are related to the actual details of the compounds' electronic band structures. However, such actual correlations between properties and band structures have been lacking, mainly because few realistic band structure calculations have been reported for the compounds in this class, a notable exception to this statement being

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the calculations performed for some europium chalcogenides.⁴ In an attempt to make further correlations possible, we are presently engaged in performing a systematic series of exploratory band structure calculations for most of the rare-earth mononictides and monochalcogenides. Some qualitative features which arise in our work are illustrated in Figure 1, which contains three of our calculated band structures for nonmagnetic states of the compounds. The group theoretical notation used in Figure 1 is the standard Boukaert-Smoluchowski-Wigner notation⁵; e.g., Γ is the center of the Brillouin zone and X is the center of the square face of the surface of the zone.

Certain common features are seen to exist in the three band structures of Figure 1. First, each has the valence bands, originating at Γ_{15} , which are primarily composed of the p-states of the respective anion. Then there are the conduction bands primarily composed of the rare-earth 6s-states, originating at Γ_1 , and the rare-earth 5d-states, originating at Γ_{25} and Γ_{12} . Of course, for a \vec{k} away from Γ the corresponding energy states can reflect more hybridization. Also present in the band structures of Figure 1 are the rare-earth f-states, or "f-bands", which have little dispersion, reflecting the well established fact that the rare-earth 4f electrons are well localized. The f-states in Figure 1(c) are off the plot at lower energies. One sees a gap exists between the valence and conduction bands in Figures 1(a) and 1(b), while the valence and conduction bands overlap in Figure 1(c). It does turn out, when one investigates the band structures for other \vec{k} directions, that whether the valence and conduction bands overlap is determined by whether the tail of the Δ_2' band has a lower energy than the Γ_{15} states. Band structures as illustrated in Figure 1 have actually been qualitatively verified by photoemission experiments reported by Eastman and Kuznetz⁶; e.g., their work shows GdS has a band structure of the type of Figure 1(b), while the band structure of EuS is of the type of Figure 1(a) except the 4f-states are slightly merged with the upper part of the valence band.

The major difficulties in performing reliable band structure calculations for the class of rare-earth compounds under discussion, as for the rare-earth metals, are connected with the f-states illustrated in Figure 1. First, it has been found^{4,7,8} very difficult to energetically locate the f-states properly in the overall band structure due to their very sensitive dependence upon the exchange contribution to the one-electron, band-theoretic, potentials. Fortunately, details of the valence and conduction band structures are not so dependent upon the exchange contribution, so calculations usually have more reliability for these states. Thus it is usually necessary to perform some ad hoc adjustment in the exchange potential for the resulting calculations to properly locate the f-states if agreement with available experimental information is desired. But one must remember that it sometimes is also just as difficult to experimentally identify and locate the compound's 4f-states due to problems associated with impurities, stoichiometry, multiple

scattering, etc., so the calculational inadequacies are not unique. Whatever the experimental case, since the calculational procedures are at present not straightforward, it is necessary to caution that resulting band structures should be considered exploratory. However, at the same time, we feel that such first-attempt exploratory calculations are of value, since they do enable the interaction process between calculational and experimental results to begin, with such interaction hopefully leading to the eventual elucidation of a given compound's actual electronic band structure.

Another difficulty one might encounter with the f-states of Figure 1 is more of a conceptual character, and is concerned with the one-electron nature of the basic band-structural model. At first thought one might envision occupying the available states of, say, Figure 1(b) according to Fermi statistics. Even though this is done for the valence and conduction bands, it is not, and must not be, done for the f-states. Rather, a "correlational-configurational" argument is invoked, meaning only a given number of the f-states are filled, resulting in the expected f^n ($n \leq 14$) configuration. This should not be too surprising, since the same state of affairs, having empty states at a lower energy than filled states, occurs in Hartree-Fock calculations⁹ for free rare-earth atoms. If such were not the case, self-consistent calculations would eventually produce a different energetic ordering of the one-particle states.

Turning to the three compounds which are the explicit purpose of this report, SmS, SmSe, and SmTe are all semiconductors under normal conditions, having band gaps (absorption edges) of, respectively, about 0.2 eV, 0.46 eV, and 0.63 eV.¹⁰ Also, these three compounds do not order magnetically, presumably due to having $4f^6$ Sm-site configurations with ground-state multiplet 7F_0 . Perhaps one of the most intriguing, and also quite recent, observations concerning the properties of these compounds is the demonstration¹⁰ that each undergoes a pressure-induced semiconductor-to-metal transition. The pressure required for the transition increases from 6.5 kbar for SmS, to the vicinity of 40 kbar for SmSe and the vicinity of 50 kbar for SmTe. At the same time, the transition occurs discontinuously for SmS, whereas it has all appearances of taking place continuously over a broad pressure range in SmSe and SmTe.

To explain the transition in all three of the samarium compounds, Jayaraman et al.¹⁰ postulated that each had a normal pressure band structure qualitatively like Figure 1(a). Then their explanation for the transitions was that application of pressure causes the gap between the 4f-states and the conduction band (the Δ_2' tail) to decrease, until at some critical pressure the conduction band merges with the 4f-states. At such merging, one 4f electron per Sm site would become delocalized,¹¹ and the compounds go metallic. However, without any other direct band-structural information being available, it was our feeling that one should also consider the possibility of the compounds having a normal pressure band structure qualitatively like Figure 1(b). With such a band structure, the pressure-induced

transition could be accounted for by having the gap between the valence band and conduction band decrease with pressure, until at some critical pressure the Δ_2 tail would have a lower energy than the Γ_{15} states and the system would then be metallic. Thus, this latter model would involve only a simple band-gap closing and not any 4f delocalization.

To help furnish calculational information that possibly might distinguish between the applicability of the above two models to, in turn, each of the compounds, we have performed numerous exploratory band structure calculations for SmS, SmSe, and SmTe. The results of our calculations indicate that the model based on Figure 1(a) applies to SmS, but the model based on Figure 1(b) applies to SmSe and SmTe. In the remainder of this report, we will outline the calculations we have done, and in so doing try to convey the above indications and the limitations that exist on such indications. However, since qualitative similarities exist in our results for SmSe and SmTe, in an attempt at brevity no further mention will be made in this report concerning SmSe.

II. APPROXIMATIONS AND CALCULATIONAL DETAILS

The major approximations, which would affect any qualitative conclusions drawn from our calculations, are all involved with the procedures used in obtaining the one-electron, band-theoretic, potentials. Although the potential procedures we have adopted are somewhat standard, since they have been applied by different investigators to numerous solids with varying degrees of success, they are by no means exact. Thus, the band structures we have calculated via these potentials can honestly be considered only as first-order approximations to the actual one-particle states possessed by the respective compounds. However, it is still our feeling that such calculated band structures have at least as great, if not greater, validity than those inferred via the practice of merely postulating band structures from indirect experimental information without the use of any calculational underpinnings.

The potentials used in this investigation were obtained from a heuristic prescription^{12,13} involving free-atom charge densities. With this prescription the potential, $V(\vec{r})$, about a given lattice site is approximated by a spherically symmetric, muffin-tin, potential $V(r) = V_C(r) + V_{ex}(r)$. Both the Coulomb part, $V_C(r)$, and the exchange part, $V_{ex}(r)$, are obtained from lattice superpositions involving free-atom charge densities; thus, the resulting $V(r)$ depends directly upon the lattice parameter being used in the calculation. That is, at a given lattice site, $V_C(r)$ is the spherically averaged sum of two components. The first component is the Coulomb potential due to the free atom at the given site, while the second component is the sum of the contributions due to tails of free-atom Coulomb potentials centered on other lattice sites in the vicinity, which overlap onto the site under consideration. A Slater-type

free-electron approximation is used for the exchange part: $V_{ex}(r) = -6\alpha[3\rho(r)/8\pi]^{1/3}$. $\rho(r)$ is the spherically symmetric lattice superposition of atomic charge densities, and obtained in a manner completely analogous to that used for $V_C(r)$. The parameter α in $V_{ex}(r)$ controls the exchange contribution to the potential, with $\alpha = 1$ being full Slater exchange. In this investigation α has been varied in order to obtain calculated band gaps, at normal pressure, in agreement with experimental band gaps. Such variation of α was done in the spirit of attempting to obtain an experimentally realistic model Hamiltonian for each of the samarium compounds.

To explicitly construct the potentials for this work, free-atom Hartree-Fock wave functions tabulated by Fischer⁹ were used. Touching muffin-tin sphere radii were then determined by requiring neighboring site potentials to be equal at the point of sphere contact. The constant value of the potential between the spheres, V_0 , was equated to the potential value at sphere contact. Band structures were calculated from the resulting potentials by use of the non-relativistic form of the Korringa-Kohn-Rostoker method as formulated by Treusch and Sandrock.¹⁴ Although for fully quantitative calculations on rare-earth systems relativistic effects cannot be neglected, due to the inherently qualitative nature of this undertaking and a desire to minimize calculational details we have, at present, limited our work by omitting relativistic effects. However, the major relativistic effect expected in the calculations would be shifts in states containing large s-components, e.g., the Γ_1 's of Figure 1. But such shifts should not be large enough to qualitatively change the band structures of Figure 1, especially since the Δ_1 bands, originating at the Γ_1 's, rise and the Δ_2 bands fall as $|\vec{k}|$ increases.

III. DISCUSSION OF RESULTS

Using the procedures outlined in the preceding section, we performed a series of band structure calculations for SmTe at its normal pressure lattice parameter (cube edge = 12.46 a.u.). During this series of calculations, only the exchange multiplier, α , was varied in order to obtain a calculated band gap in agreement with the experimental absorption edge of 0.63 eV. The calculated band gaps resulting in this series of calculations were 1.59 eV for $\alpha = 1.00$, 0.89 eV for $\alpha = 0.85$, 0.28 eV for $\alpha = 0.80$, and 0.63 eV for $\alpha = 0.844$. For $\alpha = 0.844$, the resulting calculated SmTe band structure along the major symmetry directions of the Brillouin zone is displayed in Figure 2. Notice that Figure 2 verifies our previous statement that the valence band to conduction band gap is determined by the band structure for the Γ to X direction.

After the above series of calculations fixed the value of the exchange multiplier at $\alpha = 0.844$, we performed another series of band structure calculations for SmTe involving variation of the lattice parameter but using the same α value. This series used reduced values of the lattice parameter corresponding to experimentally obtainable pressures. Part of one of the band structures resulting

in this series is displayed in Figure 3, which used a lattice parameter reduced 3% from the value used for Figure 2. Now the band gap for Figure 2 was adjusted to obtain a value of 0.63 eV by variation of the exchange multiplier α ; however, without any further variation of α , the band gap of Figure 3 has been reduced to 0.10 eV. Thus, it is seen that lattice parameter reduction decreases the calculated band gap for SmTe. The calculated band gap for SmTe as a function of lattice parameter is given by Figure 4. From this figure it is seen that the calculations indicate, as discussed earlier, that the application of pressure causes SmTe's band structure to continuously undergo a transition from the type illustrated by Figure 1(b) to the type illustrated by Figure 1(c). Also, the data of Figure 4 indicate the calculated semiconductor-to-metal transition occurs when the lattice parameter has been reduced by about 3.5%. Without the availability of detailed compressibility data for SmTe, it is not possible to express what pressure the calculations predict for the transition. However, Rooymans¹⁵ has reported SmTe lattice constants of 12.3 a.u. at 30 kbar and 11.7 a.u. at 60 kbar. So the calculated transition pressure falls approximately halfway between 30 and 60 kbar, which, when considering the approximations used in the calculations, gives very reasonable agreement with the experimental¹⁰ transition pressure of about 50 kbar.

We have also performed calculations pertaining to SmS using similar procedures as those used for SmTe. First, using the normal pressure lattice parameter (cube edge = 11.28 a.u.), the value of the exchange multiplier α was varied until the calculated gap between occupied states and the conduction band agreed with the experimental absorption edge of about 0.2 eV. For SmS, as is seen from Figure 5, in order to obtain agreement the calculational process led to the presence of the f-states between the valence and conduction bands. To further illustrate this point, for $\alpha = 1.00$ the gap between the valence and conduction bands was 2.9 eV with the f-states considerably below the valence band, for $\alpha = 0.90$ the valence-conduction gap was 2.3 eV and the f-states were still below but closer to the valence band, and for $\alpha = 0.80$ the valence-conduction gap was also 2.3 eV but the f-states had moved between the valence and conduction bands. Final adjustment gave $\alpha = 0.781$ and the band structure of Figure 5, which has a valence-conduction gap of 1.9 eV but an f-state to conduction band gap of 0.22 eV. Thus, our calculations indicate that indeed SmS has a band structure of the type illustrated by Figure 1(a), as had been postulated by Jayaraman et al.¹⁰

To further test the validity of the calculational procedures, we performed a series of calculations for SmS with α fixed at the above final value of 0.781 but varied the lattice parameter. Part of the resulting band structure for a 2% reduction in lattice parameter is shown in Figure 6. It is seen for this compression, which is equivalent to a pressure of 6 kbar,¹⁰ that the tail of the Δ_2 band has merged with the f-states, and providing 4f delocalization then occurs the system will be metallic. Since the observed transition pressure for SmS is 6.5 kbar, the agreement between our

calculations and experiment is quite reasonable.

In summary, our calculations strongly indicate that the mechanism for the pressure-induced semiconductor-to-metal transition in SmS is 4f electron delocalization, but the mechanism for SmTe (as for SmSe) is one involving simple closing of the valence to conduction band gap with pressure. If indeed such is the actual case, the experimental fact that the transition appears discontinuous for SmS and continuous for SmTe is not so mysterious.

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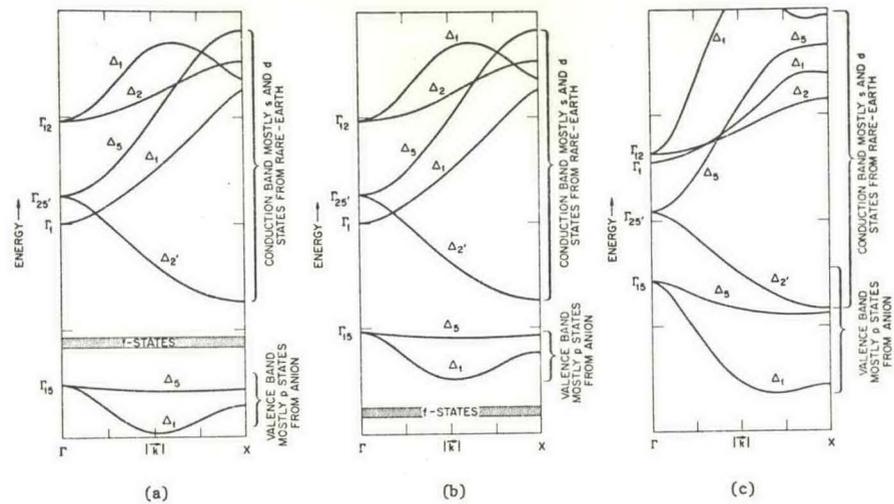


Figure 1. Some illustrative examples of variations in electronic band structures as calculated for the rare-earth monpnictides and monochalcogenides. These plots are for \bar{K} along the $\langle 100 \rangle$ direction.

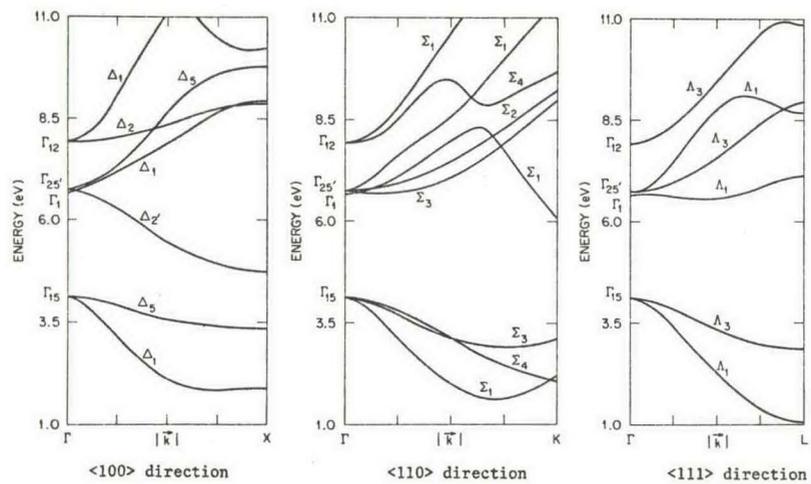


Figure 2. Calculated band structure for SmTe using an exchange multiplier of $\alpha = 0.844$ and lattice parameter = 12.46 a.u. The f-states for this calculation were below the valence band at -0.22 eV. All energies are relative to the constant value of the potential between the muffin-tin spheres $V_0 = -1.058$ ry.

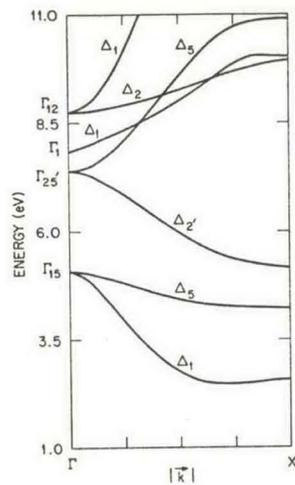


Figure 3. Results for SmTe using $\alpha = 0.844$ and lattice parameter of 12.09 a.u. The f-states for this are centered at 0.98 eV. All energies relative to the V_0 value of -1.153 ry.

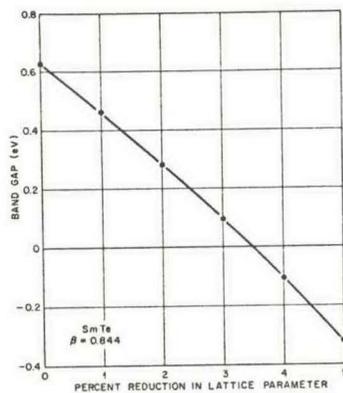


Figure 4. Band gap for SmTe as a function of percent reduction in lattice parameter from the normal value of 12.46 a.u.

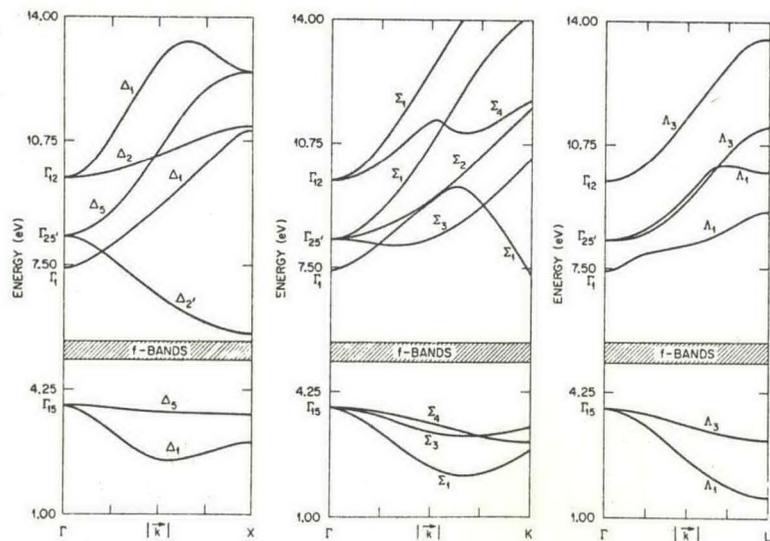


Figure 5. Calculated band structure for SmS using $\alpha = 0.781$ and a lattice parameter of 11.28 a.u. All energies are relative to the V_0 value of -1.152 ry.

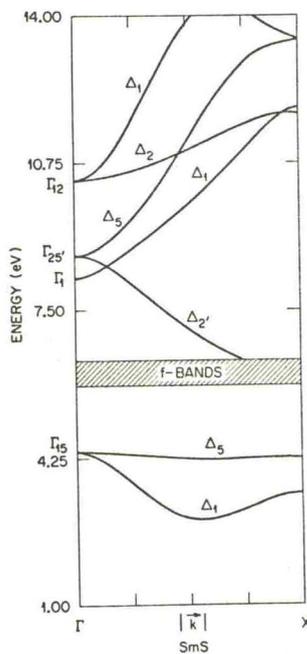


Figure 6. Results for SmS using $\alpha = 0.781$ and a lattice parameter of 11.06 a.u. All energies relative to V_0 value of -1.222 ry.

LUMINESCENT PROPERTIES OF RARE EARTH OXYSULFIDE FILMS*

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ABSTRACT

We have made LOS films of intrinsic efficiency equivalent to that of LOS powders for several activators. Because of light trapping only one ninth of the film light is directly observable. However, the films have such superior thermal conductivity compared to the powders that they sustained an excitation power density greater than $6\text{W}/\text{mm}^2$ without damage. At this excitation level, the films were brighter than the saturated brightness of the corresponding powder screen. We have made multilayer films simply by depositing LOS with one activator over LOS with a different activator. The multilayer films possessed efficient luminescence whose color was voltage dependent.

Introduction

The rare earth oxysulfides, $\text{RE}_2\text{O}_2\text{S}$ (REOS) are an isomorphic family of materials which are among the most efficient cathodoluminescent phosphors known. We felt that such materials were natural candidates for thin film luminescent devices if efficient films could be made from them. Light trapping reduces the overall efficiency of films, but their higher thermal conductivity relative to powders offers the possibility of increased excitation without thermal saturation or high temperature damage. Thus, it may be possible to achieve a higher brightness in REOS films than in the corresponding powders. Finally, the multiactivator host capabilities of REOS's suggested simple, physically and chemically compatible film layers for a voltage-selectable multicolor, multilayer cathodoluminescent screen.

Goldberg¹ has published a comprehensive review of luminescent thin film technology and properties. We recommend it to the reader as an index to luminescent film work up to 1965.

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