Electronic Structure and Excitonic Effects in $Sm_{1-x}R_xS$ Prior to Collapse

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X-ray photoemission spectra of $Sm_{1-x}R_xS$ (R=Ca, Y, Gd and Th) in the range prior to collapse ("black phase") exhibit only divalent samarium components. The $4f$ final state energy is found independent of lattice constant, but sensitive to $5d$ band screening. The fully screened final state $4f^5 5d$, ^6H, which is also involved in the interconfiguration fluctuation process, is found to reach the Fermi energy in a gradual insulator to metal transition. The results are interpreted to show that the modifications of the band structure which give rise to the phase transition are confined to the $5d$ level.

Introduction

The insulator to metal transition in SmS at a pressure of 6.5 Kb and in $Sm_{1-x}R_xS$ with increasing x for R = Gd, Y, Th, etc. is thought to take place when the narrow $4f$ level enters the broad $5d\,6s$ conduction band [1, 2]. Resistivity measurements in some of these systems have shown a change in the $4f-5d$ gap with impurity content [3]. Admittedly such a one-electron band structure model cannot provide a full description of what is generally recognized to be a complex many-electron process. Charge fluctuations require the coexistence of two configurations, here $4f^6$ and $4f^5 5d$, degenerate in energy, a situation incompatible with a simple band description [4]. X-ray photoemission measurements have been shown to provide information about the electronic structure of materials in the intermediate valence state [5]. However, the information is obtained from two $4f$ final state multiplet structures produced by the photoionization of the fluctuating initial state, and thus does not provide a complete picture of the initial state electronic structure. Moreover, the slightly filled conduction band states in the doped compounds are too close to the $4f$ level and their photoelectric cross-section at X-ray energies too small to allow them to be resolved.
Using XPS, which tests primarily bulk properties, we

did not find any evidence for the presence of trivalent samarium in the initial state in cation substituted SmS prior to collapse. We have previously shown, however, that the Sm $4f$ final state structure arising from the divalent initial state reflects the effects of Gd doping by separating into two divalent components [6]. In those measurements the absolute binding energies were not determined, leaving open a number of questions which we now address. The measurements have also been extended to include Ca, Y and Th substitution.

Experimental

The surfaces for the XPS experiment were prepared by cleaving oriented single crystals in a vacuum of $\sim 10^{-8}$ Torr in a chamber attached to the spectrometer. They were then transferred through vacuum into the main chamber of the spectrometer where they were measured in a low $\sim 10^{-9}$ Torr vacuum. Cleaved and optically flat surfaces were found to be chemically stable and the contamination remained negligible during the few hours required for the experiment. In order to locate the Fermi level the samples were coated with a thin layer of vacuum evaporated gold after the measurement, and the Au $4f$ lines and valence region recorded. In metallic

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systems this should be a reliable procedure since the Fermi levels will coincide. The Au $4f_{7/2}$ level was found to be 84.0 eV from the Fermi level, and was ultimately used as a reference because it could be located with greater precision. One interesting result is that the sulfur $2p_{3/2}$ level was found to be at 162.18 ± 0.06 eV in all samples after correction, i.e., fixed relative to the Fermi energy. This suggests that these levels can be used as internal reference standards in the study of these materials. Some earlier data for which the Au referencing procedure had not been used were found to fit well into the present systematic when the sulfur $2p$ level was used as a standard.

Since the motion of the Fermi level with doping must be quite small, less than 0.1 eV for 16% Gd, (using data for the tungsten bronzes [7] as a guide) the $2p$ level can equally well be described as fixed relative to the band structure. This is in accord with the conclusions reached regarding the oxygen levels in the cubic sodium tungsten bronzes [7] which are in some respects analogous to the sulfur levels in $Sm_{1-x}R_xS$ system.

In Figure 1c–f we show XPS spectra of the Sm $4f$ electron and valence band region of pure SmS and three substituted compounds. The concentration of the different substituents is such that comparable average lattice contraction is obtained in all cases (20% Ca, 8% Y and 7% Th).

The analysis of the Sm $4f$ final state structure [5] has been done with a model spectrum based on the calculated fractional parentage intensities of the final states [8] and energies taken from the optical spectra of Sm^{3+} in certain halides [9], Table 1. The line shape was represented by a convolution of our instrumental resolution function and a Doniach-Sunjic (DS) lineshape [10] with a lifetime width of 0.17 eV. For $\alpha > 0$ this line shape is of course rigorously applicable only in simple metals with broad conduction bands. However, in semiconductors with a gap small compared to the instrumental resolution it provides a useful approximation to the photoemission spectrum including the intrinsic excitations. The final state spectrum obtained by this process resemble those of the samarium chalcogenides giving some confidence that the parameters are satisfactory. For SmTe a good representation is obtained with α close to zero, as one might expect in an insulator, see Figure 1a.

Data for SmTe are shown in Fig. 18 of Reference 5. For SmSe and SmS values of α in the vicinity of 0.25 are required, see Figure 1b, but the fit (not shown) is not particularly satisfactory. This is a clear indication that the DS line shape with large α is not very useful in the present case. (In the earlier work [6] an *experimental* SmS spectrum was used in the analysis
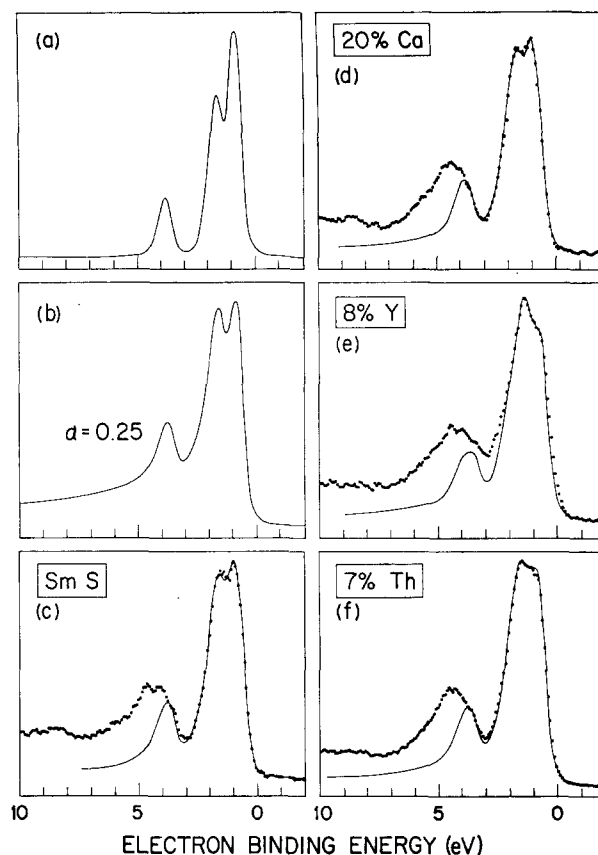

Fig. 1. Theoretical and experimental final state spectra of the $4f$ electron and valence band region of pure SmS and of Ca, Y and Th substituted SmS. (a) Theoretical final state spectrum based on the parameters of Table 1. The instrumental resolution function and a small lifetime width have been included. (b) The same as above, but including an appreciable many-body line asymmetry, (c)–(f) Fit to the data of SmS and $Sm_{1-x}R_xS$, for R=0.20 Ca, 0.08 Y and 0.07 Th, using the method described in the text. The position relative to E_F of the $^6H_{5/2}$ component as well as the intensity and displacement of the second weaker multiplet component used for the fitting procedure are given in Table 2

Table 1. Energies and Intensities of the Final State Multiplets Produced by the Photoionization of Sm^{2+}, f^6, $^7F_0$

	Energy (eV)	Intensity
$^6H_{5/2}$	0.006	0.898
$^6H_{7/2}$	0.134	2.245
$^6F_{5/2}$	0.884	1.428
$^6F_{7/2}$	0.989	0.571
$^6P_{5/2}$	2.988	0.816

of the substituted compounds, bypassing this problem.) A good fit to SmS as well as to all the data for the substituted compounds is readily obtained with α = 0.12 by simply adding a second divalent final state spectrum, displaced to grater binding energy, see Figure 1c. (For SmS the shift is 0.39 and the ampli-

Table 2

Concentration x of substituent R	Energy of the main $^6H_{5/2}$ component (relative to E_F) (eV)	Second weaker component	
		intensity relative to main component	displacement relative to main component (eV)
15 % Ca	0.97 ± 0.02	0.30 ± 0.05	0.39 ± 0.04
20 % Ca	0.98	0.30	0.39
15 % Gd	0.54	0.50	0.71
5 % Th	0.88	0.55	0.47
7 % Th	0.90	0.40	0.47
8 % Th	0.86	0.40	0.55
10 % Th	0.89	0.25	0.55
8 % Y	0.78	0.50	0.55
12 % Y	0.69	0.50	0.49
14 % Y	0.57	0.40	0.63
19 % Y	0.17	0.40	0.67

Fig. 2. Binding energy of the ^6H multiplet component of the final state spectrum of Sm^{2x} in the $Sm_{1-x}R_xS$ system (Data of Table 2)

tude 25 % of the main spectrum.) The origin of the experimental line shape distortion in SmS (points in Figure 1c), which we can to some extent represent by a DS function with large α, or better by adding a second displaced spectrum (as is the case for the fit in Figure 1c), has not been established. The electronic structure seems imcompatible with an interpretation based on shake-up or screening. The displaced component in pure SmS could correspond to samarium atoms in the surface layer [5], especially in view of its intensity which corresponds well to the fraction of surface atoms in the volume defined by the electron escape depth.

The analysis of the substituted compounds was also done in terms of two divalent spectra with separation and amplitudes as free parameters. The intensities and separation of the two divalent spectra were determined empirically so as to give the best possible fit, whose quality can be judged from Figure 1d–f. The result of the fitting procedure is given in Table 2. The main line in the present analysis corresponds to the line attributed to Sm with Gd nearest neighbour in the earlier work [6], which, even at low x values, represents the majority of the Sm. The second weaker component, which represents Sm ions with only Sm as nearest neighbour, will not be considered here because it lies further from the Fermi energy and thus does not contribute to the phase transition. It was then assumed that for those samarium atoms without impurity neighbours the d-band screening remains small.

Although this interpretation seems reasonable for small x, the substantial intensity associated with the second spectrum at larger x in the present analysis is
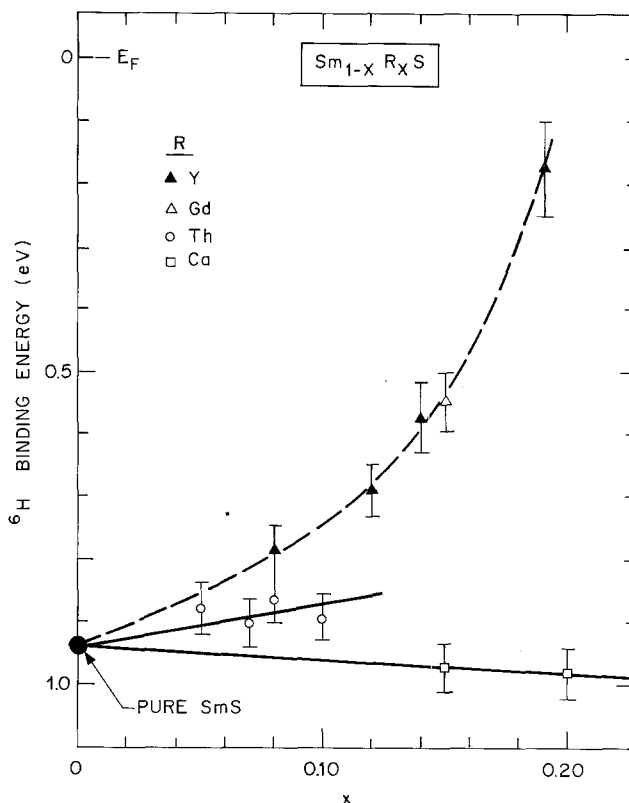
difficult to understand on this basis. A fuller interpretation depends on an understanding of the second component in pure SmS which is presumably also present in the substituted samples. Unfortunately, detailed analysis if further complicated by the possibility of an x-dependent many-body asymmetry. Further work is needed in this area.

The most important results of the present analysis are the absolute energies of the ^6H line of the main final states spectrum, see Figure 2. Note that the effect of the four substituents are distinct. Calcium produces only a very small shift away from the Fermi energy, i.e., in the sense to suppress the $I-M$ transition. Gadolinium and yttrium initially produce comparable shifts toward E_F, but that of Th is smaller. Since Th is twice as effective as Gd in promoting the $I-M$ transition, this immediately tells us that the binding energy shift is not to be interpreted as representing the cause of the phase transition. How then do we understand this concentration dependent shift? Is it related to the lattice constant or to electronic effects? Is it an initial or a final state effect?

The first point to note is that the XPS binding energy of the lowest energy multiplet in pure SmS is 0.94 eV, i.e., much larger than most estimates of the $f-d$ gap in this material which are of the order of 100 meV

[11]. The origin of this large discrepancy is not entirely clear, although it must be due to the different energy regimes of the various measurement techniques. In the spirit of Combescot and Nozières [12] two thresholds for $4f$ excitation are possible, the first, in the low energy optical regime, when the excited electron forms a *bound state* with the $4f$-hole, and the second, at higher energy, when the excited electron is delocalized and no excitonic state is produced. In this model the difference of about 0.8 eV between the two thresholds can be identified as the $4f$ *exciton* binding energy. The value for pure SmS is expected to vary with the conduction electron concentration, i.e., to decrease with increasingly effective d-screening. This is in accord with the experiment, as we shall see below. It appears clear that the $4f$ binding energy of the final state multiplet structure in XPS cannot be identified with that of the $4f$ state in other measurements.

The second observation is that the $4f$ state shifts only slightly with calcium substitution, and that the shift is in the direction of greater binding energy. This indicates clearly that the $4f$ binding energy does not depend on the lattice constant which changes significantly over the range studied. (Since calcium does not donate electrons into the $5d$ band there is no reason to expect a shift from an electronic mechanism.) The main effect of calcium substitution should be a narrowing of the empty $5d$ band because the lattice periodicity is partially destroyed by the substitution. This effect must dominate the broadening due to the decrease in the lattice constant, because the pressure for collapse increases with calcium substitution [3].

The most interesting results are those for yttrium substitution, which leads to a gradual $I-M$ transition preceded by a substantial decrease in lattice constant. It seems plausible that the electrons donated into the $5d$ band by yttrium are largely delocalized at the high concentration where the transition takes place. The $4f$ binding energy undergoes a large, nonlinear decrease with yttrium substitution, reaching a value close to zero just before the gradual collapse. One could attempt to explain this shift as a change in the initial state binding energy due to increasing population of the $5d$ band, but three observations argue against this proposal. (1) The shift is larger than the best values for the $f-d$ gap. This supports the model of Combescot and Nozière, as discussed above. (2) The shift is nonlinear with yttrium concentration. (3) The shift is larger than expected on the basis of $4f$ shifts in the cubic sodium thungsen bronzes [7]. The shift must therefore be a final state effect due to increasingly effective screening of the hole state by conduction electron. When fully screened by d electrons the final state is effec-

tively $4f^5 5d^1$, i.e., the same as one of the states involved in the interconfiguration fluctuation process. A vanishing binding energy, equivalent to a vanishing excitation energy, is exactly the condition which initiates charge fluctuations. In this sense the XPS measurements are capable of giving the most directly relevant information about the intermediate valence phenomenon.

It is interesting to note in this connection that in charge-fluctuating compounds the lowest energy multiplet of the lower-valence final state is always found at the Fermi energy [5]. This state is equivalent to the higher valence member of the two states involved in the interconfiguration fluctuation process. This is illustrated by a spectrum of partially collapsed $Sm_{0.81}Y_{0.19}S$ which shows the ^6H multiplet at the Fermi energy [13].

The data for gadolinium substitution show a comparable change in both lattice constant and $4f$ binding energy shift but are terminated by the sudden collapse at 16 % substitution. This indicates that an instability is reached before the $4f^5 5d$ state actually reaches the Fermi energy. This is the same instability which causes the sudden collapse under pressure. The interesting question is why yttrium and gadolinium produce such distinct types of behavior. The answer is to be found in the different effects which the substituents have on the $5d$ conduction band. The $4d$ electronic states of yttrium are not likely to become part of the Sm-derived $5d$ band. Yttrium, in this respect, is more like calcium. The band broadening due to the decreased lattice constant is partially counteracted by the dilution of the lattice. For gadolinium substitution there is little reason to doubt that the $5d$ band remains intact, except insofar as the presence of the trivalent ions causes a state to be split off from the bottom of the band. At very low conentrations these states resemble donor states in semiconductors. At higher concentrations they may form an impurity band which eventually merges with the Sm-derived $5d$ band, in effect lowering the band edge toward the $4f$ level. This provides a way of understanding the mechanism for the electronically generated sudden collapse in terms of a band model. Yttrium may also be less effective than gadolinium in promoting collapse simply because its $4d$ states lie higher than the $5d$ states of gadolinium.

The effects of thorium substitution are qualitatively similar to those of gadolinium, but more extreme. The small shift of the $Sm ^6H$ state in XPS indicates that electronic screening in the XPS process does not become important prior to collapse, presumably because the $4+$ substituent prevents delocalization of the electrons in the $Sm 5d$ band. Collapse occurs at smaller concentration because each tetravalent Th

formally provides two electrons to the formation of the impurity band. It also seems plausible that in SmS the $6d$ orbitals of Th have higher binding energy than those of Gd, providing a more effective way of reducing the $f-d$ gap.

The present measurements lead to the conclusion that the $I-M$ transition in $Sm_{1-x}R_xS$ is brought about by changes in the energy of the bottom of the $5d$ band. In this respect the conclusion is analogous to those reached by Batlogg et al. [14] in their studies on pure SmS under pressure, indicating that in this case chemical substitution may in a broad sense simulate pressure effects. The wide variety of behavior which is encountered with different substituents can be understood on this basis. XPS measurements show that the $4f$ binding energy is not sensitive to changes in the lattice constant, but is strongly affected by $5d$ screening. As metallic conductivity is approached the screened final ^6H state reaches the Fermi energy making possible interconfiguration fluctuation between $4f^6$ and $4f^55d$. The sudden collapse with pressure, or over a small range of x for certain substituents is described in terms of the effect of ions of valency higher than $2+$ on the bottom of the $5d$ band.

References

1. Valence Instabilities and Related Narrow-Band Phenomena (R.D. Parks, editor) pp. 3, 61, 73, 85, 153, 211, 321, 411, 419, 427, 507, 541. New York and London: Plenum Press 1977
2. Tao, L.J., Holtzberg, F.: Phys. Rev. B11, 3842 (1975)
3. Jayaraman, A., Dernier, D.P., Longinotti, L.D.: Ref. 1, p. 61 and references cited therein
4. Hirst, L.L.: Ref. 1, p. 3 and references cited therein
5. Campagna, M., Wertheim, G.K., Bucher, E.: Struct. Bonding 30, 99 (1976) and references cited therein
6. Campagna, M., Chui, S.T., Wertheim, G.K., Tosatti, E.: Phys. Rev. B14, 653 (1976)
7. Chazalviel, J.-N., Campagna, M., Wertheim, G.K., Shanks, H.R.: Phys. Rev. B16, 697 (1977)
8. Cox, P.A.: Struct. Bonding 24, 59 (1975)
9. Carnall, W.T., Fields, P.R., Rajnak, K.: J. Chem. Phys. 49, 4424 (1968)
10. Doniach, S., Sunjic, M.: J. Phys. C: Solid State Physics 3, 285 (1970)
11. Kaldis, E., Wachter, P.: Solid State Commun. 11, 907 (1972)
12. Combescot, M., Nozières, P.: J. Phys. (Paris) 32, 913 (1971)
13. Pollak, R.A., Holtzberg, F., Freeouf, J.H., Eastman, D.E.: Phys. Rev. Lett. 33, 820 (1974)
14. Batlogg, B., Schoenes, J., Wachter, P.: Phys. Lett. 49A, 13 (1974)

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