Anomalous behavior of Sm^{2+}–Sm^{3+} electronic transition in solid solutions of SmS with lanthanum

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The electronic structures of Sm, La, and Eu in $Sm_{1-x}La_xS$ and $Eu_{1-x}La_xS$ ($0 \leq x \leq 1$, $77 \leq T \lesssim 100$ K) are investigated by the x-ray K-line shift method [O. I. Sumbaev, Sov. Phys. Usp. **21**, 141 (1978)]. It is shown that although the lattice parameters of $Sm_{1-x}La_xS$ and $Eu_{1-x}La_xS$ decrease smoothly with increasing x [M. Gronau and S. Methfessel, Physica, 86–88, B + C, 218 (1977); F. Holtzberg, A. I. P. Conference Proceedings **18**, 478 (1974)], the electronic structure of Sm (the number of $4f$ electrons) in $Sm_{1-x}La_xS$ undergoes a substantial change: the valence of Sm increases relatively rapidly in the region $0 \leq x \lesssim 0.4$, and assumes at $x \approx 0.4$ a constant value independent either of temperature ($77 \leq T \lesssim 1000$ K, $x = 0.5$–0.75) or of the pressure applied to the sample ($P \approx 12$ kbar, $x = 0.5$). The valence of Sm in the collapsed phase (intermediate valence state) $m = 2.28 \pm 0.01$ and the transition limit $x \approx 0.4$ in $Sm_{1-x}La_xS$ differ substantially from the analogous quantities for alloys of SmS with sulfides of other trivalent rare-earth elements [I. A. Smirnov and V. S. Oskotskiĭ, Sov. Phys. Usp. **21**, 117 (1978)]. A comparison of the experimental data with those calculated for different variants of the electronic transition ($4f \rightarrow 5d$, $4f \rightarrow 6s$, $4f \rightarrow \infty$) [I. M. Band and M. B. Trzhaskovskaya, Tables of Electron Energy Eigenvalues and Densities near Zero and of the Mean Values in Self-Consistent Fields of Atoms and Ions, Preprint No. 91, Leningrad Institute of Nuclear Physics, 1974] shows that in this transformation the $4f$ electron is more likely to go over into the $5d$ band. The valences of La and Eu for all the investigated samples is the same as in LaS and EuS.

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INTRODUCTION

In solid solutions of SmS with monosulfides of rare earth elements (REE) [$Sm_{1-x}R_x^{3+}S$; $Sm(R^{3+})S$], an electronic transition Sm^{2+}–Sm^{3+} is observed[1] in the microscopic and macroscopic properties of the sample[2] and is accompanied by a characteristic change, independent of the type of partner (R^{3+}). The lattice parameter, color, conductivity, magnetic susceptibility, isometric and x-ray shifts, etc. change jumpwise in this transition. This is apparently due to the fact that the monosulfides of the trivalent REE have the same band structure.

An exception from this rule is the solid solution $Sm_{1-x}La_xS$, for which, with increasing lanthanum concentration, a smooth change takes place in both the color[1] and in the lattice parameter,[3] and the change of the latter is accompanied by a considerable deviation from the Vegard law. The Mössbauer data on Sm(La)S (Ref. 4) are quite similar to the analogous data for $Sm(R^{3+})S$ (R^{3+} = Gd, Tm, Y) and are identical with the data for $Sm(Ca^{2+})S$. The dependence of the lattice parameter of Sm(La)S on the concentration has a behavior similar to that of Eu(La)S, for which there should be no electronic transition because of the insufficient $4f$-$5d$ hybridization in Eu.[3]

The absence of chemical collapse in Sm(La)S is attributed in Ref. 5 to the fact that the lattice parameter of LaS($d = 5.85$ Å) is larger than the lattice parameter of $Sm^{3+}S$($d = 5.62$ Å), so that the "chemical pressure" is insufficient to "crowd out" the $4f$ electron into the conduction band. However, in the case of CeS, PrS, and NdS, whose lattice parameters are also larger than $d_{Sm^{3+}S}$,[6] a characteristic jumplike isomorphous phase transition takes place. On the other hand, the compressibility of the lattice, the position of the reflection edge,[5] and the magnetic susceptibility[7] in this system have anomalies at an La concentration $x \approx 0.3$, and these can be attributed to the Sm-valence changes suggested in Ref. 8.

These singularities in the behavior of the alloy of SmS with LaS have prompted us to investigate the electronic states of the Sm, La, and Eu ions in Sm(La)S and Eu(La)S.

EXPERIMENTAL RESULTS

The electronic states of Sm, La, and Eu in Sm(La)S and Eu(La)S alloys were determined by the x-ray line shift (XLS) method. This method and the experimental setup are described in previously published papers (see, e.g., Ref. 9). The investigated samples were produced by sintering (at near-melting temperatures) of thoroughly ground mixtures of the corresponding monosulfides in a molybdenum crucible. The obtained solid solutions had an NaCl structure with lattice parameters (Figs. 1a and 2a) and color close to those in the published data.[3,8] In addition, it was established by the XLS method that the Sm and Eu ions in the initial SmS and EuS are in the divalent state, while La in LaS is trivalent, just as Nd, Gd, and Tm are in the corresponding monosulfides.[9]

In the main experiment we measured the shifts of the K_{α_1} and K_{β_1} x-ray lines of Sm and La (or of Eu and La) in Sm(La)S [or Eu(La)S] at room temperature ($T \approx 300$ K), nitrogen temperature ($T = 77$ K), or high temperature ($T \approx 1000$ K), or else at high pressure ($P \approx 12$ kbar), relative to these quantities for the mechanical mixture SmS + LaS (or EuS + LaS) under normal conditions.

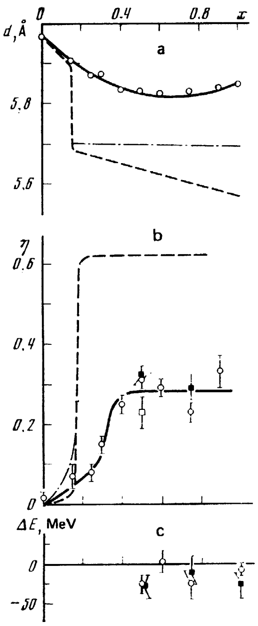

FIG. 1. Experimental dependences of the lattice parameter (d), of the degree of removal of the samarium 4f electron (η), and of the shift of the K_{α_1} x-ray line of La(ΔE) in $Sm_{1-x}La_xS$ on the composition (○ – T≈300K, ■ – T≈1000 K, □ – T = 77K a) The solid, dashed, and dash-dot lines give the values of d(x) for $Sm_{1-x}La_xS$,[3] $Sm_{1-x}Gd_xS$,[1] and $Sm_{1-x}Nd_xS$ (d(x) for Sm(Nd)S was measured in the present study on the samples investigated in Ref. 12). b) Dashed and dash-dot curves—ν(x), respectively for $Sm_{1-x}Gd_xS$ (Refs. 10 and 11) and $Sm_{1-x}Nd_xS$.[12]

In the $Sm_{1-x}La_xS$ samples at $x \gtrsim 0.4$, considerable shifts of the x-ray K lines of Sm were observed, thus attesting unequivocally to a change in the electronic structure of the Sm in this compound. The shifts and their dependence on the type of line ("facsimile") correspond to a change in the number of the $4f$ electrons of Sm, i.e., to the electronic transition Sm^{2+}, $4f^6$-Sm^{3+}. $4f^5+e$. The ratio of these shifts to the shift due to removal of one $4f$ electron (the shift for the pair of ionic compounds Sm^{2+}-Sm^{3+}) yields the fraction η of the $4f$ electrons removed in the transition, a quantity connected with the valence by the simple relation $m = m_0 + \eta$, where m_0 is the valence of the comparison reference. The mean-weighted (over the data for the K_{α_1} and K_{β_1} lines) value of η as a function of the sample composition is shown in Fig. 1b (which shows also the analogous data for Sm(Gd)S and Sm(Nd)S, obtained in Refs. 10–12. It is seen from the figure that at $0 \leqslant x \leqslant 0.4$ a relatively rapid increase of the valence of Sm in $Sm_{1-x}La_xS$ takes place, from 2 to 2.28 ± 0.01 (the mean value for the region $0.4 \leqslant x \leqslant 0.9$). The results of the measurements at nitrogen and high temperatures for the samples with $x = 0.5$ and 0.75 do not differ, within the limits of the measurement errors, from those at room temperature. Hydrostatic compression of the samples with $x = 0.5$ up to $P \approx 12$ kbar likewise does not increase the valence of Sm[$\eta(P \approx 12$ kbar$) = 0.14 \pm 0.08$].

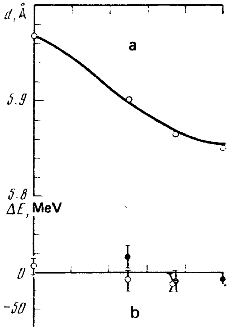

FIG. 2. Experimental dependences of the lattice parameter (d) and of the shifts of K_{α_1} x-ray lines of Eu and La in $Eu_{1-x}La_xS$ on the composition. a) Solid curve—d(x) for Eu (La)S,[3] b) ○–shifts ΔE of K_{α_1} line of Eu, ●–shifts ΔE of K_{α_1} line of La.

The XLS method makes it also possible to trace the subsequent fate of the $4f$ electron. Indeed, as shown by self-consistent calculations of the Hartree-Fock type,[13] the K-line shifts differ noticeably, depending on the final state reached by the $4f$ electron [the $6s(p)$ state, the $5d$ state, or infinity]. For example, for the K_{α_1} line of Sm $\Delta E(4f \to 6s) = -715$ MeV, $\Delta E(4f \to 5d) = -606$ MeV, and $\Delta E(4f \to \infty) = -664$ MeV. Since the change in the number of $4f$ electrons investigated by us is not an integer and the calculation agrees with experiment with ~20% accuracy in absolute value, a more reliable procedure is to compare the calculated and experimental data for the ratio $\varkappa \equiv \Delta E_{K_{\beta_1}} / \Delta E_{K_{\alpha_1}}$. Self-consistent calculations[13] yield for $\varkappa_p$ the values 2.48, 2.90, and 2.52 respectively for the transitions $4f \to 6s$, $4f \to 5d$ and $4f \to \infty$. The experimental value is $\bar{\varkappa}_{\exp} = 3.07 \pm 0.17$.

It is seen that the best agreement between the calculated and experimental data is observed for the case of the transition of the $4f$ electron to the $5d$ state ($\varkappa_p = 2.90$).[1)] Thus, it can be assumed that in the electronic transition Sm^{2+}-Sm^{3+} in Sm(La)S the $4f$ electron goes over to the $5d$ band.[2)] Allowance for the final state reached by the $4f$ electron leads to a somewhat different value of the valence of Sm in the collapsed phase, but this difference is not large and does not exceed the measurement error.

The shifts of the K lines of lanthanum in $Sm_{1-x}La_xS$ (see Fig. 1c) are close to zero regardless of the composition and temperature of the investigated samples. This means that the valence of La in these alloys remains unchanged within the limits of the measurement errors, i.e., the electronic state of lanthanum in the solid solution Sm(La)S is the same as in pure LaS. The results of the experiment for Eu(La)S are shown in Fig. 2b.

DISCUSSION OF RESULTS

The cited experimental results indicate unequivocally that the electronic transition Sm^{2+}, $4f^6$-Sm^{3+}, $4f^5 5d$ takes place in Sm(La)S. These data agree qualitatively with data on the compressibility of the lattice and on the behavior of the reflection edge in $Sm_{1-x}La_xS$ (Ref. 5) (the presence of the jumps of the indicated quantities at $x < 0.3$ and their absence at $x \gtrsim 0.3$), with the data on the magnetic susceptibility,[7] as well as with the estimate of the valence of Sm from the change of the lattice parameter of the alloy as a function of its composition.[8]

Thus, the principal mechanism of the transition in

Sm(La)S is the same as in the alloys of SmS with other trivalent REE. The details of the transition, however, are substantially different in this case from the analogous characteristics of similar systems. The lattice parameter of Sm(La)S varies smoothly, as against the jumplike change in the other $Sm(R^{3+})S$ alloys. A jumplike change takes place also in the population of the $4f$ state of Sm in Sm(Gd)S and Sm(Nd)S (Fig. 1b). The behavior of $\eta(x)$ in the case of $Sm_{1-x}La_xS$ is somewhat different: in the region $0 \leqslant x \leqslant 0.4$, the value of η increases from 0 to ≈ 0.3, and assumes a constant value at $x \approx 0.4$, just as in the case of Sm(Gd)S and Sm(Nd)S. However, the change of the valence of Sm in Sm(La)S is approximately one-half of the change for the alloys Sm(Gd)S and Sm(Nd)S($\eta_{Sm(Gd)S} \approx \eta_{Sm(Nd)S} = 0.62-0.64$; $\eta_{Sm(La)S} = 0.28 \pm 0.01$, (see Fig. 1b) and is not increased by either a change of temperature ($77 \leqslant T \lesssim 1000$ K) or by application of hydrostatic compression up to $P \approx 12$ kbar.

This difference between the changes of the valence of Sm in the alloys Sm(La)S and $Sm(R^{3+})S(R^{3+} = Gd, Nd\ldots)$ is quite appreciable.[3] The valence of Sm in the collapsed phase in $Sm_{1-x}R_x^{3+}S$, in a region far enough from critical ($x > x_{cr}$), is explained in some models[16,17] as being due to the equality of the total energies of the states of Sm^{2+} and Sm^{3+}, i.e., to the zero excitation energy of $\Delta(Sm^{2+} \rightarrow Sm^{3+})$. In this case the valence of Sm should be $m = 2.57$ (Ref. 17) for all R^{3+}. For Sm(La)S, however, this model seems to be incorrect, since the observed valence change is $\eta = 0.28$. The limit of the transition ($x \approx 0.4$) in $Sm_{1-x}La_xS$ is also substantially different (by approximately two times) from that of other $Sm(R^{3+})S$ alloys and disagrees completely with the Gronau systematics, which calls for an increase of the critical concentration with increasing z of the trivalent partner. This systematics, however, seems to be less reliable, since it is not confirmed by the well investigated cases of Sm(Gd)S,[1] Sm(Nd)S,[5] and Sm(Tm)S.[4] On the other hand, the lattice parameter of $Sm_{1-x}La_xS$ at the point $x = 0.4$ is in good agreement with the lattice parameters of other $Sm_{1-x}R_xS$ alloys (R = Pr, Tb, Dy, Ho, Gd, Th) (Refs. 2, 3) at concentrations x close to (but smaller than) critical; this can be evidence of a substantial influence of the volume of the unit cell on the transition. The results should be a decrease of x_{cr} with decreasing ionic radius of R^{3+} (i.e., with increasing z of the REE). However, the lattice parameter of the Sm(R)S alloy in the subcritical region does not obey the Vegard law (the deviation being towards smaller values of d for R = La, Pr, Nd, Gd, Y and Th and towards larger values for Tb, Dy, and Ho). This seems to distort greatly the picture of the influence of the dimension of the R^{3+} ion on the phase transition.

In the investigated solid solution Eu(La)S the shifts of the x-ray K lines of Eu and La are close to zero. The experimentally obtained change of the valence of Eu (due to the partial transition of the $4f$ electron to the conduction band) is $\bar{\eta}_{exp} = 0.019 \pm 0.014$ for $x = 0.5 \pm 0.75$, and is substantially larger than the value expected from the change of the lattice parameter ($\eta_{expect} = 0.09$). This is evidence that the electronic states of Eu and La in the Eu(La)S alloy remain unchanged (within the limits of the measurement errors).

In conclusion, the authors thank O. I. Sumbaev for valuable discussions, V. I. Kozlov, and I. I. Mosichev for help in sample preparation, L. E. Samsonov for taking care of the electronics, and Yu. I. Vasil'ev for help with the measurements.

[1] The analogous experimental value $x_{exp} = 2.45 \pm 0.05$ for the known cases of ionic divalent and trivalent samarium compounds agrees well with the calculated value x_{calc} $(4f \rightarrow \infty) = 2.52$.

[2] The 4f electron of Sm goes over to the same final state in the related compound Sm(Y)S.[14]

[3] The value obtained in Ref. 8 is $\eta Sm(La)S = 0.5{,}0{,}6$ for $x \gtrsim 0.4$, i.e., practically the same as for the other $Sm(R^{3+})S$ alloys. It must be taken into account, however, that the estimate of the valence from x-ray structure data is a less direct method (than XLS) and is therefore less accurate. In fact:
1. For the alloy $Sm_{1-x}Eu_xS$ the lattice parameter $d(x)$ is practically constant for the entire range $0 \leqslant X \leqslant 1$, whereas $\nu(x)$ increases smoothly from 0 to 0.4—0.5 (at $x = 0.8$).[12,15]
2. For the alloy $Sm_{1-x}Tb_xS$ (Ref. 3) the changes of $d(x)$ at $x < x_{cr}$ correspond to valences of $Sm(m_{sm} < 2)$ or Tb $(m_{Tb} < 3)$, which are not realized in practice (see, e.g., Ref. 9).

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