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Translated by J. G. Adashko

## Electronic mechanism of the high-temperature phase transitions in SmS and Sm<sub>1-x</sub>Gd<sub>x</sub>S

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(Submitted February 9, 1977)

Zh. Eksp. Teor. Fiz. 73, 961-966 (September 1977)

The electronic mechanism of the phase transitions in Sm<sub>1-x</sub>Gd<sub>x</sub>S [A. Yayaraman *et al.*, Phys. Rev. Lett. 31, 700 (1973)] has been investigated by the x-ray *K*-line shift method [E. V. Petrovich *et al.*, Sov. Phys. JETP 34, 935 (1972)] in a wide concentration and temperature range ( $0 \leq x \leq 0.40$ ;  $300 \leq T \leq 1000$  K). A smooth variation of the valency of samarium with increasing  $x$  has been observed at a high temperature, in contrast to the well-investigated discontinuous variation observed at room temperature [A. Yayaraman *et al.*, Phys. Rev. Lett. 31, 700 (1973); V. A. Shaburov *et al.*, Sov. Phys. JETP 41, 158 (1975)]. It has also been found that the valency of samarium increases in SmS and decreases in Sm<sub>0.81</sub>Gd<sub>0.19</sub>S with increasing temperature. It is shown that the observed effects are due to the  $4f \rightleftharpoons$  band electron transition. The valency of samarium in SmS and Sm<sub>0.81</sub>Gd<sub>0.19</sub>S varies in the range  $300 \leq T \leq 1000$  K respectively from  $m = 2$  to  $m = 2.18 \pm 0.02$  and from  $m = 2.42 \pm 0.02$  to  $m = 2.27 \pm 0.02$ . At  $T \approx 1000$  K the valency of samarium increases in the region  $0 \leq x \leq 0.40$  from  $m = 2.18 \pm 0.02$  to  $m = 2.62 \pm 0.02$ . The dependences of the Sm<sup>2+</sup>→Sm<sup>3+</sup> transition energy on the gadolinium concentration and on temperature are computed under the assumption of thermal excitation of  $4f$  electrons into the conduction band [B. C. Salest and D. K. Wohleben, Phys. Rev. Lett. 35, 1240 (1975)].

PACS numbers: 72.60.+g

### INTRODUCTION

The isomorphic phase transitions in Sm<sub>1-x</sub>Gd<sub>x</sub>S ( $B \rightarrow M$  and  $M \rightarrow B'$ <sup>[1]</sup>) were investigated by the x-ray line shift method at room and liquid-nitrogen temperatures in our previous work.<sup>[2]</sup> We discovered that to the phase transitions correspond discontinuous changes in the energy of the x-ray *K* lines of samarium, changes which form a *V*-shaped "facsimile"<sup>[3]</sup> typical of  $4f$  electrons and corresponding to changes in the valency of samarium due to  $4f \rightleftharpoons$  band electron transitions. In the transition from the semiconducting *B* phase to the metallized *M* phase ( $x \gtrsim x_{cr} \approx 0.16$ ,  $T \approx 300$  K) the valency of samarium increases discontinuously from  $m = 2$  to the value  $m = 2.62 \pm 0.03$ ; the transition from the *M* phase to the low-temperature intermediate *B'* phase ( $0.16 \leq x \leq 0.22$ ,  $T < 100$  K) is accompanied by a decrease in the valency of samarium (also discontinuously) from  $m = 2.62 \pm 0.03$  to  $m = 2.08 \pm 0.01$ .<sup>[2]</sup>

Recently, Yayaraman and his co-workers<sup>[4]</sup> observed at high temperatures ( $T > 400$  K) an abnormally larger thermal expansion of the crystal lattice of samples of Sm<sub>1-x</sub>Gd<sub>x</sub>S of the intermediate composition:  $0.16 \leq x \leq 0.22$ . (The relative change in the lattice constant was  $\Delta d/d \approx 2.3\%$  for  $x = 0.18$  in the range  $T \approx 300-900$  K.) Such a large thermal expansion of the *M* phase of

Sm<sub>1-x</sub>Gd<sub>x</sub>S is, in the opinion of these authors, due to the trapping of conduction electrons of samarium in the  $4f$  states (i. e., to the  $5d-4f$  transition) and, accordingly, to the change in the valency from  $m \approx 2.8$  to  $m \approx 2$ .

The lattice constant of Sm<sub>1-x</sub>Gd<sub>x</sub>S at a high temperature varies continuously. This circumstance makes it difficult to elucidate the mechanism of the effect and determine the changes in the valency from the crystallographic data, since the changes in the lattice constant due to the  $5d-4f$  transition are maximized by the usual thermal expansion, which in a number of cases is substantial (e. g., in EuS and NdS the ratios  $\Delta d/d \approx 1\%$  in the range  $300 \leq T \leq 1000$  K<sup>[5]</sup>).

The purpose of the present paper is to elucidate by the x-ray *K*-line shift method the electronic mechanism of the high-temperature transition in SmS and Sm<sub>1-x</sub>Gd<sub>x</sub>S and to determine the change in the valence state of the samarium atom in this transition.

### RESULTS OF THE EXPERIMENT

In the experiment we measured the shifts of the x-ray *K* lines of samarium in Sm<sub>1-x</sub>Gd<sub>x</sub>S ( $0 \leq x \leq 0.40$ ) relative to the same lines of a reference SmS sample as a function of temperature and the gadolinium concentration. The measurements were performed on a special Cau-

chois-type x-ray crystal-diffraction spectrometer with improved (in comparison with the previous<sup>[6]</sup>) luminosity. The optimization of the latter was accomplished with allowance for the elastic quasimosaic effect.<sup>[7]</sup> Calculations, done in much the same way as those performed by the authors of Ref. 8, showed that the optimum quartz plate for the measurement of the x-ray  $K$ -line shifts in the region of the rare-earth elements is a plate with  $20\bar{2}3$  reflecting planes (thickness  $T = 1.8$  mm, flexure coefficient of the reflecting planes  $k = 2 \times 10^{-4} \text{ cm}^{-1}$ ).<sup>[8]</sup> The use of such a plate enabled us to obtain a luminosity four times greater than in a plate with 1340 reflecting planes. The control of the spectrometer in the shift measurements with the subsequent processing of the results were fully automated on the basis of an "Elektronika-100" electronic computer.

The comparable samples are a thoroughly blended mixture of powdered  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  (or  $\text{SmS}$ ) and spectroscopically pure graphite placed in identical high-temperature vacuum quartz cells, whose construction is described in Ref. 9. The reference sample ( $\text{SmS}$ ) was kept at room temperature, while the temperature of the second sample ( $\text{Sm}_{1-x}\text{Gd}_x\text{S}$ ,  $0 \leq x \leq 0.40$ ) was varied in the range 300–1000 K. The system was prepared by melting together in an airtight tantalum crucible in a vacuum a well-ground  $\text{SmS} + \text{GdS}$  mixture with subsequent rapid cooling of the melt to room temperature.

In Fig. 1 we give the results of the experiments: the shifts of the  $K_{\beta_1}$  line of samarium in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  for different compositions of the sample under investigation as a function of the temperature.<sup>1)</sup> For pure  $\text{SmS}$  and a sample with a 19-percent gadolinium content a reversible effect is observed which is characterized by the variation of the energy of the  $K_{\beta_1}$  line of the heated sample. The reversibility of the effect was demonstrated in control measurements of the shifts after the high-temperature experiment (the sample under study had been cooled to room temperature). Within the limits of the measurement errors, the shifts before and after the high-temperature experiment coincide (see Figs. 1 and 2). In the  $x = 0.40$  sample the effect is absent (within the limits of the measurement errors) in the entire range of investigated temperatures.

Figure 2 depicts the behavior of the shift of the  $K_{\beta_1}$  line of samarium in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  as a function of the gad-

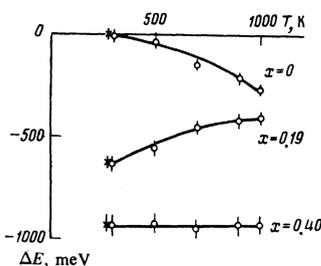


FIG. 1. Dependence of the shift of the  $K_{\beta_1}$  line of samarium in  $\text{SmS}$  (upper curve),  $\text{Sm}_{0.81}\text{Gd}_{0.19}\text{S}$  (middle curve), and  $\text{Sm}_{0.60}\text{Gd}_{0.40}\text{S}$  (lower curve) on temperature:  $\times$ ) check experiment—measurements at room temperature after the high-temperature experiment.

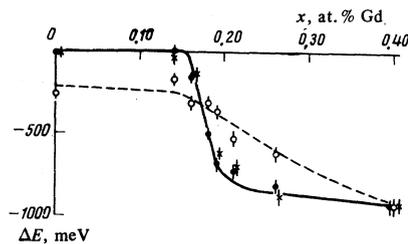


FIG. 2. Dependence of the shift of the  $K_{\beta_1}$  line of samarium in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  on the gadolinium concentration: for the continuous curve and  $\bullet$ )  $T \approx 300$  K; for the dashed curve and  $\circ$ )  $T \approx 1000$  K;  $\times$ ) control experiment: measurements at room temperature after the high-temperature experiment.

olinium concentration at room and high temperatures. The curve corresponding to the measurements at room temperature duplicates the analogous curve obtained in our previous work.<sup>[2]</sup> (The small difference between them can be connected with the different methods of obliterating the past histories: in the present work this was high-temperature annealing, while in Ref. 2 it was cooling to the temperature of liquid nitrogen.) Characteristic of the continuous curve ( $T \approx 300$  K) is a sharp transition at  $x \approx 0.16$  (the energy of the  $K_{\beta_1}$  line of samarium changes in the  $0.16 \leq x \leq 0.19$  region by almost one electron volt). The dependence at  $T \approx 1000$  K has, however, a smooth character, the  $K_{\beta_1}$ -line shift being nonzero even for  $x = 0$ .

The nature of the effect was elucidated in the study of the dependences of the shift on the type of line ( $K_{\alpha_1}$ ,  $K_{\beta_1}$ ,  $K_{\beta_{2,4}}$ ) and their comparison with the reference facsimile for a standard  $\text{SmF}_3$ - $\text{SmCl}_2$  pair considered as ionic compounds of trivalent and divalent samarium with configurations  $4f^5$  in the case of  $\text{Sm}^{2+}$  and  $4f^6$  for  $\text{Sm}^{3+}$ .<sup>[2]</sup> The results are shown in Fig. 3.

The high-temperature facsimiles ( $T \approx 1000$  K), as well as the facsimiles for  $T \approx 300$  K,  $x = 0.19$ , have a characteristic V shape similar to the shape of the reference facsimile for  $\text{Sm}^{3+}$ - $\text{Sm}^{2+}$ . This means that the valency of samarium in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  at  $T \approx 1000$  K,  $x \geq 0$  (and at  $T \approx 300$  K,  $x \geq 0.16$ ) is higher than the valency in  $\text{SmS}$  ( $T \approx 300$  K), the increase in valency being connected with a decrease in the number of the  $4f$  electrons.

From the experimental values of the  $K_{\beta_1}$ -line shifts we can find the fraction,  $\eta$ , of the  $4f$  electrons removed from the samarium atom for different temperatures and concentrations of the samples. They are equal to the ratios of the corresponding shifts to the calibration shift,  $\Delta E_{K_{\beta_1}}(\text{Sm}^{3+}, 4f^5 - \text{Sm}^{2+}, 4f^6) = -1490 \pm 26$  mV, of the  $K_{\beta_1}$  line of samarium. Using the quantity  $\eta$ , we can easily determine the dependence of the valency of the samarium atom on temperature and on the gadolinium concentration:

$$m(T, x) = 2 + \eta(T, x).$$

## DISCUSSION OF THE RESULTS AND CONCLUSIONS

The reversible variation, observed in the experiments with  $\text{SmS}$  and  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$ , of the energy of the  $K_{\beta_1}$

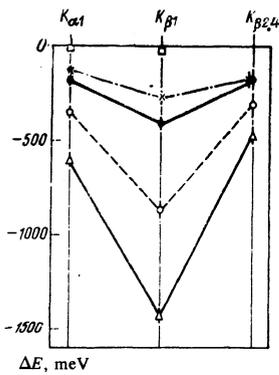


FIG. 3. Shift vs type-of-line curves (facsimiles). The thin continuous curve at the bottom and  $\Delta$ ) calibration curve for the chemical samarium compounds  $\text{SmF}_3\text{-SmCl}_2$ ; the dashed curve,  $\circ$ ) and the heavy curve,  $\bullet$ ) facsimiles for  $\text{Sm}_{0.81}\text{Gd}_{0.19}\text{S}$  respectively at  $T \approx 300$  K and  $T \approx 1000$  K; dot-dash curve and  $\times$ ) facsimile for  $\text{SmS}$  at the high temperature ( $T \approx 1000$  K);  $\square$ ) control experiment:  $\text{SmS}$  at  $T \approx 300$  K. All the shifts are given relative to the shifts for  $\text{SmS}$  at room temperature.

line of samarium with temperature is undoubtedly connected with the reconstruction of the  $4f$  shell of the samarium atom. The  $4f \rightarrow$  band transition in  $\text{SmS}$ , initiated by pressure, can thus also be initiated by temperature. (The possibility of the latter can also be predicted from the behavior of the electrical, magnetic, x-ray spectral, and other properties of  $\text{SmS}$  at high temperatures: see, for example, Ref. 5, which is a review.) However, the character and magnitude of the effect observed in  $\text{SmS}$  under pressure are different from the character and magnitude of the effect observed in the same material at a high temperature. In the first case ( $P \approx 6.5$  kbar,  $T \approx 300$  K) there occurs in the energy of the  $K$  lines of samarium a steep, jumplike change corresponding to an increase in the valency of the element from  $m = 2$  to  $m = 2.62$ .<sup>[2]</sup> In the second case the  $K$ -line energy varies continuously; the valency of samarium also increases (with increasing temperature), but this change is not large: the valency attains the value  $m = 2.18 \pm 0.02$  at  $T \approx 1000$  K. The transition in  $\text{Sm}_{0.81}\text{Gd}_{0.19}\text{S}$  has the same reversible character, but here there is observed a smooth decrease of the valency with increasing temperature from  $m = 2.42 \pm 0.02$  at  $T \approx 300$  K to  $m = 2.27 \pm 0.02$  at  $T \approx 1000$  K.

In samples with high gadolinium contents, the valency of samarium does not depend on temperature: for  $x = 0.40$ ,  $\bar{m} = 2.62 \pm 0.02$  in the entire investigated region,  $300 \lesssim T \lesssim 1000$  K.<sup>[2]</sup>

The transition in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  is smooth at high temperatures (in contrast to the discontinuous transition at  $T \approx 300$  K); the valency of samarium varies from  $m = 0.18 \pm 0.02$  to  $m = 2.62 \pm 0.02$  in the region  $0 \leq x \leq 0.40$ . The smoothness of the transition at  $T \approx 1000$  K can be regarded as a confirmation of the assumption by Yayaraman *et al.*<sup>[4]</sup> of the presence of a critical point ( $T_{\text{cr}} \approx 700$  K) in the  $T$ - $x$  diagram of  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$ .

At the same time, according to the presently most popular interconfiguration fluctuation model (see, for example, Ref. 10), the samarium ions are in a hybrid-

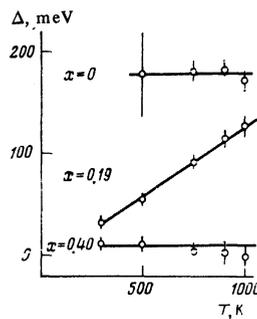


FIG. 4. Dependence of the  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$  transition energy on temperature for the  $\text{SmS}$ ,  $\text{Sm}_{0.81}\text{Gd}_{0.19}\text{S}$ , and  $\text{Sm}_{0.60}\text{Gd}_{0.40}\text{S}$  samples.

ized state (fluctuate with frequency  $\approx 10^{12} - 10^{13} \text{ sec}^{-1}$  between the  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  configurations, which are separated from each other by an energy gap  $\Delta$ ). The probability that a samarium ion is in the  $\text{Sm}^{3+}$  state is given in this model by the following expression<sup>[11]</sup>:

$$P(3+) = \left\{ 1 + \sum_i M_i^{2+(3+)} \exp(-T_i^{2+(3+)}/T) \times \exp[\Delta/(kT + \Delta H)] / \sum_i M_i^{3+} \exp(-T_i^{3+}/T) \right\}^{-1},$$

where  $M_i^{2+(3+)}$  are the multiplicities of the  $i$ -term of  $\text{Sm}^{2+(3+)}$ ,  $T_i^{2+(3+)}$  are the level energies of  $\text{Sm}^{2+(3+)}$ ,  $\Delta$  is the  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$  transition energy, and  $\Delta H$  is the energy of interaction of a  $4f$  electron with the band electrons. The thermal excitation and the mixing interaction  $\Delta H$  thus determine the population of the  $4f$  levels in the sample. According to estimates, the quantity  $\Delta H \approx 100$  K<sup>[11,12]</sup>, and at sufficiently high temperatures ( $T > 300$  K  $\gg \Delta H/k$ ), the probability  $P(3+)$  is largely determined by the thermal excitation.

From the above relations we can find the  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$  transition energy ( $\Delta$ ), using the experimental values of  $\eta$  (in our case  $P(3+) \equiv \eta$ ). In Fig. 4 we give the temperature dependences of  $\Delta$  for  $\text{SmS}$ ,  $\text{Sm}_{0.81}\text{Gd}_{0.19}\text{S}$ , and  $\text{Sm}_{0.60}\text{Gd}_{0.40}\text{S}$  samples, computed under the assumption that  $kT \gg \Delta H$ , i. e., the thermal excitation predominates in the investigated temperature region; the multiplet structure of the  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  ions does not change during the hybridization. The  $T_i^{2+(3+)}$  and  $M_i^{2+(3+)}$  values were taken from Arzhan and Kolvin's book<sup>[13]</sup>; the  ${}^6H_{5/2}\text{Sm}^{3+}$  level splitting was taken into account here.<sup>[14]</sup>

For pure  $\text{SmS}$ ,  $\Delta$  is observed to be a constant in the entire investigated temperature range; the weighted mean quantity  $\Delta = 0.18 \pm 0.01$  eV is in good agreement with the values 0.18 and 0.22 eV obtained from analysis of the magnetic and electric data.<sup>[5]</sup> For the  $\text{Sm}_{0.60}\text{Gd}_{0.40}\text{S}$  sample (the high-temperature metallized phase) the  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$  transition energy also does not depend on temperature; its weighted mean value  $\Delta = 0.009 \pm 0.002$  eV. But in  $\text{Sm}_{0.81}\text{Gd}_{0.19}\text{S}$ ,  $\Delta$  increases linearly with increasing temperature. Such behavior of the excitation energy shows that the population of the  $4f$  states in the intermediate region cannot, apparently, be explained only by thermal excitation. The existence of some inhibiting factor leading to the increase of  $\Delta$

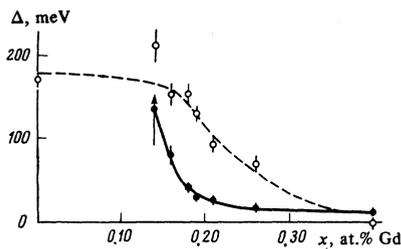


FIG. 5. Dependence of the energy of the  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$  transition in  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  on the gadolinium concentration. The dashed curve and  $\circ$ )  $T \approx 1000$  K; the continuous curve and  $\bullet$ )  $T \approx 300$  K.

can be postulated, the effective magnitude of  $\Delta$  being then well described by the linear relation  $\Delta = \Delta_0 + aT$ , where  $\Delta_0 = -0.008 \pm 0.004$  eV and  $a = (0.13 \pm 0.01) \times 10^{-3}$  eV/deg.

In Fig. 5 we show the dependences of the transition energy  $\Delta$  on the concentration of gadolinium. The latter, as the authors of Ref. 1 postulate, produces an effective internal contraction of the  $\text{SmS}$  lattice, giving rise to the drawing together of the  $4f$  levels and the bottom of the conduction band of samarium (i. e., to the decrease of the  $4f$ -band transition energy). At sufficiently high gadolinium concentrations ( $x \approx x_{cr}$ ) the chemical pressure initiates the  $4f$ -band transition. The curves in Fig. 5 corroborate this model: in the  $x \approx 0.14$ – $0.16$  region there is observed a decrease in the quantity  $\Delta$ , which drops to values equal to a few meV. The stretching of the effect at the high temperature (the dashed curve) in comparison with the effect observed at room temperature (the continuous curve) can be explained by the dependence of the transition energy on temperature for samples of intermediate composition ( $0.16 \lesssim x \lesssim 0.22$ ), see Fig. 4.

The authors are grateful to O. I. Sumbaev for a discussion of the results of the work, to A. I. Egorov for consultation on the preparation of  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$ , and to Yu. I. Vasil'ev for help with the measurements.

<sup>1</sup>All the samples were subjected before the shift measurements were performed to high-temperature annealing for the purpose of degassing them and obliterating their past history, since the latter shifts the phase transition boundary.

<sup>2</sup>However, the lattice constant of  $\text{Sm}_{0.60}\text{Gd}_{0.40}\text{S}$  varies appreciably in the region 300–900 K:  $\Delta d/d \approx 1.1\%$ .<sup>[4]</sup> This quantity is only two times smaller than the lattice constant of the  $\text{Sm}_{0.82}\text{Gd}_{0.18}\text{S}$  samples,<sup>[4]</sup> in which there occurs besides thermal expansion a change in  $d$  due to the  $4f$  transition.

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Translated by A. K. Ageyi