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Simultaneous electronic transition Sm²⁺–Sm³⁺ and Yb²⁺–Yb³⁺ in Sm₁₋ₓYbₓS

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The method of the x-ray K-line shift [O. I. Sumbaev, Sov. Phys. Usp. 21, 141 (1978)] is used to investigate the electron structure of Sm and Yb in $Sm_{1-x}Yb_xS$ ($0 \leq x \leq 1.77 \leq T \leq 1000$ K). A smooth increase of the valence of Sm with increase of x is observed, as well as a simultaneous change of the valence of Yb (at high temperature). It is shown that the observed effect is due to the departure of the $4f$ electrons of Sm and Yb into the conduction band. The valence change η_{Sm} is practically proportional to x and $\eta_{Sm} \approx 0.4$ at $x = 0.8$. The dependence of η_{Yb} on x correlates well with the concentration of the trivalent Sm ions in the sample, and reaches a value $\eta_{Yb} \approx 0.4$ at the maximum.

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1. INTRODUCTION

The mechanism of isomorphic phase transitions in solid solutions of SmS with monosulfides of trivalent rare-earth elements (REE) such as $Sm_{1-x}R_x^{3+}S$ has been established quite reliably (see, e.g., the reviews[1]). This transition is a particular case of the well known phenomenon of variable valence of the REE, and is due to the departure of the $4f$ electrons of Sm to the conduction band. It is assumed that the $Sm^{2+} - Sm^{3+}$ transition is initiated by the internal lattice ("chemical") pressure produced in the SmS lattice upon penetration of small (compared with Sm) trivalent RE atoms $d_{SmS} = 5.97$ Å; $5.8 \gtrsim d_{R^{3+}S} \gtrsim 5.4$ Å). In the phase transition these trivalent atoms are passive: unlike Sm, which acquires a valence ≈ 2.6 in the transition, the valence of R^{3+} remains unchanged.[2]

Less investigated are the electronic properties of solid solutions of SmS based on monosulfides of divalent REE ($Sm_{1-x}Eu_xS$ and $Sm_{1-x}Yb_xS$).

The parameters of the EuS and YbS lattices are 5.97

and 5.69 Å, respectively,[3] so that the "chemical" compression should produce an $Sm^{2+} - Sm^{3+}$ transition in $Sm_{1-x}Yb_xS$, analogous to the transition in $Sm_{1-x}Nd_xS$ (Ref. 2), inasmuch as $d_{YbS} \approx d_{NdS} = 5.70$ Å, and should not occur in $Sm_{1-x}Eu_xS$ because $d_{EuS} \approx d_{SmS}$. However, the anomalies typical of the isomorphic phase transition in $Sm_{1-x}Nd_xS$ (jumpwise change of the lattice parameter, semiconductor–metal transition, and change of the black color of the substance to golden yellow at $x = x_{cr} \approx 0.15$) are not observed in $Sm_{1-x}Yb_xS$ and $(0 \leq x \leq 1)$.[3] In the opinion of Jayaraman and co-workers this means that the electronic structure of the Sm ions remains unchanged in this system. In $Sm_{1-x}Eu_xS$, on the other hand, the transition $Sm^{2+} - Sm^{3+}$ does take place, although the lattice parameter has in this case, just as in $Sm_{1-x}Yb_xS$, no anomalies whatever.[3,4] (It is proposed in Ref. 4 that the transition is probably initiated by an indirect exchange interaction in the EuS magnetic matrix, which lowers the energy of the departure of the $4f$ electron of Sm to the conduction band.) Thus, it is sometimes difficult to register an electronic transition by using only crystallographic data.

The object of the present study is the electronic state of the Sm and Yb ions in $Sm_{1-x}Yb_xS$ in a wide range of sample compositions and temperatures ($0 \leq x \leq 1.77$ $\leq T \leq 1000$ K).

2. RESULTS OF EXPERIMENT

The electronic state of Sm and Yb in $Sm_{1-x}Yb_xS$ was determined by the method of the x-ray K-line shift (XLS). A description of this method as applied to the study of the mechanism of electronic phase transition can be found in our earlier papers (see, e.g., Refs. 1 and 5).[1] At room temperature we have also investigated the electric conductivity of the samples and carried out their x-ray structure analysis.

The $Sm_{1-x}Yb_xS$ samples were prepared in the following manner: A thoroughly pulverized SmS + YbS mixture was pressed into pellets ($P \approx 2000 - 3000$ kg/cm²), which were annealed in a tantalum crucible in vacuum at $T \approx 1600 - 1800$ °C. An x-ray structure analysis has shown that these samples have an NaCl structure and that the periods of the SmS and YbS lattices are close to the published data[6]: $d_{SmS} = 5.964 \pm 0.005$ Å, $d_{YbS} = 5.689 \pm 0.005$ Å. In addition, the XLS method was used to establish that the Sm and Yb ions in the initial SmS and YbS are divalent: $m_{Sm} = m_{Yb} = 2 \pm 0.03$. For samples with intermediate composition ($0 < x < 1$, $T \approx 300$ K), the lattice periods decrease practically linearly with increasing concentration (Fig. 1, dark circles). The same figure (top, dash-dot curve) shows a plot of the electric resistivity of the $Sm_{1-x}Yb_xS$ samples against composition at room temperature.

The change of the electronic state of the Sm and Yb ions in $Sm_{1-x}Yb_xS$ was revealed by the XLS (we determined in the experiments the shifts of the x-ray K lines of Sm and Yb as functions of the composition and temperature of the investigated sample, relative to those of a reference sample, made up of a mechanical SmS + YbS mixture having the same concentration x and kept
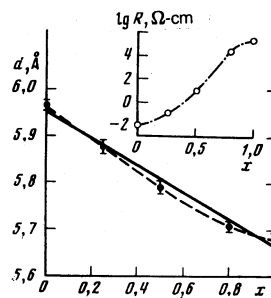

FIG. 1. Dependence of the $Sm_{1-x}Yb_xS$ lattice parameter on the composition. The inset shows the resistivity of $Sm_{1-x}Yb_xS$.

at room temperature).

Experiments at low and high temperatures were followed by control measurements of the shift, with both samples kept at room temperature. Equality of the shifts before and after the temperature experiments was evidence of the absence of irreversible changes in the samples as a result of heating (or cooling).

A study of the facsimile for the investigated samples (the pairs $Sm_{1-x}Yb_xS - [(1-x)SmS + xYbS]$ were compared) and their comparison with the calibration facsimile for the chemical compounds $SmF_3 - SmS$, $Yb_2O_3 - YbS$ (the electron structure within each pair is known and differs by one $4f$ electron) made it possible to establish unequivocally that the observed energy changes of the K lines of Sm(Yb) in the alloys are due to the removal of $4f$ electrons of Sm(Yb) to the conduction band. The experimental K-line shifts were used to determine the fractions η of the removed $4f$ electrons from the Sm(Yb) ions in the $Sm_{1-x}Yb_xS$. They are equal respectively to the ratios of the corresponding shifts and the calibration shifts of the K lines of Sm(Yb) obtained in the experiments with the chemical compounds: $\Delta E_{K_{\alpha 1}}$ $(SmF_3 - SmS) = -595 \pm 20$ meV and $\Delta E_{K_{\alpha 1}}(Yb_2O_3 - YbS)$ $= -650 \pm 33$ meV.

The experimental dependences of the degree $\eta(T, x)$ of the removal of the $4f$ electrons from the Sm and Yb ions in $Sm_{1-x}Yb_xS$ are shown in Figs. 2 and 3, respectively.

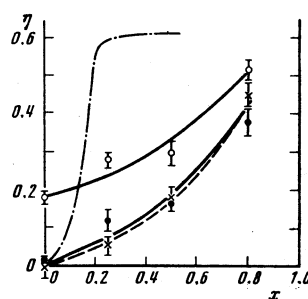FIG. 2. Change of the valence of samarium in $Sm_{1-x}R_x^{2+,3+}S$ as a function of x: solid lines—$Sm_{1-x}Yb_xS (\times - T = 77$ K, $\bullet$ $-T \approx 300$ K, $\bigcirc -T \approx 1000$ K), dashed—$Sm_{1-x}Eu_xS (T \approx 300$ K) (Ref. 2), dash-dot—$Sm_{1-x} \cdot Nd_xS (T \approx 300$ K) (Ref. 2).
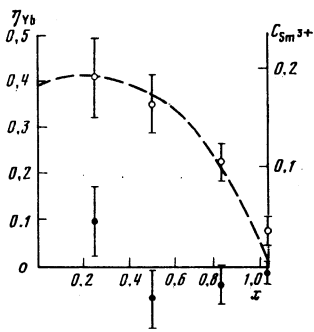
FIG. 3. Change of valence of Yb in $Sm_{1-x}Yb_xS$ ($\bullet - T \approx 300$ K, $\circ - T \approx 1000$ K). Dashed—dependence of the Sm^{3+} ion concentration in the sample ($T \approx 1000$ K) on the composition.

3. DISCUSSION OF RESULTS

As seen from Fig. 2, the $4f$ shell of the Sm ion is considerably altered: with increasing Yb concentration, the number of $4f$ electrons per Sm ion decreases smoothly (for example, at $T = 77$ K or ≈ 300 K the value of η changes from zero at $x = 0$ to ≈ 0.4 at $x = 0.8$). The slight enhancement of the degree of the transition at high temperature ($T \approx 1000$ K) can be attributed to thermal injection of the $4f$ electrons of Sm into the conduction band.

On the other hand, the dependence of the $Sm_{1-x}Yb_xS$ lattice parameter on the Yb concentration, as reported in Refs. 3 and 7, is linear[2] (it is this which gives the authors grounds for assuming that there is no electronic transition in this alloy). The dependence for our samples is also practically linear (see the solid straight line drawn by least squares on Fig. 1). However, the experimental data are in best agreement with the relation

$$d(x) = (1-x)(1-\eta(x))d_{Sm^{2+}S} + xd_{YbS} + (1-x)\eta(x)d_{Sm^{3+}S}$$

(the dashed curve in the same figure), which takes into account the presence of trivalent Sm ions in $Sm_{1-x}Yb_xS$ (here $d_{Sm^{3+}S}$ is the lattice parameter of $Sm^{3+}S$, Ref. 6).

Thus, the XLS data point unequivocally to the presence of an electronic transition in Sm, and our data on the lattice parameters do not contradict this conclusion.

The dashed and dash-dot cuvres in Fig. 2 are plots of $\eta(x)$ at room temperature for the $Sm_{1-x}Eu_xS$ and $Sm_{1-x}Nd_xS$ samples in accord with Ref. 2. Even though the lattice parameters of YbS and NdS are the same, the character and degree of the $Sm^{2+} - Sm^{3+}$ transition in $Sm_{1-x}Yb_xS$ and $Sm_{1-x}Nd_xS$ are substantially different (in the former case the transition is smooth, in the latter it is jumplike). At the same time, the analogous transition in $Sm_{1-x}Eu_xS$ is quite similar to the transition in $Sm_{1-x}Yb_xS$ [the $\eta(x)$ dependences are practically the same, even though $d_{YbS} \neq d_{EuS}$]. Thus, a single dimensional factor (the chemical pressure) alone cannot explain the character of the electronic transitions in the alloys $Sm_{1-x}R_x^{2+,3+}S$. It should depend also to a considerable degree on the concrete structure of the conduction band, whose formation is strongly influenced by

the valence (number of free electrons) of the impurity atoms.

Simultaneously with the $4f$ transition in Sm, we have observed in the $Sm_{1-x}Yb_xS$ system investigated by us (at high temperature) a $4f$ transition in Yb (a temperature reversible electronic transition Yb^{2+}, $4f^{14} - Yb^{3+}$, $4f^{13}$). This effect is illustrated in Fig. 3. At room temperature (dark circles) $\eta_{Yb} \approx 0$ (the valence of Yb is $m \approx 2$) in the entire region $0 \leqslant x \leqslant 1$. At $T \approx 1000$ K (light circles), however, the number of $4f$ electrons per Yb ion decreases (the valence of Yb increases), and the maximum value of the valence of Yb is observed at $x \approx 0.2$ and amounts to $m_{Yb} \approx 2.4$ ($\eta_{Yb} \approx 0.4$). The same figure shows dashed a plot of the concentration of the trivalent Sm ions in the sample ($T \approx 1000$ K) against the composition: $C_{Sm^{3+}}(x) \equiv \eta_{Sm}(1-x)$. The experimental $\eta_{Yb}(x)$ dependence correlates well with the $C_{Sm^{3+}}(x)$ curve. This means that the degree of the $Yb^{2+} - Yb^{3+}$ transition is proportional to the concentration of the trivalent Sm ions in the sample: $\eta_{Yb} \sim \eta_{Sm}(1-x)$.

The appearance of conducting ions in a nonconducting crystal lattice should lead in accord with percolation theory[8] to a semiconductor–metal transition at $C^{3+} \approx C_{cr} \approx 0.12$. In our case, however, this transition (at room temperature) is not observed (Fig. 1, dash-dot curve). With increasing x, a smooth increase of R takes place from values corresponding to the resistivity of SmS to values of the resistivity of YbS. The change of R in the $0 \leqslant x \leqslant 1$ region is about seven order of magnitude, and the resistivities of SmS and YbS agree well with the published data $R_{SmS} \approx 10^{-2} - 10^{-3}$ Ω-cm and $R_{YbS} \approx 10^4 - 10^5$ Ω-cm.[6]

The absence of a semiconductor–metal transition in $Sm_{1-x}Yb_xS$ at room temperature can be attributed to the fact that the number of the trivalent samarium ions produced in the $Sm^{2+} - Sm^{3+}$ electronic transition is not sufficient for the formation of conducting bridges: C_{max}^{3+} ($T \approx 300$ K) < 0.1.

In conclusion, the authors thank O. I. Sumbaev for useful discussions, A. I. Egorov for consultations on the preparation of the investigated samples, A. V. Kovalev for the x-ray structure analysis, and Yu. I. Vasil'ev for help with the measurements.

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[1] In brief, in the XLS method the shifts of the K lines are linearly connected with the change (due to the electronic transition) of the number of valence electrons of the investigated ions, and the dependence of the shift on the type of line ($K_{\alpha 1}$, $K_{\beta 1}$, $K_{\beta 2,4}$)—the "facsimile"—determines uniquely the type of electron that participates in this process.

[2] However, the accuracy with which the linear law is satisfied is not known, since the errors in the determination of d are not given.

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Elastic and inelastic scattering of Mössbauer γ quanta in a pyrolytic graphite crystal

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A method free of systematic errors is proposed for the measurement of the intensity of elastic and inelastic scattering of Mössbauer γ quanta in substances that do not contain resonant nuclei and can be in arbitrary aggregate states. The method was used to measure the intensity of elastic and inelastic scattering of 14.4 keV Mössbauer radiation along the profile of the (002) Bragg reflection and at the maxima of the reflections (004), (006), and (008) in a crystal of highly oriented pyrolytic graphite. It is shown that the existing theory of elastic scattering of x rays in mosaic crystals, as well as the theory of thermal diffuse and Compton scattering, can describe satisfactorily the experimental results. The shear modulus c_{44} and the law governing the mosaic distribution are determined, and the dimensions of the coherently scattering blocks are estimated.

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INTRODUCTION

Among the widely known methods of investigating the structure of matter and elementary excitations, such as elastic and inelastic scattering of x rays and thermal neutrons, a special place is occupied by the study of the scattering of Mössbauer γ radiation in a subtance that contains no resonant nuclei, owing to the high resolution of this method ($\sim 10^{-8}$ eV). The main idea underlying such experiments is that the Mössbauer radiation scattered from the sample is analyzed by a resonant absorber placed ahead of the detector.[1-3]

Despite the simplicity and elegance of the described[1-3] methods, a number of questions remain unanswered. These involve the allowance for the systematic errors when the background is determined and the calculation of the instrumental errors. The latter occur mainly because the luminosity of the instrument must be increased, and this leads to deviation from Bragg focusing in the Mössbauer diffractometer. This question was analyzed in detail in Ref. 4, where modifications of the procedures of Refs. 1–3 were proposed, aimed at eliminating the systematic errors in the determination of the background.

In the present study we have measured by the procedure of Ref. 4 the intensities of the elastic and inelastic scattering of 14.4-keV Mössbauer γ quanta in a highly oriented pyrolytic graphite (PG) crystal. The main structural units of this graphite are planar atomic grids in which the hydrogen atoms are located at the corners of regular hexagons. These grids are arranged in an ABABAB.... sequence as in natural graphite, forming stacks turned randomly relative to one another in the planes of the grids. Despite the considerable progress in the production of PG, it has been impossible to grow sizable artificial single crystals. It is therefore very important to accumulate experimental data on such important physical characteristics of graphite as the thickness of the stacks with regular packing and the elastic constants, particularly c_{44} (the shear modulus, which determines the critical fracture stress perpendicular to the c axis). In fact, the dimensions of the stacks with regular packing and their degree of disorientation determine the angle widths of the elastic-scattering reflections, while the elastic constants can be determined by measuring the intensity of the thermal diffuse scattering (TDS) in Bragg reflections.

Nondestructive control methods such as x-ray and γ-ray scattering are particularly attractive. Traditional measurements of the elastic constants by ultrasonic and static methods require samples of appreciable size and of special shape, whereas the method proposed by us is free of these limitations. As to the purely scientific problems, the study of graphite is of interest from the point of view of checking on the present theories of secondary extinction in TDS, inasmuch as the ex-

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