

Investigation of the mechanism of the semiconductor to metal transition in the systems $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ and $\text{Nd}_x\text{Sm}_{1-x}\text{S}$ by the method of chemical shifts of x-ray lines

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We measured the shifts of the K-series x-ray lines of the atoms Nd and Sm in the systems $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ and $\text{Nd}_x\text{Sm}_{1-x}\text{S}$ relative to NdSe, SmSe, and NdS, SmS respectively. From the values of the shifts it can be concluded that the semiconductor-to-metal transition observed in $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ at $x \approx 0.11$ (M. Avignon and J. Dumas, Sol. St. Comm. 11, 1115, 1972, and J. F. Miller *et al.*, J. Phys. Chem. Solids 25, 969, 1964) is not connected with the change of the valence state of the Nd (or Sm) atoms, as suggested by Avignon and Dumas, but is apparently attributed to the formation of conducting bridges (zones) between the trivalent Nd atoms (see Miller *et al.* and also N. F. Mott, Adv. Phys. 21, 785, 1972). Two independent phenomena of different nature and at different concentrations were observed in $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$. The first, a change in the conductivity at $x \approx 0.10$, is not connected with the change of the valence state of the Nd and Sm atoms, and has apparently the same nature as in $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$. The second is an electronic phase transition at $x \gtrsim 0.13$ and is due to the increase of the valence of Sm as a result of the "crowding out" of a 4f electron of Sm into the 5d conduction band of SmS under the influence of the effective compression of the SmS lattice following dissolution of the NdS. It is established that the valence of Sm changes in this case from 2 to 2.64 ± 0.03 . The $\text{Nd}_x\text{Sm}_{1-x}\text{S}$ system turned out thus to be quite similar to the previously investigated (V. A. Shaburov *et al.* ZhETF Pis. Red. 18, 425, 1973 and Zh. Eksp. Teor. Fiz. 68, 325, 1974) system $\text{Gd}_x\text{Sm}_{1-x}\text{S}$ by the same method.

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INTRODUCTION

The system $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$, is a semiconductor at small but undergoes an abrupt transition into the metallic state at $x_{\text{cr}} \approx 0.11$. This transition was first observed in 1964 by Miller *et al.*^[1] but its nature has not yet been finally established to this date. The existing models can be divided into two groups:

1. The models proposed by Miller *et al.*^[1] and by Mott,^[2] in which the onset of metallic conductivity at $x_{\text{cr}} \approx 0.11$ is attributed to the coming together of the Nd atoms with increasing concentration x and the formation of conducting bridges (bands). In these models it is assumed that the Nd atoms are in a trivalent state (Nd^{3+} , $4f^3$) in the entire range of concentrations.

2. The model of Avignon and Dumas,^[3,4] explains the onset of conductivity at $x \geq x_{\text{cr}}$ as being due to the transition of the Nd 4f electron of the Nd, which is initially (at $x \leq x_{\text{cr}}$) in divalent state (Nd^{2+} , $4f^3$), to the conduction band. It predicts a jumplike change of the valence of Nd (Nd^{2+} , $4f^3 \rightarrow \text{Nd}^{3+}$, $4f^3$) at $x \approx x_{\text{cr}}$.

The method of chemical shifts of the K-series x-ray lines makes it easy to observe the phenomena connected with a change in the number of 4f electrons (see, e.g.,^[5]), and consequently make an unambiguous choice between models 1 and 2. It was recently used with success in an investigation of $\text{Gd}_x\text{Sm}_{1-x}\text{S}$.^[6] We investigated by this method the system $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ in a wide range of concentrations. At the same time, we investigated the system $\text{Nd}_x\text{Sm}_{1-x}\text{S}$, which has hitherto not been investigated.

EXPERIMENTAL RESULTS AND DISCUSSION

We investigated experimentally the behavior of the K energy of the K lines of Sm and Nd, and also of the resistivity of $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ and $\text{Nd}_x\text{Sm}_{1-x}\text{S}$ as functions of the concentration x . The investigated samples were prepared by sintering in a hermetic tantalum crucible at $t \approx 1600-1800^\circ\text{C}$ of well-powdered mixtures $(\text{SmSe})_{1-x} + (\text{NdSe})_x$ and $(\text{SmS})_{1-x} + (\text{NdS})_x$, respectively. The Nd concentration was determined for each sample from the

ratio of the intensities of the $\text{K}\alpha_1$ lines of Nd and Sm. This ratio was compared with a reference curve obtained for samples made from a mechanical mixture. The Nd concentration was determined accurate to 0.2-0.3 at. %. The measurement of the resistivity was carried out at room temperature with a four-probe procedure, and the chemical shifts of the x-ray lines were measured by a scheme customarily used by us (see, e.g.^[5]).

Figure 1 shows the dependence of the shifts of the $\text{K}\beta_1$ lines of Nd and Sm, and also of the resistivity of $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$, on the concentration x (the shifts were measured relative to NdSe and SmSe, in which the Nd and Sm atoms have respectively the configurations Nd^{3+} , $4f^3$ and Sm^{2+} , $4f^6$ ^[7]). The shifts of the K line of Nd for all the investigated concentrations turned out to be close to zero. The same figure shows (dashed) the concentration dependence of the position of the $\text{Nd}\text{K}\beta_1$ line, which follows from the model of Avignon and Dumas. In this case one should expect the shift $\Delta E(\text{K}\beta_1, \text{Nd}) \equiv E(\text{Nd}_x\text{Sm}_{1-x}\text{Se}) - E(\text{NdSe})$ at all concentrations $x < x_{\text{cr}}$ to be equal to the shift between the divalent and trivalent states of Nd. The latter was measured by us experimentally using as an example the pair of compounds $\text{NdCl}_2 - \text{Nd}_2\text{O}_3$, regarded as ionic compounds of di- and trivalent Nd with configurations

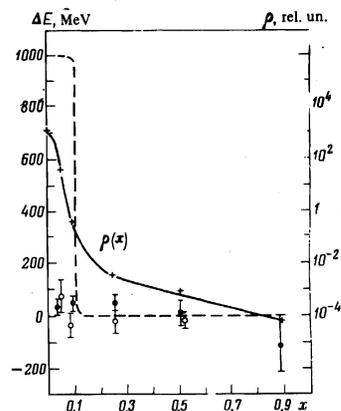


FIG. 1. Shifts of $\text{K}\beta_1$ lines of Nd and Sm and resistivity of the $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ system: \circ —shifts of $\text{K}\beta_1$ line of Nd, \bullet —shifts of $\text{K}\beta_1$ line of Sm, $+$ —resistivity; dashed curve—expected shifts of $\text{K}\beta_1$ line of Nd for the model of Avignon and Dumas^[3] (here and in the other figures, x is given in at. % normalized to unity).

Nd^{2+} , $4f^4$ and Nd^{3+} , $4f^3$ respectively; the shift turned out to be $+1000 \pm 33$ meV. At $x > x_{\text{CR}}$ the shift should be approximately equal to zero. A comparison of the expected curve with experiment offers evidence that the valence state of the Nd atoms remains unchanged in the investigated concentration interval, and makes it possible to exclude unambiguously the feasibility of the mechanism considered in the model of Avignon and Dumas.

It was also of interest to ascertain whether the semiconductor-metal transition in the $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ system is caused by the change of the valence state of the Sm atoms. It is known^[8] that SmSe undergoes under hydrostatic compression a continuous transition into the metallic state at pressures on the order of 30–40 kbar, presumably owing to the change of the state of the Sm atoms (Sm^{2+} , $4f^6 \rightarrow \text{Sm}^{3+}$, $4f^5$). Since the trivalent Nd atoms are smaller than the divalent Sm atoms, their entry into the SmSe lattice leads to an effective internal compression of the latter, and this can in principle (if this compression is strong enough) initiate a phase transition in the system $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$.

The presence of such a transition could be recorded by means of the large negative shifts of the K_{β_1} line of Sm (the complete transition Sm^{2+} , $4f^6 \rightarrow \text{Sm}^{3+}$, $4f^5$ corresponds to an Sm K_{β_1} -line shift ≈ -1400 meV^[5]). The experimental shifts of the K_{β_1} line of Sm in the system $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ (see Fig. 1) are close to zero in practically the entire range of concentrations, thus indicating that the valence states remains unchanged also for the Sm atoms (only at a concentration $x \approx 0.9$ is a negative shift possibly observed and can serve as indication of the start of the $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$ transition). Thus, we can state that in the region of the transition from the semiconductor to the metal in the $\text{Nd}_x\text{Sm}_{1-x}\text{Se}$ system there is no valence change of either the Nd or the Sm atoms, and consequently the jump in the resistivity at $x \approx 0.11$ (our measurements of the resistivity practically coincides with the results of Miller et al.^[1]) seems to be due to the mechanism proposed in the models of type 1 (see the Introduction).

A more complicated situation was observed recently in the system $\text{Gd}_x\text{Sm}_{1-x}\text{S}$.^[9, 6] Figure 2, which is plotted from data of earlier work (Ref. 6b), shows the dependence of the shifts of the K_{β_1} lines of Sm and Gd, and

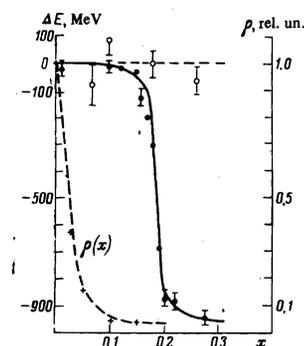


FIG. 2

FIG. 2. Shifts of the K_{β_1} lines of Gd and Sm and resistivity of the system $\text{Gd}_x\text{Sm}_{1-x}\text{S}$ [6]: \circ —shifts of K_{β_1} line of Gd, \bullet —shifts of K_{β_1} line of Sm, +—resistivity.

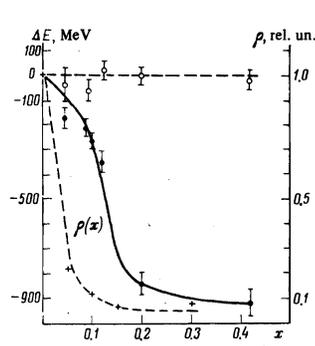


FIG. 3

FIG. 3. Shifts of K_{β_1} lines of Nd and Sm and resistivity of the system $\text{Nd}_x\text{Sm}_{1-x}\text{S}$: \circ —shifts of K_{β_1} line of Nd, \bullet —shifts of K_{β_1} line of Sm, +—resistivity.

also of the resistivity, on the Gd concentration. As seen from Fig. 2, we observe here two independent phenomena that are separated in concentration: the first, at $x \approx 0.10$, leads to a change of the resistance of the system to values typical of metal, but is not connected with the change of the valence of the Gd or Sm atom (zero shifts of the K_{β_1} lines of Gd and Sm in this concentration region); the second is responsible for the jumplike change of the volume of this system ($\Delta V/V \approx 14\%$ ^[9] and is due to the change of the valence of Sm (large negative shift of the K_{β_1} line of Sm in the region $x > 0.18$). The cause of the first phenomenon lies apparently in the formation of conducting bridges (bands) by the trivalent Gd atoms, while the second is due to the presence of an effective internal compression, which is exerted on the SmS lattice by the GdS impurities.^[1] The Gd atoms do not change their valent state and assume the role of a chemically passive press. In this case the Gd can apparently be replaced by any other trivalent lanthanoid. To check this premise, we investigated the system $\text{Nd}_x\text{Sm}_{1-x}\text{S}$.

Figure 3 shows plots of the chemical shifts of the K_{β_1} lines of Nd and Sm, and also of the resistivity, as functions of the concentration in the system $\text{Nd}_x\text{Sm}_{1-x}\text{S}$. As seen from Fig. 3, the situation here is perfectly analogous to that observed for the system $\text{Gd}_x\text{Sm}_{1-x}\text{S}$. Again there are two transitions: the first, at $x < 0.10$, is responsible for the transition of the system to the metallic conductivity, but is not connected with the change of the valences of Nd and Sm (near zero shifts of the K_{β_1} lines of Nd and Sm in this concentration region); the second, at $x \approx 0.13$, which we determine from the change of the shift of the K_{β_1} line from ~ 0 to ~ -900 meV, is due to the change of the valent state of the Sm atoms.

For a detailed explanation of the mechanism of this transition, we measured the shift as a function of the type of line (K_{α_1} , K_{β_1} , $K_{\beta_{2,4}}$) for a pair of samples, one of which beyond the phase-transition point ($x = 20$), and the other at $x = 0$ (SmS). The experimental plots of the shift against the type of line (Fig. 4) have typical V-shapes, indicating unequivocally a partial removal of the 4f electron from the Sm atom in $\text{Nd}_{0.20}\text{Sm}_{0.80}\text{S}$.

Figure 4 shows also experimental and theoretical calibration curves of the shift against the type of line, corresponding to complete removal of one 4f electron from the Sm atom. The experimental calibration curve was obtained by measuring the shifts for the pair SmF_3 – SmCl_2 , which are regarded as ionic compounds of tri- and divalent Sm with respective configurations Sm^{3+} , $4f^5$ and Sm^{2+} , $4f^6$; the curve theoretically calculated^[10] by the Hartree-Fock-Slater method for the configurations $4f^5$ and $4f^6$ of Sm agrees well with the experi-

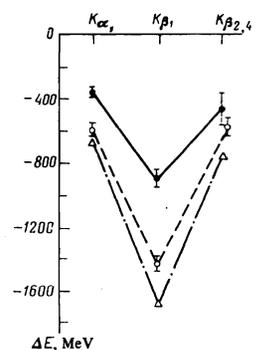


FIG. 4. Plot of shift against the type of line; solid curve—experiment for the $\text{Nd}_{0.20}\text{Sm}_{0.80}\text{S}$ – SmS sample pair, dashed—experiment for the SmF_3 – SmCl_2 sample pair, dash-dot—theoretical calculation in the Hartree-Fock-Slater model.

mental one. From the experimental shifts of $\text{Nd}_{0.20}\text{Sm}_{0.80}\text{S}$ – SmS we determined the fraction η_{Nd} of the removed 4f electrons from the Sm atoms and from $\text{Nd}_{0.20}\text{Sm}_{0.80}\text{S}$, by dividing the experimental shifts for each of the lines (K_{α_1} , K_{β_1} , $K_{\beta_2,4}$) by the corresponding experimental shifts for the standard pair SmF_3 – SmCl_2 .²⁾ The obtained value $\eta_{\text{Nd}} = 0.64 \pm 0.03$ agrees within the limits of errors (Ref. 6a) with the fractions of the 4f–5d transitions in pure SmS hydraulically compressed to 9 kbar ($\eta_{\text{P}} = 0.62 \pm 0.03$) and in $\text{Gd}_x\text{Sm}_{1-x}\text{S}$ at $x \geq 0.18$ ($\eta_{\text{Gd}} = 0.63 \pm 0.04$), thus offering evidence that the effect is of the same type in all three systems.

In conclusion, the authors thank I. M. Miftakhov and E. M. Mel'nikov for help with the measurements.

¹⁾It is known [^{8,6a}] that SmS undergoes an isomorphic phase transition due to the partial change of the valence of Sm ($\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$) at the relatively low hydrostatic pressure ≈ 6.5 kbar, and the internal effective compression turns out to be sufficient to initiate this transition.

²⁾We have subtracted from the denominator a small correction, obtained by the HFS calculation and taking account of the fact that the "pushed-out" 4f electron in $\text{Nd}_{0.20}\text{Sm}_{0.80}\text{S}$ is not removed to the ligand, as in SmF_3 , but goes over to the 5d conduction band of SmS.

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