Electron mechanism of the isomorphic phase transition in SmS

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The isomorphic ($Ce_\gamma \rightleftharpoons Ce_\alpha$ type[1,2]) phase transition in SmS[5-8] is investigated by the technique of "chemical" shift of the x-ray *K* lines. [9,10] The transition was induced either by applying pressure up to 10 kbar [6-8] or by the effective pressure arising in the SmS lattice following dissolution of GdS. [14] In the second case, the measurements are carried out for samarium and gadolinium *K* lines at both room temperature and 77°K. The effect of preliminary compression of the samples is also studied. Large (up to about 1 eV) energy changes of the samarium *K* lines are found to correspond to the phase transition. They form a V-shaped "facsimile" [10] typical of 4*f* electrons and corresponding to the increase of samarium valence due to the 4*f*-5*d* electron transition. (The valence of samarium ranges from $m = 2$ to $m = 2.62 \pm 0.03$.) The existence of a low-temperature phase of intermediate valence in samples containing gadolinium [14] is confirmed but the valence obtained is $m = 2.08 \pm 0.01$ and not $m \approx 2.5$.[14] Transition to this phase from a higher-valence phase occurs in an "explosive" manner particularly in preliminarily compressed samples. The decrease of electric conductivity observed on addition of gadolinium to the samples is found to be a process independent of the phase transition; it can probably be attributed to the "short circuit effect".[16] It is shown that the valence state of gadolinium remains unchanged during the phase transition, i.e., it plays the role of a chemically passive compressor.

INTRODUCTION

The electronic mechanism of the so-called isomorphic phase transition in metallic cerium [1] was investigated by the method of the chemical shift of the x-ray K_{α_1}, K_{β_1}, and $K_{\beta_{2,4}}$ lines in our preceding study [2]. A distinguishing feature of this first-order phase transition is the invariance of the symmetry of the crystal lattice before and after the transition, and consequently the predominant role played in the mechanism by the effect of intra-atomic electron realignment. The concrete mechanism consists in the transition of one of the inner (4f) electrons of the atom to a valence (apparently, 5d) state (see also the review [3]). Thus, this effect is a particular case of a phenomenon well known in chemistry (particularly for lanthanoids), namely variable valence; here, however, this effect is initiated by physical factors (pressure, temperature). Consequently this effect, which appeared to be unique for a long time), may be a widespread phenomenon and may be observable under certain conditions (when speaking of rare-earth elements) in compounds of Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Tm, and Yb, i.e., wherever variable valence with a 4f—5d transition is known. In a number of studies (see, in particular, the review [4]), experimental indications were observed already long ago concerning the realizability of this last effect. It appears that the most thoroughly investigated (after Ce) is at present the case of the isomorphic phase transition in SmS [5-8].

It has been shown (see, in particular [9,10]), that the phenomenon of variable valence with 4f—5d transition in rare-earth elements can be investigated most conveniently by the method of the chemical shift of x-ray K lines[1]. This method should be equally advantageous for the case of isomorphic phase transitions. Experience with cerium [2] seems to confirm this fact. We use this method here to investigate the electronic mechanism of isomorphic phase transitions in SmS and $Sm_{1-x}Gd_xS$.

EXPERIMENTAL INVESTIGATION OF ISOMORPHIC TRANSITION IN SmS AT HIGH PRESSURE

The isomorphic phase transition in SmS was initiated by hydrostatic compression of the sample. We investigated in the experiment the behavior of the Sm K-line energy as a function of the applied pressure.

The setup for the measurements of small (≥ 10 meV) displacements of x-ray lines is a special x-ray crystal-spectrometer of the Cauchois type, in the field of which are placed alternately the compared identical samples. The experimental setup is similar to that employed earlier [2], except that the low-temperature chambers have been replaced by high-pressure chambers.

Figure 1 shows schematically the arrangement of the high-pressure chamber. The investigated sample 1 is a mixture of powdered SmS (the method of preparation is described in [11]) with polyethylene, which serves as the pressure-transmitting medium. Sample 1 is located in a beryllium cone 2, which is pressed with the aid of piston 5 to the housing 3, which is made of high-strength steel and has openings for the entry and exit of the x rays. The pressure is produced by a hydrostatic press via

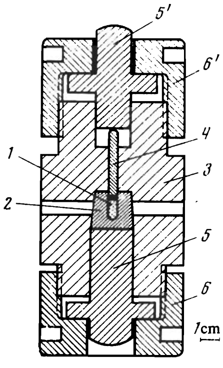

FIG. 1. High-pressure chamber used in experiments with SmS: 1—powdered mixture of SmS with polyethylene, 2—beryllium cone, 3—chamber housing, 4—small plunger, 5, 5′—lockable plungers, 6, 6′—tightening nuts.

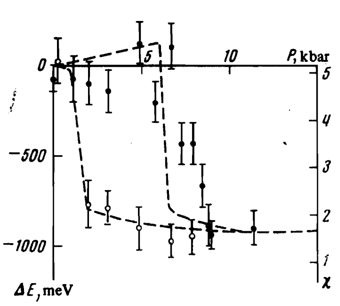

FIG. 2

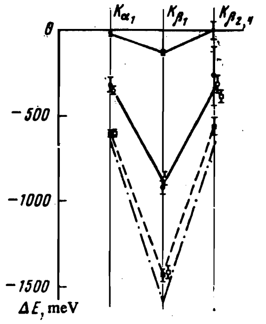

FIG. 3

FIG. 2. Pressure dependence of the shift of the K_{β_1} line of samarium in SmS. The dark and light curves were obtained respectively with increasing and decreasing pressure. The dashed line shows the analogous dependence for the magnetic susceptibility χ (in 10^{-3} emu/mole) [7].

FIG. 3. Plots of displacement vs. line type ("facsimile"). Dashed—calibration curves for the chemical compounds of samarium: □—SmF_3-$SmCl_2$, ■—SmF_3-SmS. Dash-dot—calculation after Hartree-Fock-Slater for Sm^{3+}, $4f^5$ and Sm^{2+}, $4f^6$ [13]. The thick solid line shows the collapsed phase of SmS, compressed by a pressure $P \gtrsim 9$ bar (dark circles) or by addition of gadolinium ($Sm_{1-x}Gd_xS$, x = 0.20, T ≈ 300 K—light circles). Thin solid line (top)—low-temperature (T = 77 K) phase of the intermediate valence in $Sm_{1-x}Gd_xS$ (x = 0.18). All the experimental displacements are shown relative to the uncompressed SmS at room temperature.

plungers 4 and 5′. After plunger 5′ produces the pressure, it is secured in the working position by means of locknut 6′. The nominal pressure on the sample was calculated from the value of the applied force and the area of the sample cross section. The influence of the friction in the chamber was taken into account from the forward and reverse travels of the plunger [12]. The chamber permitted stepwise application and long-duration fixation of pressures up to ≈12 kbar. In the experiment we measured the differences of the K_{β_1} line energies for two initially identical samples in identical chambers, one of which was at atmospheric pressure and the other at increased pressure.

Figure 2 shows a plot of the shift of the K_{β_1} line of Sm in SmS against pressure. A strong reversible effect is observed (the energy of the K_{β_1} line of the compressed sample decreases), which reaches approximately one electron volt at saturation and vanishes with hysteresis when the pressure is removed. The dashed line shows the pressure dependence of the magnetic susceptibility, observed by Maple and Wohlleben [7] (the scales are chosen such that the effects coincided at saturation). The agreement between the experimental points and the dashed curve is good enough to conclude that the effects are of common origin.

To explain the mechanism of the effect, we measured the plots of the displacement against the type of line (K_{α_1}, K_{β_1}, $K_{\beta_{2,4}}$)—these are the unique "facsimile" plots of the electrons [9,10]—for a pair of samples, of which one was at the phase transition point (P > 9 kbar), and the other was at atmospheric pressure. The dark circles of Fig. 3 (thick curve) show the results of this experiment. The shift vs. line type plot has a characteristic V shape. It can be compared with the calibration "facsimile" curves shown in the same figure and obtained by calculation and from experiment (dashed). The latter were measured for a "standard" SmF_3—$SmCl_2$ pair considered as ionic compounds of trivalent and divalent Sm with configurations Sm^{3+}, $4f^5$, Sm^{2+}, $4f^6$ and the pair SmF_3—SmS. Within the limits of measurement errors, the plot for SmF_3—SmS coincides with that for SmF_3—$SmCl_2$. This proves that in the uncompressed SmS the samarium is divalent, just as in $SmCl_2$.

No.	A	B	$E \equiv E_A - E_B$, MeV		
			K_{α_1}	K_{β_1}	$K_{\beta_{2,4}}$
1	SmS, $P > 9$ kbar	SmS, $P = 1$ atm	−319±43	−926±41	−258±180
2	$Sm_{0,80}Gd_{0,20}S$, $t \approx 300$ K	SmS, $t \approx 300$ K	−352±15	−923±55	−305±62
3	$Sm_{0,82}Gd_{0,18}S$, $t \approx 77$ K	SmS, $t \approx 300$ K	−38±10	−133±15	3±52
4	SmF_3	SmS	−595±20	−1430±40	−556±50
5	SmF_3	$SmCl_2$	−592±14	−1446±40	−383±43
6	Sm^{3+}, $4f^5$	Sm^{2+}, $4f^6$, $5d^1$			
	HFS calculation		−62	65	107
7	η_P		0.60±0.08	0.62±0.03	0.39±0.27
8	η_{Gd}		0.66±0.04	0.62±0.04	0.46±0.10
9	η_{Gd}^T		0.07±0.02	0.09±0.01	0.00±0.08

The forms and the absolute magnitudes of the calibration displacements are fairly well duplicated by a theoretical curve calculated (see [13]) by the Hartree-Fock-Slater method for the configurations $4f^5$ and $4f^6$ of samarium. The comparison indicates unequivocally that the valence of samarium increases under pressure at the expense of the loss of the number of 4f electrons. From the experimental shifts we can calculate the fraction η_p of the removal of the 4f electron from the Sm atom, if it is assumed that the experimental calibration shifts correspond to a complete removal of one 4f electron.

The numerical values of the shifts are listed in the Table. In line 7 are given the experimental values of η_P. They were obtained by dividing the displacements in the phase transition (line 1) by the corresponding displacements for the SmF_3—SmS compounds (line 4). We subtracted from the denominators the correction (line 6) obtained by the Hartree-Fock-Slater calculation, which takes account of the fact that the "extruded" 4f electron of SmS is not removed to the ligand, as in SmF_3, but goes over to the 5d shell of the Sm. The correction is small and hardly changes the mean-weighted value $\bar{\eta}_P = 0.62 \pm 0.03$ electron per atom.

EXPERIMENTAL INVESTIGATION OF THE ISOMORPHIC PHASE TRANSITION IN SmS DOPED WITH GADOLINIUM

In Fig. 4a, which is taken from the paper of Jayarman et al. [14], we illustrate the behavior of the $Sm_{1-x}Gd_xS$ lattice parameter as a function of the gadolinium concentration at helium and room temperatures. At x ≈ 0.16 one observes a jumplike change (decrease) of the crystal-lattice parameter. The lattice symmetry remains unchanged (it is of the NaCl type for $0 \leq x \leq 1$). It is assumed that the penetration of the Gd atoms leads to the onset of an effective internal compression of the SmS lattice as a result of the fact that the trivalent Gd atoms are smaller than the divalent Sm atoms. At sufficiently high gadolinium concentrations, the effective pressure can initiate an isomorphic phase transition in the $Sm_{1-x}Gd_xS$ system analogous to the transition produced by direct application of pressure.

Cooling the sample ($T \lesssim 100$ K) leads to formation of an intermediate phase, likewise with an NaCl-type lattice, which is stable in a small range of Gd concentrations ($0.16 < x < 0.22$). The transition is reversible:

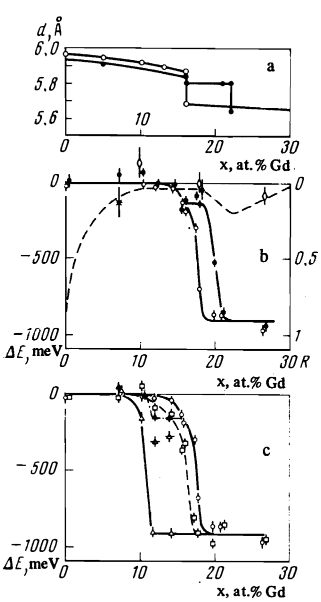

FIG. 4. Lattice parameters and shifts of K_{β_1} lines of Sm and Gd in $Sm_{1-x}Gd_xS$ vs. the amount of gadolinium impurity. a) Lattice parameter from [14] (●—T = 4.2 K, ○—T = 300 K). b) Shifts of K_{β_1} line of Sm (○, ●) and Gd (◇, ◆); dashed—dependence of resistivity (in rel. units) of our samples (beads) on x. c) Shifts of K_{β_1} line of Sm for samples at atmospheric pressure, but subjected beforehand to hydrostatic compression: □—in the course of preparation, and ▲, △—purposefully ($P \approx 10$ kbar); the hatched triangles are explained in the text. The dark points were obtained by us at low temperature (77 K) and the light ones at room temperature (≈300 K). The shifts of the Sm line were measured in all cases relative to its position in pure SmS. The shifts of the Gd line were measured relative to GdS or (at x = 0.07) relative to a mechanical SmS + GdS mixture having the same composition as the investigated sample.

heating causes the lattice parameter to assume the initial value. The authors of[14] have suggested that at $x \gtrsim 0.16$ there occurs in $Sm_{1-x}Gd_xS$ a transition of the 4f electron to the conduction band (4f—5d transition), due to the compression. Cooling causes a lowering of the "extruded" 4f level and its partial population with electrons of the conduction band, i.e., a partial inverse 5d—4f transition. By starting from the lattice parameters of the divalent and trivalent SmS and using linear interpolation, a value $\eta \approx 0.45$ was obtained in[14] for $0.16 \le x \le 0.22$ at T = 4.2 K.

Our purpose was to verify these conclusions by the method of chemical displacements of the K lines. In the experiment we registered the displacement of the K lines of Sm in $Sm_{1-x}Gd_xS$ at different concentrations of Gd relative to the corresponding Sm lines in SmS. The measurements were performed by the procedure described in[2]. The compared samples, which were pellets of powdered SmS (or $Sm_{1-x}Gd_xS$) mixed with polyethylene, were placed in identical foamed-plastic cryostats. The $Sm_{1-x}Gd_xS$ sample was kept at either room or nitrogen temperature. The $Sm_{1-x}Gd_xS$ system was prepared by sintering a well pulverized SmS + GdS mixture in a tantalum crucible at t ≈ 1600—1800°C in vacuum. The gadolinium concentration was determined for each investigated sample from the ratio of the intensities of the K lines of Gd and Sm. This ratio was compared with a reference curve obtained for samples made from the mechanical mixture (1 − x)SmS + xGdS. The accuracy with which the gadolinium concentration was determined was 0.2—0.3 at.%.

Figure 4b shows the experimental results: the shift of the K_{β_1} line of Sm for the pair of samples $Sm_{1-x}Gd_xS$ and SmS as a function of the gadolinium concentration. The light and dark circles represent the shifts at room and nitrogen temperature, respectively[2]. The behavior of the crystal-lattice parameter (Fig. 4a) and of the observed shifts as a function of the concentration is similar. The difference between the widths of the plateaus of the low-temperature branches is apparently connected with singularities of the $Sm_{1-x}Gd_xS$ phase diagram, namely the dependence of the transition boundary on the temperature (helium on Fig. 4a and nitrogen on Fig. 4b). The smearing of the transitions (the slopes of the curves) can be attributed to a certain inhomogeneity of the samples (different gadolinium contents in individual grains belonging to central or surface regions of the bead).

The nature of the effect was made clear by a study of the shifts of the K_{α_1}, K_{β_1}, and $K_{\beta_{2,4}}$ lines. Figure 3 shows the measurement results: the thick curve (light points) corresponds to x = 0.20 and T ≈ 300 K, while the thin solid line corresponds to x = 0.18 and T = 77 K. Both curves have a characteristic V shape. This indicates that the valence of Sm in $Sm_{1-x}Gd_xS$ is larger than in SmS, and the increase of the valence is due to the decrease in the number of 4f electrons.

The experimental values of the shifts and the fraction η_{Gd} of the "extruded" electrons, for the high-temperature (T ≈ 300 K) and low-temperature (T = 77 K) phases, are given in the table. The mean-weighted values are $\overline{\eta}_{Gd} = 0.63 \pm 0.04$ and $\eta^{T}_{Gd} = 0.08 \pm 0.01$ electron/atom, the latter quantity differing significantly from that obtained from the measured parameters of the $Sm_{1-x}Gd_xS$ lattice[14].

To ascertain whether the valence state of gadolinium changes in the phase transition, we measured the shifts of the K_{β_1} line of Gd (we compared the samples $Sm_{1-x}Gd_xS$ and GdF_3). Figure 4b shows the experimental results[3]. Unlike the shift of the K lines of Sm, we did not observe (within the limits of the measurement errors) any change in the energy of the corresponding Gd line.

The Gd impurity in SmS can change the electric conductivity of the sample. This is sometimes used to identify the electronic phase transition (e.g., in $Sm_{1-x}Nd_xSe$[15]). At the same time, the presence of a conducting impurity should lead, when the critical concentration is reached, to a sharp increase of the conductivity due to a mechanism that is not at all connected with the phase transition (the so-called "flow through" or "shorting" effect[16]). The dashed line in Fig. 4b shows the dependence of the resistance of our samples (beads) of $Sm_{1-x}Gd_xS$ on the gadolinium concentration. The measurements were made at room temperature by a four-probe procedure. The abrupt decrease of the resistance terminates long before the start of the phase transition.

The preparation of the working samples involves grinding and pressing them. This procedure can lead to a shift of the phase-transition boundary. This is illustrated by the dashed and solid curves in Fig. 4c (the solid curve with the circles duplicates the similar curve on Fig. 4b). These curves were obtained by investigating samples that had different prior histories, viz., the dashed curve corresponds to measurements on freshly-prepared samples, and the solid curve was obtained after cooling the same samples with liquid nitrogen and heating them to room temperature. The light triangles in the same Fig. 4c show the shifts at room temperature and atmospheric pressure for samples subjected to prior hydrostatic compression to ≈10 kbar. An appreciable shift of the phase-transition boundary to the left is observed, into the region of lower gadolinium concentration. Cooling such a previously compressed sample at atmospheric pressure to nitrogen temperature leads to a sharp decrease of the shift (dark triangles). However, the shift still remains different from zero and appears to extend the plateau corresponding to the intermediate low-temperature phase (Fig. 4b) into the region of small x (dash-dot in Fig. 4c).

The transition from the high-valence phase into a low-temperature phase of intermediate valence, first apparently observed by Jayarman et al.[14], is an even outwardly beautiful phenomenon worthy of a more detailed description. The high-valence phase in the region $x > 0.2$ consists of sparkling polycrystal of bright-gold color. When the gadolinium concentration decreases, the color changes, loses its luster, and in the region $x \approx 0.12-0.14$ the samples, which by now have been precompressed for the transition to the high-valence state, acquire the form of slightly-oxidized red copper. The constancy of the shift (see Fig.4c) indicates, however, that the valence state of this phase remains unchanged in the entire range ($0.12 \leq x < 0.30$). When cooled to liquid-nitrogen temperature, the samples are converted into fine black powder. In the region $0.16 \lesssim x \lesssim 0.20$ this process proceeds quietly and reversibly. After heating, the powder becomes gradually yellow (with a time constant of several seconds). The process can be repeated many times. In the region $0.12 \lesssim x \lesssim 0.16$ the high-valence phase obtained after the preliminary compression "explodes" upon cooling with an audible crackle, sometimes expelling fragments from the flask in which the cooling is carried. The inner surfaces of the bottle walls are coated, over a height of several centimeters, by a finely-dispersed black powder of the intermediate phase. Heating does not lead to visible changes of the color, but measurements of the shifts (see the hatched triangles in Fig. 4c) show that after the first heating a partial transition to the high-valence state takes place. Subsequent coolings and heatings gradually (after several cycles) bring the system to an equilibrium state with a shift corresponding to the dash-dot curve of Fig. 4c, and this state remains unchanged after subsequent heat cycles.

DISCUSSION OF RESULTS AND CONCLUSIONS

The reversible change of the energy of the x-ray K_{β_1} line of samarium as a function of pressure, observed in the experiment with SmS, agrees sufficiently well with in form (see Fig. 2) with the change of the magnetic susceptibility previously known for the isomorphic phase transition in SmS to be able to conclude that the effects have a common cause, i.e., thatthe energy changes are due to the phase transition. The magnitude and sign of the observed shift also agree with those expected for the isomorphic transition with the 4f–5d transition. The shape of the "facsimile" for compressed SmS (see Fig. 3, thick line, dark circles) when compared with the reference curves for the case of chemical compounds with different valences (dashed in Fig. 3) indicates most unequivocally that the compared phenomena have a common mechanism, i.e., that the isomorphic phase transition in SmS is actually a particular case of the well known variable valence with 4f–5d transition. The number of 4f electrons that are removed in the phase transition, determined from the ratio of the observed and reference shifts, is $\bar{\eta}_P = 0.62 \pm 0.03$ and is in satisfactory agreement with the value $\eta_P = 0.77 \pm 0.06$[7] previously calculated from the changes of the SmS lattice parameters observed in the phase transition.

The main effect in $Sm_{1-x}Gd_xS$ is similar in character. The "facsimile" (see the light circles joined by the thick curve in Fig. 3) are practically indistinguishable. The gadolinium seems to play here the role of a chemically passive factor that ensures only compression of the SmS lattice. Direct proof of the last statement is provided by the near-zero shifts of the Gd lines, which remain constant in the region of the phase transition (diamonds in Fig. 4b).

The obtained data lead to definite conclusions also concerning the nature of the intermediate low-temperature phase. The V-shaped "facsimile" on Fig. 3 (upper curve) allows us to conclude that in this case, too, the mechanism of the transition is connected with a decrease in the number of the 4f electrons. This decrease, however, and the corresponding increase of the valence, is small, and contradicts the previously obtained $\eta_1 \approx 0.45$[14]. The latter value was obtained in[14] by comparing (see Fig. 4a) the lattice constant for pure SmS ($x = 0$) with the constant for the intermediate phase ($0.16 \lesssim x \lesssim 0.22$). Added to it is consequently also the compression in the region $0 \lesssim x \lesssim 0.16$, which is due to the change of the valence. Our data (see Fig. 4b) show that this is incorrect, for in the region $x < 0.14$ to 0.16 the shifts are close to zero, i.e., there is no change of valence. The quantity $\bar{\eta}^T_{Gd}$, calculated from the data of[14], but including only the jumplike change of the lattice parameter at the critical concentration ($x \approx 0.16$), amounts to $\eta^T_{Gd} \approx 0.1$, in splendid agreement with our data. Thus, the intermediate (low-temperature) phase is produced in a partial transition of the 4f electron and corresponds to a samarium valence on the order of 2.1.

A comparison of the plots of the electric resistance (dashed in Fig. 4b) and of the shift of the K_{β_1} line shows that the decrease of the resistance, which can be interpreted as a semiconductor-to-metal transition, has no bearing in this case on the isomorphic phase transition (it occurs at entirely different gadolinium concentrations). It seems to be due to the mechanism of shorting the lattice by electrically-conducting metal-metal bonds of trivalent GdS and can be described within the framework of the model of flow through the lattice with statistically distributed conducting (open) sites—"valves"[16].

The rather curious phenomenon of the "explosive" transition, first observed in[14] when $Sm_{1-x}Gd_xS$ ($0.15 \lesssim x \lesssim 0.22$) was cooled to the low-temperature intermediate phase, was investigated by us also on precompressed samples (Fig. 4c). It turned out that this phenomenon can be continued into the region of somewhat lower gadolinium concentrations (down to $x \approx 0.12$), and it appears to continue into the region of the existence of the intermediate phase (dash-dot in Fig. 4c). The most interesting circumstance here is the proposed metastability, the tendency of the high temperature phase to inversion, which increases with decreasing gadolinium concentration. The quietly proceeding reversible process in the region $0.16 \lesssim x \lesssim 0.22$ (in cyclic cooling and heating) gives way at $0.12 \lesssim x \lesssim 0.15$ to irreversible and explosive processes. These phenomena can be interpreted by starting from Fig. 2 and assuming that the addition of gadolinium simply shifts the entire curve to the left, so that the pressure of the inverse transition becomes lower than atmospheric. The sample compressed along the upper branch of the hysteresis curve stores a specific energy $w = P\Delta V/V \lesssim 80\ \text{J/cm}^2$, where $P \lesssim 6$ kbar and $\Delta V/V \approx 0.14$[17], retaining this energy when the pressure is subsequently removed (following the incompleted lower curve). The cooling plays the role of a "trigger."

The explosion is a macroscopic manifestation of the "collapse" of the 5d electrons of Sm into the deeply lying 4f states, accompanied by a sharp increase in the volume (radius) of the Sm atoms. The storing of the energy of mechanical compression directly in the form of a metastable electronic state is perhaps the most interesting aspect of the phenomena under consideration.

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[1)] In view of the anomalously deep (in the radial direction) location of the 4f electron in the atom, its removal, or excitation, leads to unusually large displacements (10–20 times larger) of the K lines as compared with the effects due to 5d, 6s, or p electrons. The plots of the displacement against the type of line, i.e., the course of the effect for the lines $K_{\alpha_{1,2}}$, $K_{\beta_{1,3}}$, and $K_{\beta_{2,4}}$, have a characteristic V-shape and are practically identical for all rare-earth elements.

[2)] The room-temperature measurements were made after the low-temperature measurements, since the prior history of the sample, connected with its preparation (grinding, pressing) shifts the transition boundary (see below).

[3)] At x = 0.07 (asterisk), the shift was obtained from the pair $Sm_{1-x}Gd_xS$–$(1-x)SmS + xGdS$ (mechanical mixture of the same concentration) in order to exclude the possible spurious shift due to the strong difference between the intensities of the compared lines.

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38