Possible appearance of Sm^{3+} ions during neutron irradiation at 21 K of samarium monosulphide doped with phosphorus impurities

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Résumé. — Nous avons irradié à 21 K aux neutrons rapides, 4 échantillons de SmS dopés en phosphore (1 %). Nous avons observé un accroissement important de leur conductivité électrique, qui semble indiquer l'apparition d'ions Sm^{3+} pendant l'irradiation.

Abstract. — Four SmS samples, doped with phosphorus (1 %), have been irradiated with fast neutrons at 21 K. A high increase of their electrical conductivity has been observed which seems to be due to an appearance of Sm^{3+} ions during irradiation.

1. Introduction. — Up to now no serious investigation has been reported on point defects in valence fluctuating rare-earth chalcogenides, though point defects seem to be crucial [1] in the understanding of some of the properties of those materials. Radiation damage allows us to introduce point defects in a controlled way in the material under consideration and so is adapted to this kind of investigation.

2. Samples preparation. — The samples are prepared in two steps : 1) Low temperature diffusion of S and P vapors in Sm ($T < 700^\circ\text{C}$). 2) Fusion around 2500°C by induction heating in sealed tantalum crucibles. The crystal growth is achieved by a Bridgman technique (5 mm/hour).

3. The $\text{SmS}_{1-x}\text{P}_x$ system. — The abrupt change of the unit cell parameter (figure 1) and the related

Fig. 1. — Unit cell parameter variation versus phosphorus concentration for $\text{SmS}_{1-x}\text{P}_x$. B = black, G = gold, R = red, Bl = blue.

color change from black to gold at a phosphorus concentration between 3 to 6 % show that there is a semiconductor to metal transition associated with a valence change of Sm ions. This transition is similar to that already found for $\text{SmS}_{1-x}\text{As}_x$ [2].

We will concentrate now on $\text{SmS}_{0.99}\text{P}_{0.01}$ (black phase) which behaves like a n-type semiconductor. Figure 2 shows in a log scale, the variations of the normalised conductivities of four single crystals versus $1/T$. The observed curvature may in a first analysis be attributed to hopping conductivity in the range 100 K, 20 K ($\text{Log } \sigma \propto 1/T^4$). The large

Fig. 2. — Variation of $\text{Log } \sigma/\sigma_0$ versus $1/T$ for $\text{SmS}_{0.99}\text{P}_{0.01}$ single crystals before irradiation. $\sigma_0 = \sigma_{300\text{K}}$.

differences at low temperature between the samples are probably related to different point defect (or impurity) concentrations and distributions.

4. Experimental. — We have irradiated four $\text{SmS}_{0.99}\text{P}_{0.01}$ single crystals with fast neutrons (f.n.) at 21 K using the VINKA device [3] on the CEN-FAR Triton Nuclear Reactor. The samples were first cooled from 300 K to 21 K, then irradiated to a total flux 2×10^{17} f.n./cm² (figure 3). The samples were subsequently warmed slowly up to 300 K and finally cooled to 21 K (figure 4). The conductivity was measured continuously during the whole experiment.

Fig. 3. — Conductivity variation of $\text{SmS}_{0.99}\text{P}_{0.01}$ (sample n° 4) at 21 K during f.n. irradiation. (1) First irradiation. Instantaneous flux $\Phi_i = 1.8 \times 10^{16}$ f.n./cm². s. (2) Second irradiation $\Phi_i = 3 \times 10^{12}$. (3) The two previous curves on a same Log, Log plot. $\sigma_i = \sigma_{21\text{K}}$ before irradiation.

5. Results. — **5.1 RADIATION DAMAGE.** — Two main points should be emphasized : 1) The conductivities (σ) increase drastically during irradiation by a factor 10 to 10^4 depending on the samples. This increase is linear until the defect concentration reaches a critical value ($\Phi \approx 3 \times 10^{16}$) and then increases proportionally to Φ^3 (figure 3). 2) The results are reproducible, being identical for samples 1 and 2 which had the same conductivity before irradiation.

5.2 DAMAGE RECOVERY. — Three features are important (see figure 4) : 1) The samples remain semiconducting. 2) Annealing of defects begins only at ≈ 140 K in two steps centered around 160 K and 240 K. 3) After annealing the conductivity curves are similar to those before irradiation but show higher conductivities and less dispersion between the samples.

Fig. 4. — Temperature dependence of electrical conductivity of $\text{SmS}_{0.99}\text{P}_{0.01}$ (sample n° 4). (1) Before irradiation. (2) Effect of irradiation. (3) Annealing curve. (4) After irradiation and annealing.

6. Discussion. — From theoretical calculations [4] and assuming reasonable values for threshold displacement energies (≈ 25 eV) the atomic concentrations of displaced atoms at the end of the total irradiation are approximately 1.9×10^{-4} for S ions and 1.3×10^{-4} for Sm ions. Three possible mechanisms may be put forward to explain the $\sigma(\Phi)$ curves : 1) We have increased the number of hopping centers (point defects) and therefore the electronic mobility. 2) The damaged regions have a higher conductivity. The total conductivity is then that of an inhomogeneous medium. 3) The Sm interstitials which are submitted to high local strains change their valence to Sm^{3+} . Many of the released electrons remain localized and non conducting until a certain critical concentration is reached ($\Phi \approx 3 \times 10^{16}$). If the mobility is supposed to remain constant during irradiation, two supplementary displaced Sm at the end of irradiation contribute approximately one electron to the conduction band.

The three models proposed here support the idea of local $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$ valence change during irradiation. Further analysis and experiments are necessary to choose between them.

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