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**RARE-EARTH SEMICONDUCTORS STUDIES IN THE SOVIET UNION**

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Résumé.— Les résultats des recherches dans le domaine de physique des Semiconducteurs des terres rares en URSS sont examinés dans un exposé. On discute les résultats expérimen­taux des propriétés physiques et physico-chimiques dans le cas de ces subs­tances. L’attention principale est faite sur la discution des résultats expérimen­taux nouveaux pour SmS, EuO et la solution solide sur la base de celles-ci.

Abstract.— The investigations in the field of the physics of Rare-Earth Semiconduc­tors in the USSR are considered in this report. The experimental data on physical and physico-chemical properties of these materials are discussed. The main attention in the report is paid to the discussion of the new experimental results for SmS, EuO and some of their solid solutions.

During the past decade the study of Rare-Earth semiconductors (RES) has received increasing attention in the Soviet Union /1/. The RES research has a wide geographic dis­tribution being performed in Moscow, Leningrad, Kiev, Kharkov, Sverdlovsk, Baku, Erevan, Tbilisi, Dushanbe, Makhackhala. The following RES are investigated: EuX, SmX, Eu$_{1-x}$Ln$_x$X, Sm$_{1-x}$Ln$_x^+$, Ln$_2$X$_3$, Ln$_3$X$_4$, Ln$_x$Z$_3$, Ln$_x$Z$_4$ (where X = S, Se, Te, Ln = Rare Earth Metal (REM)), LnB$_c$ (Ln = Sm, Eu, Yb), polysulfides (Ln$_n$S$_{2n}$, Ln$_n$S$_{2n+1}$, Ln$_n$S$_{2n+2}$), pnictides (Ln$_n$Z$_3$, Ln$_n$Z$_4$, where Z = P, Sb, Bi), and complex ternary and quaternary compounds containing RE and transition metals. Investigations are made on powders, poly- and single crystals and thin films. The studies comprise optical, magneto-optical, magnetic, galvanomagnetic, electrical, thermal, thermo-electrical, acoustic, resonance, mechanical, crystallo-chemical and physico-chemical properties. The different groups study the kinetics and thermodynamics of crystal synthesis and growth as well as thin film preparation. They develop also the theory of RES. The two methods most widely used in the Soviet Union to determine the valence state of RE-ions (primarily Ce, Sm, Eu, Yb) in compounds are the following: 1) measurement of the X-ray K-line shift /2/ and 2) X-ray L$_{111}$ absorption spectroscopy /3/. Both methods give the possibility to obtain information on the valence state of RE-ion found in the bulk of a substance and permit to use the samples in the form of powders and thin films.

Work on RES is coordinated by the section conducted by the Academy of Sciences of the USSR. The RES Information Center attached to the A.F. Ioffe Physico-Technical Institute issues current RES bibliography /4/ and reviews /5,6/.

The present paper reviews only a small portion of recent results obtained on RES at a number of laboratories in the Soviet Union during the years of 1978 and 1979. The "magneto-exciton" (SmS and SmS-based solid solutions) and magnetic (EuX, Ln$_x$X$_3$, Ln$_x$X$_4$, LnB$_c$) semiconductors will be discussed in detail. A brief review of the recent results obtained on certain sulfides and complex RES will also be given below.

I. SmS.— The recent work on SmS has been devoted mostly to a) the more accurate definition of its energy band structure (the determinations of the mutual location of d and s-subbands in the conduction band and the energy gap $E_g$ between 4f-levels and conduction band), b) to the investigation of the peculiarity of semiconductor-metal phase transition under hydrostatic pressure, and finally c) to the determination of certain physical parameters of both metal -SmS (M) and semiconductor -SmS(S) modifi­cations.

As it was shown earlier /7/, the s-band
of SmS(S) is located lower on the energy scale than the d-band. This conclusion was confirmed in \(^8\), where Hall coefficient \(R_H\) and electrical conductivity \(\sigma\) were measured under uniaxial pressure (fig. 1). If the conduction band of SmS is formed by \(5d(t_{2g})\) orbitals of \(Sm^2+\) (and some orbitals of \(S_{2g}\)) \(^8\), then each of the three \(5d(t_{2g})\)-subbands should be characterized by an anisotropic effective mass. If the conduction band has s-type, then the effective mass should be isotropic. In the kinetic equation validity region the approximation of relaxation time gives:

\[
\frac{d\sigma_p}{dp} / \frac{d\sigma_\perp}{dp} = \frac{m_p}{m_\perp} = \Lambda
\]

where \(\sigma_p\) and \(\sigma_\perp\) are values of electrical conductivity parallel and perpendicular to the pressure, respectively. From figure 1 it follows that \(\Lambda = 1\). Thus we are led to the conclusion that within the experimental error the effective mass of the electrons in the conduction band should be isotropic.

On the assumption of thermal excitation of \(4f\)-electrons into the conduction band the energy for the \(Sm^{2+}\) to \(Sm^{3+}\) transition appeared to be \(0.18 \pm 0.01\) eV \(^13\). An investigation of the volume variation ratio \((\Delta V/V_0)\) at 300 K for SmS single crystals has been made in \(^16\) using a piezometer with lead as the medium for the pressure transfer. No fracture of the sample resulted from repeated direct and reverse semiconductor (B) - metal (M) transition runs. Following the fourth of fifth run the ratio \((\Delta V/V_0)\) reached a constant value and remained unaltered in subsequent runs. The values of pressure equal to 4.7 kbar (in the first run the pressure = 6.5 kbar) and 1.7 kbar for direct and reverse \(B2M\) phase transition, respectively, appeared to be characteristic for such a "trained" sample, which additionally exhibited "fine structure" in its

1. The value of \(E_g \approx 0.22\) eV was earlier obtained from data on electrical, galvano-
2. magnetic/9,10/, magnetic/11/ and thermal/7/ properties of SmS(S).
phase transition (Fig. 3).

Fig. 3: Dependence of $\frac{V}{V_0}$ on $P$ for SmS single crystal (following the fifth run)/16/.

2b. T-P phase diagram for SmS has been examined in /17/ (method of the investigation: piezometry and dilatometry up to 32 kbar, $T = 77-550K$). A curve of the isostructural $B + M_1$ phase transition has a S-shape (Fig. 4).

Fig. 4: T-P phase diagram of SmS/17/. K - critical point, 1-equilibrium line for $B$-$M_1$ transition; 2-position of $P_{cr}$ marking the onset of constant compressibility.

At $T>300K$ the ratio $\frac{d\rho}{dP}$ is positive and at $T<300K$ - negative. It was found that the critical point occurred at 700K and $\approx 8$ kbar. The compressibility was measured within 32 kbar and 298-523K. The boundary between $M_1$ and $M_2$ phases (Fig. 4) was derived from a sharp change of the compressibility at $P_{cr}$. (for $P_{cr} \geq 15-20$ kbar the compressibility became constant). Thus the T-P phase diagram for SmS has three regions: $B$ - the semiconductor phase, $M_1$ - the mixed-valence metallic phase (valence of Sm ions $m = 2.7$), and $M_2$ - metallic phase with $m=3$.

lc. When a solid is irradiated by a short laser pulse, the resulting thermal expansion, generates ultrasonic vibrations at frequencies corresponding to the Fourier-spectrum of the laser pulse. In /18/ for the amplification of the ultrasound power the SmS metallic film has been used, which under heating had a metal-semiconductor phase transition involving a large volume change /1/. In the case that the intensity of the laser beam is sufficient to heat the film to the temperature of the phase transition there is a sharp increase in the value of ultrasound amplification, which is shown in figure 5, to be an order of magnitude greater than that for a metallic Cr film treated under the same conditions.

Fig. 5: Dependence of ultrasound power on laser beam intensity for SmS and Cr films (duration of laser pulse - 40 ns; elastic wave frequency - 30 MHz).

2c. A measurement of the linear expansion coefficient $\delta (T= 80-700 K)$ for the SmS(S) has been carried out in /19/. Within 120-140 K there is "a step" in the temperature dependence $\delta$ which might be attributed to the excitation of Sm$^{+2}$ multiplet levels of higher order ($J=1, J=2$). /20/ reported new data on the homogeneity range SmS(S) and /21/ on the anomalies found in the absolute value of SmS(S) magnetic susceptibility. The normal reflection spectrum of
SmS(S) has been measured in /22/ at 300 K in the range of 0.05 - 22 eV. The result obtained for the range of 0.05 - 12 eV appeared to be in good agreement with those obtained in /23/. An absorption maximum which has been observed to occur at 14.5 eV /22/ is associated with the transfer of electrons from the deep 3s^2 shell of the sulfur to the conduction band.

The value of the plasma frequency appeared to be 2.4 eV as a result of the investigation of the thermal reflectivity of SmS metallic films, performed in /24/ for the range of 1.2 - 3.8 eV.

The rate of the metal-semiconductor phase transition in thin SmS metallic films (by heating) was estimated in /25/ and appeared to be 10^-8 s. The threshold recording energy density (E_{rec}) appeared to be 0.046 J/cm^2. The influence of various factors on E_{rec} was assessed: time and wavelength of the recording laser pulse, film thickness and substrate materials, presence of the atmosphere, and doping. A recording was made with a density of 3x10^7 bit/cm^2 /25/. In /26/ the data on holographic recording in SmS metallic films is reported. It was obtained: diffraction efficiency - 1-4%, resolution - 1500 line/mm.

2. SmS based solid solutions - The study of T-X and P-T-X phase diagrams and the determination of high and low temperature critical points for Sm_{1-x}Gd_xS /27+31/ as the valence state of Sm and Yb ions in Sm_{1-x}Yb_xS have been the main points of interests in the recent years.

A T-P-X phase diagram has been obtained in /27/ for the Sm_{1-x}Gd_xS (Figs. 6, 7). The line of the equilibrium: semiconductor-metal exhibited the S-shape for all compositions. The line of high temperature critical points was determined /27,30/. The absolute value of the critical points decrease with the increase of the concentration of Gd. At x = 0.25 and T = 100-150K there is a second low temperature critical point (K_2) on the line of isostructural phase transition /28/ (Fig.8).
The X-ray investigation of a Sm$_{0.85}$Gd$_{0.15}$S, previously subjected to hydrostatic pressure, showed that the metallic phase exists in the temperature range 160-426 K /29/. (Fig.9).

The metal-semiconductor phase transition occurs at 160 and 426 K and besides the volume changes by 10 and 8%, respectively.

Some interesting data have been obtained in /12/ on the valence state of Sm and Yb ions in Sm$_{1-x}$Yb$_x$S using the X-ray K-line shift method. The Sm valence in this solid solution increases with x (Fig. 10) in spite of the fact that the lattice constant was proved to be almost linearly decreasing from SmS to YbS. Similar effect has been observed earlier in Sm$_{1-x}$Eu$_x$S /32,33/. Also, a change of Yb valence (Yb$^{3+}$, 4f$^{14}$ → Yb$^{2+}$, 4f$^{13}$) has been observed at high temperatures (1000K).

3. EuX and EuX-based solid solutions.- One of the principal tasks facing the experimentalist has been to raise the Curie temperature ($T_C$) of EuO without changing its semiconductor properties.

Fig.10: Variation of Sm valency ($m = 2n$) in Sm$_{1-x}$Yb$_x$S with x, 1,2,3 - Sm$_{1-x}$Yb$_x$S at 77, 300 and 1000K respectively; 4 - Sm$_{1-x}$Eu$_x$S at 300K /39/; 5 - Sm$_{1-x}$Eu$_x$S at 300K /32/.

This problem has been discussed in a number of recent papers /34-37/. A significantly higher $T_C$ (130-150 K) has been obtained in Eu$_{1-x}$Yb$_x$O (x < 0.08) /34-36/ and non-stoichiometric EuO films (with excess of Eu) /37/ without changing its semiconductor properties (Fig.11).

Fig.11: Dependence of $T_C$ in Eu$_{1-x}$Ln$_x$O on lattice constant a. A - Stoichiometric EuO, $\rho \approx 10^6$ ohm.cm; Eu$_{1-x}$Sm$_x$ /34/, at point C: $x = 0.08$, $\rho \approx 10^7$ ohm.cm; Eu$_{1-x}$Yb$_x$O /38/, at point B: $x = 0.05$; Eu$_{1-x}$Gd$_x$O /6/, at point D: $x = 0.04$, $\rho \approx 10^5$ ohm.cm.

In both cases an increased $T_C$ should be attributed to the formation of the magnetic
impurity states (MIS). They occur around the Sm ions of 4f^55d^1- electronic configuration in Eu_{1-x}Sm_xO (2) and around oxygen vacancies in the films.

In Eu_{1-x}Sm_xO /35/ and Eu_{1-x}Gd_xO /40/ the presence of two Curie points: T_{C1} and T_{C2} (Fig.12,13) has been discovered.

Fig. 12: Dependence of heat capacity (1,2) and magnetocaloric effect (3) on T in Eu_{1-x}Sm_xO /35/ 1-EuO, 2,3- composition with x = 0.084. T_{C1} is very close to T_C for pure EuO and is slightly rising with x. T_{C2} shows a strong dependence on the composition of a solid solution (Fig.13). A following qualitative explanation of this phenomenon could be given. For example, in the crystals of Eu_{1-x}Sm_xO with x < 0.08 there are the regions, which are free from the Sm impurity ions - the "free phase" of EuO (3) and the regions which have magnetic quasi molecules - MIS (Sm ions of the 4f^55d^1 configuration and 12 nearest ions of Eu^2+). The "free phase" of EuO must be responsible for T_{C1}, while MIS must be responsible for T_{C2}.

4. Ln_2X_3 and Ln_3X_4.- The progress made by the Soviet investigators in the study of these materials is based on the important advances made in the development of a technique which proves efficiency in preparation of the large transparent Ln_2X_3 single crystals /41/; perfect Ln_3X_4 and Ln_2X_3 - Ln_3X_4 samples.

Extensive research of the physico-chemical properties of Ln_2X_3 and Ln_3X_4 has been under way at the various laboratories of the Soviet Union in recent years.

The X-ray investigation of Ln_2S_3 carried out in /42/ has yielded diffraction patterns of two types suggesting the possibility of two isostructural series for these compounds, namely β and β' (Fig.14).

Fig. 13: Dependence of a, T_C and paramagnetic Curie temperature Θ in Eu_{1-x}Sm_xO on x /35/.

(2) This configuration has been proved in /35,36/ from the data on the X-ray L_{111} absorption spectra.

Fig. 14: β and β' Sm_2S_3 (from X-ray measurements) /42/.

In /43/ an experiment has been made with the aim of determining the homogeneity range of the γ-phase of Ln_2S_3 - Ln_3S_4 (Ln - La, Pr, Sm, Gd, Dy.).

(3) In this regions prevails Eu^2+-Eu^2+ interaction.
The phase diagrams for the several systems have been received in /44,46/ from the data of differential thermal and X-ray analyses. Figures 15-17 demonstrate a phase diagram of a more thoroughly studied Yb-S systems.

Fig. 15: Phase diagram for Yb-S (0-62.5 at % S, P = 4.5 atm) /46/.

It exhibits two features common for the Ln-chalcogen systems: an absence of compounds in the region rich in the rare earth metals and a tendency to form a large number of phases in the region of 50-75 at % of chalcogen. A brief discussion of the diagram seems to be relevant. ε - Yb₂S₃ and δ - Yb₃S₅ (Fig.15) have been obtained as a result of a peritectical reaction at 1470 and 910°C, respectively; the homogeneity range for Yb₂S₃ is: Yb₂S₀.₉₆ - Yb₂S₁.₀₈; Yb₃S₅ (Fig.16) has been obtained at 7 kbar and 1000°C, and Yb₂S₃ - only from a solution in molten KI. γ - Yb₂S₃', δ - Yb₂S₃ - (Fig.17), Yb₂S₃ - rhombohedral, Yb₅S₇ and Yb₂S₂-x have been obtained under the high pressure (30-90 Kbar) and T = 1000-2000°C.

Magnetic and electrical properties of a series of Gd₂S₃ samples (stoichiometric and having an excess of Gd) have been studied in a wide range of temperatures and magnetic fields /47/.

A number of recent papers have been devoted to the investigation of electrical and thermoelectrical /48/ (Ln₂S₃ : Ln - Gd, Ho, Er, Yb, Lu, Sc), optical /49,50/ (Ln₂S₃ : Ln - Y, La,Yb, Dy, Ho, Er, Tm, Yb and Lu), magnetic /51/ (Sm₂S₃ - Sm₃S₄) and thermal /52/ (LaₓFe₃ - LaₓFe₄, PrₓFe₃ - PrₓFe₄) properties.

Fig. 16: "Hypothetical" Yb-S phase diagram /46/.

Fig. 17: P-T phase diagram for ε-Yb₂S₃ (60 at.%) /46/ (γ - and δ - Yb₂S₃ have been obtained from ε -Yb₂S₃ under the conditions of high pressure and temperature)

For the first time the investigation of the optical properties of the perfect La₂S₃ single crystals was carried out in /49/. A window of transparency (0.6 - 15μ) (Fig.18) was discovered.

5.Rare Earth Hexaborides.- During the past few years attention has been focused on Eu hexaboride and, specifically, on its band structure. In the model proposed by the French school /53/ the bottom of the conduc-
The variation of \( p \) with \( P \) should be ascribed to the appearance of \( \text{Eu}^{3+} \) ions or to the change of the electronic band structure of \( \text{EuB}_6 \). A measurement of X-ray K-line shift made for pressures up to 13 kbar revealed no \( \text{Eu}^{3+} \) in \( \text{EuB}_6 \) within the experimental error, thus we must imply that the decrease of \( p \) with \( P \) should be due to the altered parameters of the band structure. This conclusion was supported by the data obtained in /55/ on \( p \) measured in \( \text{EuB}_6 \) under the pressure up to 100 kbar. No semiconductor-metal phase transition was observed within this range of pressure. At \( \approx 40 \) kbar \( p \) was found to reach saturation (\( p_b \)). \( p_b \) for \( \text{EuB}_6 \) is 1100 \( \mu \text{K}\cdot\text{cm} \) as compared with 15\( \mu \text{K}\cdot\text{cm} \) for metallic \( \text{LaB}_6 \). This fact led the authors of /55/ to a conclusion that once the pressure reaches the value of 40 kbar, the conduction band absorbs the impurity level, which must be at 0.032 eV from the bottom of the conduction band. A more detailed investigation of electrical and galvano-magnetic properties of \( \text{EuB}_6 \) under the hydrostatic pressure up to 7 kbar and in the temperature range of 4.2 - 300 K has been made in /56/. The investigation of magnetic and structural properties of \( \text{EuB}_6 \), \( \text{Eu}_{1-x}\text{Ce}_x\text{B}_6 \) and \( \text{Eu}_{1-x}\text{Nd}_x\text{B}_6 \) has been reported in /57,58/ (Fig. 20 a, b).

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The investigation is focused around the phase diagrams, physico-chemical, magnetic, and thermoelectric properties.

Fig. 20 b) Dependence of a on X for Eu$_{1-X}$Ln$_x$B$_6$ 1- Eu$_{1-X}$La$_x$B$_6$/60/, 2- Eu$_{1-X}$Ce$_x$B$_6$/58a/, 3- Eu$_{1-X}$Nd$_x$B$_6$/75b/, 4- EuB$_6$-xC$_2$/70/, 5- EuB$_6$.

The materials under study may be classified into four groups:

1) The first group includes a) LnX - Me$_2$X$_3$ (Ln - Eu, Yb; Me - Ga, In; X - S, Se, Te) which exhibit two congruently melting compounds of LnMe$_2$X$_4$ and LnMe$_4$X$_7$ and b) LnX - MeX (Ln-Sn, Yb) /63-66/.

2) The second group comprises a) Ln$_2$X$_3$ - B$_2$X$_3$ (B - Sb, Bi) with one incongruently melting compound LnBX$_3$ and b) LnX - B$_2$X$_3$ within which two compounds LnB$_2$X$_4$ and LnB$_4$X$_7$ are formed /67-73/.

3) The third group consists of compounds of the type LnCrX$_3$, CrLn$_2$X$_4$, CrLn$_4$X$_7$ (X - S, Se) and LnCr$_2$X$_4$ (X - S, Se, Te; Ln - extends from Gd to Lu) /74-76/.

4) The fourth group contains the systems of the Ln$_2$O$_3$ - Gd$_2$(In$_2$)S$_3$ type /77-78/.

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