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## Increase of the Curie temperature of the magnetic semiconductor EuO

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The possibilities are considered of greatly increasing the Curie temperature of ferromagnetic solid solutions based on europium monoxide while preserving the semiconducting character of their conductivity. The experimental results of this study attest to the existence of magnetic heterogeneity in homogeneous EuO-SmO solid solutions. The discussion is carried out within the framework of the magnetic impurity state and direct excited exchange models. It is suggested that the exchange interactions are switched in the investigated solid solutions in "relay" fashion.

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From among the ferromagnetic semiconductors, particular interest attaches to divalent europium chalcogenides EuX (X=O, S, Se, Te), which are characterized by a number of unusual properties.<sup>[1]</sup> The simplicity of the crystal (and magnetic) structure (of the NaCl type) makes them convenient model objects in the theory of ferromagnetism.<sup>[2]</sup> The practical utilization of such materials is limited to the low magnetic-order temperatures—the Curie points of EuS and EuO are respectively 16 and ≈70 K. The problem of increasing  $T_C$  in these ferromagnetic semiconductors while preserving their semiconductor conductivity is therefore quite pressing.

It is known that  $T_C$  of EuO can be increased by hydrostatic compression of the crystals or by the presence of excess europium atoms in them.<sup>[3]</sup> Another way of solving this problem, by doping EuO (or EuS) with ions of trivalent rare-earth metals (REM),<sup>[4]</sup> also ensures a substantial increase of the Curie temperature (almost double in the oxides). In these cases, however, the increase of  $T_C$  is accompanied by an appreciable decrease of the activation energy of the conductivity (of the  $f-d$  transition energy), by an increase of the density of the carriers in the  $d$  band, and by an abrupt increase of the conductivity, to values  $\sigma \approx 10^2 - 10^3$  ( $\Omega\text{-cm}$ )<sup>-1</sup>.<sup>[5]</sup>

The magnetic, electric, optical, and some other properties of europium chalcogenides doped with trivalent

REM, such as La or Gd, can be explained within the framework of the model of magnetic impurity states,<sup>[6,7]</sup> according to which, the excess valence electron of the impurity is localized near the impurity atom as a result of the Coulomb interaction. Stabilization of the system and the minimum of its free energy are attained as a result of the strong  $i-f$  exchange interaction between the impurity electron and the  $4f$ -spins of the twelve nearest magnetic ions of europium. As a result, a magnetic quasimolecule is formed, characterized by a gigantic magnetic moment which is ascribed to its central ion. The onset of such a quasimolecule is accompanied by the appearance of an unusual magnetic contribution to the specific heat in the region of the Curie temperature, as was observed, for example, when EuS was doped also with gadolinium.<sup>[8]</sup> At the same time, an anomalously large increase of the ferromagnetic susceptibility takes place at  $T \geq T_C$ , leading to a positive deviation from the Curie-Weiss law.<sup>[9]</sup> It follows from the foregoing that the solution of the problem of increasing  $T_C$  of ferromagnetic semiconductors, besides being of practical importance, calls for the development of premises concerning the properties of the magnetic quasimolecules they contain. The experimental study of the latter has not yet found its due reflection in the literature.

Samokhvalov *et al.*<sup>[10]</sup> were the first to observe an

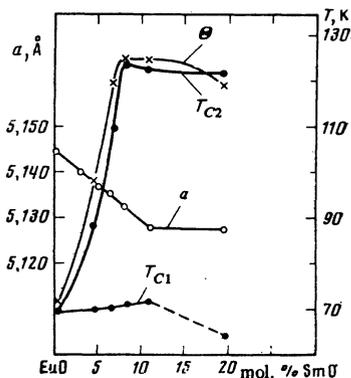


FIG. 1. Concentration dependences of the lattice parameter (a) of the ferromagnetic ( $T_{C1}$ ) and paramagnetic ( $\Theta$ ) Curie temperatures of  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  solid solutions.

increase of  $T_C$  and of the paramagnetic Curie temperature  $\Theta$  in the system of solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$ , in which the semiconducting character of the conductivity was preserved in a large region of compositions, as confirmed by an investigation of the diffuse reflection and of their electric and other properties. It must be noted that of all the REM, only Eu, Sm, and Yb are capable of forming a stable divalent state in similar structures, so that the stoichiometric solid solutions between them, particularly  $\text{EuS-SmS}$ , can preserve their semiconducting properties. One could therefore expect doping of  $\text{EuO}$  with samarium monoxide likewise to raise  $T_C$  of such solid solutions. This was indeed observed in recent investigations.<sup>[11]</sup>  $\text{SmO}$ , in contrast to  $\text{SmS}$ , does not exist under normal conditions, so that the solid solution  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  has a limited concentration region of stability. There is no information on the electronic state of samarium ions in such a solution. The present paper is devoted to their examination.

## SAMPLES AND METHODS OF THEIR INVESTIGATION

The polycrystalline finely dispersed samples of solid solutions of  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  investigated in the present paper were prepared by the method of solid-phase low-temperature oxidation.<sup>[12]</sup> One of its features is that the low reaction temperatures ensure the formation of stable solid solutions of the lower oxides of the initial REM. The sample compositions listed in Table I were determined with a Perkin-Elmer-403 atomic-absorption spectrophotometer with accuracy  $\pm 0.2\%$ . An x-ray structure and phase control of the compound was effected in  $\text{CrK}_\alpha$  radiation using VRS-3 cameras and the "DRON-3" apparatus. The concentration limits within which the solid solutions are single-phase at 1000 C were estimated from the dependence of the parameter of their crystal lattice on the composition,  $a(x)$ , shown in Fig. 1 and given in Table I. According to these data, the region in which the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  (based on  $\text{EuO}$ ) are obtained by the indicated technology single-phase is limited by the  $\text{SmO}$  content, approximately 12 mol. %. According to the x-ray analysis data, samples containing a larger percentage of  $\text{SmO}$  were always two-phase. An investigation of the single-phase compounds with the IXA-5 microanalyzer of the JEOL firm has confirmed their microhomogeneity.

The resistivity of the pressed samples was measured with direct current at room temperature and was close to  $10^8 \Omega\text{-cm}$ . An additional confirmation of the semiconducting character of the solid solutions was obtained by studying the Faraday effect<sup>[1]</sup> ( $\lambda = 7.8 \text{ mm}$ ,  $H = 5 \text{ kOe}$ ) at 80 K. It turned out, in particular, that the Faraday rotation of the compound  $\text{Eu}_{0.916}\text{Sm}_{0.084}\text{O}$  is close to 350 deg/cm. Its magneto-optical quality was also high. The single-phase solid solutions of the  $\text{EuO-SmO}$  system are apparently not inferior to pure  $\text{EuO}$  with respect to these parameters.<sup>[13]</sup>

The magnetic parameters of the samples were measured in the temperature range from 60 to 300 K and in magnetic fields from 3 to 10 kOe, using a Domenicali balance. The temperature dependences of the specific heat and of the magnetocaloric effect were investigated using an adiabatic calorimeter in one experiment. The magnetocaloric effect was measured in a longitudinal magnetic field of intensity up to 2.3 kOe and at temperatures  $T \geq 78 \text{ K}$ . The possibilities afforded by the procedures used in these measurements were reported earlier.<sup>[14]</sup>

Estimates of the Curie temperature of the solid solutions were made principally on the basis of investigations of their nonmagnetic parameters—the  $\lambda$  points on the  $C_p(T)$  polytherms and the peaks of the magnetocaloric effect. The latter practically coincided. To the contrary, the temperatures  $T_{C2}$ , determined from the  $\sigma_s(T)$  dependence, exceeds somewhat their first determinations. For example, for the compound  $\text{Eu}_{0.89}\text{Sm}_{0.11}\text{O}$  this difference reaches  $\sim 8^\circ$  (or  $\approx 6\%$ ). At lower values of  $x$ , on the other hand, the temperature  $T_{C2}$  (in the case of compounds 2 and 3) corresponds to a maximum on the  $\partial\sigma_s/\partial T$  polytherms, which, as it turned out, differs little from that established from the nonmagnetic characteristics of the samples.

Finally, to determine the electronic states of the solid solutions by x-ray  $L$ -absorption spectroscopy, we determined the electron configuration of the samarium ions. The method was based on the dependence of the energy of the absorption  $L_{111}$  maximum (corresponding to a transition of an internal  $2p$  electron to unoccupied  $5d$  states of the conduction band) on the number of  $f$  electrons in the RE ion.<sup>[15]</sup> When the number of the  $f$  electrons changes by unity, the maximum of the absorption of samarium shifts by 7.0 eV, the accuracy of the determination of its energy being  $\pm 0.2 \text{ eV}$ .

TABLE I. Structural and magnetic parameters of solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$ .

| $x$ | Composition, $x$ | $a$ , Å<br>$\pm 0.001$ | $T_{C1}$ , K | $T_{C2}$ , K | $\Theta$ , K | $M_{\text{eff}}$ , $\mu_B$ |
|-----|------------------|------------------------|--------------|--------------|--------------|----------------------------|
| 1   | 0                | 5.143                  | 68.5         | —            | 71           | 7.8                        |
| 2   | 0.048            | 5.137                  | 69           | 86           | 100          | 7.7                        |
| 3   | 0.068            | 5.133                  | 69.7         | 110          | 121          | 7.6                        |
| 4   | 0.084            | 5.131                  | 71.2         | 124          | 125          | 7.5                        |
| 5   | 0.11             | 5.128                  | 71.7         | 122          | 125          | 7.3                        |
| 6*  | 0.19             | 5.127                  | —            | 122          | 117          | 6.9                        |

\*The sample contains two phases, one of which was isostructural with  $\text{EuO}$ .

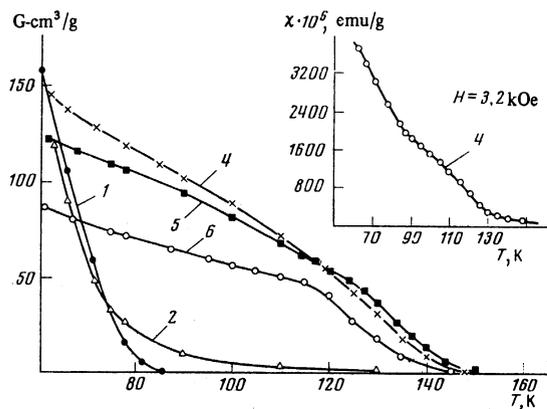


FIG. 2. Polytherms of the spontaneous magnetization of the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$ . Insert—polytherm of the magnetic susceptibility of sample No. 4 (here and below the number in the figures corresponds to the numbering in the table).

## RESULTS OF INVESTIGATION

The data shown in Fig. 1 point to a considerable increase of the Curie temperature  $T_{C2}$  of  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  solid solutions with increasing samarium content. It is typical that these substitutions of the europium ions by samarium ions in the oxide solid solution lead to observation of a decrease in the parameter of the crystal lattice. In this respect the system in question differs substantially from the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{S}$ , for which the lattice parameter remains unchanged at  $a = 5.968 \text{ \AA}$  in the entire homogeneity region.<sup>[10]</sup>

The paramagnetic Curie temperature  $\Theta$  of the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  just as the ferromagnetic point  $T_{C2}$  increases with increasing samarium content, reaching a maximum at  $x = 0.084$  (i.e., 8 mol. % SmO). Further increase of the samarium-ion concentration in the solid solution leads to a relatively weak change in the values of  $T_{C2}$  and  $\Theta$ . We note that similar regularities have been established also in<sup>[11]</sup>. On going into the two-phase region, the paramagnetic temperature apparently decreases more rapidly than  $T_{C2}$ . To be sure, however, the electric conductivity of the material increases at the same time ( $\sigma \sim 10^6 (\Omega \cdot \text{cm})^{-1}$  at  $x = 0.19$ ).

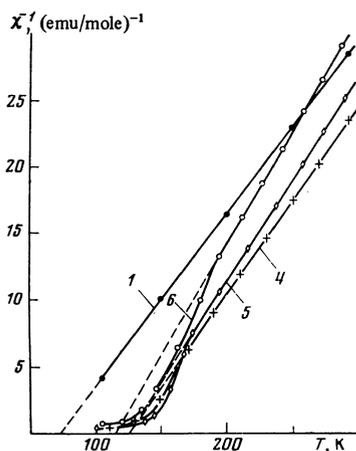


FIG. 3. Polytherms of magnetic susceptibility of the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$ .

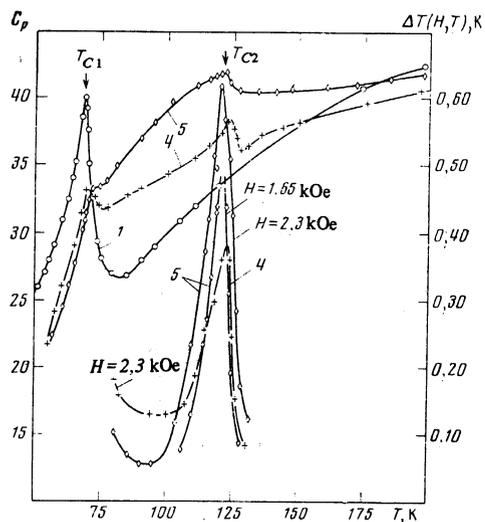


FIG. 4. Temperature dependences of the specific heat (in J/mole-deg) and of the magnetocaloric effect of samples No. 1, No. 4, and No. 5.

The polytherms of the spontaneous magnetization of the investigated samples are shown in Fig. 2. It follows from the experimental data that the magnetization of  $\text{EuO}$  in solid solutions with  $x > 0.05$  at  $T < T_{C2}$  decreases quite rapidly with increasing temperature. On the other hand, in sample No. 2 ( $x = 0.048$ ,  $T_{C2} = 86 \text{ K}$ ), this is no longer observed. It is interesting to note that this compound is characterized also by the largest difference,  $\Theta - T_{C2} = 14^\circ$ , which in turn indicates that the short-range magnetic order is preserved in it in a wide range of temperatures higher than  $T_{C2}$ . At the same time, the Curie-Weiss law for the dependence of the paramagnetic susceptibility at  $T > T_C$  (Fig. 3) is best satisfied for sample No. 1 (pure  $\text{EuO}$ ). For all the remaining solid solutions, this law holds only at temperatures above 170–180 K (whereas at lower temperatures positive deviations from this dependence are observed). In addition, for the same compounds, the Weiss constants and the effective magnetic moment per ion of metal decrease with increasing  $x$  (see the table).

A characteristic feature of the polytherms of the magnetic susceptibility and of the magnetization, measured in fields  $\leq 3 \text{ kOe}$ , is the presence on them of inflection points (see, e.g., the insert in Fig. 2). The presence of two Curie points in the solid solutions is most clearly manifest, however, on the polytherms of the specific heat and of the magnetocaloric effect (Fig. 4). The temperature  $T_{C1}$  characterizes here the low-temperature  $\lambda$  transformation in the solid solution and it is close in magnitude to the Curie temperature of "pure"  $\text{EuO}$ . The temperature  $T_{C2}$  is the Curie point of the high-temperature magnetic phase. Its value, as seen from the data in Table I, depends on the composition of the solid solution. On the polytherms of the magnetocaloric effect (owing to the limited technical means) we were able to observe peaks only in the vicinity of  $T_{C2}$ . However, the rises of the polytherms of the magnetocaloric effect, observed in the region  $T < 100 \text{ K}$ , indicate that analogous maxima will be observed also at low temperatures.

In connection with the foregoing results, it is interesting to trace the variation of the temperature  $T_{C1}$  in the solid solution  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  (Fig. 1), the value of which also increases with increasing  $x$ . For sample No. 5, its change reaches approximately  $3.2^\circ$ . The presented data correlate directly with the decrease of the lattice parameter of the solid solution. The coefficients  $\partial T_{C1}/\partial a$  calculated from them turned out to equal  $210 \text{ deg}/\text{\AA}$ , which is quite close to the results of an investigation of europium monoxide under pressure ( $\partial T_C/\partial a = 230 \text{ deg}/\text{\AA}^{[3]}$ ). Introduction of more than 12 mol. % of SmO in the solid solution, as shown by an investigation of sample No. 6, leads to loss of the single-phase property (a phase with structure of the  $\text{Eu}_2\text{O}_4$  appears besides the cubic phase) and to a certain decrease of the "effective" temperature  $\Theta$ .

It was found furthermore that at temperatures  $T \leq T_{C1}$  the specific heat of the solid solution decreases noticeably with increasing samarium content. To the contrary, as seen from Fig. 4, in the temperature interval  $T_{C1} < T < T_{C2}$  the specific heat of the solid solutions is always larger than that of EuO. Finally, at room temperature, the specific heat of the sample is practically independent of the composition and is close to the value  $C_p = 45 \text{ J/mole-deg}$  which is typical of pure europium monoxide.

## DISCUSSION OF RESULTS

It follows from the experimental data that the ferromagnetic Curie temperature of EuO (with the semiconductor conductivity preserved) can be substantially increased by dissolving in it SmO. This is evidenced by the measured Farady rotation of the polarization plane of the microwave oscillations and the resistivity of the samples, as well as, apparently, by the existence of two  $\lambda$  peaks on the  $C_p(T)$  polytherm and by the magnetocaloric effect. The latter results differ qualitatively from the data of<sup>[8]</sup>, according to which the increase of the Curie temperature in the  $\text{Eu}_{1-x}\text{Gd}_x\text{S}$  system is accompanied by an enhancement of the metallic conductivity. In addition, the polytherm of the specific heat of these solid solutions does not have a clearly pronounced  $\lambda$  anomaly, and the magnetic disorder process itself turned out to be smeared out in them in a wide temperature interval and does not have a cooperative character. The latter may be due to the metallic character of the conductivity of the compounds, i. e., to the average, on the whole, of all the possible exchange interactions between the different sorts of ions over the crystal. To the contrary, the results of the investigation of the semiconducting solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  reveal singularities of the interparticle exchange interactions. In particular, the compression of the solid-solution lattice observed with increasing  $x$ , and the growth of the temperature  $T_{C1}$ , point to an enhancement of the exchange between the europium ions  $J_{mn}$  in this compound. On the other hand, the existence of a second Curie point  $T_{C2}$  is more readily due to the presence of impurity samarium ions, which lead to the formation of magnetic impurity states and of magnetic quasimolecules. Their formation in the temperature region  $T \gtrsim T_{C1}$  indicates that a new magnetic phase is

produced, characterized by a difference of ferromagnetic exchange and by a different disorder temperature  $T_{C2}$ . The fact that this magnetic phase exists at  $T > T_{C1}$  agrees with conclusions<sup>[16]</sup> concerning the temperature region where magnetofluctuations are produced. It is typical here that the temperature  $T_{C2}$  of this solid solution reaches its maximum at an approximate constant 8 mol. % SmO—a result predicted by the theory of magnetic impurity states.<sup>[16]</sup> Since the samarium ions, if uniformly distributed in the crystal and at  $x < 0.08$ , always have twelve magnetic  $\text{Eu}^{2+}$  as the nearest neighbors, the magnetic quasimolecules produced in this case, according to the model of magnetic impurity states, have a gigantic magnetic moment connected with its central ion, i. e., the samarium ion. At  $x = 0.08$  the homogeneous crystal consists entirely of quasimolecules uniformly distributed over its volume and has a translational symmetry with a period  $\sim 2a\sqrt{2}$ . In this case the crystal has the largest spontaneous magnetization at  $T > T_{C1}$ . According to the theory,<sup>[16, 7]</sup> for a ferromagnetic exchange to take place inside a magnetic quasimolecule, the central impurity ion must have an excess electron, i. e., it must have a valence  $R^{3+}$ . The Hamiltonian of such a system is written in the form

$$H_{\text{exch}} = - \sum J_{mn} S_m S_n - 2 \sum J_{in} \sigma_i S_n - 4 \sum J_{ij} \sigma_i \sigma_j,$$

where  $J_{mn}$  is the constant of the direct exchange interaction between the  $4f$  spins  $S_m$  and  $S_n$  of the REM ions in the lattice sites  $R_m$  and  $R_n$  (interaction of the type  $\text{Eu}^{2+} - \text{Eu}^{2+}$ ,  $\text{Eu}^{2+} - \text{R}^{3+}$ ,  $\text{R}^{3+} - \text{R}^{3+}$ );  $J_{in}$  is the constant of the  $i$ - $f$  exchange between the impurity electron of the  $R^{3+}$  site and the  $4f$  spins of the  $\text{Eu}^{2+}$  ions;  $\sigma_i$  is the spin of the impurity electron, and  $J_{ij}$  describes the exchange between the impurity electrons and the spins  $\sigma_{i,j}$ . The last term in the Hamiltonian reflects, as is well known, the existence of several different effects. On the one hand, this can be band magnetism (connected with the metallic conductivity), which apparently is of no great significance in the case discussed by us, and on the other hand this can be exchanged between two impurity states or quasimolecules. This exchange determines the relative directions of the spins of neighboring quasimolecules, which depend on the ground  $s$  or  $d$  states of the electron of the samarium impurity ion. Ferromagnetic exchange between quasimolecules is realized if the electron configuration of the samarium ion is  $4f^5 5d^1$ , i. e., for the  $d$ -ground state of the impurity samarium electron.<sup>[16]</sup>

The results of the x-ray spectral investigation carried out at room temperature have shown (Fig. 5) that the energy of the absorption maximum of samarium in sample No. 4 differs from that observed in the standard SmS sample (in which the samarium ions have the configuration  $4f^6$ ). The shifts of the absorption edge indicate that in the oxide phase the samarium ion has indeed the configuration  $4f^5 5d^1$ . This corresponds formally to the configuration of trivalent samarium. However, by virtue of the possible proximity of the energies of the  $4f$  and  $5d$   $t_{2g}$  terms of samarium in the solid solution, it can be assumed that the population of its  $4f^6$  level differs from zero. Taking into account the Cou-

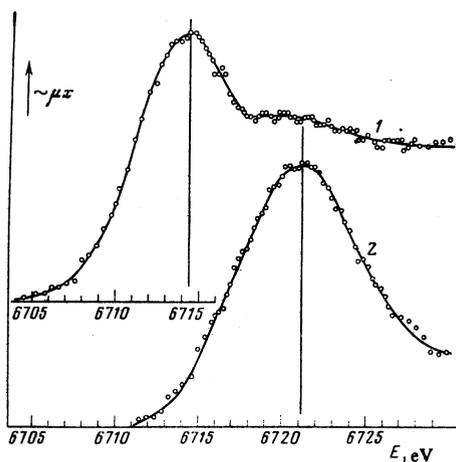


FIG. 5.  $L_{111}$ -absorption spectra of samarium ions in SmS (1) and in the solid solution  $\text{Eu}_{0.916}\text{Sm}_{0.084}\text{O}$  (2).

lomb attraction, this leads to formation of a donor level for the  $5d^1$  electron on the impurity-atom ion. Consequently, the ferromagnetic exchange, both inside the quasimolecule and between quasimolecules, is due to the samarium  $d$  electron, which causes polarization and ordering of the  $4f$  spins of the electrons of the nearest neighbors of the  $\text{Eu}^{2+}$  ions.

The fact that the exchange  $J_{in}$  and  $J_{ij}$  manifests itself only at  $T \gtrsim T_{C1}$  follows from the results of an investigation of the  $C_p(T)$  dependence of the solid solutions. In fact, since their specific heat at  $T < T_{C1}$  is lower than for pure  $\text{EuO}$  (Fig. 4), it follows apparently that there is no additional magnetic contribution to the specific heat. On the other hand, the appearance of such a contribution to the specific heat of the solid solutions at  $T > T_{C1}$  (as well as the appearance of the  $\lambda$  point in the region of  $T_{C2}$ ) cannot be connected with the lattice specific heat and reflect only the energetics of the magnetic quasimolecules and of their interactions with one another, molecules and of their interactions with one another. The existence of the latter, accompanied by the onset of a new ferromagnetic order of the solid solution at  $T > T_{C1}$ , leads to a large value of the paramagnetism and to a positive deviation of the susceptibility from the Curie-Weiss law in the temperature region  $T_{C2} < T < 170\text{--}180$  K. It appears that this temperature interval can be regarded as the region of the loss of ferromagnetic order between the magnetic quasimolecules, although this order is preserved within these quasimolecules up to higher temperatures.

Taking the foregoing into account, we can assume that the lattice component of the specific heat of the solid solution, in the region of the magnetic ordering, should not differ substantially from  $C_{lat}$  of  $\text{EuO}$  ( $\Theta_d = 350$  K). Using the estimated values of  $C_{lat}$  and  $C_m$  obtained for  $\text{EuO}$  in an earlier communication,<sup>[17]</sup> we separated the magnetic contributions made to the specific heat of the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  and due to the existence in them of magnetic quasimolecules. The data obtained thereby are shown in Fig. 6, where the shaded regions characterize the magnetic energy of the quasimolecules in compounds No. 4 and No. 5. Our estimates of the

magnetic energies and entropies of the quasimolecules for these samples turned out to equal respectively to  $\Delta H_m = 252$  and  $572$  J/mole and  $\Delta S_m = 2.1$  and  $4.6$  J/mole-deg, respectively.

The singularities of the independence of  $\Theta$  and  $T_{C2}$  of the concentration, observed<sup>2)</sup> at  $x > 0.084$ , are obviously due to the formation of complexes consisting of three quasimolecules, the ground state of which is a doublet (and therefore contributes to the magnetic parameters<sup>[6])</sup>.

From the present experimental results and from the foregoing discussion we can conclude that in the case of a crystal consisting of only quasimolecules (solid-solution concentration corresponding to a content of approximately 8 mol. %  $\text{SmO}$ ), each of them is characterized, besides the exchange  $J_{in}$ , also by an exchange interaction of the type  $J_{mn}$ —between the europium ions. In this respect, the data in question seem to serve as an additional corroboration of the model of magnetic impurity states, as well as the results of investigations made on its basis, for example of the systems  $\text{Eu}_{1-x}\text{Gd}_x\text{O}$ ,<sup>[4]</sup>  $\text{Eu}_{1-x}\text{Gd}_x\text{S}$ <sup>[8]</sup> or  $\text{Eu}_{1-x}\text{Gd}_x\text{Se}$ .<sup>[18]</sup> On the other hand, the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  with  $x > 0.08$  include already clusters with neighboring  $\text{Sm}^{2+}$  ions. Thus, under these conditions a concentration-dependent decay of the magnetic quasimolecule takes place and a new phase appears with the trivalent ions  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ . To the contrary, the solid solutions with  $x < 0.08$ , even in the case of quasimolecules uniformly distributed over the crystal, always contain regions characterized predominantly by  $\text{Eu}^{2+}\text{--Eu}^{2+}$  interaction and free of the  $\text{Sm}^{2+}$  impurity ion. These regions are microscopic groupings of the "free"  $\text{EuO}$  phase, which is in a magnetically stressed state. It is natural to expect these regions also to be the cause of the appearance of the low-temperature  $\lambda$  transition (at the temperature  $T_{C1}$ ). Since the presence of such regions cannot be directly observed by modern analysis methods (particularly, x-ray structure analysis), it was of interest to determine their contribution by indirect means—on the basis of investigations of the polytherm of the specific heat.

To this end we investigated, in the temperature region from 60 to 90 K, the specific heat of a mechanical

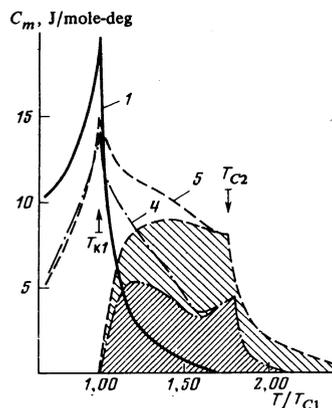


FIG. 6. Magnetic contributions to the specific heat of  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  solid solutions at  $T > T_{C1}$  (the shaded regions characterize the contributions of the magnetic quasimolecules).

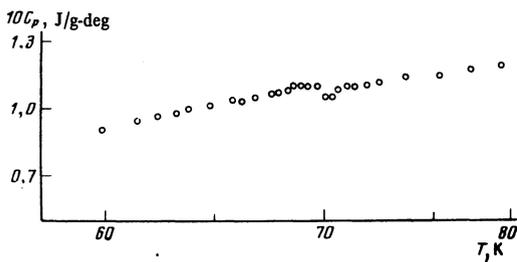


FIG. 7. Polytherm of the specific heat of the mechanical mixture (EuS + 5 wt. % EuO).

mixture of single phase EuS (with  $a = 5.967 \pm 0.001$  Å) and 5 wt. % EuO (see the table). On the x-ray pattern of this mixture, the presence of EuO is already quite clearly revealed by the [111] line. It is known that in this temperature region EuS is a pure paramagnet and its specific heat is determined in practice only by the lattice contribution.<sup>[19]</sup> Figure 7 shows the results of an investigation of the polytherm of the specific heat of the indicated mechanical mixture. It is seen from the figure that between 68 and 70 K the experimental data deviate from the smoothed  $C_p(T)$  plot by an amount greatly exceeding the measurement errors (which in turn correspond to the dimensions of the point on the figure, i. e., are less than 10%). It follows therefore that the observed anomaly is due to the magnetic contribution of the free EuO phase.

This result is similar to the results also observed in the solid solution  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  with  $x < 0.08$ , and agrees with the assumption that clusters of the EuO type are produced in it. Naturally, however, these formations cannot be identified with the EuO impurity. This follows, in particular, from the fact that the intensity of the  $\lambda$  anomaly of sample No. 4 ( $x = 0.084$ ) (Fig. 4) greatly exceeds the corresponding intensity for a mechanical mixture of close composition (EuS + 5 wt. % EuO) (see Fig. 7). In this connection one can obviously state only that the low-temperature anomaly on the polytherm of the heat capacity of the solid solutions  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$  with  $x \leq 0.084$  reflects in the main individual singularities of the  $\text{Eu}^{2+}$ - $\text{Eu}^{2+}$  exchange.

In conclusion, it is of interest to discuss the possible mechanism of the individual exchange in a magnetic quasimolecule. The direct  $\text{Eu}^{2+}$ - $\text{Eu}^{2+}$  cation-pair exchange is obviously due to a configuration transfer of electrons between the  $4f$  and  $5d$  levels of neighboring sites. This, as is well known, is reflected within the framework of the Goodenough model<sup>[20]</sup> by the parameter of the positive cation-cation interaction  $J_{mn}$ . A theoretical verification of the probability of the onset of a mixed "ground" ( $4f^7$ ) and "excited"  $4f^6 5d^1$  states in the paired  $\text{Eu}^{2+}$ - $\text{Eu}^{2+}$  molecules is given in<sup>[21]</sup>. Another type of interaction in a magnetic quasimolecule is connected with its central ion and with  $d$ - $f$  exchange via an impurity electron. Since the  $d$  electron of samarium is localized near the impurity ion, it can be regarded as virtually excited from the  $4f^6$  state to the  $5d^1$  state. The result is  $d$ - $f$  exchange between it and the localized  $4f$  electrons from the nearest environment of the  $\text{Eu}^{2+}$  ions. This type of exchange  $J_{in}$ , besides the  $J_{ij}$ ,

exchange, is responsible for the growth of  $T_C$  in the solid solution. It can be assumed that the realization of the considered exchange mechanisms reflects the observed duality of the ferromagnetic interactions in the solid solution  $\text{Eu}_{1-x}\text{Sm}_x\text{O}$ . In addition, one can apparently assume that the increase of the Curie temperature is due in this case to a gradual transformation of the exchange interactions—from the predominant exchange of the  $J_{mn}$  type, which characterizes the paired interactions, to the exchange  $J_{in}$  or  $J_{ij}$ , which is already inherent in the magnetic quasimolecule itself.

<sup>1</sup>The authors are grateful to V. I. Zakharov for its measurement.

<sup>2</sup>The quantity  $\Theta$  has in this case the meaning of a certain effective parameter.

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