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Antiferromagnet–ferromagnet and semiconductor–metal phase transitions in gadolinium sesquisulfide

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An investigation was made of the magnetic and electrical properties of Gd_2S_3 crystals in the temperature range 4.2–300°K and magnetic fields up to 70 kOe. It was found that stoichiometric Gd_2S_3 crystals are antiferromagnetic and semiconducting. Excess gadolinium increases the electrical conductivity and gives rise to indirect exchange via the conduction electrons. Increase in the excess gadolinium concentration in Gd_2S_3 crystals produces first an inhomogeneous magnetic state (a mixture of antiferromagnetic and ferromagnetic phases) and then a homogeneous ferromagnetic state. Localized ferron states of the conduction electrons appear in the doped crystals: this is equivalent to introduction of a compensating impurity. Such compensation delays the Mott transition from the semiconducting to the metallic state. An analysis is made of possible low-temperature mechanisms of conduction in magnetic semiconductors.

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1. INTRODUCTION

The indirect exchange interaction between magnetic ions via the conduction electrons in antiferromagnetic semiconductors tends to establish and maintain ferromagnetic ordering in a crystal.[1] Consequently, when the carrier density n exceeds a certain value n_F, such a semiconductor becomes ferromagnetic. A distinguishing feature of antiferromagnetic semiconductors is that the carrier-density-dependent magnetic transition does not occur abruptly at the point $n=n_F$. As shown by Nagaev,[2] there is a certain range of carrier densities $[n_A, n_F]$ in which a canted antiferromagnetic order is preferred (for energy reasons) to ferromagnetic and collinear antiferromagnetic orders. However, in the range $n>4n_A$ this canted order is unstable if short-wavelength magnons are generated.[3] Therefore, at least in the range $4n_A<n<n_F$ and possibly even at lower carrier densities the magnetic structure of a crystal should be different and have a lower energy. This structure may correspond to inhomogeneous magnetization of a crystal within the framework of a single crystal lattice which becomes split into antiferromagnetic regions with $n<n_A$ and ferromagnetic regions with $n>n_F$ (Ref. 4). The conduction electrons collect in the ferromagnetic part of the crystal and this gives rise to special features of the semiconductor–metal phase transition in antiferromagnetic semiconductors.

An inhomogeneous magnetic state has been observed earlier in europium monoselenide,[5] europium monotelluride,[6] and gadolinium sulfides.[7] The present paper reports an investigation of the characteristics of the magnetic and semiconductor–metal phase transitions in gadolinium sesquisulfide crystals.

2. EXPERIMENTAL METHOD

Gadolinium sesquisulfide Gd_2S_3 (or, equivalently, $GdS_{1.50}$) is a wide-gap semiconductor with a high electrical resistivity. One of the modifications of this compound is known as the high-temperature phase and has the Th_3P_4-type structure in which $\frac{1}{9}$ of the sites in the metal sublattice are unoccupied, i.e., are stoichiometric vacancies. The presence of such vacancies makes it possible to dissolve considerable amounts of gadolinium in excess of the stoichiometric formula. The outer-shell electrons of the excess atoms do not form valence bonds but their ionization energy decreases under the influence of the dielectric properties of the medium and they can easily be transferred to the conduction band. Therefore, introduction of excess gado-

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TABLE I. Properties of investigated GdS_x samples

Sample No.	Composition x of GdS_x	T_C, T_N, °K	N_{Gd}, 10^{18} cm^{-3}	ρ (300°K) $\Omega\cdot$cm	M_s/M_0, %	ε_1, meV
1	1.4998	4.4 T_N	2.4	1.1	–	34
2	1.488	5 T_C	150	$2.4\cdot10^{-2}$	16	15
3	1.485	15.5 T_C	180	$8.5\cdot10^{-3}$	33	9.6
4	1.480	28 T_C	240	$4.4\cdot10^{-3}$	68	1.8
5	1.475	34.5 T_C	300	$2.2\cdot10^{-3}$	85	1.1

Note. The inequality $\varepsilon_1 < kT$ is obeyed by samples 4 and 5 and, therefore, the activation energies calculated for these samples are not completely reliable.

linium makes it possible to vary the carrier density over a wide range. Gadolinium atoms occupying stoichiometric vacancies will be called donors and crystals containing these donors will be described by the formula GdS_x with $x \leq 1.50$.

The composition (second column in Table I) was determined by gas chromatography.[8] X-ray phase analysis showed that all the samples consisted of a single phase and has the Th_3P_4-type structure. The lattice constant did not vary by more than ~0.04% in the investigated range of compositions.

The magnetic and electrical measurements were carried out on the same samples, which were rectangular parallelepipeds with typical dimensions $1.5\times1.5\times6$ mm. These samples were cut from separate blocks (of linear dimensions up to 10 mm) of fused ingots. The magnetic properties were determined with a vibration magnetometer. The electrical conductivity and Hall emf were measured by the conventional dc compensation method employing a potentiometer or an electrometer, depending on the resistance of the sample.

3. RESULTS OF MEASUREMENTS

The temperature dependence of the magnetic susceptibility χ of sample 1 has a maximum at[1)] $T_N = 4.4°$ K (Néel temperature), typical of antiferromagnets; in the paramagnetic range its magnetic susceptibility obeys the Curie–Weiss law with a characteristic temperature $\Theta \approx -10°$ K. Curve 1 in Fig. 1 gives the temperature dependence of the projection of the magnetic moment M_H along an external field $H = 50$ Oe applied to sample

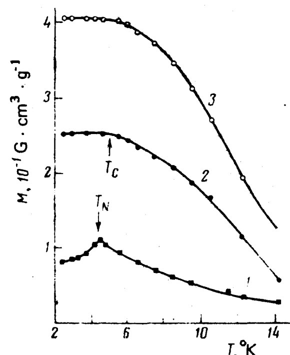

FIG. 1. Temperature dependences of the specific magnetic moment in magnetic fields H(Oe): 1) 50 (sample 1); 2) 25 (sample 2); 3) 40 (sample 2).

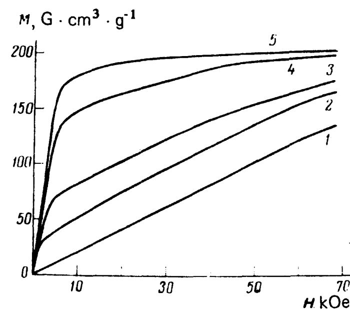

FIG. 2. Dependences of the specific magnetic moment of GdS_x samples on the external magnetic field at $T = 4.2$°K. The curves are labeled in the same way as samples in Table I.

1. The $M_H(T)$ curves of samples 2–5 are typical of ferromagnets. Their moment is practically independent of temperature in the range $T < T_C$ in accordance with the expression $M_H = H/4\pi N$ (Ref. 9), where N is the demagnetization factor, provided the magnetic field is weak so that the domain structure is retained; at temperatures $T > T_C$, ferromagnetic domains are destroyed and the magnetic moment decreases rapidly with rising temperature. Curves 2 and 3 in Fig. 1 gives the dependences $M_H(T)$ for sample 2 obtained in various external magnetic fields. The temperature dependences of the magnetic moments of samples 3–5 are similar. The critical temperatures T_C and T_N deduced by the method of kinks in the temperature dependences of the magnetization[9,10] in weak magnetic fields ($H \to 0$) are listed in the third column of Table I.

Figure 2 shows the dependences of the magnetization on the magnetic field at $T = 4.2°$ K obtained for five GdS_x samples of different compositions. Curves are similar to the magnetization curves of iodine-doped EuTe, in which antiferromagnetic and ferromagnetic phases coexist.[6] We can see from Fig. 2 that all the samples, except sample 1, have a spontaneous magnetic moment (the magnetization increases rapidly with the field when the latter is weak) and the spontaneous moment rises on deviation from the $GdS_{1.50}$ stoichiometric composition. It should be pointed out that the magnetic saturation moment of sample 5 (with the greatest deviation from stoichiometry among our samples) is identical, within the limits of the experimental error, with the theoretical saturation moment $M_0 = 190$ cgs emu/g of a homogeneous ferromagnetic crystal.

We also investigated the temperature and magnetic-field dependences of the electrical resistivity of samples of GdS_x. Attempts to determine the carrier density by measuring the Hall coefficient in fields up to 10 kOe were successful only in the case of sample 1 ($n = 2\times10^{18}$ cm^{-3} at $T = 300°$ K). For other samples we were unable to identify the Hall emf against the voltage drop caused by a nonequipotential configuration of the Hall probes. Therefore, in the case of samples 2–5 we were forced to estimate the conduction electron density on the assumption that, at sufficiently high temperatures, each excess gadolinium atom contributed one electron to the conduction band (the sign of the room-temperature thermoelectric power of all samples corresponded to n-type conduction). The concentration of the gadolinium

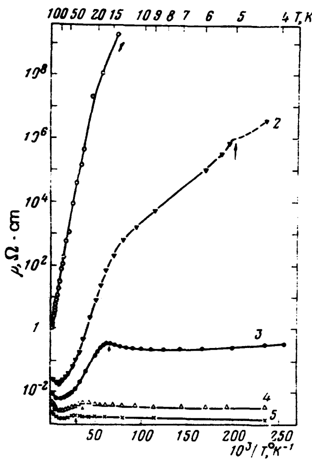

FIG. 3. Temperature dependences of the resistivity of GdS_x samples (on a logarithmic scale). The curves are labeled in the same way as in Fig. 2. The arrows identify the Curie points of samples 2-5.

donors N_{Gd} in each of the samples was deduced from the chemical composition, found by gas chromatography, and from the x-ray density. The results of calculations of the donor concentration are presented in the third column of Table I. Since the electron density in sample 1, deduced from the Hall emf and the results of gas chromatographic analysis were in satisfactory agreement, it was concluded that the values of N_{Gd} given in Table I for samples 2–5 represented satisfactorily the true values of the free-electron density in these samples as well. This was supported by the observation that, as reported below, the lower limit n_F of the existence of homogeneous ferromagnetic order estimated in accordance with Nagaev's theoretical paper[2] for an antiferromagnetic semiconductor is only one third of the electron-gas density in sample 5, which is practically totally ferromagnetic.

Figure 3 shows the experimental results of an investigation of the temperature dependence of the electrical resistivity $\rho(T)$. It is clear from this figure that at high temperatures the dependences $\rho(T)$ are typical of semiconductors and can be used to find the activation energy ε_1. The values of ε_1 are listed in the last column of Table I. As in the case of conventional nonmagnetic semiconductors, they decrease on increase in the donor concentration, which is due to a reduction in the energy gap between the donor levels at the bottom of the conduction band because of the overlap of the wave functions of electrons localized at these donors.

The curve $\rho(T)$ for sample 2 has, in addition to a region with ε_1, another activated region with $\varepsilon_2 < \varepsilon_1$ which is located at lower temperatures. Three activated regions with $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$ are observed for sample 1 at different temperatures.

The dependences $\rho = f(10^3/T)$ for the three samples with the highest excess gadolinium concentrations have maxima. Such maxima are typical of heavily doped ferromagnetic semiconductors (see, for example, Ref. 1) and are located near the Curie point T_C. The shift of the maximum toward higher temperatures, exhibited by

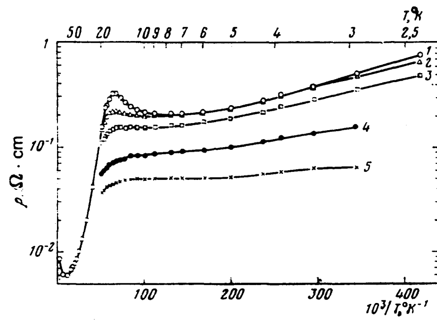

FIG. 4. Temperature dependences of the electrical resistivity of sample 3 (on a logarithmic scale) in magnetic fields H(kOe): 1) o; 2) 1; 3) 3; 4) 5; 5) 9.

the curves in Fig. 3 on increase in the gadolinium donor concentration, indicated that T_C rises in agreement with the results of the magnetic measurements. The amplitude of the resistivity maximum decreases from sample 3 to sample 5. For sample 2 this maximum is barely distinguishable near T_C (curve 2 in Fig. 3 is shown dashed for this temperature range). Thus, we may conclude that the amplitude of the resistivity maximum of gadolinium sulfide considered as a function of the N_{Gd} concentration is itself a curve with maximum.

At temperatures exceeding that corresponding to a region with the activation energy ε_1 (see footnote of Table I) the dependences $\rho(T)$ of samples 2–5 pass through a minimum, which is followed by an increase in the resistivity with rising temperature. As in the case of nonmagnetic heavily doped semiconductors, this increase in the resistivity is probably due to the enhancement of the carrier scattering by lattice vibrations.

All the investigated GdS_x samples exhibited a large (in the absolute sense) negative magnetoresistance. Figure 4 shows the dependences $\rho(T)$ for sample 3 obtained in various external magnetic fields. It is clear that the resistivity of this sample depends weakly on temperature in the range 3–20°K in field $H = 9$ kOe and that the behavior of the negative magnetoresistance in

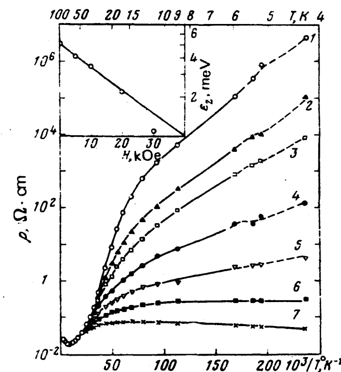

FIG. 5. Temperature dependences of the electrical resistivity of sample 2 (on a logarithmic scale) in magnetic fields H(kOe): 1) 0; 2) 5; 3) 10; 4) 20; 5) 30; 6) 40; 7) 50. The inset gives the dependence of the activation enerby ϵ_2 of sample 2 on magnetic field based on curves 1-5 in the same figure.

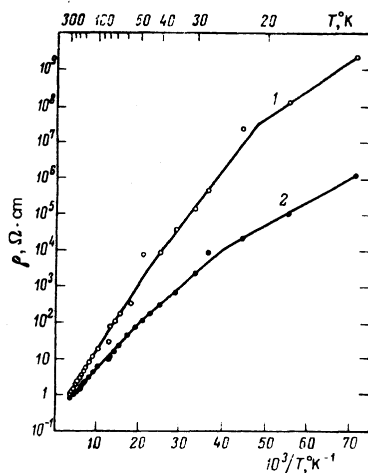

FIG. 6. Temperature dependences of the electrical resistivity of Sample 1 (on a logarithmic scale) in magnetic fields H(kOe): 1) 0; 2) 50.

this range is essentially governed by the behavior of $\rho(T)$ in $H=0$.

The temperature dependence of the resistivity in magnetic fields exhibited by the more heavily doped samples 4 and 5 is similar to that shown in Fig. 4, except that their resistivity and negative magnetoresistance decrease monotonically with temperature in the ferromagnetic temperature range ($T < T_C$).

The negative magnetoresistance has the highest absolute value in sample 2 (Fig. 5). In this case the magnetoresistance rises monotonically as a result of cooling from 40 to 4.2°K. The magnetoresistance of sample 1, with the lowest gadolinium donor concentration, is negative and it decreases with rising temperature (Fig. 6) throughout the range 14–300°K.

4. DISCUSSION OF EXPERIMENTAL RESULTS

As pointed out earlier, introduction of donor atoms into an antiferromagnetic semiconductor leads to a situation in which antiferromagnetic and ferromagnetic phases may coexist in a certain range of the electron-gas densities. The density n_F, above which a homogeneous ferromagnetic order is established in a crystal, is given by the expression[2]

$$n_F=4|J|N_c/A, \quad |J|S=z|I|S^2=kT_N. \tag{1}$$

Here, I is the integral representing the direct exchange between the z nearest neighbors in the magnetic sublattice; S is the total spin of the magnetic atoms; A is the s–f exchange integral; N_c is the cation concentration. Our calculations based on Eq. (1) were carried out assuming that $kT_N=0.38\times10^{-3}$ eV ($T_N=4.4$°K) and that the gadolinium atom concentration was $N_K=2\times10^{22}$ cm^{-3}; the s–f exchange integral was estimated by Stoppels and Savatzky[11] from the width of the ESR line and from the shift of the g factor exhibited by gadolinium-doped lanthanum sulfide crystals: its value was 0.1 eV. We then found $n_F=0.9\times10^{20}$ cm^{-3}.

This density n_F is quite close to the electron-gas densities deduced by us from the results of gas chromatography of samples 2–5. One should add that, as shown by Kashin and Nagaev,[4] inhomogeneous states may exist also in a certain range of $n > n_F$. This is due to the fact that return to the antiferromagnetic order in a part of a crystal results in an additional gain in the energy of the direct exchange between the magnetic atoms. Hence, we can assume that the magnetization curves of Fig. 2 can be explained on the assumption that antiferromagnetic and ferromagnetic phases coexist in samples 2–5.

Three regions can be distinguished in curves 2–5 in Fig. 2. In the first region (weak magnetic fields) the magnetization of the ferromagnetic part of a crystal occurs until saturation is reached. Further rise of H (second region) increases the magnetic moment of the crystal much more slowly because of the magnetization of its antiferromagnetic parts. This probably explains why the curves in Fig. 2 are parallel to one another in moderate magnetic fields and can be described by

$$M(H)=M_s(T)+\chi(T)H, \tag{2}$$

where M_s is the saturation moment of the ferromagnetic part; $\chi(T)$ is the susceptibility of the antiferromagnetic part. In our opinion, the parallel nature of the $M(H)$ curves in moderate magnetic fields indicates that the electron density in the doped antiferromagnetic phase remains practically zero, because all the electrons are concentrated in the ferromagnetic phase.

The curves in Fig. 2 become nonparallel in strong magnetic fields (third region) probably because of an increase in the volume occupied by the ferromagnetic part or because charge delocalization from the ferromagnetic phase alters the indirect exchange interactions in the antiferromagnetic phase and this may affect the field in which the sublattice collapse takes place. It should be stressed that the range of magnetic fields in which the $M(H)$ curves of the doped samples are parallel to the corresponding curve of sample 1 becomes narrower on increase in the doping.

The experimental curves in Fig. 2 allow us to estimate the value of M_s for each of the investigated crystals: according to Eq. (2), this value can be found by extrapolating the dependence $M(H)$ from moderate magnetic fields to $H=0$. Then, using the saturation moment of the homogeneous ferromagnetic crystal, we can find the ratios M_s/M_0 for samples 2–5 at $T=4.2$°K (sixth column of Table I), which represent the proportion of the volume of the sample which is in the ferromagnetic state.

The results of the electrical measurements indicate that the excess gadolinium atoms contribute free electrons. These electrons mediate indirect exchange between spins of the magnetic atoms and establish a ferromagnetic order throughout the crystal (sample 5) or a part of it (samples 2–4), as indicated by the curves in Figs. 1 and 2. The electrons collect in the ferromagnetic phase (collective ferron states). The loss in the Coulomb and kinetic energies due to such electron-gas condensation is balanced out by the gain in the s–f exchange energy, which results in an effective attraction

between electrons.[1] When the gadolinium donor concentration is sufficiently low (as in sample 1), the ferron state may acquire individual character. In each such state, one electron is localized and it creates a ferromagnetic microregion whose size is about three lattice constants. The conditions for the appearance of individual ferrons may differ considerably from the analogous conditions for the collective localization of the electron gas.[1]

The influence of the magnetic order on the electrical properties of GdS_x crystals is manifested primarily by the maxima of the dependences $\rho(T)$ exhibited by the most heavily doped samples 3–5 (Fig. 3). The reasons for the appearance of these maxima in the dependences exhibited by magnetic semiconductors near T_C are still not clear. For example, Zil'bervarg and Nagaev[12] attribute them to the localization of the conduction electrons resulting from the simultaneous influence of the potential of defects and of magnetization fluctuations (localized ferrons). In our crystals these defects are the excess gadolinium atoms. They also ensure the appearance of electrons in the conduction band. Therefore, increase in N_{Gd} establishes conditions necessary for the capture of electrons by fluctuations of the magnetic moment. Since the electron energy decreases on increase in the local magnetization, fluctuations of the magnetic moment are linked by positive feedback to fluctuations of the free-electron density. However, the latter fluctuations decrease as $n^{-1/2}$ on increase of n, in accordance with the laws of statistical thermodynamics. This factor should predominate beginning from certain values of N_{Gd}. Thus, an increase in the low-temperature carrier density from sample 3 to samples 4 and 5 [in this temperature range the resistivity of sample 3 is more than two orders of magnitude higher than the resistivity of samples 4 and 5 (Fig. 3)] reduces the amplitude of the maximum.

Since an external magnetic field suppresses the magnetization fluctuations and destroys localized ferrons, its application should reduce the amplitude of the maximum, i.e., it should give rise to a negative magnetoresistance at temperatures close to T_C, which is observed for sample 3 (see Fig. 4) and for samples 4 and 5.

As pointed out earlier, in the temperature range $T < T_C$, samples 4 and 5 exhibit not only a maximum of $\rho(T)$ but a monotonic fall of the resistivity on increase in T, which can be explained by an increase in the degree of order in the ferromagnetic phase, which increases the carrier mobility. However, in sample 3 with a lower excess gadolinium concentration, a similar maximum at $T \sim T_C$ changes to a minimum (at $T \approx 8°$K), which is followed by a rise of the resistivity. This type of dependence $\rho(T)$ for sample 3 at $T < 8°$K can be explained by confinement of the conduction electrons to nonoverlapping ferromagnetic drops. We shall consider this aspect in greater detail.

According to Kashin and Nagaev,[4] near n_F there is a critical concentration $n_T < n_F$ at which the ferromagnetic part of the crystal in which the conduction electrons can move changes from multiply connected (in the range $n < n_T$) to singly connected (for $n > n_T$). The electrical conductivity of an inhomogeneous magnetized magnetic semiconductor consisting of a conducting ferromagnetic phase and a nonconducting antiferromagnetic phase is analogous to the problem of the electrical conductivity of a nonmagnetic semiconductor with large-scale fluctuations of the electric potential which distorts the bottom of the conduction band. This problem was considered by Shklovskiĭ and Éfros.[13]

Bearing in mind that a considerable proportion of the volume of sample 4 is in the ferromagnetic state ($M_s/M_0 \approx 68\%$), we may conclude that in this sample and in the more heavily doped sample 5 ($M_s/M_0 \approx 85\%$) the ferromagnetic regions are singly connected, i.e., these samples obey the inequality $n > n_T$. The proportion of the volume occupied by the ferromagnetic phase in sample 3 ($M_s/M_0 \approx 33\%$) is probably insufficient for the formation of a singly connected ferromagnetic region, i.e., in this sample the carrier density is less than the critical value n_T. Therefore, at sufficiently low temperatures the conduction electrons are confined to ferromagnetic drops and this is why the resistivity rises at $T < 8°$K (curve 1 in Fig. 4). We recall that ferromagnetic regions in this sample appear at temperatures below 16°K. Application of an external magnetic field delocalizes the carriers and flattens the dependence $\rho(T)$ at $T < 8°$K. Since the degree of localization of the electrons in ferromagnetic drops increases at lower temperatures, a magnetic field should reduce more effectively the electrical resistivity at such temperatures, i.e., the negative magnetoresistance should rise in this part of the curve on approach to $T \to 0$, which is observed experimentally (Fig. 4).

The carrier density in sample 3 is thus less than the critical value n_T. Electron density in sample 2 is even lower, i.e., it also obeys the inequality $n < n_T$. The lower electron–gas density in sample 2, compared with sample 3, is responsible for the lower Curie temperature ($T_C \approx 5°$K), governed by the intensity of the indirect exchange via the electrons, and it also reduces the relative volume occupied by the ferromagnetic phase ($M_s/M_0 \approx 16\%$). In this case a consequence of a reduction in the excess gadolinium concentration is the fact that the resistivity maximum near T_C of sample 2 is barely visible and the conduction process is activated in a wide range of temperatures.

The least doped sample 1 is a nondegenerate semiconductor and its conduction is activated throughout the temperature range 14–300°K (Fig. 3). It is clear from Fig. 3 that the temperature dependences of the resistivity of sample 1 plotted as $\rho = f(10^3/T)$ have three linear regions, each of which has a different conduction mechanism with its own activation energy ε_i. In this case the dependence $\rho(T)$ can be written in the form

$$\rho^{-1} = \sum_{i=1}^{3} \rho_i^{-1}, \quad \rho_i = \rho_{0i} \exp\left(\frac{\varepsilon_i}{kT}\right). \tag{3}$$

Such a dependence $\rho(T)$ is well known in the physics of semiconductors and, as established in a number of papers, all three activation energies ε_i depend on the degree of compensation, i.e., on the ratio of the donor and acceptor concentrations. We shall show later that

the magnetic-field-induced change in the nature of the $\rho(T)$ curves of GdS_x samples with low excess gadolinium concentrations can be explained by assuming a magnetic-field dependent compensation of these crystals.

There was no attempt to introduce deliberately any acceptors into our crystals. However, the individual ferrons around neutral donors, capable of capturing an additional electron from another donor atom, can act as acceptors in the GdS_x samples. Essentially, the formation of such an individual ferron reduces to the appearance of a negatively charged donor D^- near which a local ferromagnetic order is established by a fluctuation and this facilitates localization of an additional electron. The donor atom from which an electron is captured then goes over to the state D^+. Hence, it follows that the appearance of an individual ferron is equivalent to introduction of two acceptor atoms because each D^+ and D^- pair can no longer give up electrons to the conduction band. Therefore, the degree of compensation K can be defined as the ratio of twice the concentration of individual ferrons N_f to the concentration of donor atoms N_D, i.e., $K=2N_f/N_D$.

It is clear from this discussion that the appearance of a donor in the D^+ state in our crystals can be due to the ionization of an electron to the conduction band or a capture of an electron by a ferron state. The former occurs at high temperatures. However, at low temperatures when the value of kT is insufficient for the ionization process, the donors appear in the D^+ state mainly because of the second factor.

We have pointed out above that all three activation energies ε_i in Eq. (3) depend on the degree of compensation of a nonmagnetic semiconductor. However, since in the case of our samples the degree of compensation depends on the magnetic field which destroys individual ferron states,[14] we may expect ε_i of GdS_x crystals to depend strongly on H. This was checked by determining the dependences $\rho(T)$ for samples 1 and 2 in various magnetic fields. The results are presented in Figs. 5 and 6.

It is clear from these figures that all three activation energies ε_i are strongly dependent of the magnetic field. We recall that the part of the dependence $\rho(T)$ with the activation energy ε_1 describes the temperature dependence of the carrier density in the conduction band. As shown by Davis and Compton for n-type germanium crystals,[15] the dependence of ε_1 on the degree of compensation is sublinear.

The experimental curves in Fig. 5 cannot be used to find the analytic dependence $\varepsilon_1=f(H)$ because the $\rho(10^3/T)$ curves deviate from linearity in each of the regions. However, the results indicate that the dependence of ε_1 on the degree of compensation of GdS_x crystals in qualitatively identical with the corresponding dependence for n-type germanium.[15] In fact, in weak magnetic fields (when the ferron concentration is high and the degree of compensation is large), there is a rapid fall in ε_1, whereas in high fields H (when the ferron concentration is lower and the degree of compensation is small), the fall of ε_1 on increase of the magnetic field slows down.

At lower temperatures (<45° K and <15° K for samples 1 and 2, respectively) the band conduction mechanism changes to a different mechanism with a lower activation energy ε_2. According to Fritzsche,[16] the activation energy ε_2 of nonmagnetic semiconductors describes the transfer of an electron from a neutral donor D^0 to another neutral donor. This seems most likely because only the D^0 donor state should occur in the ground state of a nonmagnetic semiconductor in this temperature range if there is no compensation by an acceptor impurity. However, in the case of magnetic semiconductors the ground state of a crystal may be characterized by the presence of D^0 as well as of donors in the other two charge states D^+ and D^- (individual ferrons). The existence of donors in the last two charge states gives grounds for assuming that the most probable conduction mechanism is now the transfer of electrons from D^- to D^+, which corresponds to the region with an activation energy ε_2 exhibited by a magnetic semiconductor.

Since a magnetic field destroys individual ferrons, its application reduces the donor concentration in the D^+ and D^- states and increases the donor concentration in the D^0 state. Thus, in the limiting case of a strong magnetic field a magnetic semiconductor may exhibit—in this temperature range—the same conduction mechanism as found in nonmagnetic semiconductors. Therefore, we cannot exclude the possibility that the activation energy ε_2 of sample 1 changes from a value corresponding to the transfer of charge from an individual ferron D^- to an ionized donor D^+ (in $H=0$) to a finite nonzero value corresponding to the transfer of an electron from D^0 to D^0 in a field $H=50$ kOe.

It is clear from Fig. 5 that, in contrast to sample 1, the activation energy ε_2 of sample 2 is reduced by a magnetic field practically to zero (in fields 40 and 50 kOe the resistivity of this sample is independent of temperature, which is typical of metallic conduction). This difference in the behavior of $\rho(T)$ of samples 1 and 2 in strong magnetic fields seems to indicate that the gadolinium donor concentration required for the Mott transition in GdS_x crystals lies somewhere between the values of N_{Gd} in these two samples. We recall that the Mott transition of n-type nonmagnetic semiconductors to the metallic state is hindered by the compensation with an acceptor impurity. Similarly, the Mott transition in our sample 2 is prevented by the compensation associated with the existence of ferron states. An external magnetic field destroys these states and restores the conditions necessary for the transition to the metallic states.

Another possible explanation of the disappearance of the ε_2 and ε_3 can be based on the ideas put forward by Kashin and Nagaev.[4] According to these authors, the formation of localized ferrons reduces the Bohr orbit radius a_H. Hence, it follows that, whereas at low temperatures the Mott criterion of "collectivization" of the donor electrons $a_H n^{1/3}>0.25$ is not satisfied, it may be obeyed at higher temperatures T because then the Ferron states are destroyed. In our case the Mott transition is induced by a magnetic field of sufficiently high

intensity, which also destroys the localized electron states.

The change in the activation energy ε_2 in a magnetic field, based on the experimental curves of Fig. 5, is plotted as an inset in the same figure and can be represented analytically by the expression $\varepsilon_2 = \varepsilon_2^{(0)}\exp(-H/H_c)$ with the parameters $\varepsilon_2^{(0)} = 49$ meV and $H_c = 25$ kOe. Here, H_c should be regarded as the field in which ferrons become dissociated and the compensation disappears. The assumption of compensation by individual ferrons explains also the fact that in the more heavily doped sample 3 the conduction in the paramegnetic temperature range in $H=0$ is activated.

Further cooling of sample 1 gives rise to a region of $\rho(T)$ with the activation energy ε_3. In the case of nonmagnetic semiconductors the conduction corresponding to this activation energy is attributed to electron transfer from neutral D^0 to ionized D^+ donors (see, for example, Ref. 17). The value of ε_3, like the energies ε_1 and ε_2 depends on the degree of compensation.

In the case of magnetic semiconductors we must bear in mind that cooling may result in energy preference not for individual ferrons but for larger ferron clusters consisting of a few (for example two or three) donor atoms. Their existence does not give rise to a spontaneous moment. However, such a cluster contains shared electrons and it is characterized by a higher local magnetization. Consequently, in the temperature range characterized by the activation energy ε_3 it is most probable that the conduction mechanism in sample 1 reduces to the transfer of an electron from such a ferron cluster to an ionized donor. The value of ε_3 should be governed by the competition of the following two factors. On the one hand, the local magnetization makes the spins of the shared electrons parallel and the filling of the energy states by these electrons in accordance with the Pauli principle has the result that the detachment of electrons from higher energy levels of such a cluster requires less energy than the detachment from an individual ferron. On the other hand, the local magnetization itself prevents electron detachment. Therefore, the application of a magnetic field which equalizes the magnetization throughout a crystal should lower the activation energy ε_3. Moreover, this field destroys ferron clusters. Consequently, for sample 1 in the region with the activation ε_3, as in the region with the energy ε_2, we may expect the conduction mechanism typical of nonmagnetic semiconductors if the applied magnetic field is sufficiently high.

If we assume that the field 50 kOe destroys practically completely the ferron states in sample 1, we can compare the experimentally determined value $\varepsilon_3 = 13$ meV with the theoretical expression of Shklovskiĭ *et al.*[18] obtained for the case of conduction involving electron jumps from D^0 to D^+ in the $K \ll 1$ case:

$$\varepsilon_3 = 0.99 e^2 N_D^{1/3}/\varkappa. \tag{4}$$

Here, e is the electron charge and $\varkappa$ is the permittivity. If we assumed that $\varkappa$ of our crystals is 15, which is justified because the permittivities of monatomic semiconductors Ge and Si and of the majority of III-V and IV-VI compounds are close to this value, we find from Eq. (4) that $\varepsilon_3 = 12.7$ meV. This is in good agreement with the above experimental value of ε_3 and it shows that the conduction mechanisms in magnetic semiconductors subjected to strong magnetic fields are analogous to those in nonmagnetic semiconductors.

5. CONCLUSIONS

Our results show that the γ phase of gadolinium sesquisulfide is an antiferromagnet with an ordering temperature $T_N = 4.4$°K. The results of a study of the electrical and magnetic properties of GdS_x samples suggest the following physical picture. The excess gadolinium atoms in these crystals act as donors. The electrons in lightly doped crystals are in individual ferron states, which can exist in a wide temperature range. An increase in the gadolinium donor concentration imparts collective nature to the ferron states at low temperatures and a crystal assumes a magnetically inhomogeneous state. In such a crystal the electrons collect in the ferromagnetic region. The Curie temperature and the relative volume occupied by the ferromagnetic phase increase on increase in the electron density, whereas the electrical and magnetic properties of the antiferromagnetic phase are not affected.

The existence of individual ferrons is equivalent to an effective compensation. This compensation delays the Mott transition. The application of an external magnetic field destroys such compensation and restores the conditions necessary for the Mott transition.

At low temperatures the conduction in lightly doped gadolinium sulfide crystals subjected to zero magnetic field is different from that observed in nonmagnetic semiconductors. However, in strong magnetic fields the conduction mechanisms in gadolinium sulfide are similar to those found in nonmagnetic semiconductors.

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[1)]In an earlier investigation[5] of Gd_2S_3 crystals we reported an underestimated value of T_N, which was due to an error in the temperature measurement.

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Low temperature phase transition in samarium

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The crystal structure of α-samarium was investigated in the temperature interval 4.2–300 K. It has been established that the low-temperature transition at $T = 14.5$ K, just at $T = 106$ K, is a second-order phase transition. Both phase transitions are due to successive onset of antiferromagnetic order respectively in layers with hexagonal symmetry of the environment ($T_{N_h} = 106$ K) and in layers with cubic symmetry of the environment ($T_{N_c} = 14.5$ K) in a nine-layer hexagonal compact lattice. At both critical points, the jumps of the linear expansion coefficients are highly anisotropic; $\Delta\alpha_\perp < 0$ and $\Delta\alpha_\parallel > 0$. The singularity of the thermal expansion is most strongly pronounced at $T_{N_c} = 14.5$ K. It is concluded from the calculation of the temperature dependence of the energy of spontaneous deformation of the crystal lattice in the magnetically disordered state that the spontaneous magnetic moment of the cubic sublattice is larger than the moment of the hexagonal sublattice.

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It was shown in an earlier study[1] of the crystal structure of α-Sm in the interval 77–300 K that the paramagnetism–antiferromagnetism transition that occurs at $T = 106$ K is of second order from the thermodynamic point of view. A subsequent neutron-diffraction investigation[2] of single-crystal samarium has established that below 106 K only 2/3 of the atoms of its rhombohedral lattice are antiferromagnetically ordered, and the positions of these atoms correspond to hexagonal close packing (h-layers), while 1/3 of the atoms in positions corresponding to cubic close packing (c-layers) produce a magnetically ordered state below 14 K. The magnetic moments of the atoms of both layers are directed along the c axis and form somewhat different collinear antiferromagnetic structure. Whereas for the hexagonal positions the ferromagnetic layers are normal to the c axis, for the cubic positions they are parallel to the $(10\bar{1}1)$ planes. The results of the measurement of the magnetic susceptibility of samarium single crystals[3] can also be adequately interpreted by representing this crystal as an antiferromagnet with a c axis.

In this paper we continue the structural investigation of α-Sm into a temperature region that includes a second phase transition. The measurement was made in a cryostat where the sample temperature was continuously varied in the interval 4.2–300 K by a stream of cold helium gas. The sample temperature was measured with differential thermocouples; a Cu – Au + 0.01% Fe was used in the interval 4.2–40 K, and a copper–constantan thermocouple above 40 K.

The object of the investigation was, as before, a polycrystalline sample with a large-grain structure, produced by recrystallization annealing.

The single-crystal reflections were recorded on the x-ray diffractometer chart from the (0018) planes ($2\theta \sim 104°$) in CrK_α radiation and from the (220) planes ($2\theta \sim 116.4°$) in CuK_α radiation. This made it possible to measure the parameters of the crystal lattice with accuracy $\Delta a_i/a_i = \pm 1.10^{-5}$. The position of the diffraction peak was fixed in temperature steps of 1–2 K, and in steps decreased to 0.2 K in the phase-transition region.

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