

PHYSICS OF MAGNETIC PHENOMENA

EXTRAORDINARY MAGNETIC PROPERTIES OF $\text{Ca}_{1-x}\text{Eu}_x\text{S}$ AND $\text{Sr}_{1-x}\text{Eu}_x\text{S}$ SOLID SOLUTIONS

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The electron paramagnetic resonance (EPR) spectra and the stationary magnetic susceptibility are investigated for $\text{Ca}_{1-x}\text{Eu}_x\text{S}$ and $\text{Sr}_{1-x}\text{Eu}_x\text{S}$ solid solutions ($0.00005 < x < 0.0032$). The EPR spectrum of Eu^{2+} in both matrices contains a wide structureless line in addition to the narrow lines of the superfine structure characteristic of ions with high local symmetry. Because of the extraordinary temperature dependence of this line in CaS:Eu , it is associated with strongly interacting magnetic centers, namely, exchange-coupling pairs and chains or more complex clusters of magnetic ions. At the same time, the dependence of the stationary magnetic susceptibility in the temperature range 4.2–50 K has no peculiarities for CaS:Eu and SrS:Eu and obeys the Curie law.

INTRODUCTION

Alkaline-earth sulfides (AES) activated by rare earths have been investigated since the end of the last century, when Lenard [1] prepared the first flash luminophores sensitive to infrared light. AES luminophores were used in the first night-vision devices. They still remain promising cathodo-, electro-, and thermoluminophors up to now. In addition to their applied significance, these solid solutions are interesting for fundamental research of the luminescence and magnetism of diluted magnetic dielectrics. This is demonstrated by works devoted to spin glasses prepared from $\text{Sr}_{1-x}\text{Eu}_x\text{S}$ solid solutions (for example, see [2]). However, the magnetic properties of highly diluted solutions with a structure typical of luminophors were studied only to refine the charge state and charge transformations of europium in luminophors [3, 4]. The data on CaS:Eu published in [4] demonstrate that for low impurity concentrations ($x < 5 \cdot 10^{-3}$), the solid solutions are nonuniform and that impurity cations may cluster. The clusters containing magnetic ions engender extraordinary magnetic properties observed, for example, in solid solutions of manganese in chalcogenide systems [5, 6]. In particular, the electron parametric resonance (EPR) spectra of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ solid solutions of manganese included a wide line whose width increased with decreasing temperature [6].

The wide structureless line in the EPR spectrum of solid europium solutions in AES may also indicate the interactions of Eu^{2+} ions in these matrices. We note that the SrS:Eu and CaS:Eu spectra were published repeatedly [4, 7], but the nature of the wide line, as a rule, was not discussed. In [8] it was pointed out that this line is caused by the Eu^{2+} impurity. It always accompanies the well-known spectrum of Eu^{2+} centers with high local symmetry (cubic or octahedral). It was also speculated that this wide line is caused by $\text{Eu}^{2+}\text{-Eu}^{2+}$ pair centers and that the possible superfine structure (SFS) of two neighboring nuclei was not resolved in a powdered sample because of averaging of the angular dependences of spectral lines over possible orientations of microcrystals in a magnetic field. Nevertheless, the temperature and the concentration dependences of this line have not yet been studied, and its nature has not yet been elucidated. At the same time, investigations [9] of the Eu^{2+} EPR in alkali-halide crystals are known, where the similar wide structureless line was attributed to the europium ion segregation in the disintegration of a solid solution.

In the present work, the data on the wide structureless EPR line generated in $\text{Ca}_{1-x}\text{Eu}_x\text{S}$ and $\text{Sr}_{1-x}\text{Eu}_x\text{S}$ solid solutions ($0.00005 < x < 0.0032$) prepared under equivalent conditions are compared. The concentration-induced broadening of SFS of lines in the EPR spectrum of isolated Eu^{2+} centers, associated with the dipole-dipole interaction of paramagnetic ions, is also

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TABLE 1. Concentration of implanted Eu and the fraction of Eu^{2+} estimated from the Curie constant for $\text{Ca}_{1-x}\text{Eu}_x\text{S}$ and $\text{Sr}_{1-x}\text{Eu}_x\text{S}$ solid solutions

Sample	Implanted Eu (x)	C , $\text{K}\cdot\text{cm}^3/\text{g}$	χ_0 , cm^3/g	Fraction Eu^{2+}/Eu
CaS:Eu_5/0	0.00005	$2.375\cdot 10^{-6}$	$-3.54\cdot 10^{-7}$	0.43
CaS:Eu_10/0	0.00010	$3.17\cdot 10^{-6}$	$-3.56\cdot 10^{-7}$	0.29
CaS:Eu_20/0	0.00020	$6.63\cdot 10^{-6}$	$-3.73\cdot 10^{-7}$	0.30
CaS:Eu_40/0	0.00040	$13.61\cdot 10^{-6}$	$-3.76\cdot 10^{-7}$	0.31
CaS:Eu_80/0	0.00080	$22.81\cdot 10^{-6}$	$-3.71\cdot 10^{-7}$	0.26
CaS:Eu_160/0	0.00160	$39.45\cdot 10^{-6}$	$-2.66\cdot 10^{-7}$	0.23
CaS:Eu_320/0	0.00320	–	–	–
SrS:Eu_5/0	0.00005	$1.517\cdot 10^{-6}$	$-2.57\cdot 10^{-7}$	0.46
SrS:Eu_10/0	0.00010	$3.552\cdot 10^{-6}$	$-2.20\cdot 10^{-7}$	0.54
SrS:Eu_20/0	0.00020	$3.51\cdot 10^{-6}$	$-2.75\cdot 10^{-7}$	0.27
SrS:Eu_40/0	0.00040	$9.006\cdot 10^{-6}$	$-2.27\cdot 10^{-7}$	0.34
SrS:Eu_80/0	0.00080	$25.88\cdot 10^{-6}$	$-2.50\cdot 10^{-7}$	0.49
SrS:Eu_160/0	0.00160	$43.47\cdot 10^{-6}$	$-3.00\cdot 10^{-7}$	0.41
SrS:Eu_320/0	0.00320	$76.08\cdot 10^{-6}$	$-3.90\cdot 10^{-7}$	0.36

compared. The measurements of the temperature dependences of the stationary magnetic susceptibility of the given solid solutions are discussed.

MEASUREMENT PROCEDURE

Polycrystalline (powdered) CaS:Eu and SrS:Eu samples (Table 1) were prepared from especially clean AES produced by the reduction of the corresponding sulfates in dry cleared hydrogen at 900-950°C. The europium impurity was implanted in the form of very clean (for luminophors) Eu_2O_3 or EuS . The samples were activated by annealing in sulfur vapor and a protective argon atmosphere. During annealing, the microcrystals were recrystallizing and growing, despite the low temperature compared to the melting point. All the CaS:Eu samples were annealed at 1150°C, and the SrS:Eu samples were annealed at 1050°C. The samples contained less than 10^{-5} at. % of Cr, Co, Ni, Fe, and Pb, less than 10^{-4} at. % of Mn, and less than 10^{-2} at. % of alkaline metals and halogens. Despite the fact that the content of dissolved oxygen reached $(5-10)\cdot 10^{-1}$ at. %, no separate oxide or oxisulfide phases arose. The oxisulfide europium phase was detected only in samples not annealed for recrystallization in sulfur vapor (they are not used in the present work).

The molar concentration of bivalent europium (Table 1) was estimated from the Curie constant under the assumption of noninteracting paramagnetic ions, for which the relation

$$\chi - \chi_0 = \frac{x_{\text{Eu}^{2+}} \cdot N_A \cdot g^2 \cdot \mu_B^2 \cdot S \cdot (S+1)}{3 \cdot M \cdot k_B \cdot T} = \frac{C}{T}$$

holds, where χ is the magnetic susceptibility per unit mass, N_A is the Avogadro number, g is the Landé factor, μ_B is the Bohr magneton, S is the total spin ($S = 7/2$ for Eu^{2+}), M is the molar mass of the parent substance ($M = 72.144$ for CaS and $M = 119.684$ for SrS), k_B is Boltzmann's constant, C is the Curie constant, and x is the bivalent europium concentration in molar fractions.

The EPR spectra were measured with a Varian E-4 X-range spectrometer with a Varian E-257 nitrogen-temperature attachment, which allowed the temperature of the sample to be changed from 100 to 500 K. The interface of the EPR spectrometer with a personal computer allowed the spectra to be recorded in digital form and the mathematical data processing to be performed. The spectral line width was determined as the difference, in G, between the corresponding maximum and minimum (the peak-to-peak difference).

The stationary magnetic susceptibility was measured with a SKVID magnetometer [10] in the constant magnetic field $H \cong 0.07$ T in the temperature range $2 \text{ K} < T < 50 \text{ K}$. To perform the measurements, the samples were sealed in quartz bulbs, whose contributions to measurable counts were insignificant and practically independent of the temperature, and evacuated. A gaseous medium, required for fast establishment of thermal equilibrium, was created in bulbs through the diffusion of helium

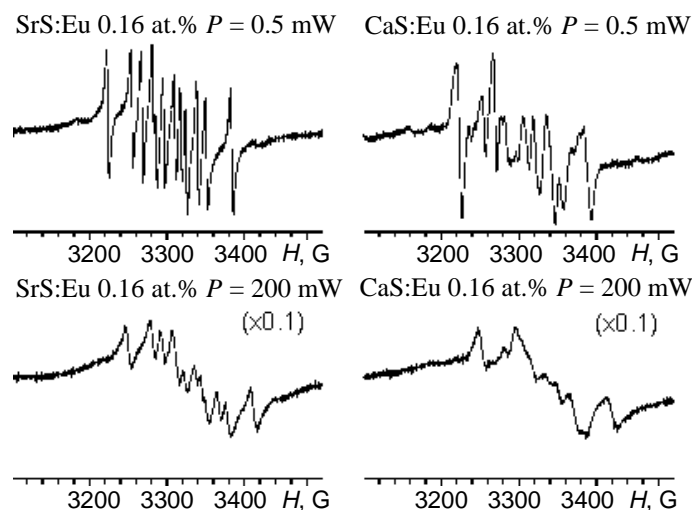


Fig. 1. Comparison of EPR signal saturation for a 400-fold increase of the microwave power for CaS:Eu and SrS:Eu with identical europium concentrations (0.16 at. %). The spectra were recorded at $T = 300$ K.

through the bulb walls. For weighed quantities of about 100 mg, the error in measuring the magnetic susceptibility was about $5 \cdot 10^{-9} \text{ cm}^3/\text{g}$.

RESULTS AND DISCUSSION

We investigated the dependences of EPR spectra on the microwave power (Fig. 1), the europium concentration, and the temperature. It turned out that the spectrum of the isolated Eu^{2+} ions with partially resolved SFS from ^{151}Eu and ^{153}Eu nuclei and the spectrum of the wide structureless line depended differently on the microwave power (Fig. 1). The saturation with increasing power was much more weakly manifested for the wide line than for the Eu^{2+} SFS lines. This allows these superimposed signals to be separated to some extent and facilitates their interpretation. Different patterns of saturation indicate a higher rate of spin relaxation for centers responsible for the wide line compared to that of the Eu^{2+} isolated ions. The structureless line width was practically equal to the separation between the extreme SFS components of the spectrum of Eu^{2+} ions in the highly-symmetric local environment. This indicates its coupling with doubly charged europium ions. It is possible that this line represents the spectrum of Eu^{2+} ions with the completely unresolved structure. The disappearance of the structure can be caused by concentration (dipole-dipole) line broadening or broadening due to exchange interactions. The wide line can be associated with exchange-coupled centers, because its intensity depends extraordinarily on the temperature (see below).

With increase in the europium concentration in samples, individual SFS components of Eu^{2+} ion spectrum with high local symmetry are broadened, and the wide line intensity, but not its width (Fig. 2a), increases. The increase of the europium concentration causes the average distance between the neighboring magnetic ions to decrease and hence the dipole-dipole contribution to the EPR line width of the Eu^{2+} ions with high local symmetry to increase (Fig. 2b). The dependence of the line width on the europium concentration is significantly nonlinear for CaS:Eu, for which the noticeable difference between the radii of Eu^{2+} (0.117 nm) and Ca^{2+} (0.100 nm) ions substituted by the Eu^{2+} ions may lead to the accumulation of the Eu^{2+} ions, for example, near the domain boundaries or in the region of dislocations, where partial volume compensation is possible.

The temperature dependence of the wide line also differs from the behavior of SFS components in the conventional spectrum of Eu^{2+} ions. The temperature variations of narrow SFS lines are typical of isolated paramagnetic ions, whereas the wide line variations for calcium sulfide are typical of strongly interacting magnetic centers (Fig. 3). The area under the wide line for CaS:Eu increases upon heating the sample up to 250 K. With further heating, the intensity of this line decreases. This behavior of the EPR spectrum can be attributed to strong exchange interaction of the Eu^{2+} ions. Thus, the ground state of antiferromagnetically-coupled pair of identical spins is nonmagnetic (zero total spin) [11]. But with increasing temperature, the excited magnetic level, which contributes to the EPR signal, is populated. The intensity of the EPR signal from each pair decreases, whereas the number of EPR-active pairs, on the contrary, increases with temperature. This yields a characteristic curve with the maximum at a temperature of about the exchange integral J . Since such large values of J are not typical for

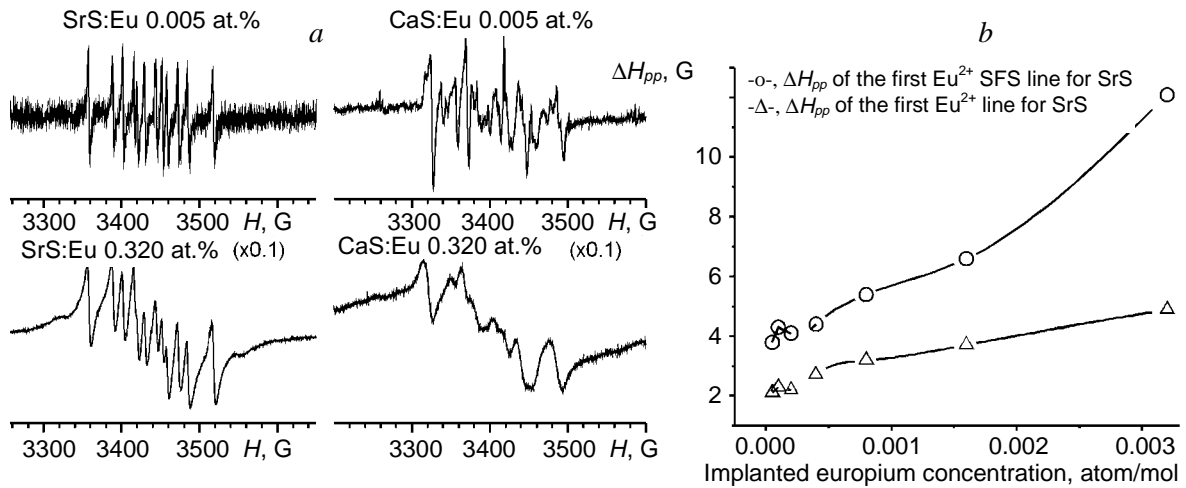


Fig. 2. EPR spectra of SrS:Eu and CaS:Eu samples with the minimum (above) and maximum (below) europium concentrations (a). The spectra were recorded for the microwave power $P = 0.5$ mW at $T = 300$ K. The concentration (dipole-dipole) broadening of the first low-field SFS line in the Eu^{2+} ion spectrum with high local symmetry (b).

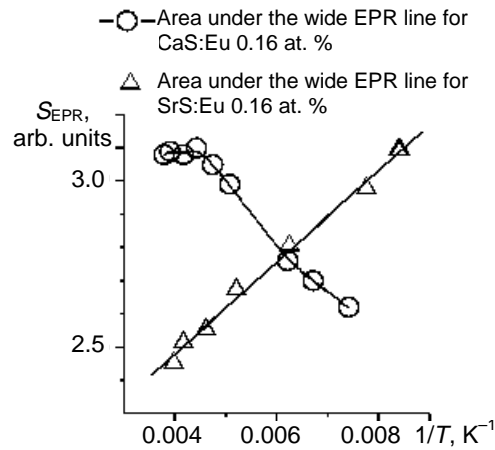


Fig. 3. Dependence of the area under the wide EPR line on the reciprocal temperature for SrS:Eu and CaS:Eu samples with identical europium concentrations (0.16 at. %). The spectra were recorded for the microwave power $P = 200$ mW.

europium chalcogenides, it is reasonable to assume that the wide line is produced by rather large clusters of exchange-coupled Eu^{2+} ions rather than by individual pairs. This is also indicated by the complete disappearance of any signal structure. For isolated exchange-coupled pairs, the interval between superfine components is halved compared to individual atoms [12]. When large groups of atoms are included in the exchange, the superfine structure completely disappears [12]. The fact that the position and width of the structurless line coincide with the position and spread of the SFS spectrum of the Eu^{2+} ions with high local symmetry, also indicates that the wide line may be associated with the Eu^{2+} ions of such clusters, where they are subject to the action of fields that reduce their local symmetry. The last conclusions are also valid for SrS:Eu, where the wide EPR line is similar in many respects to that for CaS:Eu, except the temperature dependence. The peculiarities of the temperature dependence of the wide line in SrS:Eu can be detected at lower temperatures.

The experimentally observed dependence of the static magnetic susceptibility on the temperature is well described by the Curie law ($\chi = \chi_0 + C/T$). An attempt at approximating the experimental dependence by the Curie-Weiss law yielded very small values (of the order of 10^{-9} K) of the Curie paramagnetic temperature. The Curie constants and the parameters χ_0 for all the examined samples are given in Table 1. For CaS:Eu samples with a europium concentration less than 0.01 at. %, χ_0 corresponds to the diamagnetic contribution of pure calcium sulfide. With increase in the europium concentration, χ_0

increases. The reverse tendency was observed for SrS:Eu. Apparently, the mechanisms of formation and stratification of solid Eu solutions in calcium and strontium sulfides differ. This is also confirmed by the EPR data (see Figs. 2 and 3). Nevertheless, the values of the Curie constants (Table 1) in both cases showed the monotonic increase of the magnetic moment with the implanted europium concentration. The difference between the EPR data and the magnetic research is most likely due to the fact that the variations of $\chi(T)$ characterize the integral contribution of all magnetic moments, whereas the EPR reflects selectively the contribution of individual europium centers. The decrease of the fraction of bivalent europium with increase of the concentration of implanted europium impurity (Table 1) was more pronounced for CaS:Eu than for SrS:Eu. The strong concentration line broadening of the EPR spectrum of highly symmetric Eu^{2+} centers and the abnormal temperature dependence of the area under the wide line are also manifested for CaS:Eu. This can be due to large local stresses arising from the discrepancy between the Eu^{2+} and Ca^{2+} radii (see above). The zero Curie paramagnetic temperature and the absence of peculiarities in the temperature dependence of the magnetic susceptibility for CaS:Eu and SrS:Eu, found in the magnetic measurements, may be due to mutual compensation of the superexchange parameters J_1 and J_2 ($J_1 \approx J_2$, $J_1 < 0$, and $J_2 > 0$) [13].

Thus, clusterization of europium impurity at very small concentrations ($x \approx 0.0001$) is typical of $\text{Ca}_{1-x}\text{Eu}_x\text{S}$ and $\text{Sr}_{1-x}\text{Eu}_x\text{S}$ solid solutions. This is indicated by the formation of the wide structureless EPR line. At the same time, the dependence of the stationary magnetic susceptibility on the temperature obeys the Curie law with high accuracy in the temperature range 4.2–50 K, despite the noticeable exchange interactions of Eu^{2+} ions manifested through the EPR spectra.

REFERENCES

1. V. Klatt and P. Lenard, *Wied. Ann.*, **38**, 90 (1889).
2. C. Pappas, M. Meissner, G. Schmidt, *et al.*, *Physica*, **B165**, Pt. 1, 185–186 (1990).
3. M.-L. Yu. Allsalu, M. I. Danilkin, V. D. Kuznetsov, *et al.*, *Vestn. Mosk. Univ., Ser. 3, Fiz., Astron.*, **30**, No. 2, 97–99 (1989).
4. M. Pham-Thi, N. Ruelle, E. Tronc, *et al.*, *Jpn. J. Appl. Phys.*, **33**, No. 4A, Pt. 1, 1876–1884 (1994).
5. D. G. Andrianov, N. M. Pavlov, A. S. Savel'ev, *et al.*, *Fiz. Tekh. Poluprovodn.*, **14**, No. 6, 1202–1212 (1980).
6. S. Ozeroff and P. Kizom, *Semimagnetic Semiconductors* [Russian translation], Mir, Moscow (1992).
7. A. A. Manenkov and A. M. Prokhorov, *Dokl. Akad. Nauk SSSR*, **107**, No. 3, 402–404 (1956).
8. M. Danilkin, M. Must, É. Pedak, *et al.*, *Zh. Prikl. Spektrosk.*, **62**, No. 3, 186–191 (1995).
9. V. B. Laizan, in: *Radiation Physics III. Ionic Crystals* [in Russian], Znanie, Riga (1965), pp. 95–102.
10. V. D. Kuznetsov, *Prib. Tekh. Eksp.*, No. 4, 196–201 (1985).
11. A. Abraham and B. Bleaney, *Electronic Paramagnetic Resonance of Transition Ions. Vol. 1* [Russian translation], Mir, Moscow (1972).
12. S. A. Al'tshuler and B. M. Kozyrev, *Electronic Paramagnetic Resonance of Compounds of Transition Elements* [in Russian], Nauka, Moscow (1972).
13. A. Bruno and J. P. Lascaray, in: *High Magnetic Fields in Semiconductor Physics II, Springer Series in Solid-State Sciences. Vol. 87* (1989), pp. 509–512.