Investigation of the energy gap in SmB_6 by the ESR method

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The electron spin resonance of rare-earth impurities in a mixed-valence compound SmB_6 was investigated in a wide range of temperatures. It was established that a gap in the electron spectrum, amounting to ≈ 50 K at $T = 0$ K, decreased on increase in temperature and disappeared at $T = 150$ K.

1. INTRODUCTION

Mixed-valence compounds can be divided into two classes, depending on their low-temperature behavior: metallic compounds with a ground state having the characteristics of a Fermi liquid and substances of the "semiconductor" type with a narrow gap near the Fermi level. A typical representative of the second class is SmB_6. The existence of a gap $\Delta \approx 40$–60 K in the low-temperature spectrum of electron excitations in SmB_6 has been established by a variety of methods,[1–5] including the ESR method.[6,7] The problem of the origin of this gap is still a matter of controversy. The gap has been attributed to the *f-d* hybridization,[8] Wigner crystallization,[9] exciton pairing of *d* electrons with *f* holes,[10] etc. The discrepancies between the predictions of the various theories are significant at finite temperatures: for example, the gap predicted by the hybridization theory does not vary with temperature, whereas the exciton gap appears as a collective effect and disappears at temperatures of the order of the gap itself. It would therefore be desirable to obtain experimental information on the excitation spectrum at finite temperatures.

We investigated the temperature dependence of the ESR spectrum of impurity spins in SmB_6 and obtained for the first time evidence of disappearance of the gap at high temperatures. Our results (first reported briefly in Ref. 11) were in good agreement with the conclusions reached in Ref. 12 as a result of an analysis of the lattice properties of SmB_6.

2. EXPERIMENTAL METHOD

Our ESR measurements were made on powder and single-crystal samples of SmB_6 containing Gd^{3+}, Eu^{2+}, Er^{3+}, and Sm^{3+} ions, and on powders of LaB_6 doped with Gd^{3+} ions. The purity of samarium used in the preparation of these samples was 99.95% and that of boron was 99.99%. Single crystals were grown from molten solutions. The maximum size of a single-crystal plate was $2 \times 1 \times 0.1$ mm. Measurements on single crystals were made only at $T = 1.7$–4.2 K because the signal intensity was low. Powders were prepared by several methods: samples designated as No. 1 were prepared by melting together the components taken in the stoichiometric ratio, first in an induction furnace and then in an arc furnace. The size of individual grains in a powder was 10–15 μ, i.e., it was less than the thickness of the skin layer. Small single crystals grown from molten solutions were ground in a mortar and passed through a 50-μ sieve. The result was powder No. 2. Powder No. 3 was prepared by fast quenching of the samples and it was characterized by a higher number of defects. Better penetration of an electromagnetic field into a sample was ensured by dissolving a powder in molten paraffin. Measurements were made in a wide range of temperatures from 1.7 to 150 K at a frequency of 9.4 GHz.

3. RESULTS OF MEASUREMENTS

The spectra of the Gd^{3+} and Eu^{2+} ions in the investigated powders represented a single line with the g factor 1.92 ± 0.02, which depended weakly on temperature. The signal due to Er^{3+} consisted of a double line due to a Γ_8 quartet with $g = 4.4$, which disappeared on heating to 12 K, and a single line due to an excited Γ_8 doublet with $g = 5.83$. Figures 1–3 show the temperature dependences of the resonance line width δH for the Gd^{3+}, Eu^{2+}, and Er^{3+} ions (in the last case due to a Γ_6 doublet) in SmB_6 powder at temperatures $T = 1.6$–150 K. At low temperatures $T < 20$ K similar dependences for Gd^{3+} and Eu^{2+} can be found in Ref. 13. These dependences have two characteristic features: a) a step in the region of $T \approx 6$–10 K for the Er^{3+} and Gd^{3+}

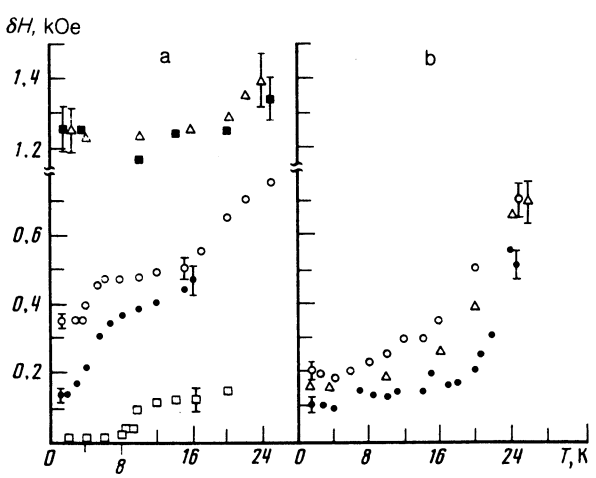

FIG. 1. Temperature dependences of the ESR line width obtained for SmB_6 at low temperatures for different impurities: a) Gd^{3+} (●—0.1%; ○—1%; △—1%, ▲—1% quenched samples; ■—5%), Er^{3+} (□—0.02%); b) Eu^{2+} (●—0.03%; ○—0.5%; △—5%).

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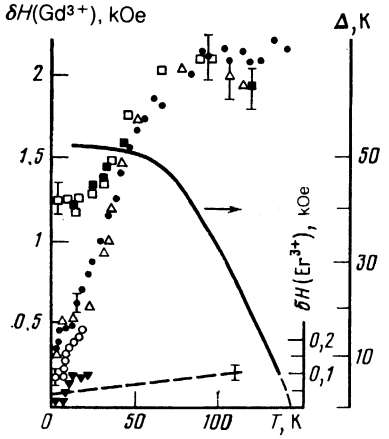

FIG. 2. Temperature dependences of the ESR line width of Gd^{3+} ions (○—0.1%; ●—1%; No. 1; △—0.8%, No. 2; □—0.8%, No. 3; ■—5%) and of Er^{3+} ions (▼—0.02%) in SmB_6. The dashed curve represents $La_{0.99}Gd_{0.01}B_6$ and the continuous curve is the temperature dependence of the energy gap in $Sm_{0.99}Gd_{0.01}B_6$.

impurities; b) a steep rise of the line width exhibited by all the samples when their temperature is increased. The strong dependence of the low-temperature line width on the preparation method, and on the nature and concentration of impurities, is due to the dipole-dipole interactions and the static scatter of the g factors due to imperfections of the crystal structure.

A singularity in the temperature dependence of the line width of trivalent ions at $T \approx 10$ K corresponds to a minimum in the rate of relaxation T_1^{-1} of the spins of the boron nuclei in SmB_6, which occurs in the same range.[14,15] An interpretation of this minimum has been proposed on the hypothesis that, in particular, low-energy collective magnetically active excitations appear in SmB_6, attributed in Ref. 14 to the Wigner crystallization of the $4f$ electrons.

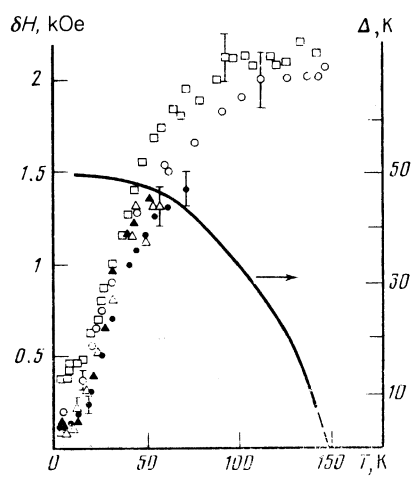

FIG. 3. Temperature dependences of the ESR line width of Eu^{2+} ions (●—0.03%, No. 1; △—0.04%, No. 2; ○—0.5%; ▲—5%) and Gd^{3+} ions (□—1%, No. 1) in SmB_6. The continuous curve is the temperature dependence of the energy gap in $Sm_{0.995}Eu_{0.005}B_6$.

The reason for a step in the dependence $\delta H(T)$ was studied by determining the low-temperature ESR spectra of SmB_6 single crystals containing Eu^{2+}, Gd^{3+}, Er^{3+}, and Sm^{3+} ions. An analysis of these spectra and of their angular dependences revealed the following. Local crystal fields acting on the Eu^{2+} ions have a cubic symmetry at all the impurity concentrations (0.1, 1, and 5 at.%).

The Gd^{3+} ions exhibit an ESR signal not only of the cubic, but also of the axial symmetry. An increase in the concentration of this impurity as well as quenching of a sample increases also the relative number of the active centers.

The ESR spectra of the trivalent erbium ions also indicate that the crystals contain not only cubic centers of the Γ_8 symmetry (reported earlier in Ref. 16), but also centers which are subject to an axial crystal field and are characterized by $g_\perp = 2.72$ and $g_\parallel = 2.27$. Moreover, when a sample is heated to 10–15 K, an additional line with a strong angular dependence (with the g factor varying from 1.31 to 3.18) is observed and it is clearly due to the excited Γ_8 quartet.

All the single crystals exhibit the ESR signal of the Sm^{3+} ions in a field of tetragonal symmetry and characterized by $g_\parallel = 0.42$ and $g_\perp = 0.79$.

We can thus see that in the case of trivalent ions there are local distortions of the cubic symmetry and the distortion axis is parallel to a fourfold axis. This may be due to the fact that because of the inter-action of an "excess" charge of a trivalent ion with a vacancy, the gadolinium and erbium ions occupy preferentially locations near vacancies in the samarium sublattice.

The qualitative difference between the behavior of the ESR line width of powders with Gd^{3+} and Er^{3+} from those with Eu^{2+} at $T \approx 10$ K (presence or absence of a step) is also clearly due to a difference in the valences of these ions.

In all probability the replacement of samarium with an "average" valence of ~ 2.5 by a trivalent ion results in localization of an excess electron near an impurity. Since the permittivity of SmB_6 is high, amounting to $\varepsilon \sim 10^3$ (Ref. 4), we may assume that the excitation energy of this impurity state is low, of the order of 10 K. Therefore, at these temperatures we can expect a steep rise of the rate of relaxation of the impurity spin due to modulation of the exchange interaction of an ion with a quasilocalized electron.

This singularity of the relaxation of the trivalent ion spins makes it possible to interpret differently the nuclear relaxation minimum mentioned above. We may assume that at low temperatures the decay of the nuclear magnetization is largely due to the interaction of foreign rare-earth impurity ions. Since the rate of relaxation of the nuclei is proportional to the relaxation time of the impurity spins, a strong reduction of the latter on increase in temperature in the region of $T \approx 10$ K should give rise to a minimum in the dependence $T_1^{-1}(T)$ for the nuclei of the trivalent impurity.

The most interesting feature in the problem formulated above is the behavior of the ESR signal at high temperatures, when the resonance line of any sample increases rapidly on increase in temperature (Figs. 2 and 3). In the range $T > 40$ K the line width is practically independent of the nature of the impurity ion, its concentration, and method used to pre-

pare the samples. The size of the individual grains in a powder is almost comparable with the thickness of the skin layer throughout the investigated range of temperatures, so that the g factor is determined (as in the case of insulators) by the maximum of the absorption curve. Figure 4 shows typical ESR signals obtained at low and high temperatures. The signal amplitudes differ approximately by two orders of magnitude. At $T \geqslant 150$ K the resonance cannot be observed reliably.

The resonance line broadening in the range $T > 20$ K is in all probability due to the exchange interaction between the impurity and the f electrons of Sm. This is supported also by the smallness of the usual Korringa relaxation of Gd^{3+} in LaB_6 (Fig. 2), when f energy band is located far from the Fermi level. The exponential rise of δH can be explained by the presence of a gap in the spectrum, but calculations carried out in the f-d hybridization model with a constant gap fail to give a satisfactory description of $\delta H(T)$. Moreover, such a description cannot be provided by using a dependence of the type

$$\delta H(T) = \delta H(0)\, T^{\alpha} \exp(-\Delta/T).$$

The general form of $\delta H(T)$ resembles the dependences reported for systems in which the gap Δ is a function of temperature and decreases on increase in temperature. In particular, the temperature dependence of the line width resembles somewhat the behavior of the line width in the spectra of superconductors. There are also theoretical arguments[10] in favor of the hypothesis that the gap in SmB_6 is not of the single-particle type (i.e., caused by simple f-d hybridization), but is of collective origin. In this case we can again naturally expect the gap to decrease on increase in temperature.

In view of this situation, we attempted to describe the behavior of $\delta H(T)$ using a dependence of the type

$$\delta H(T) = \delta H(0) \exp[-\Delta(T)/T].$$

In fact, it is then possible to achieve a much better agreement with the experimental results. The dependence $\delta(T)$ obtained in this case shows that the gap which at $T \leqslant 40$ K amounts to $\Delta \approx 50$ K decreases on increase in temperature and this is particularly steep in the region of $T \approx 100$ K.

4. DISCUSSION OF RESULTS

There is a simple mechanism which can alter the density of states and fill the gap as temperature rises: this mechanism is the damping of electron excitations due to their interaction with phonons. Simple estimates indicate that this mechanism can hardly account for the observed temperature dependence of the gap. The damping of electron states at finite temperatures is described by $\gamma \sim T^3/\Theta_D^2$ ($\Theta_D = 373$ K is the Debye temperature of SmB_6 given in Ref. 12) and, for example, at $T \approx 100$ K it amounts to $\gamma \approx 6$ K which is much less than the change in the gap observed experimentally (Figs. 2 and 3). We shall therefore assume that a change in the gap with temperature is a real effect due to its collective origin. A more detailed analysis requires adoption of a specific model of the origin of the gap and we shall select the model of an excitonic insulator. The gap is attributed to the exciton pairing of holes from the f shell with d electrons from the conduction band. In a mixed-valence phase a small gap exists in the ground state precisely in those cases in which the densities of the d electrons and of the f holes are the same (SmB_6, SmS, TmSe). On the other hand, exciton pairing is possible in this situation; the equality of the densities of electrons and holes is the condition for the formation of an excitonic insulator.

As mentioned above, we shall assume that the resonance line broadening at $T > 20$ K is mainly due to relaxation of the transverse component of the impurity spin to the partly filled f band. Relaxation of the localized spin in an exciton insulator is considered in Refs. 17 and 18. Calculations are reported there of the longitudinal relaxation rate T_1^{-1} in the approximation of identical electron and hole energy bands. At high temperatures we have $T_2^{-1} = T_1^{-1}$ so that in our case the calculations can be carried out similarly with small complications because of the difference between the effective masses and exchange integrals of the d and f electrons.

We shall assume that J_d and J_f are the exchange integrals of the interaction of impurities with a d electron and an f hole, and N_d and N_f are the densities of states in the corresponding energy bands at the Fermi level. The rate of relaxation of the transverse magnetization of the impurity spins is

$$T_2^{-1} = 2\pi T f(\Delta)\,(b_f^2 + b_d^2)\,\{1 + \alpha[1 - f(\Delta)]\,(\Delta/2T)\ln(2\Delta\tau)\}, \tag{1}$$

where

$$f(\Delta) = [1+\exp(\Delta/T)]^{-1}, \quad b_i = J_i N_i; \quad \alpha = (b_f + b_d)^2/(b_f^2 + b_d^2),$$

$\Delta = \Delta(T)$ is the exciton gap; τ^{-1} is the momentum relaxation time. Equation (1) differs from the corresponding formula in Ref. 17 by a coherence factor α: in Eq. (1) its value is $0 \leqslant \alpha \leqslant 2$, whereas in Refs. 17 and 18 it is $\alpha = 2$.

The dependence $\delta H(T)$ for Gd^{3+} is described by Eq. (1) with $b_d = -0.62 \times 10^{-2}$, $b_f = -2.32 \times 10^{-2}$, and $\tau^{-1} = 1$ K on condition that the gap $\Delta(T)$ depends on temperature as is shown in Fig. 2. A similar fitting for Eu^{2+} gives the values $b_d = -0.74 \times 10^{-2}$, $b_f = -2.23 \times 10^{-2}$, and $\tau^{-1} = 1$ K, as well as the temperature dependence of the gap shown in Fig. 3. It is clear from the figures that the low temperature gap is 50 K and it hardly varies up to $T = 50$–70 K; a strong reduction in the gap begins in the region of 100 K and at $T_c = 150$ K the gap disappears. However, it is possible that the gap does not fill completely.

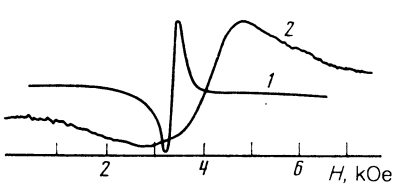

FIG. 4. Electron spin resonance spectrum of gadolinium ions (1%) in SmB_6 at different temperatures: 1) 4.2 K; 2) 100 K.

It should be stressed that the existence of free parameters b_d, b_f and τ is not of fundamental importance: the main points are the existence of a gap which varies with temperature and an increase in the density of states at the gap edges. The existence of maxima in the density of states $N(\varepsilon)$ near the gap edges in SmB_6 is confirmed by the results of optical measurements.[4] On the other hand, a maximum of $\delta H(T)$, associated with the appearance of a gap near T_c and clearly noticeable in the case of superconductors, is in our case quite weak because $T_c > \Delta(0)$.

As expected, the value of πb_d^2 is of the order of the temperature coefficient of the Gd^{3+} line width in the case of LaB_6. When the width of the d energy band is ≈ 5 eV, the exchange integral is $J_d = -0.03$ eV. The interaction of the impurity with the f electrons of Sm^{3+} is via the conduction band and we then have $j_f = cJ_d VN_d$, where c is a number of the order of unity and V is the matrix element of the f-d hybridization. In the case of mixed-valence compounds for a strong Hubbard repulsion the role of the exchange integral between the f and d electrons is played by V, instead of by the usual expression V^2/ε_f, which is valid in the case of deep f levels characterized by $\varepsilon_f > V$. We also have $N_f \propto \delta^{-1}$, where $\delta = \pi V^2 N_d$ is the width of the f band. We can find the experimental values of b_f assuming that $V = 0.3$ eV and $c = 0.6$; this gives $J_f = -10^{-3}$ eV and $\delta = 0.05$ eV, which seems reasonable.

A considerable shift of the g factor amounting to $\Delta g = -0.08$ is exhibited by all the samples. It can be estimated from $\Delta g = b_d + \gamma b_f$; the appearance of a factor $\gamma = [(4/3)J(J+1)]^{1/2}$ is due to the degeneracy of the state Sm^{3+} characterized by $J(Sm^{3+}) = 5/2$. For these values of b_i, we find that $\Delta g = -0.08$, which agrees with the observed shift.

5. CONCLUSIONS

These results show that an anlysis of the temperature dependences of the ESR line width for the Ge^{3+} and Eu^{2+} impurities leads to the conclusion that the electron energy spectrum of SmB_6 has a gap which decreases with temperature and becomes small at $T = 150$ K. Evidence that the gap of SmB_6 depends on temperature and disappears at $T \approx 150$ K was also reported in Ref. 12, where an analysis was made of the temperature dependences of the lattice constant and of the elastic moduli.

A good agreement with the experimental $\delta H(T)$ curve can be obtained in the model of an excitonic insulator, when the fitting procedure gives reasonable values of the parameters (exchange integrals J_d and J_f, densities of states N_d and N_f) and makes it possible to explain also the shifts of the g factors. However, it must be stressed that these results do not depend critically on the actual gap formation model and cannot be regarded as proving such a model. It is probable that similar results could also be obtained employing the Wigner crystallization model.[9,12]

The mechanism of formation of gap is possibly not purely excitonic, because it is difficult to reconcile the relatively small gap at $T = 0$ K, which amounts to $\Delta = 50$ K, with a fairly high value of the "critical temperature" $T_c = 150$ K. However, on the whole it seems to us that the collective origin of the gap and its temperature dependence have been established quite firmly.

[1)]P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow.

[1]J. W. Allen, B. Batlogg, and P. Wachter, Phys. Rev. B **20**, 4807 (1979).
[2]G. Guntherodt, W. A. Thompson, F. Holtzberg, and Z. Fisk, Phys. Rev. Lett. **49**, 1030 (1982).
[3]I. Frankowski and P. Wachter, Solid State Commun. **40**, 885 (1981).
[4]P. Travaglini and P. Wachter, Phys. Rev. B **29**, 893 (1984).
[5]S. von Molnar, T. Theis, A. Benoit, A. Briggs, J. Flouquet, J. Ravex, and Z. Fisk, in: Valence Instabilities (Proc. Intern. Conf., Zurich, Switzerland, 1982, ed. by P. Wachter and H. Boppart), North-Holland, Amsterdam 1982, p. 389.
[6]T. S. Al'tschuler, M. M. Zaripov, and V. N. Mironov, VII Vsesoyuznyĭ simpozium po spektroskopii kristallov aktivironvannykh ionami redkozemel'nykh i perekhodnykh metallov. Tezisy dokladov (Abstracts of Papers presented at All-Union Symposium on Spectroscopy of Crystals Activated with Rare-Earth and Transition Metal Ions), Leningrad, 1982, p. 11.
[7]C. M. Jackson, K. Y. M. Wong, M. Hardiman, *et al.*, Bull. Am. Phys. Soc. **28**, 270 (1983).
[8]N. F. Mott, Philos, Mag. **30**, 403 (1974).
[9]T. Kasuya, K. Takegahara, T. Fujita, T. Tanaka, and E. Bannai, J. Phys. (Paris) **40** Collq. 5, C5-308 (1979).
[10]D. I. Khomskii, in: Quantum Theory of Solids (ed. by I. M. Lifshitz), Mir., M., 1982, p. 70.
[11]T. S. Al'tshuler, V. N. Mironov, G. G. Khaliullin, and D. I. Khomskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 28 (1984). [JETP Lett. **40**, 754 (1984)].
[12]T. Kasuya, M. Kasaya, K. Takegahara, T. Fujita, T. Goto, A. Tamaki, M. Takigawa, and H. Yasuoka, J. Magn. Magn. Mater. **31-34**, 447 (1983).
[13]K. Kojima, M. Kasaya and Y. Koi, J. Phys. Soc. Jpn. **44**, 1124 (1978).
[14]M. Takigawa, H. Yasuoka, Y. Kitaoka, T. Tanaka, H. Nozaki, and Y. Ishizawa, J. Phys. Soc. Jpn. **50**, 2525 (1981).
[15]O. Pena, M. Lysak, D. E. MacLaughlin, and Z. Fisk, Solid State Commun. **40**, 539 (1981).
[16]H. Sturm, B. Elschner, and K. H. Hock, Phys. Rev. Lett. **54**, 1291 (1985).
[17]K. Maki and K. Nakanishi, J. Low Temp. Phys. **5**, 55 (1971).
[18]B. G. Idlis and Yu. V. Kopaev, Fiz. Tverd. Tela (Leningrad) **20**, 1383 (1978) [Sov. Phys. Solid State **20**, 796 (1978)].

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