Observation of the temperature dependence of the energy gap in SmB_6 by the EPR method

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The EPR of Gd and Eu impurities in the compound SmB_6 with intermediate valency is investigated. It is established that the gap in the electron spectrum, equal to ~ 50 K at $T = 0$, decreases with increasing temperature and apparently vanishes at $T \sim 150$ K.

1. Compounds with intermediate valency can be divided into two classes, depending on their behavior at low temperatures: compounds of the "metallic" type, which have a ground state with the characteristics of a Fermi liquid, and materials of the "semiconducting" type with a narrow gap near the Fermi level. The typical representative of the second group is SmB_6. The presence of a gap Δ on the order of 40–60 K at low temperatures in the spectrum of electronic excitations in SmB_6 was established by various methods.[1–3] The nature of this gap is still disputed. The gap has been attributed to the *f-d* hybridization,[4] Wigner crystallization,[5] excitonic pairing of *d* electrons with *f* holes,[6] etc. There is a substantial disagreement between the predictions of different versions of the theory at finite temperatures: The hybridization gap does not change with temperature, while the exciton gap arises as a collective effect and vanishes at temperatures on the order of the gap itself. In this connection, it is desirable to have experimental data on the excitation spectrum at finite temperatures.

In this letter we investigate the temperature dependence of the EPR spectrum of impurity spins in SmB_6 and we give evidence for the first time that the gap vanishes at high temperatures.

2. The measurements were performed at a frequency of 9.4 GHz in the temperature range 1.7–140 K in SmB_6 powders with gadolinium and europium impurities. The EPR signal from the Gd^{3+} and Eu^{2+} ions with a g-factor of 1.92 ± 0.02, which is nearly independent of temperature, was observed. At temperatures below 20 K the width of the resonance line, δH, which depends on the concentration and type of magnetic impurity (Figs. 1a and 1b), is attributable to the usual factors (dipole-dipole interaction, unresolved fine structure, spread in the g-factors near defects, etc.). In this region, our data correlate with the results of Ref. 7, in which analogous studies were performed in SmB_6 at low temperatures.

From the viewpoint of the problem stated above, the most interesting behavior is that of the EPR signal at high temperatures, when the resonance line in all samples is broadened rapidly with increasing temperature (Figs. 1a and 1b). At $T \gtrsim 150$ K the EPR could not be observed reliably.

3. The observed broadening of the EPR line is most likely associated with the exchange interaction of impurities with the *f* electrons of Sm^{3+}. This is also suggested

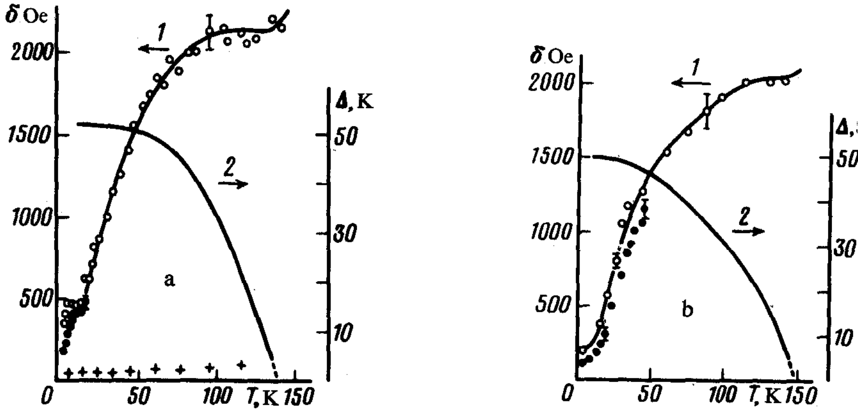

FIG. 1. Temperature dependence of the width of the EPR line $\delta H(T)$ in $Sm_{1-x}Gd_xB_6$ (a) and $Sm_{1-x}Eu_xB_6$ (b) at x. ○ – 0.01 and ● – 0.001. Curve 1 is the calculation using Eq. (1). Curve 2 shows the temperature dependence of the gap Δ. The plus sign is the width of the line $\delta H(T)$ in $La_{0.99}Gd_{0.01}B_6$.

by the smallness of the usual Korringa relaxation in LaB_6 (Fig. 1a), in which the f-band is situated far from the Fermi level. The exponential growth of δH at low temperatures can be explained by the presence of a gap in the spectrum. However, calculations in the f-d hybridization model with a constant gap did not lead to a satisfactory description of the dependence $\delta H(T)$. This dependence is externally slightly reminiscent of the behavior of the line width in superconductors. It may be, however, that the gap in SmB_6 arises as a collective effect produced as a result of excitonic pairing of d electrons with f holes, for example.

Let J_d and J_f be the exchange integrals of the interactions of impurities with a d electron and an f hole, and let N_d and N_f be the state densities of the corresponding bands at the Fermi level. For the relaxation rate T_2^{-1} of the impurity spin we find

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

where $\Delta = \Delta(T)$ is the excitonic gap, and τ is the momentum relaxation time. Expression (1) differs from the corresponding equation in Ref. 8 by the concreteness factor α: in (1) we have $0 \leqslant \alpha \leqslant 2$, whereas in Ref. 8 $\alpha = 2$.

4. 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, if the gap $b_d = -0.74\times 10^{-2}$ and $b_f = -2.23\times 10^{-2}$, and $\Delta(0)\tau = 50$ depends on the temperature as in Fig. 1a. An analogous fit for Eu^{2+} gives the values $b_d = -0.74\times 10^{-2}$ and $b_f = -2.23\times 10^{-2}$, and $\Delta(0)\tau = 50$ and the temperature dependence of the gap plotted in Fig. 1b.

As expected, the quantity $J_d \sim -0.03$ is on the order of the temperature slope of the line width for LaB_6. With a d-band width of ~ 5 eV the exchange integral is $J_f \sim cJ_d VN_d$ eV. The impurity interacts with the f electrons of Sm^{3+} through the conduction band, and $J_f \sim cJ_d VN_d$, where c is a number on the order of unity and V is the matrix element of f-d hybridization. (Under the conditions of variable valency and with strong Hubbard repulsion the role of the exchange integral between f and d electrons is played by V, instead of the usual expression $\sim V^2/|E_f|$, which is valid for a deep f level $|E_f| \gg V.N_f \sim \delta^{-1}$, where $\delta = \pi V^2 N_d$ is the width of the f band.) To obtain the experimental value of b_f we must set $V \sim 0.3$ eV and $c \sim 0.6$; in this case $J_f \sim 10^{-3}$ eV and $\delta \sim 0.05$ eV, which is entirely reasonable.

The displacement of the g-factor is estimated to be $\Delta g = b_d + \gamma b_f$; the appearance of the factor $\gamma = [J(J+1)/(3/4)]^{1/2}$ is caused by the degeneracy of the state of Sm^{3+} with $J(Sm^{3+}) = 5/2$. For the values of b_i found above, the quantity $\Delta g \simeq -0.08$ consistent with the observed displacement.

5. The results presented above indicate that the gap in SmB_6 arises in a coherent manner, at a finite temperature T_c on the order of 150 K. It is possible that the mechanism for the formation of the gap is not purely excitonic, since T_c greatly exceeds the magnitude of the gap $\Delta(0) \sim 50$ K.

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