# Effect of pressure on the correlation gap in a compound with intermediate valency $SmB_6$

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It is found that the correlation gap $E_9$ in $SmB_6$, which under normal pressure $\sim 4$ meV, decreases under the action of pressure $p$ and vanishes at $p \approx 55$ kbar. In the pressure range $p > 60$ kbar, the resistance of $SmB_6$ as a function of temperature $R(T)$ exhibits a metallic behavior, which indicates a pressure-induced transition of samarium in $SmB_6$ from the state with intermediate valency $\nu$ [$\nu$(Sm) = 2.6 at $p = 0$] to integer valency $\nu = 3$ for $p > 60$ kbar.

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**1**. Samarium hexaboride is a samarium compound with fluctuating valency (CFV)[1] with a Fermi level $\varepsilon_F$, intersecting a very narrow $4f$ band with a density of states $g(\varepsilon)$, exceeding approximately 100-fold the density of states in wide bands of normal metals. At $p = 0$, the valence $\nu$ of samarium in $SmB_6$ is 2.66.[2] Since the compounds of the type $R^{2+}B_6$ (R is an ion of a rare-earth element) are semiconductors,[2] and $R^{3+}B_6$ are analogs of closely valent metals,[2] one would expect, therefore, that $SmB_6$ would also be a metal with $g(\varepsilon_F) \neq 0$. However, in reality, $SmB_6$ is a semiconductor, in which the gap $E_g$ is (2–4) meV, i.e., near $\varepsilon_F$ on a background of a relatively high density of states $g(\varepsilon)$, there is an extremely narrow and deep gap (see insert a in Fig. 1).

The reason for the presence of this gap has not yet been completely understood. There are theories relating its presence to the Wigner crystallization,[2] as well as models[3] that examine the interelectronic correlation and CFV, which leads to the appearance of the so-called hybridization gap.

Recently, it was found[4,5] that the weak semiconducting behavior of $R(T)$ in the "gold" phase of SmS is suppressed at $p \gtrsim 20$ kbar, which is interpreted as a pressure-

  

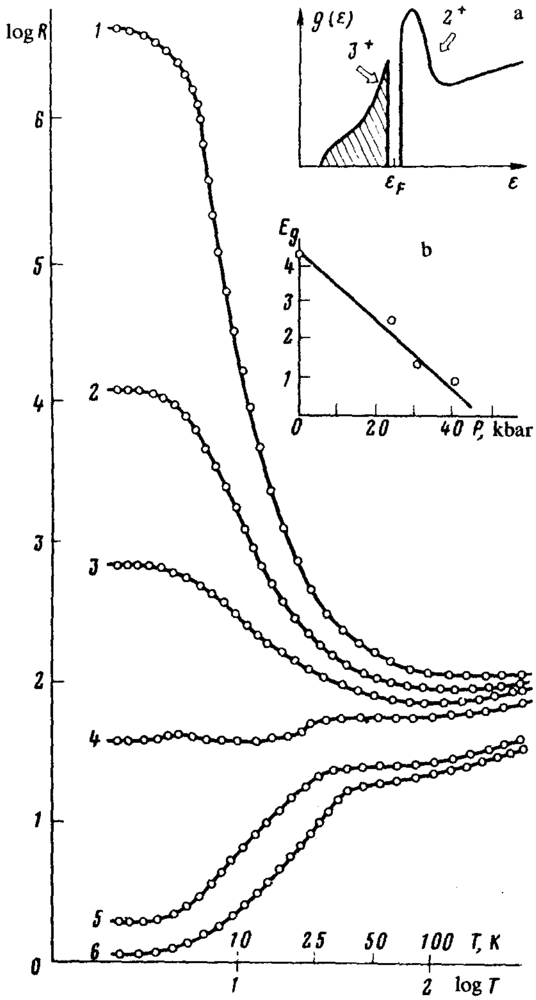


FIG. 1. Temperature dependence of the resistance $R(T)$ in $SmB_6$ under different pressures (in kbar). 1) 0, 2) 24, 3) 40, 4) 57, 5) 70, and 6) 108. The insert illustrates the behavior of the density of states $g(\varepsilon)$ (a) and the dependence of the gap size $E_g$ on the pressure $p$ (b).

induced transition to a trivalent state of Sm in SmS, accompanied by disappearance of the correlation gap near $\varepsilon_F$. However, the existence of a gap in SmS in the "gold" phase is not reliably established at the present time.

In contrast to SmS, the presence of a gap near $\varepsilon_F$ in $SmB_6$ is confirmed by different methods[6–8] and does not give rise to any doubts. In this connection, it was of interest to investigate the effect of pressure on the temperature and field dependences of the resistance $R$ in single-crystalline specimens of $SmB_6$.

2. The measurements were performed under pressure up to 110 kbar in magnetic fields up to 50 kOe in the temperature range 2–300 K. Single crystals of $SmB_6$ with

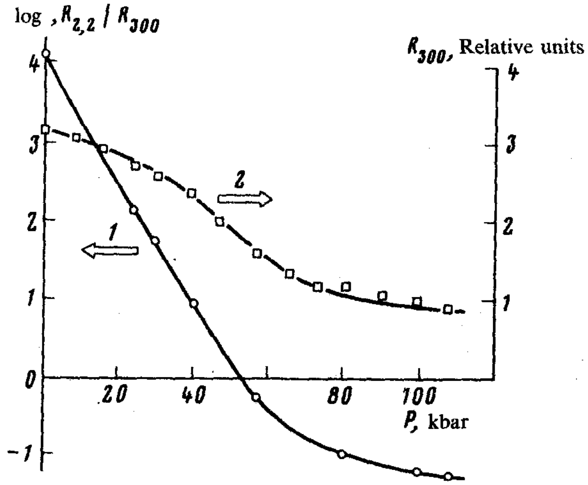


FIG. 2. Pressure dependence of the reduced resistance at low temperatures (1) and the resistance at $T = 300$ K (2).

$T_{melt} \approx 2800$ K and a resistance ratio of $R$ (4.2 K)/$R$ (300 K) $\cong 2\times 10^4$ were grown at the Institute of Problems in Material Engineering of the Ukrainian Academy of Sciences (Kiev).

**3.** Under the action of pressure, the resistance ratio $R$ (2.2 K)/$R$ (300 K) decreases (see Fig. 2, curve 1). The size of the gap $E_g$, determined from the slope of the linear sections of the dependences $\log R = f(1/T)$, decreases simultaneously. At $p \simeq 55$ kbar, $E_g$ vanishes (see insert b in Fig. 1). At $p > 55$ kbar, the dependence $R(T)$ becomes metallic (curves 4, 5, and 6 in Fig. 1). The characteristic feature of curves 4–6 is the presence of a distinct inflection in the temperature region 4–40 K. Above this region, $R$ is a weakly linear function of $T$. The ratio $R$ $(p = 0)/R$ $(p = 108$ kbar) at $T = 300$ K is equal to 4 and increases to $2.5\times 10^6$ when $T$ decreases to 2.2 K.

It is interesting to note that at $p = 57$ kbar (curve 4 in Fig. 1), the decrease in $R$ with a decrease in temperature in the range $10 < T < 300$ K as 10 K is approached is replaced by a Kondo increase (see curve 1 in Fig. 3). Then, with further cooling, in the temperature range 3.5–3 K, the resistance decreases abruptly by 4%.

At pressures up to 40 kbar, the magnetoresistance is negative $\Delta R(H)/R_0 = 4.7\times 10^{-6} H^2$, and at pressures exceeding 60 kbar, it is positive: $\Delta R(H)/R_0 = 6.8\times 10^{-6} H^2$ ($H$ is in kilo-oersteds).

**4.** A change in the temperature dependence of $R$ as a function of $T$ under pressure (Fig. 1) can be interpreted as follows. Since at $p = 0$ the valance of Sm in $SmB_6$ is $\nu = 2.66$, the $4f$ level is less than half filled: filled states correspond to $\nu$(Sm) = 2 with the magnetic moment $\mu = 0$; unfilled states correspond to $\nu$(SM) = 3 with $\mu \neq 0$. By analogy with the "gold" phase of SmS[4,5] and TmSe,[9] it may be conjectured that in $SmB_6$ the $4f$ level is also displaced under pressure upwards relative to $\varepsilon_F$. It is then logical to attribute a decrease in $E_g$ (insert b in Fig. 1), on the one hand, to a decrease

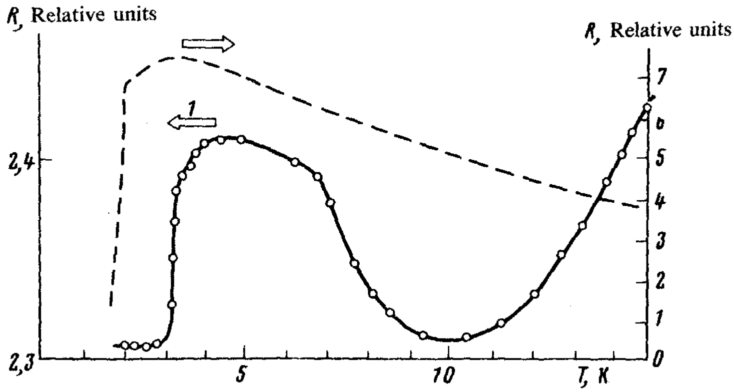


FIG. 3. Temperature dependence of the resistance in $SmB_6$ and in $CeB_6$ at $p = 0$ (2).

in the density $g_{4f}(\varepsilon_F)$ of the $4f$ states and, on the other hand, to an increase in the degree of $f$-$d$ hybridization, since in $SmB_6$ the number of electrons in the $d$ band is equal to the number of states of $Sm^{3+}$ in the $4f$ band, which increases with increasing pressure (insert a in Fig. 1). Both the decrease in $g_{4f}(\varepsilon_F)$ and the intensification of hybridization lead to a decrease in the interelectronic correlations, which must lead to a decrease in $E_g$.

At $p \gtrsim 60$ kbar, the shape of the curves $R(T)$ is analogous to the dependences of $R$ on $T$ for $CeAl_2$($T > 4$ K)[10] and $CeSn_3$,[11] for which the region of the inflection is related to the splitting of the magnetic states of $Ce^{3+}$ in a crystal field. From this point of view, the metallic behavior of $R(T)$ in $SmB_6$ and the change in sign of the magnetoresistance at $p \gtrsim 55$ kbar could correspond to a transition to the trivalent state of Sm in $SmB_6$, when $SmB_6$ turns out to be the analog of a univalent metal. However, the possibility that metallic behavior of the resistance $R(T)$ also appears in the phase with the intermediate valency, when the valence of Sm is close to 3, but is not yet an integer, has not been ruled out.

We note that, in contrast to CFV with Ce and Eu, in which the states with the highest valence of the rare-earth metal are nonmagnetic (in $Ce^{3+}$, $J = 5/2$ and in $Ce^{4+}$, $J = 0$), in CFV with Sm the opposite occurs: in $Sm^{2+}$, $J = 0$, while in $Sm^{3+}$, $J = 5/2$. As a result of this, the increase in the valency of Sm in CFV does not lead to a decrease in the density of magnetic centers (as for Ce and Eu), but to an increase in this density.

If we assume that at a pressure 57 kbar, the valence of Sm ions in $SmB_6$ is equal to 3, while $J = 5/2$, then at this pressure, $SmB_6$ is a unique analog of $CeB_6$, in which the Ce ions are trivalent and have $J = 5/2$.

We can assume in this case that the jump in the resistance in $SmB_6$ at $p = 57$ kbar and $T = 3.4$ K (curve 1 in Fig. 3) has the same nature as in $CeB_6$ at $p = 0$ and $T = 3.2$ K (curve 2 in Fig. 3), i.e., it is a result of a transition to the antiferromagnetic state. The absence of an analogous transition in $SmB_6$ at high pressures (curves 5 and 6 in Fig. 1) is apparently explained by the pressure-induced decrease in the transition temperature.

Thus $SmB_6$, a semiconducting CFV with a correlation gap in $\varepsilon_F$, just as SmS and TmSe, goes over under compression to a metallic state.

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