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High-pressure induced modifications in the hybridization gap of the intermediate-valence compound SmB_6

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We have carried out the measurements of high-pressure ^{11}B-nuclear magnetic resonance on the intermediate-valence compound SmB_6 to investigate the effects of pressure on Sm $4f$ states and the quasiparticle band. From the measurements of spin-lattice relaxation time, just below the critical pressure P_c of nonmagnetic-magnetic phase transition, we find that quasiparticle bandwidth clearly decreases with pressure, while the insulating gap is almost constant or slightly increases. The latter is consistent with the result of a band-structure calculation. These pressure induced modifications in the band structure indicate the enhancement of the density of states of the quasiparticles when approaching P_c. The pressure dependence of the Sm $4f$ states and the origin of the insulating gap are well explained in terms of exchange interactions between conduction and $4f$ electrons.

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Lanthanide-based compounds classified as heavy fermion (HF) compounds show a rich variety of physical properties, for example, magnetic ordering, enhanced effective mass of electrons, and intermediate valence (IV), depending on the magnitude of exchange interactions J_{cf} between conduction and $4f$ electrons. In such a material, if the Fermi level sits in a gap derived from hybridization between conduction and $4f$ electrons, the material behaves as a semiconductor, which is called a "Kondo insulator."

SmB_6 is one of a few materials in which one finds many important features arising from the interactions between conduction and f electrons. Sm ions in this compound are in an IV state: the valence at room temperature is ∼2.6 [1,2]. The electrical resistivity, which is almost temperature independent above ∼50 K, increases by several orders of magnitude as temperature decreases below ∼50 K. This is evidence for opening of a relatively small insulating gap (50–100 K) [3,4]. The gap is suppressed by the application of pressure, and subsequently SmB_6 becomes metallic, according to transport measurements [5]. Simultaneously, it shows a magnetically ordered ground state above critical pressure P_c(= 6–10 GPa) [6–8]. The appearance of the metallic and magnetic phase above P_c should involve drastic changes in the Sm $4f$ sates and the structure of related bands. However, to date, because of a lack of many basic characteristics near P_c, for example the specific heat and the susceptibility, the detailed $4f$ states under pressure have not been clarified. Moreover, quite recently the surface conducting states at low temperatures in SmB_6 have attracted much attention as one of the candidates for topological Kondo insulators [9]. To uncover such a novel physics as well, one needs reliable understanding of fundamental bulk properties.

Let us recall the simple description of J_{cf} which is useful to understand pressure induced changes between localized and delocalized characters. For a $4f^1$ electron system, J_{cf} is expressed as

$$J_{cf} \sim \frac{|V|^2}{\varepsilon_F - E_f}, \tag{1}$$

when the Coulomb repulsion U between two f electrons in the same orbital is sufficiently large. Here, ε_F is the Fermi energy, E_f is the energy level of the $4f$ electron, and V is assumed k-independent hybridization. Generally, the application of pressure increases $|V|$ in any $4f^n$ electron systems. For the Ce^{3+} ion, E_f rises with pressure due to an increase in the Coulomb repulsion, leading to a decrease in $\varepsilon_F - E_f$. Consequently, J_{cf} (therefore Kondo temperature T_K) increases with pressure, as indeed observed in many Ce-based compounds under pressure. On the other hand, for the Yb^{3+} state with a $4f^{13}$ configuration, one can consider E_f to be a $4f$ hole level. Therefore E_f lowers as a function of pressure, and both $|V|$ and $\varepsilon_F - E_f$ are expected to increase with pressure. In this context, the P dependence of J_{cf} in Yb-based compounds is nontrivial. However, from the fact that many Yb-based compounds show the localization of the $4f$ hole under pressure, E_f is supposed to be more sensitive to pressure than $|V|$.

For the Sm^{3+} state with a $4f^5$ configuration, the situation may be similar to the case of the Yb^{3+} state owing to spin-orbit coupling, namely, it has one $4f$ hole within the $J = 5/2$ multiplet. Note that Eq. (1) is valid in the so-called HF systems where E_f is deep enough to ε_F, which may not be the case in the IV compounds including SmB_6 at ambient pressure. However, $|V|$ and $\varepsilon_F - E_f$ are crucial factors controlling the $4f$ states between the localized and delocalized regimes in the IV systems, and the right-hand side of Eq. (1), $|V|^2/(\varepsilon_F - E_f)$, will be still a meaningful parameter on the condition that U is sufficiently larger than $|V|$.

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In this paper, we report ^{11}B-nuclear magnetic resonance (NMR) measurements of SmB_6 up to 6 GPa. Although the maximum pressure does not reach P_c, we have succeeded in improving experimental accuracy compared to our old works under pressure [10–12], and the present NMR measurement brought us rich information about pressure-driven changes in the $4f$ states. Advantages of studying the Sm based Kondo insulator are as follows.

(i) If the narrow gap is actually caused by the hybridization between conduction and f electrons, one can obtain knowledge about the P dependence of $|V|$ by measuring the gap at different pressures.

(ii) The different P dependence of the bandwidth (or T_K for the HF systems) from that of $|V|$, which is characteristic of one $4f$ hole systems, helps us to identify a prime parameter controlling the gap.

From the present study, we found that the pressure causes narrowing of the quasiparticle band and the localization of $4f$ holes, while the size of the gap is almost constant or slightly increases with pressure. The experimental results indicate that the density of states (DOS) of the quasiparticle band in SmB_6 is enhanced when approaching P_c, analogous to a tendency for Yb-based IV compounds toward the HF region by the application of pressure.

A single crystal of SmB_6 was prepared by the floating melting zone technique [13], and we used a powdered sample for the NMR measurements. High-pressure measurement at 2 GPa was carried out in a piston-cylinder pressure cell made of nonmagnetic NiCrAl/CuBe alloy with polyethylsiloxane as a pressure transmitting medium [14]. Measurements above 3 GPa were achieved by using a modified Bridgman anvil cell. A sample container made of Teflon was filled with an equal mixture of Fluorinert FC 70 and FC 77 as a pressure transmitting medium. We employed nonmagnetic CuBe plates surrounding the Teflon capsule, because the present measurements were conducted in a strong magnetic field. The details of this pressure cell are given elsewhere [15,16]. The ^{11}B-NMR measurements (nuclear spin $I = 3/2$) were performed using a standard spin-echo technique with a phase-coherent pulsed spectrometer. NMR lines were obtained by sweeping frequency. The details are described in our previous paper [17]. T_1 was measured at a central line ($1/2 \leftrightarrow -1/2$) with a signal rf-pulse saturation method. All NMR measurements were carried out at a fixed field of about 7.5 T. To grasp the P dependence of quasiparticle gap magnitude, we also performed the density functional calculations with the WIEN2K package [18].

Information on the insulating gap can be obtained from the T dependence of $1/T_1$. According to the Korringa process, $1/T_1$ reflects the DOS as follows:

$$1/T_1 = A^2 \int d\varepsilon \rho(\varepsilon)^2 f(\varepsilon)[1 - f(\varepsilon)], \qquad (2)$$

where $\rho(\varepsilon)$ is the DOS, $f(\varepsilon)$ is the Fermi distribution function, and A is a coefficient associated with the hyperfine coupling constant. The experimental data of $1/T_1$ are shown in Fig. 1(a). The T dependence at ambient pressure is almost consistent with previous reports [4,19]. Generally, at high temperatures in a narrow-band system, i.e., $T > W/k_B$ where W is the bandwidth, Eq. (2) gives T-independent behavior of $1/T_1$.

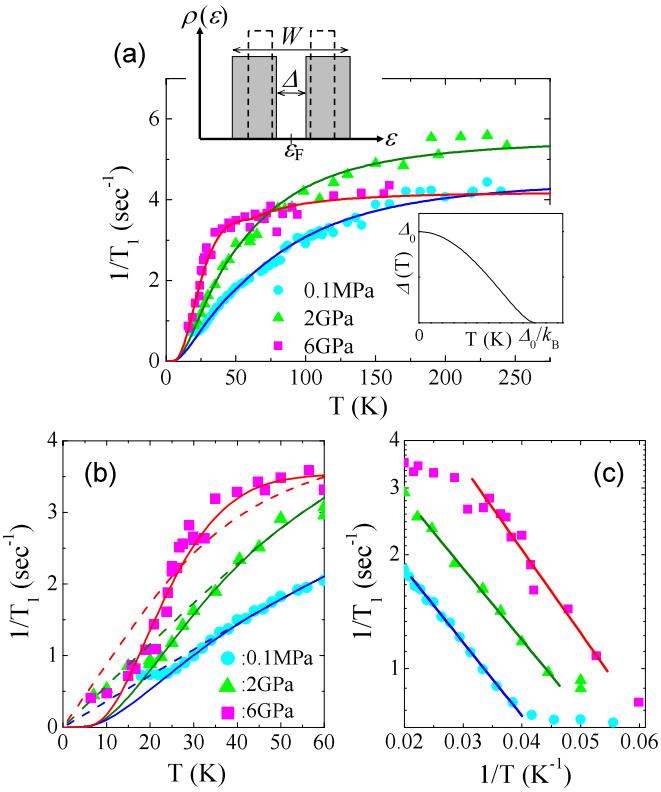

FIG. 1. (a) T dependence of $1/T_1$ measured at ambient pressure (circles), 2 GPa (triangles), and 6 GPa (squares). The solid lines represent least-squares fits of Eq. (2) with our model to the data. Inset (upper left): Schematic drawing of the band structure. The broken line indicates $\rho(\varepsilon)$ under pressure. Inset (lower right): T dependence of $\Delta(T)$. See text for details. (b) T dependence of $1/T_1$ below 60 K along with the same solid lines shown in Fig. 1(a). The broken lines were obtained by assuming $\Delta(T) = 0$ with other fit parameters giving the solid lines. Therefore the broken lines indicate the relation of $1/T_1 \propto T$ below ~40 K at ambient pressure and 2 GPa and below ~30 K at 6 GPa. (c) The plot of $1/T_1$ on a semilogarithmic scale as a function of $1/T$. The solid lines are least-squares fits of the data by the exponential form $1/T_1 \sim \exp(-\Delta_{est}/k_B T)$.

Indeed, such a T dependence is observed for $T > 300$ K in SmB_6 [4]. On the other hand, as temperature decreases below $T \sim W/k_B$, the T dependence crosses over from $1/T_1 \sim$const. to $1/T_1 \propto T$. This is exactly observed in the present data for $T > 40$ K at ambient pressure. Therefore, the much weaker T dependence down to ~50 K observed at 6 GPa suggests a significant decrease in W by pressure. Note that the rapid decrease below ~30 K at 6 GPa is not ascribed to the occurrence of a long-range magnetic order, since the NMR line does not show any significant broadening nor shift down to 2 K [12,17]. The steeper T dependence than $1/T_1 \propto T$, observed for $T < 40$ K at ambient pressure and 2 GPa and for $T < 30$ K at 6 GPa, arises from a decrease in the DOS at the Fermi energy level due to gap opening [see Fig. 1(b), where the broken lines represent the relation of $1/T_1 \propto T$ in the low T regions].

In order to discuss the P dependence of band structure more quantitatively, we fit Eq. (2) to the experimental data by assuming the structure of $\rho(\varepsilon)$, which is illustrated in

the upper left inset of Fig. 1(a). The model is based on that proposed by Takigawa *et al.* [4], where magnetic fluctuations are neglected [20]. The two peaks of $\rho(\varepsilon)$ just above and below ε_F represent the quasiparticle bands. In the relevant parameter range, the exact $1/T_1$ expression for this model can be approximated [12] by an exponential form $1/T_1 \approx \exp(-\Delta_{est}/k_B T)$, leading to the simple gap estimate of Fig. 1(c), which indicates that Δ_{est} does not depend on pressure or slightly increases at 6 GPa. For our detailed analysis, we introduced the T dependence of the insulating gap Δ [see the lower right inset of Fig. 1(a)]. Since the formation of the gap is associated with the interactions between conduction and f electrons, it is natural to expect that the gap is T dependent: namely, the gap is fully developed at low temperatures, while it is considerably reduced far above a characteristic temperature of the interaction. Actually, such a T dependence is evident from recent experimental and theoretical works [21–23]. This effect needs to be taken into account to reproduce the data at 6 GPa where the quasiparticle bandwidth is substantially reduced, as described below. We adopted a simple function of $\Delta(T) = \Delta_0[1 - (k_B T/\Delta_0')^2]^\beta$ with $\beta = 3/2$ and $\Delta_0' = \Delta_0$ which reproduces our data [12,24]. The much less steep T dependence of $\Delta(T)$ than of $\beta = 1/2$, the mean-field value for a second-order phase transition, reflects the crossover nature of gap opening in SmB_6.

Note that we used only the data above about 20 K for the analysis in order to avoid influences from complex properties at low temperatures. The low-temperature features of SmB_6 cannot be accounted for within a single gap regime. For example, T_1 strongly depends on magnetic field, and its T dependence clearly deviates from what is expected from Eq. (2) as described below. Caldwell *et al.* suggested that the in-gap states dominate the T_1 relaxation below 10 K [19]. Moreover, the electrical resistivity shows saturating behavior below ~4 K after a deviation from an activation-type T dependence upon cooling. On the other hand, T_1 above about 20 K is almost independent of field.

The results of fitting reproduce the experimental data fairly well [solid lines in Fig. 1(a)]. Parameters extracted from least-squares fits are presented in Table I. The most striking effect of pressure is a substantial reduction in W, implying the localization of $4f$ holes. On the other hand, Δ_0 was found to increase slightly, which is consistent with the P dependence of Δ_{est}. The decrease in A under pressure may be associated with the localization of the $4f$ holes which is expected to reduce transferred hyperfine field from the Sm ions. In this context, the reduction of A is consistent with the decrease in W, although it is hard to identify the P dependence of each hyperfine field component. The comparison of the solid lines with the broken ones in Fig. 1(b) reveals how the peculiar T

TABLE I. Parameters extracted from the fits Eq. (2) to the T_1 data at different pressures. See text and Ref. [12] for details.

P	W/k_B	Δ_0/k_B	Δ_{est}/k_B	$A(P)/A(0)$
0.1 MPa	504 K	43 K	44 K	1.0
2 GPa	382	50	43	0.96
6 GPa	191	63	50	0.59

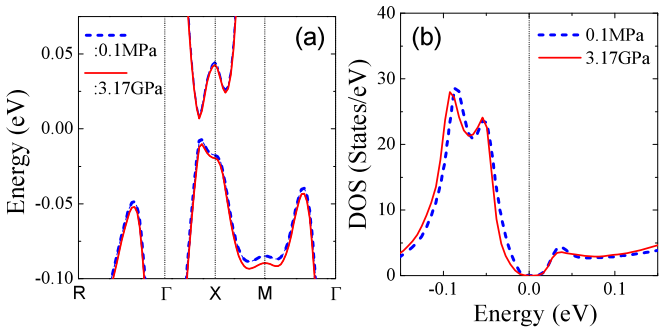

FIG. 2. Expanded views of (a) calculated energy-band structure along the high-symmetry lines and (b) the DOS for SmB_6, both at ambient pressure (broken lines) and at 3.17 GPa (solid lines).

dependence of $1/T_1$ at 6 GPa emerges. Here, the broken lines were obtained by setting $\Delta(T)$ to zero among the fit parameters giving the solid lines. According to our calculation using the above-mentioned model, $1/T_1$ shows weak T dependence down to roughly $T \sim W/2k_B$. Moreover, the opening of the gap enhances $\rho(\varepsilon)$ in Eq. (2) and then causes an increase in $1/T_1$ just below $T \sim \Delta_0/k_B$. This is significant at 6 GPa as well as the substantial decrease in W, and these effects explain the anomalously weak T dependence down to about 50 K.

In order to test whether or not the gap can be actually increased by pressure as indicated by the analyses of $1/T_1$, we have performed band-structure calculations [12] using the experimental data of the lattice parameters under pressure [17]. Previous band calculations for SmB_6 indicate the presence of a small direct hybridization gap at the Fermi level [25,26]. Figure 2(a) shows the P dependence of the energy-band structures. The energy-band dispersions along the high-symmetry line indicate the presence of a small energy gap at the Fermi level (0 eV) near the X symmetry point, which is consistent with previous studies [25,26]. This hybridization gap becomes slightly larger at 3.17 GPa due to the downward shift of the $4f$ bands with $j = 5/2$. Indeed, we can see in Fig. 2(b) that the DOS just below the Fermi level is much suppressed. These results are in good agreement with our experimental observations, although strictly speaking the mass renormalization effect due to the Kondo effect should be taken into account.

According to the nondegenerate periodic Anderson model, the direct hybridization gap is related with the hybridization by $\Delta_{dir} \sim |V|$. Therefore the obtained P dependence of the gap is in agreement with the expected P dependence of $|V|$ as mentioned before: as pressure increases, $|V|$ increases due to the shrinkage of the lattice or is not very sensitive to pressure. Thus, the experimental results suggest that the gap in SmB_6 closely relates with $|V|$ rather than with W, although it is often discussed that the gap in the Kondo insulators relates with T_K which roughly scales with W. The weak P dependence of Δ_0 approaching P_c obviously suggests the first-order nature of the insulating-metallic transition of SmB_6. In this context, the result is consistent with that of recent resistivity measurements: the residual resistivity is almost constant up to P_c, followed by a drop at P_c [7], and the activation gap also shows discontinuous vanishing at P_c [7,27]. However, the present P dependence of Δ_0 is opposite to what has been believed

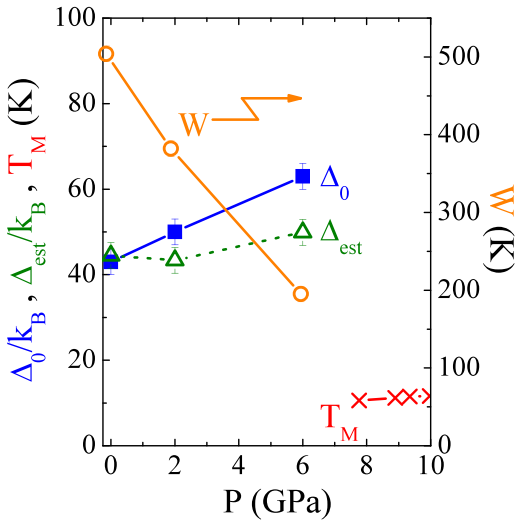

FIG. 3. T-P phase diagram of SmB_6. Bandwidth W (open circles) and insulating gaps Δ_0 (solid squares) and Δ_{est} (open squares) are presented as a function of pressure. We also plot the magnetic ordering temperature T_M (crosses) [8].

from previous transport measurements [5,7]. The origin of this discrepancy has not been clarified yet. We note that the transport measurements preferentially probe the metallic properties in a sample, while T_1 is more directly connected to the DOS of the quasiparticle band.

Finally, we summarize the P dependences of W, Δ_0, and Δ_{est} in Fig. 3, along with that of magnetic ordering temperature T_M [8]. As pressure increases, W significantly decreases, while the gap is almost constant or slightly increases. These pressure induced modifications in the band structure should lead to the enhancement of the DOS of the quasiparticle band on the assumption that the number of quasiparticles is constant. A schematic drawing is given at the upper left of Fig. 1(a) (broken lines). Interestingly, although such an enhanced DOS derived from the underlying interactions between conduction and f electrons is essentially similar to that in the HF compounds, it might be undetectable by usual transport and specific-heat measurements because of lack of carriers in SmB_6. The obtained results are consistently explained by a manner similar to what is expected for many Yb-based compounds: namely, E_f is lowered more sensitively than $|V|$ is increased as a function of pressure. We stress that the $4f$ holelike regime characteristic of Yb and Sm compounds, in which $|V|$ and W tend to move in different directions with pressure, allowed us to observe clearly the intimate relationship between the insulating gap and the hybridization in SmB_6.

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