High-Pressure Ground State of SmB_6: Electronic Conduction and Long Range Magnetic Order

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High-pressure ^{149}Sm nuclear forward scattering of synchrotron radiation and specific heat measurements have been performed on the intermediate valent Kondo insulator SmB_6. The results show that at a critical pressure $p_c \approx 6$ GPa, where the charge gap closes, a first order transition occurs to a magnetically ordered state, which shows typical features of trivalent samarium compounds. The similarity with SmS stresses the role of local correlations and gives important insight into the debate on the local or itinerant character of the f electrons in heavy fermion systems.

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The intermetallic compounds based on anomalous lanthanides (Ce, Yb, Sm, etc.) have attracted considerable interest in the past decades owing to their rich variety of condensed matter phenomena (e.g., intermediate valence, heavy fermion behavior). An example of unconventional f electron compounds are the so-called Kondo insulators or narrow-gap semiconductors (SmB_6, YbB_{12}, golden SmS) [1]. At high temperatures they behave like an array of independent localized moments interacting with itinerant conduction electrons, whereas at low temperatures they develop clear narrow-gap properties. It is generally thought that the gap formation in these materials originates from the hybridization of a narrow f band with broad enough conduction bands of s, p, and d type. Despite continuous experimental and theoretical efforts in the last 40 years, several fundamental questions do not yet have an answer.

At ambient pressure SmB_6, which crystallizes in the cubic CsCl-type structure, is a homogeneous mixed valent (intermediate valent) semiconductor [1–4]. Its valence ($v = \sim 2.6$ at ambient pressure and room temperature) increases smoothly, reaching the fully trivalent state only above ~ 22 GPa [4,5]. The electrical transport properties are characterized by different regimes, associated with various energy scales. Above ~ 70 K the resistivity and the number of carriers are those of a metal [6,7], while in the range between 70 and 5 K the resistivity increases by several orders of magnitude due to the opening of a gap $E_g \sim 10$–20 meV [7]. Below 5 K the resistivity saturates. The gap was shown to close at a pressure p_c in the range between 4 and 7 GPa [8–11]. The ground state of high-pressure SmB_6 is very similar to that found in metallic Kondo lattices displaying the properties of a magnetically enhanced Fermi liquid [10]. The magnetic form factor as determined by neutron diffraction at ambient pressure is that expected for divalent samarium [12], as also observed in other Kondo insulators like golden SmS or TmSe [13]. In the excitation spectrum, besides the extremely broadened intermultiplet transitions $^7F_0 \rightarrow {}^7F_1$ of Sm^{2+} and $^6H_{5/2} \rightarrow {}^6H_{7/2}$ of Sm^{3+}, a sharp excitation at 14 meV appears below ~ 100 K [14,15] and is attributed to the "true" intermediate valent wave function of the gapped state [16].

In this Letter, we present clear evidence that above p_c, where the insulating gap closes, long range magnetic order appears. This result was obtained by performing high-pressure ^{149}Sm nuclear forward scattering (NFS) of synchrotron radiation and specific heat measurements in a diamond anvil cell. Our data show that at about 6 GPa a likely first order transition occurs from a low-pressure state, which shows short range magnetic correlations, into a magnetically ordered state with a saturated moment of $\sim 0.5 \mu_B$ and an ordering temperature of ~ 12 K, stable to at least 26 GPa. Our findings strongly support the idea that in the metallic state above p_c the wave function of the Sm ions is dominated by the trivalent configuration, with a Γ_8 quartet crystal field ground state, despite the fact that a pure trivalent state is reached only at very high pressure.

Samarium hexaboride single crystals were grown by a standard aluminum flux technique [17,18] and were found to be single phase by x-ray diffraction. The ^{149}Sm NFS measurements were performed on powders of isotopically enriched (to 97%) Sm, while the specific heat was measured on single crystals. High pressure was generated by using diamond anvil cells with nitrogen or argon as the pressure transmitting medium. The specific heat measurements were performed at the CEA Grenoble using a setup described in Ref. [19], while the ^{149}Sm NFS measurements (resonant energy $E_0 = 22.494$ keV; 5/2-7/2 transition) were performed at beam line ID22N [20] of the ESRF in Grenoble. The setup used is described in Ref. [21]. NFS is related to the Mössbauer effect and allows one to determine the magnetic hyperfine field B_{hf}, the ordering temperature T_m, and the electric quadrupole splitting ΔE_Q.

The analysis of the NFS spectra was performed with the package MOTIF [22].

Figure 1 shows some selected ^{149}Sm NFS spectra collected for pressures up to 26 GPa at temperatures of 200 K (left panel) and 3 K (right panel). At 200 K for all pressures one observes spectra characteristic of unsplit nuclear levels; i.e., quadrupole or magnetic interactions are absent as expected for Sm ions in a nonmagnetic (either paramagnetic or diamagnetic) state and in a cubic symmetry. The same type of spectra is measured in the whole pressure range between 0 and 26 GPa for temperatures higher than ~50–100 K. At lower temperatures the spectral shape changes in a more or less pronounced way depending on pressure. One can distinguish three pressure regimes. For $p < 6$ GPa combined hyperfine interactions with extremely broad distributions are present at the ^{149}Sm nuclei. For $p > 10$ GPa a clear quantum beat structure appears at low temperatures (see Fig. 1) indicating that the nuclear levels are split by well defined hyperfine interactions. An intermediate regime, with probably the coexistence of the low-pressure and high-pressure phases, is found for $6 < p < 10$ GPa.

The graphs in Figs. 2(a) and 2(b) show the pressure and volume dependence of the average values of B_{hf} and ΔE_Q as determined from the fits of the spectra measured at 3 K [23]. The volume dependence on pressure at 3 K has been determined by powder x-ray diffraction measurements performed along with the NFS and yields an ambient pressure bulk modulus $B_0 = 138(10)$ GPa. At ambient pressure we obtain $B_{hf} = 33(20)$ T and $\Delta E_Q = -0.1(1)$ mm/s. The distribution of the hyperfine parameters shows that approximately 70% of the Sm nuclei feel zero hyperfine interactions, while for the remaining 30% the magnetic hyperfine field varies in the range between 40 and 170 T. Although this model supposes the magnetic moments at the Sm ions to be static, our suggestion is that slow fluctuations (with a period $\tau > 10^{-8}$ s) are present, which appear as almost static on the time scale of the NFS measurements. The values of B_{hf} and ΔE_Q stay almost unchanged up to a pressure of 5.3 GPa and then increase rapidly to reach values of 246(10) T and $-1.3(1)$ mm/s, respectively, at 9.7 GPa. At the same time the widths of the distributions of the hyperfine parameters decrease considerably. For a further increase of the pressure up to 26 GPa only a slight variation of both B_{hf} and ΔE_Q is observed. At this pressure we find

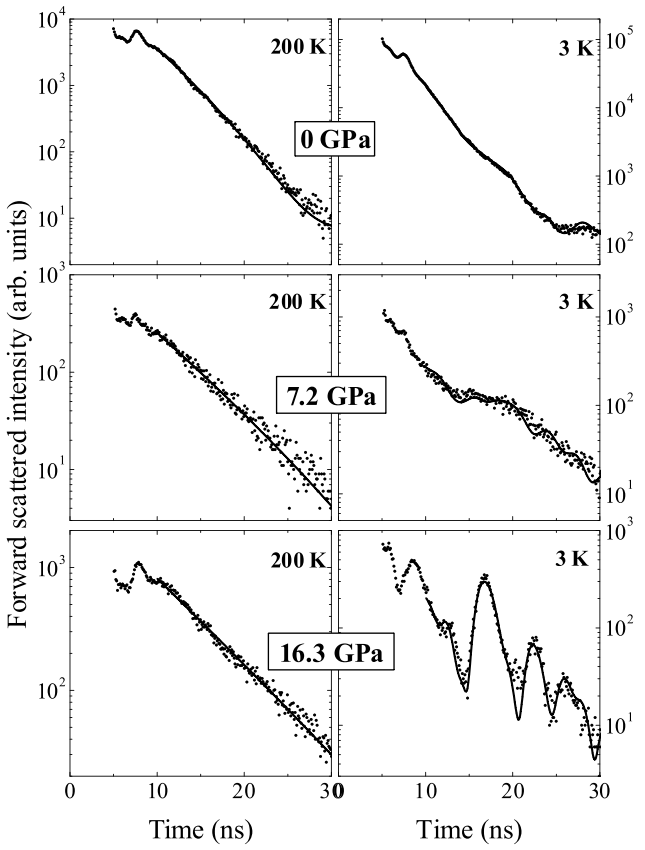

FIG. 1. The ^{149}Sm NFS spectra of SmB_6 at $T = 200$ K (left) and $T = 3$ K (right) for some selected pressures. The dots represent experimental data points, while the lines are fits.

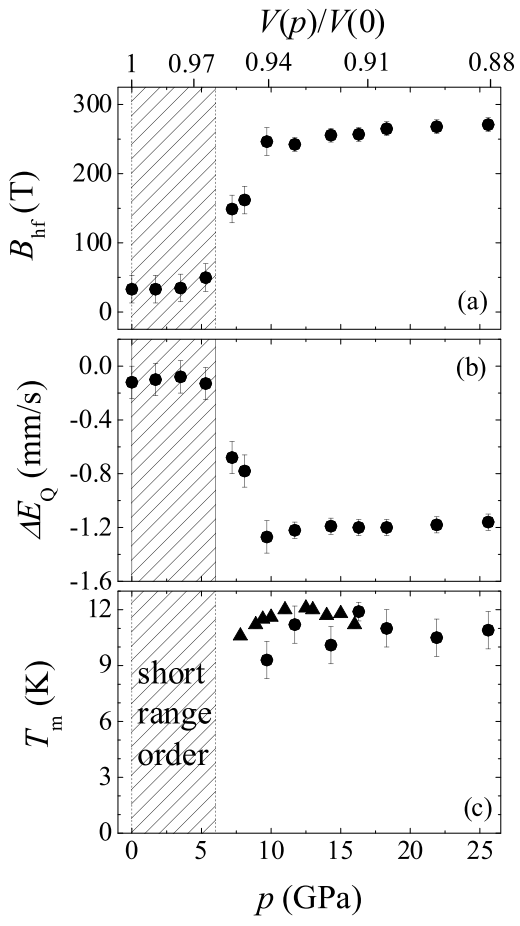

FIG. 2. Pressure and volume dependence of (a) the average magnetic hyperfine field B_{hf} at 3 K, (b) the average electric quadrupole interaction ΔE_Q at 3 K, and (c) the ordering temperature T_m as determined by NFS (full circles) and specific heat (full triangles).

$B_{hf} = 271(10)$ T and $\Delta E_Q = -1.2(1)$ mm/s. SmB_6 undergoes therefore a pressure-induced phase transition from a low-pressure phase to a high-pressure phase, starting at $p > 5.3$ GPa. The coexistence of the two phases observed for $5.3 < p < 9.7$ GPa and the discontinuous change of the hyperfine parameters suggest a first order transition. The pressure interval 5.3–9.7 GPa covers the range around p_c, where the semiconducting gap closes.

At ambient pressure, although several techniques have not evidenced the presence of long range magnetic order down to the lowest temperatures (50 mK) [14,15,24,25], ^{11}B NMR experiments show that dynamical magnetic correlations may set in below ~15 K [26], although their intrinsic character is not established. These findings and our results suggest therefore that the low-pressure phase of SmB_6 is characterized by the presence of magnetic moments which are slowly fluctuating. The closing of the gap in SmB_6 seems therefore to be associated with the onset of long range magnetic order. The presence of large hyperfine interactions at the Sm nuclei for $p > 5.3$ GPa can be supposed to arise from the ordering of the Sm moments.

The confirmation of a phase transition at high pressure is given by ac-calorimetry measurements. Figure 3 shows the specific heat as recorded in the ac microcalorimetric experiment at 4.7 and 11 GPa. No phase transition can be detected at low pressure (4.7 GPa), but at high pressure (11 GPa) the signal indicates a phase transition at a temperature $T_m = 12$ K. A clear signature of a specific heat anomaly appears for all pressures above ~7 GPa at a temperature of ~12 K [only weakly dependent on pressure up to 16 GPa, see Fig. 2(c)], while no anomaly occurs for lower pressures. The presence of the specific heat anomaly indicates that a phase transition occurs at $T_m = 12$ K for $p > 7$ GPa, which can be associated with the long range ordering of the Sm magnetic moments.

At the phase transition the aspect of the NFS spectra changes abruptly, and their analysis reveals that the hyperfine interactions decrease discontinuously as the temperature increases through T_m (see Fig. 4). Above T_m, i.e., in the paramagnetic state, B_{hf} and ΔE_Q have finite average values with broad distributions, at least up to temperatures of the order of 50–100 K. This behavior is reminiscent of the one observed at low temperature in the low-pressure phase. The transition at T_m appears to be of the first order, as the hyperfine parameters show almost no temperature variation in the range between 3 K and T_m and then decrease abruptly within 1 K.

Figure 4 shows the temperature dependence of the hyperfine parameters for three typical pressures (0, 8.1, and 25.6 GPa). No characteristic ordering temperature appears at low pressure ($p < 6$ GPa). The absence of any specific heat anomaly for pressures lower than 7 GPa confirms that in the low-pressure phase there is no transition to long range magnetic order and that the nonzero average values of the hyperfine interactions are rather due to short range magnetic correlations, with moments which may be slowly fluctuating.

In the magnetically ordered state, the average saturation values of the hyperfine parameters are close to the values expected for a pure Γ_8 cubic crystal field ground state ($B_{hf} = 250$ T and $\Delta E_Q = -1.7$ mm/s), under the assumptions that the Sm ions are trivalent in the ordered phase and that the exchange interactions are so weak as not to mix the ground multiplet ($^6H_{5/2}$) with excited ones. In this case the ordered magnetic moment would amount to $\sim 0.5 \mu_B$. Although the first assumption may not be com-

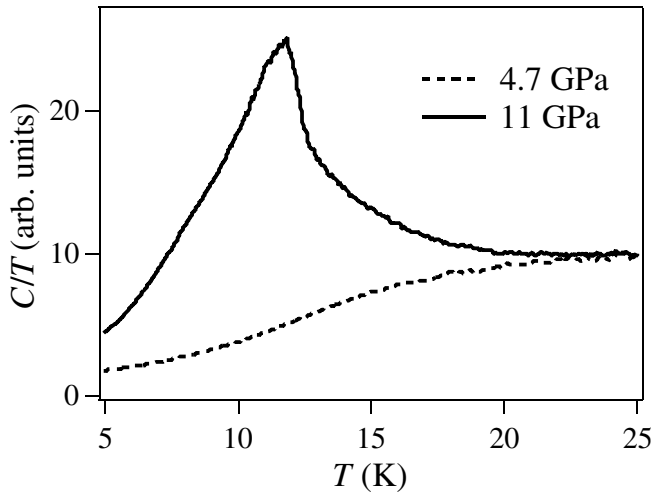

FIG. 3. Temperature dependence of the specific heat of SmB_6 at different pressures above and below $p_c \approx 6$ GPa.

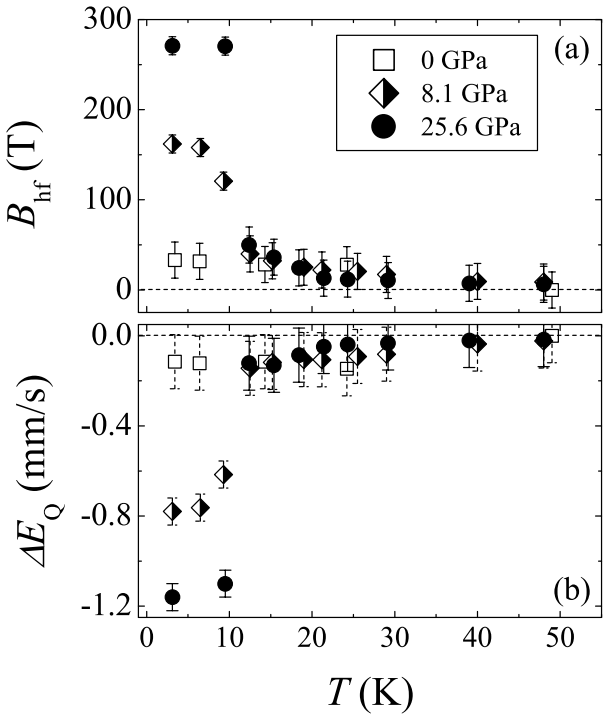

FIG. 4. Temperature dependence of (a) the average magnetic hyperfine field B_{hf} and (b) the average electric quadrupole interaction ΔE_Q as determined by NFS at various pressures.

pletely justified for SmB_6 at low pressures, as the Sm valence has been measured to be less than three below 20 GPa [4,5], the entrance into the trivalent state is not signalled by any dramatic change of the magnitude of the hyperfine parameters. Therefore, the system seems to behave as if it were trivalent even when the valence is as low as ~ 2.7, and the magnetic order appears when SmB_6 is still clearly intermediate valent.

The parameter that drives the transition from the short range magnetic correlations at low pressure to the long range order at high pressure seems therefore not to be in connection with a dramatic change of the $4f$ relative occupation number n_f (defined as 0 for divalent and 1 for trivalent samarium, so that the valence is $v = 2 + n_f$) but rather in close relationship with the appearance of metallic conduction above p_c. The great interest is that the same phenomena have been recently reported for the intermediate valent gold phase of SmS [21]. The similarity between SmB_6 and SmS concerns the appearance of long range magnetism at the onset of the metallic conduction as well as the appearance of a Γ_8 ground state above p_c. This common behavior is not obvious since the two crystal structures are quite different; thus the hybridization is known to be strong only for SmB_6 (see the band calculations of Refs. [27,28]) and point charge models predict Γ_7 and Γ_8 ground states for SmS and SmB_6, respectively. Obviously the physics in the intermediate valence state is dominated by local d-f correlations. Our result supports the picture where at low pressure ($v = 2.6$, $n_f = 0.6$) the 0.6 electrons per Sm atom which should be released from the localized $4f$ to the $5d$ conduction band remain instead quite localized on a Sm atom and its neighbors [16,29]. This gives rise to a Sm electronic configuration which is close to that of purely divalent Sm and explains the formation of a low temperature gap. In this low-pressure phase, for the trivalent configuration the Kondo energy ($k_B T_K$) prevails over the crystal field splitting (C_{CF}) and the magnetic moments cannot interact due to their uncorrelated fast fluctuations. However, increasing the pressure leads to a crossover where the Kondo energy reaches the value of the crystal field splitting. In this crystal field ground state, the Sm^{3+} configuration can live for long enough for the establishment of a long range magnetism. This statement agrees with the observation that for Ce heavy fermion compounds long range magnetic ordering occurs only when $T_K < C_{CF}$, i.e., only for quasitrivalent cerium compounds. The extension to a higher degree of intermediate valence for Sm or Yb, as compared to Ce, may reflect basic differences in the pressure variation of T_K, because of the difference in the equilibrium relations $Sm^{2+} \leftrightarrow Sm^{3+} + 5d$ and $Ce^{3+} \leftrightarrow Ce^{4+} + 5d$ [30].

The underlying message to general perspectives of $4f$ heavy fermion systems is that correlations seem to preserve the microscopic local character of one valence configuration even when the valence mixing is large. The Ce case might be singular as the itinerant character of the $4f$ electrons prevails due to the larger extension of its $4f$ shell.

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