SmB_6: Kondo Insulator or Exotic Metal?

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High pressure resistivity and Hall effect measurements on SmB_6 show that the activation gap Δ vanishes discontinuously between 45 and 53 kbar, yielding at high pressures a mass-enhanced Fermi liquid phase. The low temperature transport is dominated by extended states in the gap with unusual superunitarity scattering properties, and a carrier density which grows almost exponentially with reduced Δ, saturating below 45 kbar near 0.15 electron per unit cell. Our results are inconsistent with hybridization gap models and suggest a striking parallel to Mott-Hubbard insulators.

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The relationship between magnetism and small insulating gaps is an extremely subtle yet fascinating problem, common to all families of strongly correlated materials. The continuing importance of this question is reflected in the recent renaissance of interest in the family of f-electron-based Kondo insulators, intermetallics having small transport and spin gaps about the Fermi level. Many experimental properties of these small gap insulators are described by identifying the indirect insulating gap Δ as a hybridization gap [1–3], arising from the coherent hybridization of Kondo compensated magnetic moments. Δ is proportional to the Kondo temperature T_K, the energy difference between the conduction electron and local moment singlet and triplet states. Consequently, band filling is the sole determinant of whether an insulating or metallic ground state is realized. Variations in pressure, composition, and magnetic fields can be expected to alter the magnitude of a hybridization gap, in some cases driving continuous insulator-metal transitions of the band-crossing type.

There is considerable controversy whether this hybridization gap scenario provides a complete description of the Kondo insulators. For instance, while the mean-field solution of the Kondo lattice model neglects long-range magnetic interactions, it has been proposed [3] that these correlations may drive first-order transitions with magnetic field, temperature, or pressure from Kondo compensated insulator to magnetically ordered metal. Charge degrees of freedom may also play an important role in gap formation [4], and are essentially ignored in the Kondo lattice model. By analogy to Mott-Hubbard insulators, the insulating state may have a similar intrinsic instability as external variables modify the band structure and correlations. Unlike the continuous insulator-metal transition envisaged in the hybridization gap scenario, all three of these alternatives encompass a discontinuous vanishing of Δ with pressure, magnetic field, or even temperature.

The stability of the insulating gap Δ is consequently a key piece of evidence in determining whether a hybridization gap description of the so-called Kondo insulators is complete. Accordingly, we have investigated the stability of the insulating gap in SmB_6 to high pressures. We chose SmB_6 for both the availability of high quality, single crystals as well as results from previous studies [5,6] indicative of gap suppression in the vicinity of 60 kbar.

We have extended these early measurements not only by a more exhaustive resistivity study but also by supplementing this information with Hall effect measurements. Our conclusions are qualitatively different, finding not only that the gap vanishes discontinuously with pressure, but also at low pressure that the ground state of SmB_6 has unusual metallic properties, despite the presence of the gap. The high pressure phase is very similar to that found in stable valence Kondo lattices, displaying the properties of a magnetically enhanced Fermi liquid.

Single crystals of SmB_6 were prepared from aluminum flux, and were carefully screened for a resistivity increase of at least 10^4 between room temperature and 4.2 K. High pressures were generated in a Bridgman anvil cell. A superconducting lead manometer [7] was used to establish the pressure dependence of the SmB_6 activation gap, which served as the pressure standard in subsequent Hall effect measurements. At the highest pressures, no gap is present and pressures were inferred from previously measured force-pressure relationships. We stress that the resistivity and Hall effect measurements reported here were performed simultaneously on the same sample at the same pressure. The electrical resistivity of SmB_6 is plotted as a function of temperature in Fig. 1(a), for pressures ranging from 1 bar to 66 kbar. As demonstrated in Fig. 1(b), the measured resistivity is well described at 45 kbar and below by a parallel combination of an activated term, dominant above $\sim$5 K, and constant residual term ρ_0, accounting for the temperature independent resistivity found below $\sim$3.5 K. The activation gap Δ extracted from these fits is plotted in Fig. 2(a) and is suppressed

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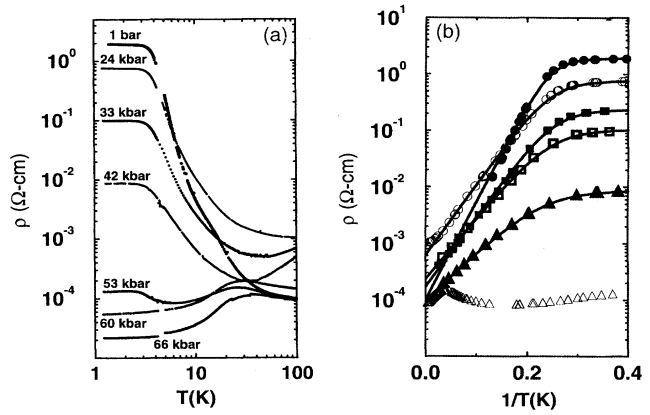

FIG. 1. The electrical resistivity ρ as a function of temperature (a) and inverse temperature (b). (b) ○ = 1 bar, ○ = 24 kbar, □ = 25 kbar, □ = 33 kbar, △ = 45 kbar, and △ = 53 kbar. The solid lines in (b) are fits by the function $[\rho(T)]^{-1} = [\rho_0(P)]^{-1} + (\rho_{\rm act}(P)\exp[\Delta(P)/k_BT])^{-1}$, described in the text.

linearly ~0.5 K/kbar from its ambient pressure value of 41 K. Above 45 kbar, the resistivity is metallic and it is no longer possible to extract an activation gap.

Our measurements indicate a gap instability at a critical pressure P_c between 45 and 53 kbar, in disagreement with the conclusions of previous workers [5,6], who found that Δ vanished continuously near 60 kbar. In one of these studies [5] the sample was of demonstrably lower quality than our own, with a significantly smaller ambient pressure $\Delta = 33$ K and a much smaller $\rho_0 \sim 10$ mΩ cm, both symptomatic of Sm vacancies or defects introduced in powdering [8]. Our measurements suggest that the gap instability is a feature only of the highest quality samples, as P_c increases markedly with reduced sample quality, passing out of our experimental pressure window of 180 kbar for $\rho_0 \lesssim 0.1$ Ω cm. We further believe that the simple activation fits used to determine Δ in both earlier experiments were overly weighted by the temperature independent resistivity below ~3.5 K, particularly near P_c. Figure 1(b) demonstrates that near P_c the range

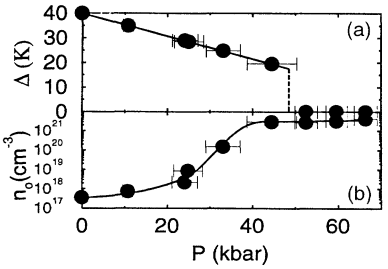

FIG. 2. The pressure dependences of the activation gap Δ (a) and residual carrier density $n_0 = 1/R_H(T = 0)$ (b). Dashed line indicates approximate pressure for disappearance of Δ. Solid lines are guides for the eye.

of temperatures over which simple activation fits are linear becomes increasingly limited and problematic to define with increased pressure. In contrast, our parallel resistor formulation provides uniformly good fits over this pressure range, and consequently yield a more accurate determination of Δ.

Since there is no evidence in SmB_6 for a discontinuous structural change at or below 60 kbar [9], the sudden disappearance of Δ suggests that it is not a simple hybridization gap, for in that case the insulator-metal transition occurs by band crossing and the gap is suppressed continuously to zero. A valence instability can be similarly discounted, as high pressure x-ray absorption measurements [10] find that the Sm valence increases smoothly from +2.6 to +2.75 between 1 bar and 60 kbar.

We have used Hall effect measurements to study the evolution of the carriers in the vicinity of P_c. The Hall constant R_H is plotted as a function of $1/T$ in Fig. 3 for pressures ranging from 1 bar to 66 kbar. We find that R_H is negative for temperatures T between 1.2 and 40 K and at all pressures, as well as independent of magnetic fields as large as 18 T. As has been previously noted at 1 bar [11], R_H is both large and extremely temperature dependent with a maximum at 4 K, at each pressure becoming temperature independent below ~3 K. It has been proposed [12] that this temperature dependence for R_H is characteristic of Kondo lattices, reflecting a crossover from high temperature incoherent to low temperature coherent skew scattering. However, similar maxima in $R_H(T)$ occur in doped semiconductors as in-gap impurity states dominate intrinsic activated processes with reduced temperature [13].

We do not address the full temperature dependence of R_H here, instead limiting our discussion to the

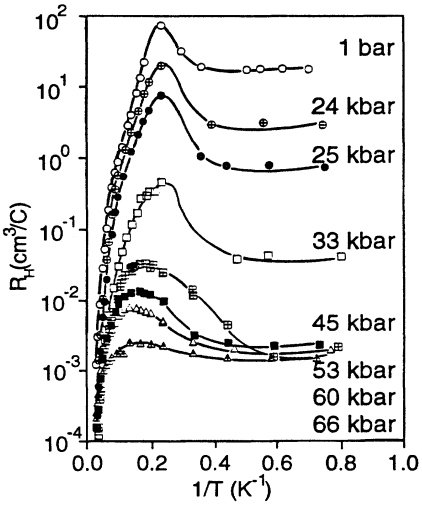

FIG. 3. The absolute value of the Hall constant R_H of SmB_6 as a function of inverse temperature.

lowest temperatures, where R_H is temperature independent at all pressures. $R_H(T \to 0)$ most generally has contributions both from the ordinary Hall effect and from anomalous skew scattering from defects. The latter is expected to be only weakly temperature dependent [12], and we estimate from our data (Fig. 3) a maximum magnitude of 10^{-4} cm^3/C. We conclude that the $T \to 0$ Hall constant is dominated at every pressure by the ordinary Hall effect, in principle requiring a multiple band analysis [11,13]. However, the simultaneous observation at every pressure of temperature independent Hall constant and resistivity below ~3 K suggests that a single band of electrons dominates the low temperature transport, allowing the identification $R_H(T \to 0) \simeq 1/n_0 e$. This simplification is further validated by high pressure x-ray absorption measurements [10], which link the pressure-induced increase in electron density to increases in the Sm valence.

The low temperature, ambient pressure transport reveals unexpected new properties of the ground state of SmB_6. In agreement with previous reports [11,14], we find a residual resistivity $\rho_0 = 1.9\ \Omega$ cm and single band electron density $n_0 = 3.6 \times 10^{17}$ cm^{-3}. The finite resistivity indicates that as $T \to 0$, the transport is dominated by extended states which pin the Fermi level within the gap. It is natural to assume that these states result from residual impurities or lattice defects, as in ordinary semiconductors, and indeed Mott's criterion $n_0^{1/3} a_H \gg 0.25$ for impurity band conduction is satisfied. The length scale for transport a_H can be estimated using the excitonic expression [15] $a_H = (0.53\ \text{Å})\kappa m/m^*$. Optical conductivity measurements [16] provide values for the static dielectric constant κ and mass enhancement m^*/m of 1500 and 1.5, respectively, yielding a rather extended state $a_H \sim 500$ Å, consistent with our observation of finite, metallic resistivity at the lowest temperatures.

Nonetheless, the magnitude of the residual resistivity makes an impurity band interpretation untenable in SmB_6. Specifically, if we assume that the band of extended states inferred from the 1 bar metallic resistivity has a Fermi wave vector $k_F = (3\pi^2 n_0)^{1/3} = 2 \times 10^6$ cm^{-1} and scatters at most at the unitarity limit from an unknown concentration of scattering centers N_i, we can use Friedel's equation [17] to place a lower bound on N_i: $\rho_0 \leq 4\pi\hbar N_i/e^2 k_F$. An unphysically large concentration of scattering centers, at least 80 per unit cell, is required to explain the observed residual resistivity. Superunitarity scattering indicates that the scattering centers have become extended, presumably through strong many-body interactions as in the heavy fermion compounds [18]. Significantly, superunitarity scattering is observed only below P_c in SmB_6, as the disappearance of Δ is accompanied by a sharp reduction of ρ_0 below the maximum unitarity value.

Compelling evidence that the metallic states which dominate the low temperature, low pressure transport are intrinsic is found in the evolution of this band as pressure suppresses the gap. As depicted in Fig. 2(b), the carrier density n_0 is extremely pressure dependent, increasing almost four orders of magnitude between 1 bar and 45 kbar. At 45 kbar and above, n_0 increases only slowly, and with no apparent feature accompanying the disappearance of the activation gap between 45 and 53 kbar. Since the density of both simple impurity and "Kondo hole" [19] states is determined by a fixed defect concentration, this extraordinary sensitivity to pressure argues that these carriers are primarily intrinsic, present even in pristine SmB_6.

The net increase in electron concentration of 0.15 per unit cell which we observed between 1 bar and 45 kbar is exactly accounted for by the simultaneous increase in Sm valence from 2.6 to 2.75 identified in x-ray absorption measurements over the same pressure range [10]. These measurements suggest that the electrons originally localized in Sm $4f$ orbitals at 1 bar are continuously transferred to the Fermi level under pressure, and are the origin of the extended, mass-enhanced electron band which increasingly dominates the low temperature transport. We believe that the closest analog for these in-gap states in SmB_6 is found in the mean-field treatment of the Mott-Hubbard transition [20]. That is, the magnetically enhanced many-body states which appear in the gap are precursors of the strongly interacting metal obtained by the destabilization of the gap. In support of this view, we have identified just such a metallic state at high pressures in SmB_6.

Above P_c, the temperature dependences of the Hall constant and resistivity of SmB_6 are completely typical of stable valence f-electron lattice systems. Both $R_H(T)$ and $\rho(T)$ display maxima, signalling a crossover from high temperature incoherent scattering to low temperature coherent scattering [12,21]. For temperatures in the range $1 \leq T \leq 4$ K, $\rho(T)$ is quadratic in temperature $\rho(T) = \rho_0 + AT^2$. A has a magnitude comparable to that of moderate mass heavy fermion compounds like $CeRu_2Si_2$ [22], decreasing from 0.6 to 0.12 $\mu\Omega$ cm/K^2 as the pressure is increased from 60 to 66 kbar. We conclude from these observations that the ground state of high pressure, gapless SmB_6 is identical to that of normal Kondo lattices: coherent Fermi liquid with substantial magnetic enhancement of the quasiparticle mass. Although we have somewhat limited data, the characteristic energy scale for the quasiparticle interactions $T^* \propto 1/\sqrt{A}$ decreases sharply, and the mass enhancement $m^*/m \propto \sqrt{A}$ correspondingly increases as P_c is approached from above. We propose that the strong correlations responsible for gap formation in SmB_6 at low pressure survive as quasiparticle mass enhancement in the high pressure, gapless state. However, as the low pressure gapped states in SmB_6 are already metallic, we stress that the vanishing of the gap is not accompanied by a metal-insulator transition.

To summarize, our results on SmB_6 indicate that its gap cannot be the result of simple Kondo hybridization,

since its discontinuous vanishing is not accompanied by a reduction in crystal symmetry. There is no indication in our measurements of magnetic order in the high pressure metallic state, evidence against a critical role for long-range magnetic correlations. In addition, our high field measurements [23] suggest that the activation gap Δ is almost completely insensitive to magnetic fields as strong as 18 T. The magnitude and pressure dependence of the lattice constant [9], as well as high pressure x-ray absorption measurements [10], similarly show no sign of a discontinuous valence change associated with the disappearance of the gap, indicating that, unlike systems such as SmS [24], charge fluctuations do not solely dictate gap stability. Finally, since metallic states appear in the preformed gap and are largely unaffected by the collapse of the gap, no insulator-metal transition accompanies the gap instability, an observation which when paired with the strong magnetic enhancement of the high pressure metallic state makes a striking parallel to similar observations in classic Mott-Hubbard systems such as V_2O_3 [25]. Nonetheless, it remains a challenge to provide a theoretical basis for this connection between the apparently disparate Kondo and Mott-Hubbard systems.

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