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Low-temperature thermal expansion of SmB_6: Evidence for a single energy scale in the thermodynamics of Kondo insulators

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We have measured the thermal expansion of the Kondo insulator SmB_6 from 5 to 80 K using a sensitive capacitance dilatometer. There is a pronounced negative anomaly in the linear expansion coefficient α, of electronic origin, which achieves a local minimum of -5×10^{-6} K^{-1} at 45 K. We interpret this anomaly as a Schottky-like contribution arising from transitions across a semiconducting energy gap $E_g \simeq 140$ K. Although there are several energy scales in the problem, a Grüneisen analysis indicates that the thermodynamics is driven by a single energy, which we identify as the gap energy.

SmB_6 is a prototypical member of a class of narrow-gap semiconductors known as Kondo insulators.[1] Gap formation in these materials is thought to arise through the hybridization of a narrow f band with a broad conduction band, with each unit cell containing an even number of electrons. The semiconducting energy gap E_g is a natural energy scale for these systems, but since Kondo insulators are also mixed valent,[1,2] other energies, such as the valence fluctuation temperature T_0, or the Kondo temperature T_K, may be expected to play an important role.

Both a small energy gap in the quasiparticle excitation spectrum and the coupling of unstable $4f$ ions to the lattice are expected to produce marked effects in the specific heat and thermal expansion of Kondo insulators.[3] Transitions across a semiconducting gap will contribute a Schottky-like term to the specific heat that goes roughly as dn/dT, where n is the carrier density. If in addition the bands are narrow, dn/dT becomes large and this term can easily dominate the specific heat. The thermodynamic consequences of valence fluctuations are well documented[4-8] but imperfectly understood. The entropy of a mixed-valent system is given by[8] $s = R[\nu \ln(g_n) + (1-\nu)\ln(g_{n+1}) - \nu \ln(\nu) - (1-\nu)\ln(1-\nu)]$. Here R is the gas constant, g_n and g_{n+1} are the degeneracies of the $4f^n$ and $4f^{n+1}$ levels, and $\nu = N_n/(N_{n+1} + N_n)$, where N_n and N_{n+1} are the numbers of ions in the $4f^n$ and $4f^{n+1}$ configurations. If the valence changes with temperature we expect a term in the specific heat $C_v = T(\partial S/\partial T)_V$

and a change in the lattice constant since the $4f^{n+1}$ configuration has a 20–30 % larger ionic volume than the $4f^n$ configuration.[6] Phenomenologically, most of these effects are amenable to a scaling analysis,[3,7] in which it is assumed that the volume dependence of the electronic contribution to the free-energy density is determined entirely by the volume dependence of a characteristic energy E_0. This allows the introduction of an electronic Grüneisen parameter $\Omega_e = -\partial \ln E_0/\partial \ln V$ in terms of which most thermodynamic quantities can be calculated. For mixed-valent metals such as $CeSn_3$ and $CePd_3$ the valence fluctuation temperature T_0 is the characteristic energy; experimentally, peaks are observed in the specific heat and thermal expansion coefficient at about $T_0/2$.[3,7]

For Kondo insulators in general and SmB_6 in particular, the temperature dependence of the valence is an open question. Estimates of the valence based on lattice parameters[9,10] are problematic because the concomitant large changes in compressibility can introduce significant errors. Other methods often do not agree. In SmB_6, for example, L_{III} x-ray absorption measurements indicate a valence change from 2.53 at 4.2 K to 2.60 at 300 K,[10] whereas Mössbauer isomer-shift measurements[11] are unable to detect any valence change. This is an important issue for thermodynamics, because it can be shown[6,8] that for sufficiently high temperatures the mixed-valent contribution to the entropy is $S = R \ln(g_n + g_{n+1})$. For SmB_6, $g_n = 6$, $g_{n+1} = 1$, and the mixed-valent contribution to the entropy is expected to be $S = R \ln(7) = 16.18$

$J\,mol^{-1}\,K^{-1}$, which is a sizable contribution.

In this paper we present measurements of the linear expansion coefficient of SmB_6 from 5 to 80 K. Using the linear expansion coefficient of LaB_6 as a reference, we estimate the electronic contribution to the thermal expansion of SmB_6. Similarly, we use the specific heat data of Kasuya *et al.*[12] on SmB_6 and Peysson *et al.*[13] on LaB_6 to estimate the electronic contribution to the specific heat of SmB_6. We find that both the specific heat and thermal expansion anomalies are well described by a simple semiconductor model consisting of two narrow bands and an energy gap $E_g \simeq 140$ K. We calculate the electronic Grüneisen parameter Ω_e, and find that it is constant over most of the measured temperature range: this is strong evidence that the thermodynamics is derived from a single characteristic energy—the semiconducting energy gap. To test this identification we use Ω_e to predict the pressure dependence of the gap $\partial \ln E_g/\partial P$. Reasonable agreement with experiment is obtained.

Single crystals of SmB_6 and LaB_6 were grown in an argon atmosphere out of an aluminum flux. The flux was removed with sodium hydroxide and the crystals were characterized using magnetic susceptibility, resistivity, and powder x-ray diffraction. The thermal expansion measurements were performed using a capacitance dilatometer with a detection limit $\Delta d \cong 0.01$ Å. The temperature was swept at 2 mK/sec from 4 to 80 K, and the capacitance was measured every 20 mK. A similar measurement was performed on a Cu reference sample, allowing the cell effect to be subtracted out. The lengths of the SmB_6 and LaB_6 samples were 2.96 and 3.02 mm, respectively, and the measurements were performed along the [100] direction. A detailed description of the apparatus and measurement technique will be presented elsewhere.[14]

In Fig. 1 we plot the linear expansion coefficient α vs temperature for SmB_6. The negative sign of α is not unusual for a strongly correlated system; that the origin of the negative expansion is electronic (nonlattice) can be seen by comparing $\alpha(T)$ of SmB_6 to that of LaB_6 [Fig. 2(b)], an isostructural material with no f electrons. In the inset to Fig. 1 we show the small peak in $\alpha(SmB_6)$ that occurs at $T \simeq 11.5$ K. This anomaly is almost certainly of electronic origin, since its magnitude is larger than we expect for the lattice expansion of a material like SmB_6, with a high melting point and a high Debye temperature. Similar anomalies in the specific heat of SmB_6 were observed by Nickerson *et al.*[15] and were found to depend on the method by which the SmB_6 was grown; above 18 K, however, the specific heat was found to be independent of growth technique. Because this anomaly appears to be sample dependent, and because it occurs at an energy an order of magnitude smaller than those of interest in this paper, we will ignore it in the following analysis.

In Fig. 2(a) we show the specific heat data of Kasuya *et al.*[12] on SmB_6 and Peysson *et al.*[13] on LaB_6. We assume that the difference in specific heat between these isostructural compounds is a fair approximation to the anomalous electronic contribution of SmB_6, while keep-
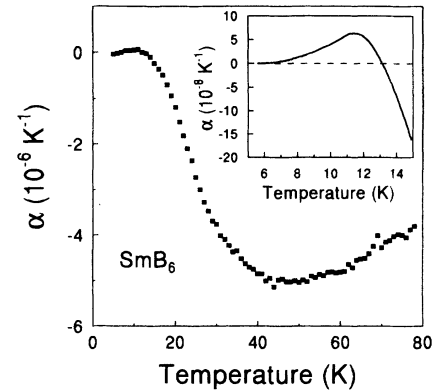

FIG. 1. Linear expansion coefficient $\alpha(T)$ vs T for SmB_6; $\alpha(T)$ was determined by numerically differentiating the length vs temperature data obtained from capacitance dilatometry. The inset shows the low-temperature expansion coefficient on a magnified scale; in this case, $\alpha(T)$ was determined by differentiating a cubic spline interpolation.

ing in mind that all such subtraction schemes have severe limitations. No effort was made to correct for the difference in mass between La and Sm or for the small linear term in the specific heat of LaB_6 due to the presence of free carriers. In Fig. 2(b) a similar analysis is performed using the thermal expansion coefficient of LaB_6 to extract the electronic contribution to the expansion of SmB_6. LaB_6 has its own low-temperature anomaly, in that the expansion is negative below 14 K. This tends to magnify the positive anomaly in the estimated electronic contribution to the expansion of SmB_6, but this is a small effect.

In the hybridization gap picture,[1] the gap is thought to form within a narrow peak in the electronic density of states at the Fermi energy. We model this system using narrow valence and conduction bands of width W_v and W_c and a semiconducting energy gap E_g [inset, Fig. 3(b)]. The number of conduction electrons in this model
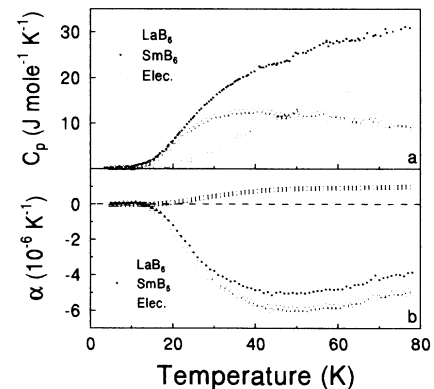

FIG. 2. (a) Specific heat of SmB_6 (after Ref. 12), LaB_6 (after Ref. 13), and the difference $C_p(SmB_6)-C_p(LaB_6)$ which represents the electronic contribution to the specific heat of SmB_6 (see text). (b) Linear thermal expansion coefficient of SmB_6, LaB_6, and the difference $\alpha(SmB_6)-\alpha(LaB_6)$.
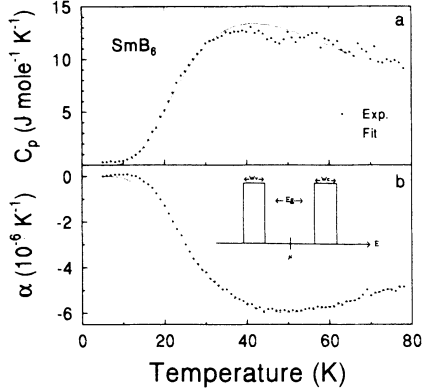
FIG. 3. (a) The electronic contribution to the specific heat of SmB$_6$ and a fit using the procedure described in the text. (b) The electronic contribution to the thermal expansion of SmB$_6$, and a fit as described in the text. The inset depicts the simple model used to fit the data; W_v and W_c are the widths of the valence and conduction bands, E_g is the semiconducting energy gap, and μ is the chemical potential determined self-consistently as described in the text.

is given by

$$n_e = \int \frac{2N}{W_c} f(E) dE, \tag{1}$$

where N is the number of unit cells, $f(E)$ is the Fermi function $f(E) = \{\exp[(E - \mu)/k_B T] + 1\}^{-1}$, and the integration is over the conduction band. Similarly, we have for the number of holes

$$n_h = \int \frac{2N}{W_v} [1 - f(E)] dE. \tag{2}$$

Here the integration is over the valence band. The chemical potential μ is determined at each temperature from the condition $n_e = n_h$. Once μ is found, we can calculate the total energy U:

$$U = \int_{\substack{\text{cond} \\ \text{band}}} \frac{2N}{W_c} E f(E) dE + \int_{\substack{\text{val} \\ \text{band}}} \frac{2N}{W_v} E f(E) dE. \tag{3}$$

The heat capacity C_v is found by differentiation: $C_v = (\partial U/\partial T)_v$. In Fig. 3(a) we plot the electronic contribution to the specific heat and a fit using the approach outlined above with fitting parameters $W_v = 55$ K, $W_c = 100$ K, and $E_g = 135$ K. It should be emphasized that in this model the number of electrons per unit cell is fixed at two; the proper magnitude of the specific heat emerges naturally from the analysis.

If a scaling relationship is obeyed, the thermal expansion is related to the specific heat through a (constant) electronic Grüneisen parameter:

$$\Omega_e = \frac{(\Delta\beta)V}{(\Delta C_p)\chi_s}. \tag{4}$$

Here $\Delta\beta$ is the electronic contribution to the volume thermal expansion, V is the molar volume, ΔC_p is the electronic contribution to the heat capacity, and χ_s is the background adiabatic compressibility. Using Eq. (4) and

the model discussed above, we fit the thermal expansion with the parameters $W_v = 60$ K, $W_c = 120$ K, $E_g = 145$ K, and $\Omega_e = -10.6$; these values for W_c, W_v, and E_g are nearly the same as those used to fit the specific heat. The 50-K elastic constant data of Nakamura et al.[16] on LaB$_6$ were used to calculate the background χ_s needed in Eq. (4). The results of the fit appear in Fig. 3(b). The deviation between experiment and fit below 20 K is most likely due to the positive-going low-temperature anomaly discussed earlier. If we simply use Eq. (4) and the measured data, we find that $\Omega_e \simeq -11$ over most of the measured temperature range $(20 < T < 80$ K).

The above analysis implies that the semiconducting gap energy drives the thermodynamics of SmB$_6$. To test this identification we recall that if a characteristic energy E_0 determines the thermodynamics of a system then the electronic Grüneisen parameter can be identified with the volume dependence of this characteristic energy:[3,7] $\Omega_e = -\partial \ln E_0 / \partial \ln V$. A simple thermodynamic transformation gives $(1/E_0)\partial E_0/\partial P = \Omega_e/B_T$ where B_T is the isothermal bulk modulus. Using the room-temperature value of B_T measured by King et al.,[17] $B_T = 139$ GPa, we find that $(1/E_0)\partial E_0/\partial P \simeq -0.008$ kbar^{-1}. In order to compare with experiment, we note that SmB$_6$ metallizes at about 70 kbar,[18] which implies $(1/E_0)\partial E_0/\partial P \simeq -0.014$ kbar^{-1}. The agreement is quite reasonable, and supports the identification of the gap energy as the characteristic energy.

The value of the gap determined from the fits, $E_g \simeq 140$ K, is in excellent agreement with gaps obtained from infrared spectroscopy[19,20] and has nearly the same energy as an interesting magnetic excitation recently reported by Mignot et al.[21] that appears to be coupled strongly to the gap. This gap value is also comparable to the single-ion Kondo temperature $T_K = 100$–300 K which can be estimated from inelastic neutron scattering.[22] We note that inelastic neutron scattering also finds evidence for a second energy scale,[23] estimated to be 10^2–10^3 K, that is associated with intermultiplet transitions and provides a measure of the interconfigurational interaction energy. As discussed in Ref. 22, it is the width of these inelastic peaks and not their energy that reflects the energy scale of the valence (and associated spin) fluctuations.

The question remains: What is the role of mixed valence in the thermodynamics of SmB$_6$? For one thing, the sign of the thermal expansion coefficient is in agreement with what one would expect for a mixed-valent Sm compound. As the system is warmed, entropy considerations favor the configuration with a higher degeneracy. For Sm the smaller Sm^{3+}(f^5) configuration has $J = \frac{5}{2}$ and $g_n = 2J + 1 = 6$ whereas Sm^{2+}(f^6) has $g_{n+1} = 1$; the smaller ion has the greater degeneracy, so one would expect a negative expansion coefficient. This is what we observe, but it does not automatically follow that the valence has changed more than an infinitesimal amount. Furthermore, the elastic constant measurements of Nakamura et al.[16] on SmB$_6$ show a peak in the compressibility at about the same temperature that the specific heat peaks. This peak in the compressibility almost certainly arises through deformation potential coupling arising from the presence of a gap. Because Sm^{2+} ions are

more compressible than Sm^{3+} ions[26] the compressibility data imply that the valence is moving toward Sm^{2+}; the thermal expansion, on the other hand, implies that the valence is moving toward Sm^{3+}. It is possible that the increased compressibility allows the valence to remain nearly constant as the lattice parameter changes; this would explain the lack of a mixed-valent contribution to the low-temperature thermodynamics. Another, more exciting, possibility is that the semiconducting energy gap is derived from or is directly proportional to the valence fluctuation temperature. Again, the thermodynamics would be determined by a single energy scale; in this case, however, small contributions to the specific heat and thermal expansion arising from a change in valence with temperature would be difficult, if not impossible, to distinguish from contributions arising from transitions across a narrow gap.

In conclusion, we find that the low-temperature thermodynamics of SmB_6 is consistent with a hybridization gap model. A Grüneisen analysis indicates that a single characteristic energy—the semiconducting energy gap—drives the thermodynamics.

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