Electron correlations in Sr(Sm)B_6

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(Received 22 September 1997)

We present and discuss electronic correlation effects in slightly doped $Sr_{1-x}Sm_xB_6$ for which the concentrations of magnetic centers and itinerant electrons are low and approximately equal, and compare its properties with those of SrB_6 and SmB_6. For $x=0.03$ the low-temperature conductivity σ exceeds $\sigma(x=0,\ T=0)$ and $\sigma(x=1,\ T=0)$ by more than two orders of magnitude and the electronic specific heat reveals a strong enhancement of the electronic density of states at the Fermi level E_F, not observed in the concentrated compound SmB_6. [S0163-1829(98)01817-7]

Strong correlation effects among itinerant charge carriers are known to occur in a variety of metallic rare-earth and actinide compounds at low temperatures. This phenomenon is usually observed at low temperatures in materials where the cations with partially filled f-electron orbits occupy regular sites of the crystal lattice and where the density of itinerant charge carriers is comparable to that of common simple metals.[1] Correlation effects are also observed in metallic matrices with only a small concentration of magnetic ions.[2] The screening of the magnetic moments via conduction electrons induces a narrow peak of electronic density of states at the Fermi energy E_F, which may be verified by various types of experiments.[1,2] In this work we aim at investigating the interplay between magnetic moments and conduction electrons for a case where the conditions are substantially altered in the sense that a low concentration of magnetic impurities is introduced into a compound with a low concentration of conduction electrons.

For our purpose a particularly well-suited class of materials is provided by cubic hexaborides with divalent and trivalent cations. LaB_6 is a good metal with approximately one conduction electron per unit cell[3] and observations of correlation effects in $La_{1-x}Ce_xB_6$ with x of the order of a few at. % are well documented in the literature.[4,5] SrB_6, in which the cations adopt a divalent configuration, is known to be a poor metal at low temperatures, and the concentration of itinerant charge carriers is very low, of the order of 10^{-4} electrons per unit cell.[6] Band-structure calculations indicate that for divalent cubic hexaborides the electronic features depend very critically on details of the band structure in the vicinity of the X point of the Brillouin zone.[7] Slight variations in the interatomic distances between the B atoms are expected to provoke changes from a tiny band overlap to a complete gapping of the electronic excitation spectrum at E_F. Another hexaboride that is close to a metal-insulator transition is SmB_6, for which there is convincing experimental evidence that with decreasing temperature, a large part of the electronic states in the vicinity of E_F is removed.[8,9] The corresponding gap formation is not quite complete, however, leaving a residual small number of itinerant electrons at very low temperatures. Previously, the corresponding remaining electrical conductivity was ascribed to impurity or defect induced itinerant states,[10] but the more intriguing possibility of observing the intrinsic feature of an incomplete gap formation, akin to similar phenomena in unconventional superconductors,[11] should not completely be excluded.

We therefore have chosen to introduce a few at. % of Sm atoms on Sr sites of SrB_6. If the Sm ions adopt their trivalent configuration each such ion will add both one magnetic moment based on the $f^5 J=5/2$ Hund's rule ground state and one additional conduction electron, thereby enhancing the metallic character of the material. The latter conjecture is confirmed by measurements of the electrical resistivity of both SrB_6 and $Sr_{0.97}Sm_{0.03}B_6$, the results of which are shown in Fig. 1. A Curie-Weiss-type temperature variation of the magnetic susceptibility of the Sm doped material[12] provides

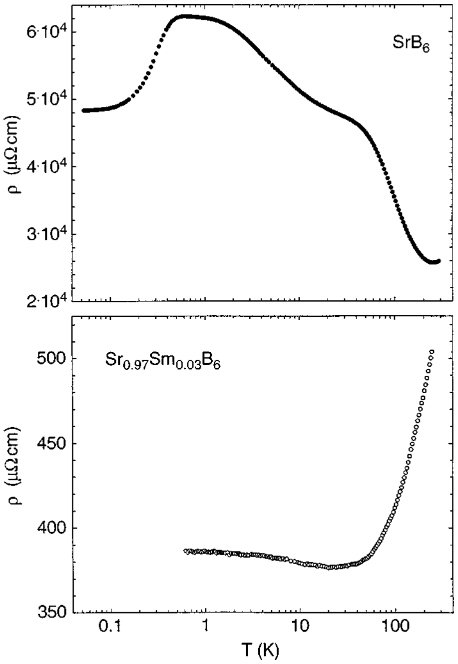

FIG. 1. Temperature dependences of the electrical resistivities of SrB_6 (upper panel) and $Sr_{0.97}Sm_{0.03}B_6$ (lower panel) below room temperature.

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evidence for the presence of isolated magnetic moments. Below we intend to demonstrate the different situations that emerge from the interactions between magnetic moments and conduction electrons with low and high concentrations by comparing low-temperature thermal and transport properties of SrB_6, $Sr_{0.97}Sm_{0.03}B_6$, and SmB_6.

All the data that are presented have been obtained from measurements using single crystalline samples grown from A1 flux.[6] For each of the three compounds, the measurements have been made using the same single crystal. The electrical resistivity ρ was measured using a four probe low-frequency ac technique and the specific heat C_p was obtained by employing a relaxation-type method. The low-temperature ac magnetic susceptibility was measured with a common mutual inductance setup and the primary magnetic-field amplitude was less than 1 Oe.

As may be seen in Fig. 1, both the magnitude and the temperature dependence of the electrical resistivity are significantly different for SrB_6 and $Sr_{0.97}Sm_{0.03}B_6$. The low-temperature residual resistivities differ by two orders of magnitude. As pointed out in Ref. 6, the temperature variation of ρ of SrB_6 is of ambivalent character. The Sm-doped material first reveals a positive slope $\partial\rho/\partial T$ below room temperature. At about 20 K, $\rho(T)$ passes through a shallow minimum and the subsequent negative slope persists below this minimum temperature. Although it is not obvious from our plot in Fig. 1, the resistivity increases linearly with decreasing temperature below 5 K with a slope of -0.8 $\mu\Omega$ cm/K, without any tendency to saturation down to 0.35 K. The resistive behavior of this dilute alloy is again quite different from $\rho(T)$, often observed, of SmB_6. In this latter case, the room-temperature resistivity is about half of that of our Sm-doped SrB_6 but, as found previously,[8,10] increases monotonically with decreasing temperature. Below 50 K the negative slope increases dramatically and ρ increases a few orders of magnitude but settles at a finite value of the order of 0.1 Ω cm,[13] as $T\rightarrow 0$. Thus the two compounds containing Sm ions in low and high concentration, respectively, appear to adopt rather different ground states. The $\rho(T)$ increase of SmB_6 is not exponential in $1/T$ at low temperatures and therefore the removal of electronic states close to the Fermi energy does not result in the formation of a complete gap, in accordance with the nonzero conductivity at very low temperatures of these[13,14] and other samples.[10] The linear temperature variation of $\rho(T)$ of Sm-doped SrB_6 with a negative slope is obviously unusual and, in spite of the resistivity minimum, is not compatible with a simple Kondo-type behavior that might appear as the most obvious choice for explaining the physical properties of slightly doped SrB_6.

The results of the specific-heat measurements at low temperatures also reveal distinct differences in the behavior of these compounds. For SrB_6 a small excess specific heat C^{ex}, in addition to the expected contribution due to lattice excitations, develops below 5 K, increasing with decreasing temperature. More details concerning $C^{ex}(T)$ of SrB_6 at very low temperatures may be found in Ref. 6. The replacement of 3% Sr atoms by Sm changes this behavior dramatically, as may be seen in Fig. 2, where the specific-heat data for both compounds, obtained at temperatures between 0.06 and 18 K, are plotted in the form of C^{ex}/T vs T for $T<6$ K. For $Sr_{0.97}Sm_{0.03}B_6$ the excess specific heat sets in at 15 K. Here again, C^{ex} is obtained by subtracting the lattice contribution from the measured specific heat. The corresponding C^{ex}/T ratio increases significantly with decreasing temperature below 12 K and reaches a maximum of about 85 mJ mole f.u. K^2 at 1.2 K. The subsequent decrease at lower temperatures is intercepted at approximately 0.2 K by another steep increase towards temperatures below 0.1 K.

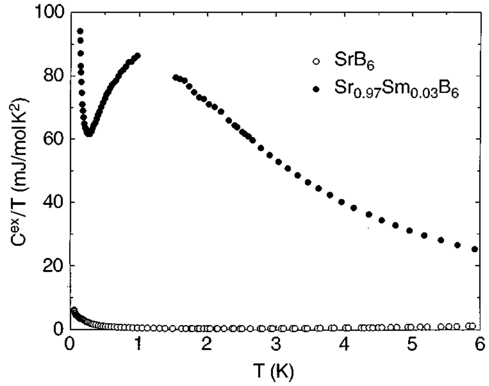

FIG. 2. Comparison of the excess specific heat (see text) in the form of C^{ex}/T vs T for SrB_6 and $Sr_{0.97}Sm_{0.03}B_6$ between 0.06 and 6 K.

As mentioned above, we also compare the excess specific-heat data of the Sm-doped SrB_6 with that obtained for SmB_6. This comparison is made in Fig. 3. The C^{ex}/T ratio of SmB_6 below 6 K is about one order of magnitude smaller than that for doped SrB_6. Taking into account the loss of occupied electronic states close to E_F of SmB_6, this observation is not suprising and indicates that the large low-temperature excess specific heat of $Sr_{0.97}Sm_{0.03}B_6$ is of electronic origin. Nevertheless, the distinct maximum of C^{ex}/T of the dilute alloy appears to have its strongly reduced counterpart for SmB_6, for which it is slightly shifted to approximately 1.5 K.

Considering both Figs. 2 and 3, there is no doubt that strong enhancements of the density of electronic states $D(E_F)$ due to scattering centers carrying a magnetic moment also occur in materials with a very much reduced concentration of itinerant charge carriers. Comparing room-temperature resistivity data, $Sr_{0.97}Sr_{0.03}B_6$ has about a factor of 50 less conduction electrons than LaB_6 for which, as men-

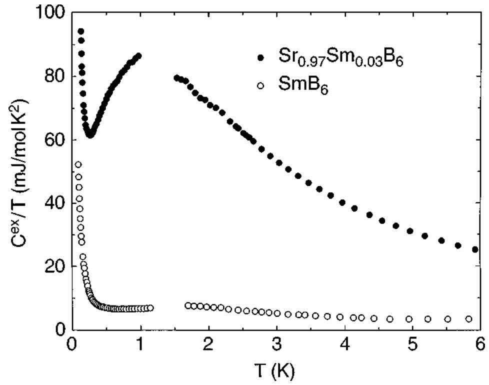

FIG. 3. Comparison of the excess specific heat (see text) in the form of C^{ex}/T vs T for SmB_6 and $Sr_{0.97}Sm_{0.03}B_6$ between 0.06 and 6 K.

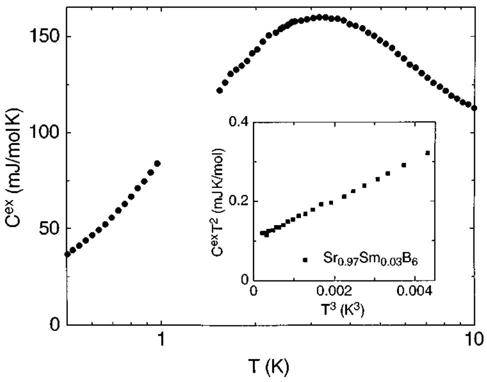

FIG. 4. Excess specific heat (see text) of $Sr_{0.97}Sm_{0.03}B_6$ between 0.5 and 10 K on a logarithmic temperature scale. The inset emphasizes $C^{ex}(T)$ at very low temperatures in a plot of C^{ex}/T^2 vs T^3 (see text).

tioned, many-body effects due to Ce impurities have previously been reported.[4,5] The total excess entropy S^{ex} observed for $Sr_{0.97}Sm_{0.03}B_6$ is adequately accounted for by considering a contribution of $k_B\ln4$ per Sm impurity, supporting the interpretation that the Sm ions adopt a trivalent configuration and that the crystal electric-field splitting leaves a Γ_8 quartet state of the $J=5/2$ multiplet as the ground state.[15]

At very low temperatures the specific heat of $Sr_{0.97}Sm_{0.03}B_6$ is very well described (see inset of Fig. 4) via

$$C^{ex}T^2=a+\gamma T^3, \tag{1}$$

where a and γ are the prefactors of C_p contributions proportional to T^{-2} and T, respectively. If we interpret the linear-in-T term as revealing the density of electronic states at E_F, the γ value is compatible with 1.5 J/mole Sm K^2. The corresponding characteristic temperature

$$T^*=S^{ex}/\gamma=(R\ \ln4/1.5)=7.7\ \mathrm{K} \tag{2}$$

should be compared with $T_{max}=3.2$ K, the temperature of the maximum C^{ex} displayed in Fig. 4, which is approximately half of the value of T^*, a relation that is a common result of models describing correlation effects induced by magnetic impurities in good metals.[16–19] The same models also account for the general shape of the $C^{ex}(T)$ curve, plotted on a logarithmic temperature scale, which is shown in Fig. 4. In the temperature range of the maximum of C^{ex} we have also observed a shallow maximum of the ac susceptibility. We further note that χ_{ac} is constant below 1 K, confirming the compensation of the magnetic moments carried by the Sm impurities.

The appearance of a C_p contribution varying at T^{-2} at very low temperatures is usually associated with excitations between nuclear energy levels split by internal magnetic or electric fields at the sites of the nuclei. In our case the cause for this contribution is not entirely clear, because we have no independent indication of static internal magnetic fields due to moment ordering or freezing. The only possibility might be the existence of substantial electric-field gradients at the Sm sites that would, by interaction with the nuclear electric quadrupole moment, lift the degeneracy of the nuclear levels of ^{147}Sm nuclei. In view of the low concentration of Sm atoms, the natural abundance of ^{147}Sm of 14% and the moderate value of its nuclear quadrupole moment, this interpretation should only be regarded as a remote possibility which, with the present status of information, cannot entirely be discarded. In this sense we have to accept that the additional excess specific heat of $Sr_{0.97}Sm_{0.03}B_6$ at very low temperatures, which to a lesser extent is also present in SmB_6 (see Fig. 3), remains unexplained.

Apart from this uncertainty we conclude that the screening of magnetic moments also prevails in metals with low conduction-electron concentrations. It appears that the compensation of magnetic moments is also achieved, if the concentration of moments and itinerant charge carriers are approximately equal. This observation may offer a new way of looking at intermediate valence-type phenomena,[20] as they have previously been discussed for SmB_6, for example. According to the results presented here, the crossover from an enhancement of the electronic density of states at E_F to the formation of partial gaps in the electronic excitation spectrum at E_F may be studied in the series of $Sr_{1-x}Sm_xB_6$ compounds with varying x.

The work at ETH Zürich profited from financial support of the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung. Work at Los Alamos was done under the auspices of the U.S. Department of Energy. Z.F. and J.L.S. acknowledge financial support of the Japanese New Energy and Industrial Technology Development Organization (NEDO). One of us (H.R.O.) would like to thank the Center for Materials Sciences of Los Alamos National Laboratory for its support and hospitality during part of this work.

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