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Kondo insulators

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Abstract

We discuss Kondo insulators in the context of recent experimental results. These experiments address the questions of the relationship of spin and charge excitations, the temperature dependence of the gap, and the existence of 'failed' insulators.

The small class of f-element compounds known as Kondo insulators are all in a certain sense 'valence' compounds: the f-elements that are present in these compounds have unstable valence, with the valence corresponding to the non-magnetic f-state of the element satisfying the valence requirements of the other elements in the material. A few cases require special consideration, but it is also the case that semiconducting analogs exist for these materials, with the f-element replaced by an isovalent element. The problem can be viewed as a very simple limiting case of the correlated electron lattice: exactly one half-filled band interacting with one occupied f-level. This also corresponds to a simple limiting case of the Kondo lattice with one conduction electron to screen one moment at each site.

The general properties of these materials are characterized by a small gap [1]. High-temperature Curie–Weiss magnetic susceptibility evolves into low-temperature paramagnetism on the same temperature scale describing the rise in resistivity at low temperature. This scale also gives the temperature development of the Hall constant, and, to the extent that we have the data, the Hall number describes as well the temperature development of the magnetic susceptibility: each carrier corresponds to one f-moment [2]. This comparison is not easy to make in all cases (such as SmB_6), and in fact the data set is not at all complete. There is also an anomalous part to the thermal expansion which tracks the moment evolution [3].

It is not just the magnetic moments accompanying excitations across the low temperature gap that distinguishes these semiconductors from the conventional ones. Optical conductivity studies in $Ce_3Bi_4Pt_3$ show that the gap only opens below a characteristic temperature T^* approximately equal to 0.6Δ, the mean field expression [4, 5]. In addition, the spectral weight lost at low energies when the gap opens is not recovered until an energy of order 10Δ.

While the gap has been studied in inelastic neutron scattering in polycrystalline $Ce_3Bi_4Pt_3$ and found to be approximately twice the activation energy derived from transport measurements [6], a more complete study via neutrons has been made on single-crystal CeNiSn [7], the only non-cubic crystal structure so far known to harbor Kondo insulators [8]. The gap in this material is quite small, of order 10 meV, and was actually discovered to be well defined only in certain directions in phase space. Additionally, and perhaps not unrelated, there exists evidence that a small concentration of heavy conduction electrons remain at low temperatures in parallel with the gap [9].

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The question thus naturally arises as to whether the Kondo-insulating materials actually are true insulators at low temperature or whether an intrinsic small conduction-electron carrier concentration is present. In this connection several experimental findings are relevant. The first point to make is that the presence of the gap as $T \to 0\,K$ does not depend on whether or not residual conductivity is found [10]. It has also been observed in CeNiSn that seemingly cleaner samples, as judged by the smallness of the sample-dependent Curie tail at lowest temperature, have higher limiting conductivities at low temperature than samples with larger Curie tails [9]. A similar conclusion has been drawn from the pulsed-field ρ_{xx} and ρ_{xy} measurements of Boebinger et al. on $Ce_3Bi_4Pt_3$ [11]. Below 10 K and above 50 T, ρ_{xx} and ρ_{xy} become field- and temperature-independent at finite values corresponding to approximately 0.02 carriers per formula unit (Fig. 1). The data for SmB_6 are similar to that for $Ce_3Bi_4Pt_3$, but correspond to a characteristic energy scale which is several times larger, so a field-independent regime, if it exists, has not been reached [12]. Aspects of the residual resistivity of SmB_6 as a function of pressure have been discussed in [13].

Optical studies on the intermediate-valent material $CePd_3$ have also found a gap which opens at low temperatures with a substantial Drude piece remaining [5, 14]. Again, the spectral weight is redistributed over an energy an order of magnitude larger than the gap. We note that in the intermediate-valent compound $CeSn_3$, a gap-like feature develops at low temperature with weight redistribution only in the vicinity of the gap [5]. This is what would be expected in connection with a Kondo resonance in a metal.

An interesting result was found in Gd-EPR experiments in SmB_6 by Wiese et al. [15]. The $g = 2$ resonance could be seen below 10 K in their Al-flux-grown crystals. However, an entirely different spectrum evolved on cooling below 6 K. Their explanation for this result is that the extra electron brought by trivalent Gd into the lattice becomes bound in some kind of singlet state. Interestingly, inelastic neutron scattering in pure SmB_6 [16] has identified a feature at low temperatures which may be the corresponding entity. There seems to be a sample-to-sample variation here as well: the EPR feature was seen in Al-flux-grown samples but not in zone-refined ones.

In this regard, Raman experiments in SmB_6 are interesting [17]. We first note that the Raman scattering sees clearly that the gap opens only below a characteristic temperature, although the weight in the spectrum redistributes itself only in the vicinity of the gap (Fig. 2). Here, however, there is no optical sum rule. As the gap opens, a feature appears in the gap at 135 cm^{-1} with $d_{x^2-y^2}$ symmetry (Fig. 3). This is likely to be the same object seen in the inelastic neutron scattering. Whether or not it is

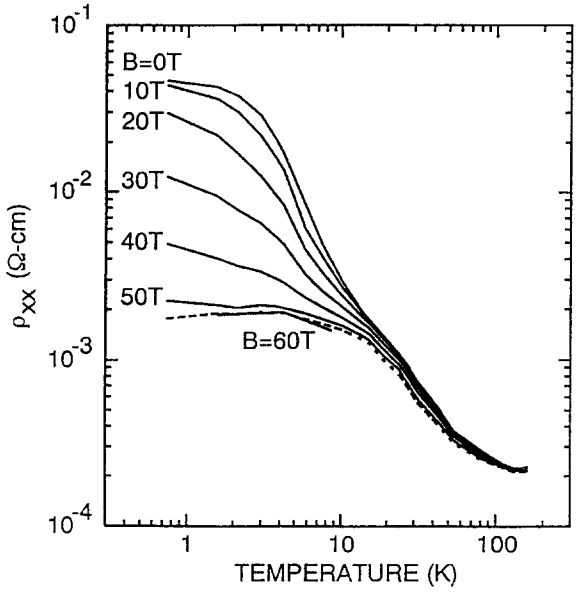

Fig. 1. Longitudinal resistivity versus temperature at fixed magnetic field for $Ce_3Bi_4Pt_3$. The dashed line is $B = 55$ T data. Note that the resistivity is relatively constant for $T < 10$ K and $B > 50$ T. After Ref. [11].

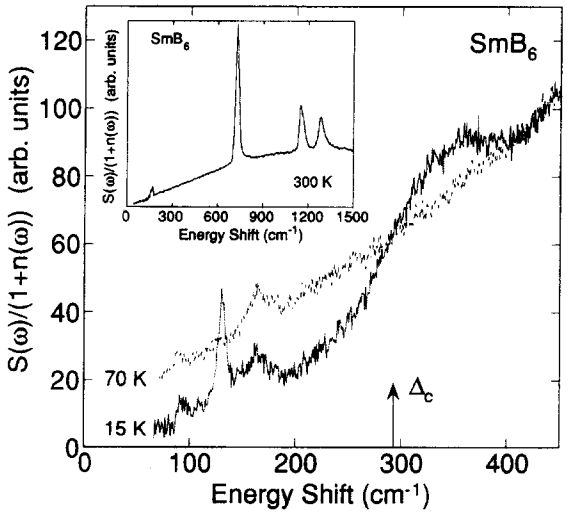

Fig. 2. Comparison of the 70 K and 15 K $A_{1g} + E_g + T_{2g}$ symmetry Raman scattering response function for SmB_6. A suppression of electronic Raman scattering below $\omega = 290\,cm^{-1}$, and a redistribution of electronic scattering strength to higher energies is apparent due to the development of a charge gap. The inset shows the room-temperature, high-frequency Raman scattering response function. After Ref. [17].

related to what Wiese et al. observed in the Gd-EPR is not known of course. The symmetry of this excitation is consistent both with the type of object Wiese et al. postulated and with a crystal-field excitation. In regards to the latter possibility, we note that it is unusual to see crystal-field excitations in apparently mixed-valent ions, but this again cannot be ruled out.

The final point to make here concerns the nature of the phase diagram in e/n (charge/moment) phase space in the vicinity of the $e/n = 1$ point characterizing the Kondo insulators. Nothing is really known about what general features could be shared by this class of materials. It is known that CeNiSn doped with Cu becomes magnetic at the 10% Cu doping level [18]. Additionally, Co-doping for Ni has been found to lead to a first-order valence transition, at certain concentrations, as a function of temperature [19]. Much remains to be done here to elucidate our picture of these materials. It may be that the way to approach the physics is by asking what is the single impurity limit of the Kondo effect in an insulator.

FeSi shows a number of similarities to the Kondo insulators [1, 20]. These similarities include loss of high-temperature Curie–Weiss magnetic susceptibility on a temperature scale comparable to the gap evident in transport properties [21, 22], $\chi'(q, \omega)$ being q-independent as $\omega \to 0$ [23], doping-induced magnetic order [24], and a temperature-dependent gap which opens at low temperature with spectral weight shifted over an energy scale an order of magnitude larger than the gap [25]. There is controversy on this last point: in an extensive set of measurements on a single crystal of FeSi, the large shift in spectral weight accompanying the opening of the gap was not seen [26]. It should be pointed out, however, that this particular sample was, in fact, considerably more metallic in its properties than that measured in the original optical experiments [25].

Raman scattering experiments on FeSi also show the gap clearly opening with lowering temperature [27], very much as in SmB_6. The gap in FeSi is approximately 600 K, as measured by transport. Raman sees the gap opening below 250 K, with a width of 760 cm^{-1} (Fig. 4). As in the case of SmB_6, Raman sees the spectral weight redistributed only in the vicinity of the gap. Again, however,there is no spectral-weight sum rule for Raman intensity. The Raman data, as indicated by the observed phonon lines, also reveal that the electron–phonon coupling is quite strong. Phonon coupling is also important in the rare-earth cases, as inferred from the marked temperature-dependent lattice-parameter variations.

We see no a priori reason for thinking that transition metal compounds cannot share some of the same physics as the unstable-valent rare-earth compounds. It is common to think of a progression of properties from, for example, Ce to U to magnetic transition elements, based on the idea of progressively less localization of the 4f → 5f → 3d electrons. It is curious that we do not have a clean example of a 5f Kondo insulator: the candidates

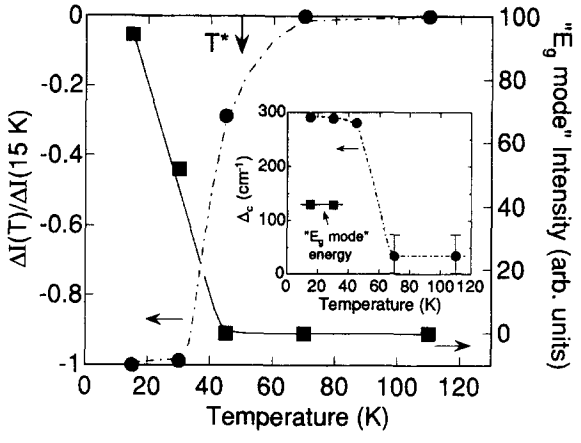

Fig. 3. Filled circles: Temperature dependence of the fractional change in integrated electronic spectral weight below $\Delta_c = 290\,cm^{-1}$, $\Delta I(T)/\Delta I(T = 15\,K)$, where $\Delta I(T) = I(T) - I(340\,K)$, and $I(T)$ is the integrated electronic spectral weight associated with the Raman response function $R''(\omega)$ below $\omega = \Delta_c$ for SmB_6. Open squares: Temperature dependence of the integrated 'E_g mode' intensity. Inset: Plot of Δ_c as a function of temperature (filled circles), where Δ_c is the energy below which electronic Raman scattering intensity in $R''(\omega)$ is suppressed with decreasing temperature. For comparison the 'E_g mode' energy is also plotted as a function of temperature (open squares). After Ref. [17].

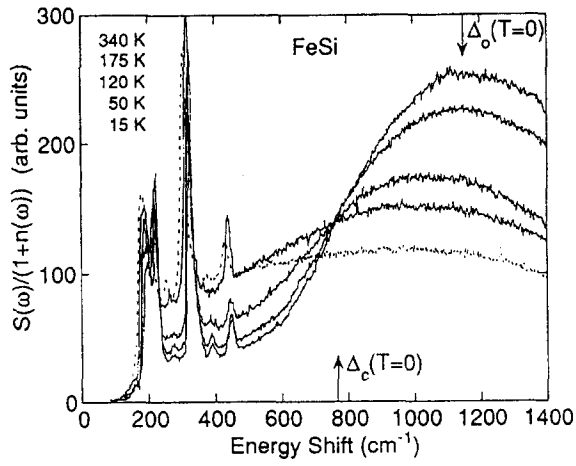

Fig. 4. Temperature dependence of the A + E + T symmetry Raman-scattering response function, $R''(\omega) = S(\omega)/[1 + n(\omega)]$, of FeSi, showing the development of a gap, Δ_0, in the electronic continuum at low temperatures, and the transfer of scattering strength to the peak near Δ_0. After Ref. [27].

so far appear to have a stable U^{+4} configuration. Possibly UNiSn is close, but its low-temperature magnetic transition drives the material metallic.

Part of the argument concerning the appropriate way to look at FeSi has been based on the assertion that band structure calculations are adequate to account for its properties [28]. This appears to be only partially true. It is not the case that the temperature dependence of the optical conductivity can be accounted for by simple thermal excitations. Neither is $\chi(T)$ accounted for in this way. In addition, photoemission studies show the development of an extremely sharp polaron-like feature at the Fermi edge at low temperatures, again indicative of important many-body correlations in the physics [29, 30].

The qualitative picture that emerges is one in which a particular set of crystal structures are particularly disposed, at suitable electron count, to the Kondo insulating ground state: the physics involves a single half-filled conduction band mixing with one occupied magnetic level per site. It appears that this magnetic level can be a d- or an f-level. There is a significant spectral weight shift seen in the optical conductivity as this state develops, corresponding, loosely speaking, to the formation of a weakly bound, non-magnetic state at low temperature. The development of this ground state occurs below a temperature of order 0.6Δ. The transition is continuous, although we see no reason why it might not happen via a first-order phase transition in some cases. A suspected feature of the ground state is that $\chi'(q, \omega)$ as $\omega \to 0$ is q-independent. Whether or not oxide materials can partake of this same physics remains to be determined.

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