Magnetic impurities in Kondo insulators and the puzzle of samarium hexaboride

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Impurities and defects in Kondo insulators can have an unusual impact on dynamics that blends with effects of intrinsic electron correlations. Such crystal imperfections are difficult to avoid, and their consequences are incompletely understood. Here we study magnetic impurities in Kondo insulators via perturbation theory of the s-d Kondo impurity model adapted to small bandgap insulators. The calculated magnetization and specific heat agree with recent thermodynamic measurements in samarium hexaboride (SmB\textsubscript{6}). This qualitative agreement supports the physical picture of multichannel Kondo screening of local moments by electrons and holes involving both intrinsic and impurity bands. Specific heat is thermally activated in zero field by Kondo screening through sub-gap impurity bands and exhibits a characteristic upturn as the temperature is decreased. In contrast, magnetization obtains a dominant quantum correction from screening by virtual particle-hole pairs in intrinsic bands. We argue that this physical picture also has the potential to explain the bulk-like de Haas-van Alphen quantum oscillations in SmB\textsubscript{6}, through the effect of Landau quantization in intrinsic bands on the Kondo screening of impurity moments.

I. INTRODUCTION

Impurities within Kondo insulators are distinct from the typical electron and hole-type impurities in semiconductors\textsuperscript{1,2}. A popular physical picture is that the formation of a Kondo insulating ground state is predicated on a coherent lattice of localized moments that develop singlet correlations with mobile electrons.\textsuperscript{2} When impurities break translational symmetry and disturb the coherence of the ground state, they become “Kondo holes” in the Kondo lattice. The theory of non-magnetic Kondo holes has been studied extensively, revealing a novel impurity band at dilute concentrations and a collapse of the insulating state at moderate and higher concentrations.\textsuperscript{3,4}

Experimental results on impurities and defects in Kondo insulators show an analogy to the Kondo impurity model, including a resistance minimum for dilute La doping in CePd\textsubscript{3} and impurity-driven localization in La-doped CeNiSn.\textsuperscript{5,6} In addition to non-magnetic impurities, rare earth elements with substantial magnetic moments (e.g., Gd, Eu) are common impurities in Kondo insulators.\textsuperscript{7,8} Their presence also disrupts the coherent Kondo insulator state, yet the experimental consequences of their magnetic degrees of freedom have largely been overlooked.

The theory of magnetic impurities in metals has a long history.\textsuperscript{9–20} Magnetic impurities in insulators have attracted much less attention so far. Nevertheless, theoretical studies of Kondo screening in gapped systems (insulators and superconductors) have reached an important result that a Kondo singlet state does form at low temperatures, just like in metallic systems, if the gap is of the order of Kondo temperature or smaller.\textsuperscript{21,22}

The most-studied Kondo insulator, samarium hexaboride (SmB\textsubscript{6}), is a strongly correlated “heavy fermion” material and a proposed strong topological insulator (TI) with time-reversal (TR) symmetry.\textsuperscript{23–25} The former has been established in numerous experiments over several decades now,\textsuperscript{23–26} while the evidence for the latter is recent and growing.\textsuperscript{24–27} As a correlated TR-invariant TI, SmB\textsubscript{6} could exhibit novel physical phenomena including an exotic bulk ground state and correlated topologically protected surface states (a 2D Dirac heavy-fermion system).\textsuperscript{28–30} Experimental evidence is mounting that surface states in SmB\textsubscript{6} are effected by interactions, either among the intrinsic degrees of freedom (e.g. mediated by a collective mode), and/or involving impurities (such as Sm vacancies, which are known to proliferate at the surface).\textsuperscript{31–35} The possibility of strongly interacting surface states gives SmB\textsubscript{6} special importance among the expanding family of topological materials.

Several experimental studies of SmB\textsubscript{6} have recently observed puzzling dynamics consistent with metallic behavior,\textsuperscript{36–38} despite measurements showing that SmB\textsubscript{6} is an electric and thermal-transport DC insulator in the bulk,\textsuperscript{39–41} with a spectroscopically clear gap to all excitations.\textsuperscript{42–43} In particular, Corbino geometry transport measurements show unambiguously the insulating nature of the bulk.\textsuperscript{44} Measurements of de Haas-van Alphen (dHvA) effect in quantum oscillations\textsuperscript{45} have indicated a possible 3D bulk Fermi surface in SmB\textsubscript{6}, involving quasiparticles that couple to the external magnetic field but do not transport charge; other similar measurements, however, have been interpreted as resulting from 2D surface dynamics.\textsuperscript{46} Optical conductivity\textsuperscript{47} shows a continuum-like density of states that absorb light at sub-gap energies, but with a frequency dependence that extrapolates to a vanishing DC conductivity. On the other hand, inelastic neutron scattering has not detected any apparent magnetic spectral weight in the energy range 0.15 – 13 meV below the energy of the coherent spin-exciton. The implication of this absence of scattering is that the putative low-energy degrees of freedom respon-
sible for these dynamics must be non-magnetic, have a very small moment, or be related to impurities and defects. Their footprint is seen thermodynamically as an up-turn in the low-temperature dependence of the linear specific heat \( (C/T) \) with decreasing temperature, and perhaps also by neutrons as a finite lifetime of the coherent exciton mode \( \gamma_{\text{coherent}} \).

The observed subgap degrees of freedom in SmB\(_6\) could be a window into an exotic correlated ground state. The most obvious ground state candidate inspired by quantum oscillations and specific heat is a gapless spin or Majorana liquid with a neutral Fermi surface. Charge-neutral quasiparticles would not conduct DC currents, but could in principle couple non-minimally to an external magnetic field – for example, if the spinons were sufficiently large to allow their internal charged constituents (an electron and a holon) to independently interact with the field at short-enough length and time scales. This kind of coupling is likely not engaged in quantum oscillation experiments, which rely on Landau quantization of the density of states in DC magnetic fields. Also, spinons may be at odds with a few other probes: heat transport measurements seem to rule out a Fermi liquid contribution of any kind, while explaining the optical spectroscopy result in terms of spinons would require an unlikely existence of many spinon bands that enable photon absorption at broadly distributed energies without momentum transfer. Moreover, spinons were not evident in low-energy neutron scattering studies. Other proposed explanations of quantum oscillations that attempt to circumvent a neutral Fermi surface may also be at odds with some experimental results, although careful consideration may be able to reconcile relevant energy and field scales. More recently, impurities and defects have been proposed as the cause of bulk dHvA oscillations.

In this paper we explore an explanation of SmB\(_6\) puzzles related to impurities, without ruling out the prospect of an exotic ground state. Our analysis builds upon studies of perplexing impurity effects in SmB\(_6\), which show moment-screening and dramatic enhancement of the low-energy density of states. We argue that these experiments find an explanation in a multi-channel Kondo screening of impurity moments, which is facilitated by electrons and holes in both intrinsic and impurity bands of a small-gap insulator. Our conclusions obtain from a perturbative calculation of magnetization and specific heat in an insulating s-d Kondo model, and hence should apply to generic small-gap materials with localized magnetic impurities. We will also argue that many of the remaining puzzling behaviors in SmB\(_6\) could be attributed to the dynamics of localized magnetic moments introduced by impurities in a correlated Kondo insulator environment.

Our previous thermodynamic studies included measurements of magnetization and specific heat in a variety of samples with different controlled levels of impurity doping. Magnetization incorporates a background Van Vleck component related to Sm\(^{2+}\), which was subtracted. The remaining magnetization shows the temperature and field dependence typical for a paramagnet of decoupled magnetic moments. We can independently extract the effective moment and concentration of impurities from the magnetization \( m(\mu_0 H) \). We found that the concentration of magnetic moments was proportional to the amount of gadolinium doping, sensitive to the hundreds of ppm level. Hence, magnetization is a highly-sensitive characterization tool for a wide range of common magnetic impurities in SmB\(_6\). Furthermore, the linear specific heat \( (C/T) \) at zero field shows a marked deviation from the typical insulating or even metallic behavior. It features an up-turn in its temperature dependence as the temperature is lowered well below the characteristic scale set by the SmB\(_6\) gap – and hence does not exhibit an apparent exponential suppression characteristic of thermal activation in the measured temperature range. This specific heat feature is proportional in its amplitude to the amount of doping. Isolated magnetic moments due to low-density impurities in an insulator do not have capacity to store heat in zero field, so the observed specific heat must be attributed to their interaction with some additional degrees of freedom – which, naively, are either gapless or live at very low energy scales in order to produce a non-thermally activated response.

A. Summary of the analysis and conclusions

In this paper we propose an explanation of the recent magnetization and specific heat measurements in SmB\(_6\), and indirectly address the puzzling metallic-like behaviors of SmB\(_6\) seen by other probes. We argue that most experimental observations are consistent with a quantum and thermally-activated screening of localized magnetic moments introduced by rare earth impurities in a small-bandgap insulator. Indeed, such screening is possible even in gapped systems at low temperatures – provided that the Kondo temperature scale \( k_B T_K \) is comparable or larger than the gap \( \Delta \), which likely is the case in Kondo insulator.

The simplest theoretical model of a Kondo insulator with magnetic impurities is the following adaptation of the s-d model’s Hamiltonian:

\[
H = \sum_s \left[ \int d^3 k \left( E_{s k} \psi_{s k}^\dagger \psi_{s k} - J \sum_{i=1}^{N_i} \mathbf{S}_{r_i} \cdot \mathbf{\sigma}_{s r_i} \frac{1}{2} \psi_{s r_i}^\dagger \psi_{s r_i} \right) \right].
\]

The Kondo insulator’s intrinsic quasiparticles are described by field operators \( \psi_s \) in two bands \( s = \pm 1 \) separated by a gap, and \( N_i \) local moments scattered at locations \( \mathbf{r}_i \) are described by spin operators \( \mathbf{S}_{r_i} \). This minimalistic model focuses only on the Kondo interaction \( J \) between the magnetic impurities and quasiparticles, without seeking to capture the nature of the ground state, correlations among quasiparticles or collective modes in a Kondo insulator. The main simplification built into the
model is the treatment of both quasiparticles and local moments as effective \( S = \frac{1}{2} \) spin degrees of freedom with the same coupling to the external field. This reduces the technical complexity of calculations without jeopardizing the qualitative nature of conclusions. However, since magnetic impurities like gadolinium have a large moment, the price to pay is an inadequate description of underscreening that takes place in the low-temperature Kondo state.

We calculate magnetization up to saturating fields and specific heat in zero field using perturbation theory in the model (1). Our main results can be summarized by the following corrections to magnetization density \( \delta m \) and zero-field specific heat \( \delta c \) in a Kondo insulator:

\[
\delta m = \begin{cases} 
- c_1 \nu_i \left( \frac{Jp}{\Delta} \right)^2 \frac{\beta \tanh(\beta \hbar)}{\cosh^2(\beta \hbar)} & , \beta \Delta \gg 1 \\
c_2 \nu_i Jp^3 \left( \frac{\beta}{\beta \Delta} \right)^n \frac{\tanh(\beta \hbar) [1 + \cosh^2(\beta \hbar)]}{\cosh(\beta \hbar)} & , \beta \Delta \ll 1
\end{cases}
\]

\[
\delta c \approx \begin{cases} 
c_3 \nu_i k_B \left( \frac{Jp^3}{\Delta} \right)^2 \frac{1}{\beta \Delta} & , \beta \Delta \gg 1 \\
c_4 \nu_i k_B (\beta Jp^3)^2 & , \beta \Delta \ll 1
\end{cases}
\]

These are only the dominant corrections to the response of decoupled quasiparticles and local moments. \( c_{1,2,3,4} \) are positive numerical coefficients, \( \beta = (k_B T)^{-1} \) is inverse temperature, \( h \) is the Zeeman energy of both quasiparticle and impurity spins aligned with the external magnetic field (assumed to be the same for simplicity), \( 2\Delta \) is the bandgap (\( \Delta \gg h, k_B T \)), and \( n_i = N_i / V \) is the concentration of impurity moments. A microscopic momentum scale \( p \), determined from the high-energy quasiparticle spectrum, is combined with the Kondo coupling \( J \) to produce an energy scale \( j = Jp^d \). We use the units with \( h = 1 \). Perturbation theory is controlled by the parameter \( x = j / \Delta \) that can be small even in the limit \( \Delta \lesssim k_B T_K \propto \exp(-1 / Jp) \) where Kondo screening can occur (\( p \) being the average density of electron states available for screening).

The essential features of the above response functions are: (i) specific heat is thermally activated unless the Kramers degeneracy of local moments is lifted or gap closed; (ii) magnetization is not thermally activated – it receives a quantum correction at the second order of perturbation theory by virtual particle-hole pairs that screen the local moments. A thermally activated component of magnetization is also found at the first order of perturbation theory, but it is not dominant at low temperatures.

The properties of the calculated \( \delta c \) and \( \delta m \) that are immediately consistent with the experiment include: (i) the system is an electric insulator, (ii) both corrections of thermodynamic responses are proportional to the impurity concentration \( n_i \), (iii) magnetization is reduced in comparison to that of isolated moments (i.e. the effective moment of impurities is renormalized to a smaller value as antiferromagnetic Kondo screening with \( J < 0 \) takes place), (iv) magnetization is not thermally activated, and (v) specific heat shows an upturn as the temperature is reduced, albeit only in the thermally activated regime.

\( \beta \Delta < 1 \). However, difficulties arise with attempts to fully understand specific heat: an upturn in some samples is experimentally seen down to millikelvin temperatures. This can be reconciled with the present model only if the electron spectrum features an extremely small gap, much smaller than the intrinsic \( 2\Delta \sim \sim 19 \meV \) gap of \( \text{SmB}_6 \).

In order to resolve the problem of having an insulating transport behavior with an apparent presence of screened extrinsic magnetic moments in \( \text{SmB}_6 \), we suggest that multiple insulating Kondo channels give rise to the observed thermodynamics. Optical conductivity provides evidence of a density of states that spans the sub-gap range of energies. This has been explored theoretically in the “Kondo hole” picture, when an in-gap impurity band locks the Fermi-level or comes with lower-energy localized magnetic excitations. Micro-gaps \( \Delta_i \) can develop as the impurity bands form and create a new channel for Kondo screening that appears not thermally activated in the specific heat measurements of some samples. In this scenario, the upturn of specific heat is very much like a Schottky anomaly, but controlled by a Kondo effect. Variability in this temperature range of the heat capacity is clearly related to impurities and defects, and previous analysis of heat capacity on other samples has included Schottky anomalies to partially account for the upturn in linear heat capacity. At the same time, magnetization can be contributed both by the impurity and the intrinsic electron-hole channels, since the latter is not thermally activated. Hence, the calculated response functions exhibit all essential features of their measured counterparts in the experiment (see Fig. 1).

FIG. 1. Impurity magnetization of moments with \( 8\mu_B \) at 10 K (e.g. as for \( \text{Gd} \)). The amplitude of the correction is modified by impurity concentration, especially through changes in the gap scale, known to be sensitive to impurities and defects. \( A_{J, \eta} \) encompasses the constant prefactor in Eq. 2. Inset shows that at high fields the full unscreened impurity moment is recovered.

It will become apparent later that the momentum scale \( p \) is related to the gap \( \Delta \), cut-off energy \( W \) and the average density of states \( \rho \) in the electron bands associated...
with a Kondo channel:

\[ p^3 \sim \rho W \left( \frac{\Delta}{W} \right)^3. \]  

(3)

Therefore, if we compute from (2) the ratio of the dominant magnetization correction magnitudes in the intrinsic \((\Delta_0)\) and impurity \((\Delta_i)\) Kondo channels:

\[
\frac{\delta m_i^{(0)}}{\delta m_i^{(1)}} \sim \frac{(J \rho_0)^2/\Delta_0}{J p_i^2} \left( \frac{\beta \Delta_i}{\Delta} \right) \sim \frac{p_0}{p_i} \frac{\Delta_0}{\Delta_i} \frac{W_i}{W_0}^3, \]  

(4)

we can find a natural possibility realized with \(\Delta_0 \gg \Delta_i\) and \(p_0 \gg p_i\), that the quantum contribution of the intrinsic channel is notably larger than the thermal contribution of the impurity channel (even in the perturbative limit \(J \rho_0 W_0/\Delta_0 \ll 1\)). Note that the energy cut-offs \(W\) are limited both by the bandwidths and microscopic properties of the Kondo interaction (e.g. spatial range), so it is not unnatural to have comparable scales \(W_0 \sim \Delta_0\), and even \(W_i \sim W_0\) when impurity levels fill up the gap.

In simple words, the thermodynamic experiment\(^{2}\) may be revealing a thermal correction to specific heat in the impurity Kondo channel and a quantum correction to magnetization in the intrinsic Kondo channel. Both are determined at the second order of perturbation theory and proportional to \(J^2\). This interpretation is of particular importance because the coefficient of the specific heat now matches that of the correction to magnetization, the scaling found empirically in our previous experiment.\(^{6}\)

This is a distinct contrast to the metallic s-d model, where corrections to specific heat are \(\propto (J \eta)^4\) and magnetization corrections are \(\propto J \eta\), with \(\eta\) being the density of states at the Fermi energy. Given that the scaling was consistent over more than two orders of magnitude of impurity concentration, this model represents a substantial improvement over a direct comparison to the metallic Kondo impurity effect for the case of SmB\(_6\).

Moreover, dHvA quantum oscillations in SmB\(_6\) can also be qualitatively explained from the perspective of our model. If the magnetization measured in dHvA experiments comes mostly from the impurity local moments, then it must be sensitively affected, via Kondo coupling, by Landau quantization of the intrinsic insulator’s bands in the applied magnetic field. When magnetic field is gradually varied in an experiment, the amount of Kondo screening, and hence magnetization, oscillates as it follows the oscillatory changes in the bandgap and particle/hole density of states. The strength of Kondo screening is controlled by the independent scale \(J\), which could be relatively large. Most importantly, Kondo screening is a quantum effect even in an insulator – thermal activation is not required as in other prominent interpretations of quantum oscillations.\(^{6,6,7}\)

Note that Sm vacancies can raise the valence of SmB\(_6\) toward the magnetic Sm\(^{3+}\) valence, and thus lead to similar magnetic impurity effects as doped magnetic rare earths.

The rest of the paper presents technical details of theoretical calculations. A detailed description of the model is discussed in section II A, followed by a review of the thermodynamics of decoupled insulating electrons and local moments in section II B. First order perturbative calculations are presented in section II C 1. The second order calculations of magnetization and specific heat are presented in sections II C 2 and II C 3 respectively.

II. PERTURBATION THEORY OF AN INSULATING KONDO IMPURITY MODEL

Here we analyze thermodynamics of an s-d model of Kondo impurities in an insulator, using perturbation theory. We calculate magnetization in an external magnetic field up to saturation, and specific heat in zero field. It turns out that magnetization corrections to the response of isolated local moments are dominated by a quantum process at the second order of perturbation theory in which virtual particle-hole pairs screen the local moments via Kondo coupling. In contrast, the zero-field specific heat is thermally activated but shaped by processes that also start at the second order of perturbation theory. These results provide foundation for the physical picture we build – and conclusion that Kondo-like impurities likely play a major role in the puzzling metallic-looking dynamics of SmB\(_6\).

A. Model

The s-d model we study is given by the Hamiltonian:

\[
H_{sd} = \int \frac{d^d k}{(2\pi)^d} \Psi_k^\dagger h_0 \Psi_k - J \sum_{i=1}^{N_v} \mathbf{S}_i \cdot \mathbf{\Psi}_i^\dagger \frac{1}{2} \sigma \mathbf{\Psi}_i. \]  

(5)

It describes a band insulator of electrons and localized magnetic moments in \(d\) dimensions coupled by the Kondo term \((J)\). We use a simple band-insulator energy spectrum

\[
E_{sk} = \sqrt{\epsilon_k^2 + \Delta^2 - \mu}, \]  

(6)

with a band index \(s = \pm 1\) and bandgap \(2\Delta\), obtained from a non-interacting two-orbital Hamiltonian:

\[
h_0 = \begin{pmatrix}
\epsilon_k - \mu & 0 & \Delta & 0 \\
0 & \epsilon_k - \mu & 0 & \Delta \\
\Delta & 0 & -\epsilon_k - \mu & 0 \\
0 & \Delta & 0 & -\epsilon_k - \mu
\end{pmatrix}. \]  

(7)

This representation is compatible with spinor field operators \(\Psi\) whose components \(\psi_{n,\alpha}\) are labeled by an orbital index \(n \in \{1, 2\}\) and spin \(\alpha\):

\[
\Psi = \begin{pmatrix}
\psi_{1\uparrow} \\
\psi_{1\downarrow} \\
\psi_{2\uparrow} \\
\psi_{2\downarrow}
\end{pmatrix}. \]  

(8)
For simplicity, we work with $\epsilon_k = v |k|$ that makes the momentum dependence $E_{\text{sk}}$ formally relativistic at high energies; this microscopic feature is ultimately collected into a single momentum scale and otherwise not essential for our conclusions.

Local moments sit at randomly scattered positions $r_i$ and have an average concentration $n_i = N_i / V$ in the system of volume $V$. We consider spin $S = \frac{1}{2}$ local moments and represent their spin operators

$$S_{r_i} = z^\dagger_{r_i} \sigma z_{r_i}$$

in terms of two-component field operators $z^\dagger$, $z$ for electrons localized at impurity sites ($\sigma$ is the vector of Pauli matrices). We assume that the moments are too far apart to interact with one another.

We calculate magnetization density $m(h, T)$ and specific heat $c(h, T)$ as functions of the applied magnetic field $h$ and temperature $T$:

$$m = \frac{\partial h}{\partial T} , \quad s = \frac{\partial g}{\partial T} , \quad c = T \frac{\partial s}{\partial T} ,$$

from the free energy density $g$:

$$g = - \frac{k_B T}{V} \log(\Xi) .$$

The partition function $\Xi$ is obtained from the imaginary-time path-integral in grand canonical ensemble, with chemical potentials $\mu$ for mobile electrons and $-i\lambda$ for impurity electrons:

$$\Xi = \int Dz Dz^\dagger D\psi D\psi^\dagger \exp \left\{ - \int_0^\beta \frac{d\tau}{\beta} \right\}$$

$$= \sum_s \int \frac{d^4 k}{(2\pi)^4} \psi^\dagger_{sk} \left( \frac{\partial}{\partial \tau} + E_{\text{sk}} - \mu + h \sigma^z \right) \psi_{sk}$$

$$- J \sum_{s, s'} \sum_{i=1}^{N_i} S_{r_i} \int \frac{d^4 k}{(2\pi)^4} \frac{d^4 k'}{(2\pi)^4} e^{i(k' - k) \cdot r_i} U_{sk, s' k'} \psi^\dagger_{sk} \sigma^z_{sk} \psi_{s' k'}$$

$$+ \sum_i \left( z_i^s \frac{\partial z_i^s}{\partial T} - h z_i^s \sigma^z z_i + i \lambda z_i^s \right) ,$$

where $\beta = (k_B T)^{-1}$ and $k_B$ is Boltzmann constant. For simplicity, we assume that mobile and localized electrons couple the same way to the magnetic field $h$. Representing the Kondo coupling in the band basis, with two-component band spinors $\psi_{sk}$, requires the following vertex function:

$$U_{sk, s' k'} = \frac{\Delta^2 + \left( \sqrt{\epsilon_k^2 + \Delta^2 - \epsilon_k} \right) \left( \sqrt{\epsilon_{k'}^2 + \Delta^2 - \epsilon_{k'}} \right)}{2 \sqrt{\left( \Delta^2 + \epsilon_k^2 - \epsilon_k s' \sqrt{\epsilon_{k'}^2 + \Delta^2} \right) \left( \Delta^2 + \epsilon_{k'}^2 - \epsilon_{k'} s' \sqrt{\epsilon_k^2 + \Delta^2} \right)}} \delta_{ss'}.$$  

**B. Unperturbed free electrons and local moments**

We proceed by calculating $\Xi$ first at the zeroth order of perturbation theory $J = 0$. In this case, $\Xi = \Xi_c \Xi_m$ factorizes into the textbook expressions for the grand canonical partition functions of free “conduction” electrons ($c$) and local moments ($m$):

$$\log(\Xi_c) = V A_d e^{-\Delta} \cosh(\beta \mu) \cosh(\beta h)$$

$$\log(\Xi_m) = N_i \log \left[ 2 \cosh(\beta h) \right] ,$$

where:

$$A_d = 4 S_d \Gamma \left( \frac{d}{2} + 1 \right) (2\beta \Delta)^{d/2} , \quad S_d = \frac{2 \pi^{d/2}}{\Gamma \left( \frac{d}{2} \right)}$$

and $\Gamma$ is Gamma function. Magnetization density $m$ and specific heat $c$ of electrons in a band-insulator are thermally activated:

$$m_c = A_d e^{-\beta \Delta} \cosh(\beta \mu) \sinh(\beta h)$$

$$s_c = k_B A_d e^{-\beta \Delta} (\beta \Delta) \cosh(\beta \mu) \cosh(\beta h)$$

$$c_c = k_B A_d e^{-\beta \Delta} (\beta \Delta)^2 \cosh(\beta \mu) \cosh(\beta h) .$$
Note that \( \mu = 0 \) corresponds to the Fermi energy sitting at the middle of the band-gap, and the field dependence is meaningful only in small fields \( h \ll \Delta \). The contribution of decoupled local moments with concentration \( n_i \) is:

\[
m_m = n_i \tanh(\beta h) \\
c_m = k_B n_i \left( \frac{\beta h}{\cosh^2(\beta h)} \right)
\]

at any temperature and magnetic field. The magnetization of local moments exhibits a linear dependence on small magnetic fields \( \beta h \ll 1 \) and saturates in large magnetic fields \( \beta h \gg 1 \). The same overall behavior of the measured magnetization in doped \( \text{SmB}_6 \), proportional to the doping concentration \( n_i \), provides evidence that the doped impurities carry magnetic moments. However, the isolated magnetic moments have no heat capacity in the absence of magnetic field \( (h = 0) \), which is where an excess specific heat is observed in the experiment. This means that the doped local moments in \( \text{SmB}_6 \) must be coupled to additional degrees of freedom. We discuss this coupling next.

### C. Perturbation theory

The perturbative expansion of the free energy \([11]\) is the sum of connected vacuum Feynman diagrams:

\[
\log(\Xi) = \log(\Xi_c) + \log(\Xi_m) + \sum_{n=1}^{\infty} F_n
\]

where \( \Xi_c \) and \( \Xi_m \) are given by \([14]\) and \( F_n \) is the sum of \( n^{th} \) order diagrams. The bare propagators of conduction electrons and \( D \) of local moments are given by matrices operating in the two-component spinor space:

\[
G(s, k, \omega_n) = \frac{1}{i\omega_n - (E_{sk} - \mu) + i\hbar \sigma_z}
\]

\[
D^{ij}(\Omega_n) = \frac{\delta_{ij}}{i\Omega_n - i\lambda + i\hbar \sigma_z}
\]

\( i, j = 1, \ldots, N_i \) enumerate impurity sites, and \( \omega_n, \Omega_n \) are Fermionic Matsubara frequencies that take values \( \omega_n = (2n + 1)\pi/k_B T \) for integer \( n \). The matrix elements of these propagators, indexed by \( \alpha, \beta = \pm 1 \) spin-projection states along the \( \hat{z} \) axis are:

\[
G_{\alpha\alpha'}(s, k, \omega_n) = \frac{1}{2} \sum_{\sigma = \pm 1} \frac{\delta_{\alpha\alpha'} + \sigma \sigma' \delta_{\alpha\alpha'}}{i\omega_n - (E_{sk} - \mu - i\hbar \sigma)}
\]

\[
D^{ij}_{\beta\beta'}(\Omega_n) = \frac{\delta_{ij}}{2} \sum_{\sigma = \pm 1} \frac{\delta_{\beta\beta'} + \sigma \sigma' \delta_{\beta\beta'}}{i\Omega_n - i\lambda + i\hbar \sigma}.
\]

The bare vertex for the Kondo coupling at \( \omega + \Omega = \omega' + \Omega' \) is:

\[
V_{\alpha\alpha', \beta\beta'}(\omega, s, k; \omega', s', k'; i, \Omega; j, \Omega') =
\]

\[
= -\frac{J}{2\beta} \delta_{ij} e^{i(k-k')r_i} \sigma_{\alpha\alpha'} \sigma_{\beta\beta'} U_{sk, s'k'}
\]

\[
= -\frac{J}{2\beta} \delta_{ij} e^{i(k-k')r_i} (2\delta_{\alpha\beta} \delta_{\alpha\alpha'} - \delta_{\alpha\alpha'} \delta_{\beta\beta'}) U_{sk, s'k'}
\]

with \( U_{sk, s'k'} \) given by \([13]\).

#### 1. First order corrections

The first-order connected vacuum diagram shown in Fig.2(a) is:

\[
F_1 = (-1)^2 \frac{J}{2\beta} (2\delta_{\alpha\beta} \delta_{\beta\alpha'} - \delta_{\alpha\alpha'} \delta_{\beta\beta'})
\]

\[
\times \sum_s \sum_{\omega_n, \Omega_n} \int \frac{d^dk}{(2\pi)^d} G_{\alpha\alpha'}(s, k, \omega_n) D^{ii}_{\beta\beta'}(\Omega_n) U_{sk, s'k'}
\]

Since the electron propagator makes a tadpole loop at the vertex, momentum and band conservation reduces the vertex function \([13]\) to the trivial form \( U_{sk, s'k'} \rightarrow 1 \). The tadpole represents an intra-band process that must be thermally activated because a fully occupied or empty band at zero temperature cannot exhibit spin fluctuations needed for the Kondo interaction. We use the following identities to calculate the sums over repeated spin indices:

\[
\delta_{\alpha\alpha'}(2\delta_{\alpha\beta} \delta_{\beta\alpha'} - \delta_{\alpha\alpha'} \delta_{\beta\beta'}) = 0
\]

\[
\sigma_{\alpha\alpha'}^z(2\delta_{\alpha\beta} \delta_{\beta\alpha'} - \delta_{\alpha\alpha'} \delta_{\beta\beta'}) = 2\sigma_{\alpha\alpha'}^z
\]

\[
\sigma_{\alpha\alpha'}^z(2\delta_{\alpha\beta} \delta_{\beta\alpha'} - \delta_{\alpha\alpha'} \delta_{\beta\beta'}) = 2\sigma_{\alpha\alpha'}^z + 4
\]

The first identity together with \([20]\) implies that any diagram with a tadpole vanishes in zero field. Substituting these identities and \([20]\) in \([22]\) gives us:

\[
F_1 = \frac{J n_i V}{2} \sum_{\sigma, \sigma' = \pm 1} \sum_s \int \frac{d^dk}{(2\pi)^d} \frac{\sigma}{\sigma'}
\]

\[
\times \sum_{\omega_n, \Omega_n} \frac{i\omega_n - (E_{sk} - \mu - i\hbar) i\Omega_n - i\lambda + i\hbar \sigma}{i\Omega_n - i\lambda + i\hbar \sigma'}.
\]

The summation over Matsubara frequencies is carried out by the standard procedure. After a few straight-forward steps we arrive at:

\[
F_1 = \frac{J n_i V}{2} \frac{1}{1 - \tanh^2(\frac{\beta \mu}{2})} \frac{1}{1 - \tanh^2(\frac{\beta \lambda}{2})} \frac{1 - \tanh^2(\frac{\beta h}{2})}{1 - \tanh^2(\frac{\beta h}{2})} \frac{1}{1 - \tanh^2(\frac{\beta h}{2})}
\]

\[
\times \sum_s \int \frac{d^dk}{(2\pi)^d} \frac{1}{1 - \tanh^2(\frac{s\beta \sqrt{\nu^2 + \Delta^2} - \beta \mu}{2})} \frac{1}{1 - \tanh^2(\frac{s\beta \sqrt{\nu^2 + \Delta^2} - \beta \mu}{2})} \frac{1}{1 - \tanh^2(\frac{s\beta \sqrt{\nu^2 + \Delta^2} - \beta \mu}{2})}.
\]
Using $\epsilon_k = v k$ allows us to easily introduce a dimensionless energy $\xi = \beta \sqrt{\epsilon_k^2 + \Delta^2}$ and rewrite momentum integrals as:

$$
\int \frac{d^d k}{(2\pi)^d} = \frac{S_d}{(2\pi \beta v)^d} \int_0^\infty \frac{d \xi}{\beta \Delta} \left[ \xi^2 - (\beta \Delta)^2 \right]^{d/2 - 1}. \tag{25}
$$

After some trigonometric simplifications we arrive at:

$$
F_1 = \frac{J \beta n_i V}{2} \left( \frac{S_d}{(2\pi \beta v)^d} \frac{\sin^2(\beta h)}{\cosh(\beta h) + \cosh(\beta i \lambda)} \right) \times \sum \frac{d \xi}{\beta \Delta} \left[ \xi^2 - (\beta \Delta)^2 \right]^{d/2 - 1}
\times \frac{J n_i V}{2} \frac{\sin^2(\beta h)}{\cosh(\beta h) + \cosh(\beta i \lambda)}.
\tag{26}
$$

A thermally activated quantity:

$$
\eta = \frac{S_d \Gamma}{(2\pi \beta v)^d} \left( \frac{2(\beta \Delta)^{d/2}}{\sinh(\beta h) + \tanh(\beta h)} \right) \times 2 \beta e^{-\beta \Delta} \cosh(\beta \mu), \tag{27}
$$

with the units of a density of states plays the same role as the density of states at the Fermi energy in a Kondo metal.

Finally, we substitute the Popov-Fedotov chemical potential $\lambda = i\pi/2 \beta$ for localized electrons and obtain from (10) and (11) the first order corrections to (17):

$$
\delta g = -n_i k_B T J n_i \sinh(\beta h) \tanh(\beta h), \quad \delta m = n_i J n_i \left[ \sinh(\beta h) + \frac{\tanh(\beta h)}{\cosh(\beta h)} \right]. \tag{28}
$$

in the limit $\beta \Delta \gg 1$, $\Delta \gg |h|, |\mu|$. We see that the Kondo correction to the response of free moments is exponentially sensitive to small magnetic fields, but still thermally activated until the extreme limit $|h| \sim \Delta$.

A decent approximation for $\delta m$ in the $\beta \Delta \ll 1$ limit is given by the above formula with a modified parameter:

$$
\eta \approx \frac{(\Delta/\beta v)^d}{2 \pi v} \frac{S_d C (\beta \Delta)^{-d}}{\cosh(c \beta \Delta)}. \tag{29}
$$

The “constants” $C$ and $c$ can be determined by a numerical fit to the exact integral in (26) at small fields.

Kondo screening reduces the intrinsic magnetization of free moments in the case of antiferromagnetic coupling $J < 0$, since thermally generated particles and holes try to form spin singlets with local moments. This happens in a linear fashion at small fields, i.e. through a renormalization of the impurity magnetic moment. At zero temperature, the Kondo correction to magnetization stays strictly zero until $|h| \gtrsim \Delta$, when it suddenly jumps. Note that free moments at zero temperature immediately saturate in any Zeeman field, and this behavior is not disturbed by the Kondo effect in an insulator.

Specific heat vanishes in zero field at this order of perturbation theory because $\delta g = 0$ at $h = 0$. We will find a finite thermally activated correction to specific heat only at the second order, where magnetization also acquires its dominant non-activated quantum correction.

Another form of the above result:

$$
\delta m = \text{const} \times n_i \beta J \left( \frac{mv}{2\pi} \right)^d \left[ \frac{\sinh(\beta h) + \tanh(\beta h)}{\cosh(\beta h)} \right] \tag{30}
$$

provides a more transparent comparison to the second-order quantum correction that was discussed in the introduction; $m = \Delta/v^2$ is the effective mass of low-energy quasiparticles and holes, and $p = mv/2\pi$ is a microscopic energy scale that converts the raw Kondo coupling $J$ to an energy scale $j = J p^d$. It is not hard to see by dimensional analysis that the temperature and field dependence of thermodynamic functions are not qualitatively affected by the precise electron dispersion $\epsilon_k$, even in the presence of a spin-orbit coupling. Such details of the electron spectrum can be collected into dimensionless numerical factors and a momentum scale $p$. Using the present model, we can relate $p$ to more objective characteristics of the spectrum:

$$
p^d \sim \left( \frac{\Delta}{v} \right)^d = \left( \frac{\Delta}{W} \right)^d \left( \frac{W}{v} \right)^d = \rho W \left( \frac{\Delta}{W} \right)^d \tag{31}
$$

such as an energy cut-off $W$ and the average density of electron states $\rho$ that can contribute to Kondo screening (note that $\Lambda \sim W/v$ is a cut-off momentum in the present model, so that $\rho \sim W^{-1} A^d$).

2. Second order corrections: magnetization

Here we calculate magnetization of a Kondo insulator at the second order of perturbation theory. In contrast to the case of a Kondo metal, the dominant part of magnetization in a Kondo insulator appears only at this order – it originates from virtual particle-hole excitations generated by the Kondo coupling even at $T = 0$. Specific heat, however, must remain thermally activated as long as Kramers degeneracy (of local moments) is not lifted or the gap closed.

There are three second order connected vacuum diagrams that appear in the free energy expansion, shown in Fig. 2(b)-(d). The diagrams (b) and (c), which contain tadpoles, vanish in zero magnetic field and otherwise are thermally activated. We will thus start with the most important diagram (d), which is thermally activated in
zero field, and finite at $T = 0$ when $h \neq 0$:

$$F_{2d} = \frac{(-1)^2}{2} \left( \frac{J}{2\beta} \right)^2 \sum \sum \sum \sum \int \frac{d^d k}{(2\pi)^d} \frac{d^d k'}{(2\pi)^d}$$

$$\times e^{i(k-k')(\tau_n-\tau'_n)} U_{sk,s'k'} U_{sk',sk}$$

$$\times (2\delta_{\alpha_1' \beta_1'} \delta_{\beta_1' \alpha_1} - \delta_{\alpha_1 \alpha_1'} \delta_{\beta_1 \beta_1'}) (2\delta_{\alpha_2 \beta_2'} \delta_{\beta_2' \alpha_2} - \delta_{\alpha_2 \alpha_2'} \delta_{\beta_2 \beta_2'})$$

$$\times \sum_{\alpha_3 \beta_3} \delta G_{\alpha_3 \beta_3} (s,k,\omega_n) G_{\alpha_3 \beta_3} (s',k',\omega_n')$$

$$\times D_{\beta_1 \beta_2} (\Omega_n) D_{\beta_1' \beta_2'} (\Omega_n + \omega_n - \omega_n').$$ (32)

The Green’s functions of mobile and localized electrons are given by [20]. The Kronecker symbol $\delta_{\alpha \beta}$ and the Pauli matrix $\sigma_{\alpha \beta}$ in these formulas contract differently their spin indices with the vertices, so we need the means to manage all the terms generated by contractions. To that end, we introduce four new summation variables $\tau_n = \pm 1$ to represent the numerators of the four Green’s functions in $F_{2d}$:

$$\delta_{\alpha \alpha'} + \sigma_{\alpha \alpha'} \sigma = \sum_{\tau_n = \pm 1} \left[ \frac{1 + \tau_n}{2} \delta_{\alpha \alpha'} + \frac{1 - \tau_n}{2} \sigma_{\alpha \alpha'} \right]$$

in the order $n = 1, 2, 3, 4$ of their appearance in (32). The contraction of spin indices reduces to the following factor that depends on $\tau_n$:

$$S(\tau_n) = \frac{1}{2} \left( 1 + \prod \tau_n \right) \left[ \begin{array}{c} 2 + 3 \tau_n - 3 \tau_n - 3 \tau_n + 3 \tau_n \\ 2 \tau_n - 2 \tau_n - 2 \tau_n + 2 \tau_n \end{array} \right],$$ (33)

and we have:

$$F_{2d} = \frac{n_i V}{512} \left( \frac{J}{2\beta} \right)^2 \sum_{\tau_n \sigma_n} \sum_{\omega_n \omega'_n} \sum_{\Omega_n \Omega'_n} \int \frac{d^d k}{(2\pi)^d} \frac{d^d k'}{(2\pi)^d}$$

$$\times \sum_{\Omega_n \Omega'_n} i \omega_n - (E_{sk} - \mu - \sigma_1 h) i \omega_n' - (E_{sk'} - \mu - \sigma_2 h)$$

$$\times \sum_{\Omega_n \Omega'_n} i \Omega_n - i \lambda + \sigma_3 h i \Omega_n' - i \lambda + \sigma_4 h$$

$$\times \left( U_{sk,s'k'} \right)^2.$$ (34)

The impurity site $(i, j)$ summation is reduced to the number $N_i = n_i V$ of impurity sites in the volume $V$, and we applied $U_{sk,s'k'} = U_{sk',sk}$ according to [13]. This expression is ready for the lengthy but straight-forward summation over Matsubara frequencies:

$$\sum_{\omega_n \omega'_n} \sum_{\Omega_n} \sum_{\Omega'_n} \frac{1}{i \omega_n - (E_{sk} - \mu - \sigma_1 h) i \omega_n' - (E_{sk'} - \mu - \sigma_2 h)}$$

$$\times \frac{1}{i \Omega_n - i \lambda + \sigma_3 h i \Omega_n' - i \lambda + \sigma_4 h}$$

$$= \beta^3 \left\{ K_1 + K_2 \right\},$$ (35)

with:

$$K_1 = \frac{2 \cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}{\cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)} - \frac{2 \cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}{\cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}$$

$$\times \frac{2 \cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}{\cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}$$

$$\times \frac{2 \cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}{\cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)} - \frac{2 \cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}{\cosh \left( \frac{\beta (\sigma_3 - \sigma_4) h}{2} \right)}$$

$$\times M_{1/2} \left( \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 \right) \frac{h}{2\Delta} W$$

$$+ O(\varepsilon) .$$
Putting everything together into (34) and writing compactly \( \chi = (\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)h/2\Delta \), we obtain:

\[
F_{2d} = \frac{n_V \beta^4}{512} \left( \frac{J}{2\beta} \right)^2 \sum_{\tau_n} S(\tau_n) \Pi_n [1 + \sigma_n + (1 - \sigma_n)\tau_n] \\
\times \frac{S^2_2}{\beta \Delta} \left( \frac{mv}{2\pi} \right)^{2d} \left[ -\frac{\sinh(\beta h) M_2 (\chi, \frac{W}{\Delta})}{\cosh(\beta h)} \right] \\
+ \frac{2 \cosh \left( \frac{\beta(\tau_n - \tau_h)h}{2} \right) M_1 (\chi, \frac{W}{\Delta})}{\cosh \left( \frac{\beta(\tau_n + \tau_h)h}{2} \right) + \cosh \left( \frac{\beta(\tau_n - \tau_h)h}{2} \right)} + \cdots
\]

up to the thermally activated terms (\cdots). Finally, we sum over \( \sigma_n \) and \( \tau_n \) to obtain a relatively simple expression:

\[
F_{2d} = n_V \beta J^2 \left( \frac{mv}{2\pi} \right)^{2d} S^2_2 M_1 (0, \frac{W}{\Delta}) \times 2 + 3 \cosh(\beta h) \cosh(2\beta h) \left[ \cosh(\beta h) \right]^2 + O(e^{-\beta\Delta})
\]

We have introduced the effective mass \( m = \Delta/v^2 \) of particles and holes, and grouped various factors by meaning. The essential factor that reveals the nature of the second-order perturbative process is \( \beta(j^2/\Delta) \), where \( j = J/p^d \) is the energy gain of the Kondo coupling between a local moment and a virtual particle-hole pair that intrinsically costs energy \( \Delta \). The residual factor of \( \beta \) is eliminated in the free energy density \( q = g_0 - (k_B T/V) F_2 \), so the obtained second-order correction is purely a quantum-mechanical shift of the ground state energy. Thermally generated and activated terms have been neglected here.

The exact dependence of \( F_2 \) on the cut-off scales in \( M_1 \) is tied to the high-energy dispersion of electrons and holes. Using a more realistic non-relativistic dispersion \( e_k \) only changes the definition of the momentum scale \( p \) that shapes the effective Kondo energy scale \( j = J/p^d \).

The full free energy is contributed also by the dia-grams in Fig.2(b,c). With the gained insight, we can easily rule out the diagram (b) as an important contrib-utor because its mobile electron tadpole loops describe only intra-band virtual processes that must be thermally activated or vanish in the absence of magnetic field. In contrast, the diagram (c) contains a particle-hole bubble, which describes inter-band virtual processes. Since particle-hole pairs can be generated by the Kondo inter-acation even at zero temperature, we ought to explicitly calculate this diagram. We know only that this diagram vanishes in zero field due to its tadpoles. The initial for-mula for the diagram (c) is:

\[
F_{2c} = \frac{(-1)^3}{2} \sum_{ij} \sum_{\Omega_n \Omega'_n \omega_n \omega'_{n'}} \int \frac{d^d k}{(2\pi)^d} \frac{d^d k'}{(2\pi)^d} \\
\times e^{i(k-k')(r_i-r_j)} U^*_{s_k,s'_k} U_{s'_k,s_k} \\
\times (2\delta_{\alpha_i,\alpha'_j} - \delta_{\alpha_i,\alpha'_j})(2\delta_{\beta_i,\beta'_j} - \delta_{\beta_i,\beta'_j}) \\
\times G_{\alpha_i\alpha'_j}(s_k, \omega_n) G_{\alpha_i\alpha'_j}(s'_k, \omega_n) \\
\times D_{\beta_i\beta'_j}(\Omega_n) D_{\beta_i\beta'_j}(\Omega'_n).
\]

We will first contract all spin indices. After some manipulations, we arrive at:

\[
F_{2c} = \frac{1}{2} \sum_{ij} \sum_{\omega_n \omega'_{n'}} \int \frac{d^d k}{(2\pi)^d} \frac{d^d k'}{(2\pi)^d} \\
\times e^{i(k-k')(r_i-r_j)} U^*_{s_k,s'_k} U_{s'_k,s_k} \\
\times \frac{1}{(\mu - h\sigma)} \int \frac{d^d k'}{(2\pi)^d} \\
\times \sum_{\Omega_n \sigma = \pm 1} \frac{\sigma}{i\Omega_n - i\lambda + h\sigma} \right)^2.
\]

Summing up Matsubara frequencies yields:

\[
F_{2c} = \frac{J}{2\beta} \sum_{ss'} \int \frac{d^d k}{(2\pi)^d} \frac{d^d k'}{(2\pi)^d} \\
\times \frac{2 \cosh(\beta h)}{\cosh(\beta h)} \\
\times \frac{2 \sinh(\beta h)}{\cosh(\beta h)} \\
\times \frac{2 \sinh(\beta h)}{\cosh(\beta h)} \\
\times \frac{2 \sinh(\beta h)}{\cosh(\beta h)} \\
\times \frac{\sinh(\beta h)}{\cosh(\beta h)}
\]

This diagram involves a non-trivial summation over the impurity positions \( r_i \). Diagrams of this kind can generate RKKY-type interactions between proximate local moments. The summation over \( r_i \) and \( r_j \) is equivalent to the summation over \( \delta r = (r_i + r_j) \) and \( \delta r = r_i - r_j \). In a particular realiza-tion of impurity disorder, the impurity sites \( r_i \) are randomly scattered with some average spatial separation \( a \). However, the distribution of \( \delta r \) is expected
to significantly and broadly extend below $|\delta r| < a$ because there are many neighboring impurities separated by arbitrarily short distances on the scale of the entire sample. Assuming that impurity locations are not mutually correlated, the translationally invariant distribution of $\delta r$ allows us to treat it as a continuous uniform random variable (it gets averaged over the entire system volume). Therefore, we may approximate:

$$\sum_{ij} e^{i(\mathbf{k} - \mathbf{k}')(r_i - r_j)} \approx \sum_{r} \frac{1}{a^d} \int d^d \delta \mathbf{r} e^{i(\mathbf{k} - \mathbf{k}') \delta \mathbf{r}}$$

(47)

$$= \frac{N_i}{a^d} (2\pi)^d \delta(\mathbf{k} - \mathbf{k}') = \frac{n_i V}{a^d} (2\pi)^d \delta(\mathbf{k} - \mathbf{k}')$$

$$= n_i^2 V \times (2\pi)^d \delta(\mathbf{k} - \mathbf{k}')$$

where $N_i = n_i V \sim V/a^d$ is the total number of impurities.

Once $\mathbf{k}'$ becomes equal to $\mathbf{k}$, the vertex function $U_{sk, s'k'} \rightarrow \delta s s'$ becomes trivial and forces the two electron propagators to carry the same band index. However, we must take the limit $\mathbf{k}' \rightarrow \mathbf{k}$ and $s' = s$ carefully because the integrand of (46) becomes singular:

$$\lim_{\mathbf{k}' \rightarrow \mathbf{k}} \frac{2 \sinh(\beta(E_{sk} - \mu))}{\cosh(\beta(E_{sk} - \mu)) + \cosh(\beta \Delta)} \frac{2 \sinh(\beta(E_{s'k'} - \mu))}{\cosh(\beta(E_{s'k'} - \mu)) + \cosh(\beta \Delta)}$$

$$= \frac{2 \beta}{|\cosh(\beta(E_{sk} - \mu)) + \cosh(\beta \Delta)|^2} \left(1 + \cosh(\beta(E_{sk} - \mu)) \cosh(\beta \Delta)\right)^2$$

(48)

Resolving the singularity this way and then integrating disorder is physically motivated because the distribution of $\delta r$ is infra-red cut off by the system size, just like the quantized values of momentum $\mathbf{k}$. We should obtain some thermodynamic effect from very small $|\mathbf{k}' - \mathbf{k}|$, as captured here. We now have:

$$F_{2c} = \frac{n_i^2 V^3}{8} \left(\frac{J}{2\beta}\right)^2 \left[\frac{2 \sinh(\beta \Delta)}{\cosh(\beta \Delta)}\right]^2$$

$$\times \sum_s \int \frac{d^d k}{(2\pi)^d} \frac{1 + \cosh(\beta(E_{sk} - \mu)) \cosh(\beta \Delta)}{|\cosh(\beta(E_{sk} - \mu)) + \cosh(\beta \Delta)|^2}$$

$$= \mathcal{O}(e^{-\beta \Delta})$$

(49)

There is no need to calculate any further because this diagram is clearly thermally activated: $\beta |E_{sk}| \geq \beta \Delta \gg 1$ makes the denominator with $\cosh(\beta(E_{sk} - \mu))$ exponentially large at any magnetic field $|h| \ll \Delta$. Also, physically, no particle-hole processes remain after impurity-position summation.

In conclusion, we have now established that quantum contributions to free energy up to the second order of perturbation theory come only from (43). Using Popov-Fedotov chemical potential $i \lambda = i\pi/2\beta$ and (10), (11) we find the following second order corrections:

$$\delta g = -n_i k_B T_0 \left[2 + \frac{1}{\cosh^2(\beta h)}\right] + \mathcal{O}(e^{-\beta \Delta})$$

$$\delta m = -2n_i T_0 \frac{\tanh(\beta h)}{\cosh^2(\beta h)} + \mathcal{O}(e^{-\beta \Delta}),$$

(50)

where we defined a temperature scale $T_0$ by:

$$k_B T_0 = S_d^2 M_1 \left(\frac{W}{\Delta}\right) \times \frac{J}{(2\pi)^d} \frac{4m_v}{2\pi}.$$  

(51)

The intrinsic magnetization of local moments is linearly suppressed at small fields by Kondo screening that involves quantum fluctuations of virtual particle-hole pairs. However, this correction fades away at large fields $h > k_B T$ in a thermally activated fashion. Similarly, $\delta m$ fades away both in the limits of zero and infinite temperature when $h$ is kept fixed.

3. Second order corrections: specific heat in zero field

The quantum correction to free energy $\delta g$ in (50) loses temperature dependence in zero field and hence does not provide a correction to specific heat. We must examine the thermally activated terms $\mathcal{O}(e^{-\beta \Delta})$ in order to find a second order correction to specific heat. To that end, we go back to the diagram in Fig. 2(d) and specialize to the case $h = 0$. The other two second-order diagrams have tadpoles and vanish in zero field.

The calculation in $h = 0$ is considerably simpler because the Green’s functions (20) reduce to:

$$G_{\alpha \alpha'}(s, \mathbf{k}, \omega_n) = \frac{\delta_{\alpha \alpha'}}{i\omega_n - (E_{sk} - \mu)}$$

$$D^{ij}_{\delta \beta}(\Omega_n) = \frac{\delta_{\delta \beta} \delta_{ij}}{i\Omega_n - i\lambda}.$$  

(52)

Substituting in (22) and using the first spin-index identity of (23) quickly gives us:

$$F_{2d} = \frac{3}{2} \left(\frac{J}{\beta}\right)^2 n_i V \sum_{\omega_s, \omega_n} \sum_{s, s'} \int \frac{d^d k}{(2\pi)^d} \frac{d^d k'}{(2\pi)^d}$$

$$\times U_{sk, s'k'} U_{s'k', sk} \frac{1}{i\omega_n - (E_{sk} - \mu)} \frac{1}{i\omega_n - (E_{s'k'} - \mu)}$$

$$\times \frac{1}{i(\Omega_n - \lambda)} \frac{1}{i(\Omega_n + \omega_n - \omega_n') - \lambda}.$$  

(53)

Summing up the Matsubara frequencies results with an expression analogous to (35) and (36):

$$F_{2d} = \frac{3}{16} \frac{\beta J^2 n_i V}{\cosh^2(\frac{\beta \Delta}{2})} \sum_{s, s'} \int \frac{d^d k}{(2\pi)^d} \frac{d^d k'}{(2\pi)^d} \left(U_{sk, s'k'} \right)^2 K_1$$

(54)

with:

$$K_1 = \frac{\tanh(\frac{\beta(E_{sk} - \mu)}{2}) - \tanh(\frac{\beta(E_{sk} - \mu)}{2})}{E_{sk} - E_{s'k'}}.$$  

(55)
where \( \xi = \beta \sqrt{\epsilon^2 + \Delta^2} \) and \( \xi' = \beta \sqrt{\epsilon^2 + \Delta^2} \). From this point on, we will separately consider the low-temperature \( \beta \Delta \gg 1 \) and high-temperature \( \beta \Delta \ll 1 \) limits – both are accessible in perturbation theory when the energy scale \( J^2(mv/2\pi)^2\beta/\Delta \) is small enough.

In the low-temperature regime, we can approximate \( \sinh(\xi) \approx \cosh(\xi) \approx \frac{1}{2} \xi^2 \) because \( \xi > \beta \Delta \gg 1 \). This leads to:

\[
Q_1 = Q_1^{(0)} - 4 \cosh(\beta \mu) \left[ u^2 e^{-\xi} - e^{-\xi'} \right]
+ (1 - u^2) \frac{e^{-\xi} + e^{-\xi'}}{\xi + \xi'} + O(e^{-2\beta \Delta}) ,
\]

where \( Q_1^{(0)} \) is the non-thermally activated part that we dealt with in section 11C.2. Substituting in (54) yields:

\[
F_{2d} = F_{2d}^{(0)} + \frac{n_i V}{\cosh^2 \left( \frac{\beta \lambda}{2} \right)} \frac{\beta J^2}{\Delta} \left( \frac{mv}{2\pi} \right)^2 e^{-\beta \Delta} \cosh(\beta \mu) \\
\times M' \left( \frac{W}{\Delta}, \beta \Delta \right) + O(e^{-2\beta \Delta}) ,
\]

where:

\[
M' (w, \beta \Delta) = \frac{3S^2}{2} \int_0^w dx \int_0^x dy \left( (x+1)^2 - y^2 \right) \left( x + y(x + y + 2) \right)^{\frac{3}{2} - 1} \left( (x+y)(x+y+2) \right)^{\frac{3}{2} - 1} \times e^{-\beta \Delta x} \left[ u^2 \sinh(\beta \Delta y) \right] \left( 1 - u^2 \right) \cosh(\beta \Delta y) \frac{y}{x+1} + 2 \left( 1 - u^2 \right) \frac{\tanh \left( \frac{\xi}{2} \right) - \tanh \left( \frac{\xi'}{2} \right)}{\xi - \xi'}
+ 2 \left( 1 - u^2 \right) \frac{\tanh \left( \frac{\xi}{2} \right) + \tanh \left( \frac{\xi'}{2} \right)}{\xi + \xi'}
= 1 - \frac{(\beta \Delta)^2}{12} \left[ (x+1)^2(2u^2+1) + y^2(3-2u^2) \right] + \cdots
\]

The remaining integration over \( x \) is temperature-independent, so we conclude:

\[
F_{2d} \approx F_{2d}^{(0)} + \frac{n_i V}{\cosh^2 \left( \frac{\beta \lambda}{2} \right)} \frac{\beta J^2}{\Delta} \left( \frac{mv}{2\pi} \right)^2 e^{-\beta \Delta} \cosh(\beta \mu) e^{-\beta \Delta} + O(e^{2\beta \Delta}) ,
\]

where \( C \) is a constant and \( T_0 \) is a Kondo temperature scale introduced in (51). It follows that (\( \lambda = i\pi/2\beta \)):

\[
\delta y = \delta y^{(0)} - 2Cn_i k_B T_0 \cosh(\beta \mu) e^{-\beta \Delta} + O(e^{2\beta \Delta})
\]

\[
\delta c = 2Cn_i k_B \frac{k_B T_0}{\Delta} \cosh(\beta \mu) (\beta \Delta)^{-\frac{3}{2}} e^{-\beta \Delta} + O(e^{2\beta \Delta})
\]

in the low-temperature \( \beta \Delta \gg 1 \) limit.

Next, we analyze the high-temperature limit. For simplicity, we will take \( \cosh(\beta \mu) \approx 1 \) and then expand (56) in powers of \( \beta \Delta \ll 1 \):

\[
Q_1 \approx 2u^2 \left[ \tanh \left( \frac{\xi}{2} \right) - \tanh \left( \frac{\xi'}{2} \right) \right]
+ 2 \left( 1 - u^2 \right) \left[ \tanh \left( \frac{\xi}{2} \right) + \tanh \left( \frac{\xi'}{2} \right) \right]
= 1 - \frac{(\beta \Delta)^2}{12} \left[ (x+1)^2(2u^2+1) + y^2(3-2u^2) \right] + \cdots
\]

Since \( x \) is integrated out up to \( w = W/\Delta \), where \( W \) is the bandwidth, this expansion is actually in powers of \( \beta W \) – which we assume to be small. The ensuing condition \( T \gg \Delta \) is the only path available in the present insulating model toward a specific heat that exhibits a Schottky-like upturn when temperature is reduced over a certain range, as seen in the experiments on SmB\(_6\). This forces us to interpret carefully the meaning of the gap \( \Delta \), given that the upturn is seen down to millikelvin temperatures. An interpretation of our results and experiments is discussed in the introduction; here, we simply finish presenting the derivations. Substituting \( Q_1 \) into \( F_{2d} \) yields:

\[
F_{2d} \approx \frac{n_i V}{\cosh^2 \left( \frac{\beta \lambda}{2} \right)} \left[ C_1 - C_2(\beta \Delta)^2 + \cdots \right] ,
\]
and then \((i\lambda = i\pi/2\beta)\):
\[
\delta g \approx -2n_i \beta \Delta k_BT_0 \left[ C_1 - C_2(\beta \Delta)^2 + \cdots \right]
\]
\[
\delta c \approx 4n_i k_BT_0 \left[ C_1 - 6C_2(\beta \Delta)^2 + \cdots \right].
\]

The constants \(C_1 > 0\) and \(C_2\) depend on \(W/\Delta\). We see that \(\delta c \propto T^{-2} \rightarrow 0\) in the high-temperature limit. Therefore, \(\delta c(T)\) must have a peak at intermediate temperatures, in a manner analogous to Schottky anomaly – but here generated via the Kondo coupling \((T_0 \propto J^2)\).

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