Gap-Anisotropic Model for the Narrow-Gap Kondo Insulators

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A theory is presented which accounts for the dynamical generation of a hybridization gap with nodes in the Kondo insulating materials CeNiSn and CeRhSb. We show that Hund's interactions acting on virtual $4f^2$ configurations of the cerium ion can act to dynamically select the shape of the cerium ion by generating a Weiss field which couples to the shape of the ion. In low symmetry crystals where the external crystal fields are negligible, this process selects a nodal Kondo semimetal state as the lowest energy configuration.

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Kondo insulators share in common with the Mott insulators a gap which is driven by interaction effects [1,2]. Unlike Mott insulators, they undergo a smooth cross-over into the insulating state, where a tiny charge and spin gap develops. These materials are generally regarded as a special class of a heavy fermion system, where a lattice Kondo effect between the localized spins and conduction electrons forms a highly renormalized band-insulator [3,4].

The smallest gap Kondo insulators, CeNiSn and CeRhSb, do not naturally fit into this scheme: they appear to develop gapless excitations. Early measurements showed a drastic increase of the electrical resistivity below 6 K [5], but very pure samples of CeNiSn display metallic behavior [6]. NMR measurements are consistent with an electronic state with a "V-shaped" component to the density of states [7]. These results, together with other transport properties [8–11] point to the formation of a new type of semimetal with an anisotropic hybridization gap.

Ikeda and Miyake (IM) [12] recently proposed that the Kondo insulating ground state of these materials develops in a crystal field state with an axially symmetric hybridization potential that vanishes along a single crystal axis. This picture accounts for the V-shaped density of states, and provides an appealing way to understand the anisotropic transport at low temperatures, but it leaves a number of puzzling questions. In CeNiSn and CeRhSb, the cerium ions are located at sites of minimal monoclinic symmetry, where the low-lying f state is a Kramers doublet

$$|\pm\rangle = b_1|\pm 1/2\rangle + b_2|\pm 5/2\rangle + b_3|\mp 3/2\rangle, \quad (1)$$

where $\hat{b} = (b_1, b_2, b_3)$ could point anywhere on the unit sphere, depending on the details of the monoclinic crystal field. The IM model corresponds to three symmetry-related points in the space of crystal field ground states,

$$\hat{b} = \begin{cases} (\mp\frac{\sqrt{2}}{4}, -\frac{\sqrt{5}}{4}, \frac{3}{4}) \\ (0, 0, 1) \end{cases}, \quad (2)$$

where a node develops along the x, y, or z axis respectively. What mechanism selects this special semimetal out of the manifold of gapped Kondo insulators? Neutron scattering results show no crystal field satellites in the dynamical spin susceptibility of CeNiSn [13], suggesting that the crystal electric fields are quenched: is the selection of the nodal semimetal then a many body effect [14]?

In this Letter, we propose that this selection mechanism is driven by Hund's interactions among f electrons in the cerium ions. Hund's interactions play an important role in multi-f-electron ions [15]. In the Kondo semimetal, the cerium ions are in a nominal $4f^1$ state, but undergo valence fluctuations into f^0 and f^2 configurations. We show that the memory effect of the Hund's interactions in the f^2-state induces a kind of Weiss field which couples to the shape of the cerium ion. When this field adjusts to minimize the Hund's interaction energy, the nodal IM state is selected.

To develop our model, we classify each single-particle f configuration by a "shape" ($a = 1, 2, 3$) and a pseudospin quantum number ($\alpha = \pm 1$), where

$$\begin{aligned} f^\dagger_{1\pm}|0\rangle &\equiv |\pm 1/2\rangle, \\ f^\dagger_{2\pm}|0\rangle &\equiv |\pm 5/2\rangle, \\ f^\dagger_{3\pm}|0\rangle &\equiv |\mp 3/2\rangle. \end{aligned} \quad (3)$$

There are eight multipole operators,

$$[\mathbf{\Gamma}]^a = f^\dagger_{b\sigma}\Lambda^a_{b,c}f_{c\sigma}, \qquad (a = 1, 8), \quad (4)$$

which describe the shape of the cerium ion, where the Λ^a matrices are the eight traceless SU(3) generators, normalized so that $\mathrm{Tr}[\Lambda^a\Lambda^b] = \delta^{ab}$. We shall describe the low energy physics by an Anderson model $H = H_o + H_f$, where

$$H_o = H_c + \sum_{ja\sigma} V[c^\dagger_{a\sigma}(j)f_{a\sigma}(j) + \mathrm{H.c}], \quad (4)$$

and $H_c = \sum_{\mathbf{k}\sigma}\epsilon_{\mathbf{k}}c^\dagger_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}$ describes a spin-1/2 conduction band hybridized with a lattice of localized f-states. The operator

$$c^\dagger_{a\alpha}(j) = (N_s)^{-\frac{1}{2}}\sum_{\mathbf{k},\boldsymbol{\sigma}} e^{-i\mathbf{k}\cdot\mathbf{R}_j}\mathcal{Y}^\sigma_{a\alpha}(\hat{\mathbf{k}})c^\dagger_{\mathbf{k}\boldsymbol{\sigma}} \quad (6)$$

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creates a conduction electron in a $l = 3$, $j = 5/2$ Wannier state at site j with shape-spin quantum numbers (a, σ), N_s is the number of sites, and

$$\mathcal{Y}^{\sigma}_{a\alpha}(\hat{\mathbf{k}}) = Y_3^{m_J-\sigma}(\hat{\mathbf{k}})\,(\tfrac{1}{2}\sigma, 3m_J - \sigma \,|\, \tfrac{5}{2}m_J)$$

defines the form factors, in terms of spherical harmonics and the Clebsh-Gordon coefficients of the $j = 5/2$ f^1-state [16], where $m_J \equiv m_J(a, \alpha)$ maps the spin-shape quantum numbers to original azimuthal quantum number of the f-scattering channel. Following previous authors [17], we regard H as a low energy Hamiltonian, so that hybridization strength V is a renormalized quantity, that takes into account the high energy valence and spin fluctuations.

The term

$$H_f = \sum_j \left\{ E_f n_f(j) + \frac{U}{2}[n_f(j) - 1]^2 - \frac{g}{2}\mathbf{\Gamma}_j^2 \right\} \quad (8)$$

describes the residual low-energy interactions among the f electrons: the second term is a Coulomb interaction term. The third term is a Hund's interaction which favors $4f^2$-states with maximal total angular momentum. In an isotropic environment, this interaction would take the form $-\frac{g}{2}\mathbf{J}^2$, where $\mathbf{J}$ is the total angular momentum operator, but in a crystalline environment it takes on a reduced symmetry which we model in a simplified form by $-\frac{g}{2}\mathbf{\Gamma}^2$. In general, the Hund's interaction is only invariant under discrete rotations so that fluctuations into the f^2-state enable the system to sample the crystal symmetry even when the conventional crystal field splittings are absent.

Suppose the crystal electric field term were unquenched, so that $H \to H - \sum \boldsymbol{\alpha} \cdot \mathbf{\Gamma}_j$. The shape of the cerium ion $\langle \mathbf{\Gamma}_j \rangle = \mathbf{\Gamma}$ is determined by the condition that the energy is stationary with respect to variations in $\mathbf{\Gamma}$,

$$N_s^{-1}\delta\langle H_o\rangle/\delta\mathbf{\Gamma} = \boldsymbol{\alpha} + g\mathbf{\Gamma}\,. \quad (9)$$

The second term is a feedback or "Weiss" contribution to the crystalline electric field, created by fluctuations into the $4f^2$-state. Generally, the induced field Γ will follow the crystalline electric fields $\boldsymbol{\alpha}$, but in situations where the valence and spin fluctuations are rapid enough to quench the external crystal electric field [13], then $\boldsymbol{\alpha} = 0$, and the Weiss field becomes free to explore phase space to minimize the total energy. In such a situation, the shape of the cerium ion is determined by the interactions, rather than the local conditions around each ion.

To explore this process, we carry out a Hubbard-Stratonovich decoupling of the interactions,

$$H_f(j) \to f_j^{\dagger}[(E_f + \lambda_j)\underline{1} + \mathbf{\Delta}_j \cdot \underline{\mathbf{\Lambda}}]f_j + E_o[\lambda_j, \mathbf{\Delta}_j], \quad (10)$$

where

$$E_o[\lambda_j, \mathbf{\Delta}_j] = \left(\frac{\mathbf{\Delta}_j^2}{2g} - \frac{\lambda_j^2}{2U} - \lambda_j\right), \quad (11)$$

Here $\mathbf{\Delta}^a(j) \sim -g\mathbf{\Gamma}^a(j)$ is a dynamical Weiss field, and f_j denotes the spinor $f_j \equiv f_{a\sigma}(j)$. Note that, in the path integral, the fluctuating part of λ_j, associated with the suppression of charge fluctuations, is imaginary. We now seek a mean-field solution where the Weiss field $\lambda_j = \lambda$ and $\mathbf{\Delta}_j = \mathbf{\Delta}$, and $E(\lambda_j, \mathbf{\Delta}_j) = E_o$. Such an expectation value does not break the crystal symmetry. However, the selected crystal field matrix $\mathbf{\Delta} \cdot \mathbf{\Lambda}$ must adjust to minimize the total energy. Supposing we diagonalize this matrix, writing $\mathbf{\Delta} \cdot \underline{\mathbf{\Lambda}} = U\underline{\mathbf{\Delta}}_o U^{\dagger}$, where $\underline{\mathbf{\Delta}}_o = \mathrm{diag}(\Delta_1, \Delta_2, \Delta_3)$ and $\Delta_1 > \Delta_2 > \Delta_3$. In the basis, $\tilde{f}_{a\sigma}(j) = U^{\dagger}_{ab} f_{b\sigma}(j)$, the crystal field is diagonal. In practice, the strength of the Hund's interaction g is so large that the excitation energies $\Delta_{1,2} - \Delta_3$ substantially exceed the Kondo temperature. In this case, the mean-field Hamiltonian must be projected into the subspace of the lowest eigenvalue. In the hybridization, we therefore replace

$$c_j^{\dagger} f_j = c_j^{\dagger}\underline{U}\,\tilde{f}_j \to b_a[c^{\dagger}_{a\sigma}(j)\tilde{f}_{\sigma}(j)], \quad (12)$$

where $\tilde{f}_{\sigma}(j) \equiv \tilde{f}_{3\sigma}$ (dropping the superfluous index "3") describes the lowest Kramers doublet and $b_a \equiv U_{a3}$. To satisfy the constraint $\langle n_f \rangle = 1$, the energy of the lowest Kramers doublet must be zero, i.e., $E_f + \lambda + \Delta_3 = 0$. We then arrive at the mean-field Hamiltonian

$$H^* = H_c + V\sum_{\mathbf{k}}[\phi_{\sigma\alpha}(\mathbf{k})c^{\dagger}_{\mathbf{k}\sigma}f_{\alpha\mathbf{k}} + \mathrm{H.c.}] + N_s E_o\,, \quad (13)$$

where $\phi_{\sigma\alpha}(\mathbf{k}) = \sum_a b_a \mathcal{Y}^{\sigma}_{a\alpha}(\hat{\mathbf{k}})$ is the dynamically generated form factor of the hybridization [16]. The transformed hybridization is no longer rotationally invariant: all information about the anisotropic wave function of the cerium ion is now encoded in the vector $\hat{\mathbf{b}}$.

The quasiparticle energies associated with this Hamiltonian are

$$E^{\pm}_{\mathbf{k}} = \epsilon_{\mathbf{k}}/2 \pm \sqrt{(\epsilon_{\mathbf{k}}/2)^2 + V^2_{\mathbf{k}}}\,. \quad (14)$$

Here, the hybridization can be written in the convenient form $V^2_{\mathbf{k}} = V^2\Phi_{\hat{b}}(\hat{\mathbf{k}})$ where $\Phi_{\hat{b}}(\hat{\mathbf{k}}) = (1/2)\sum_{\alpha,\sigma}|\sum_a b_a \mathcal{Y}^{\sigma}_{a\alpha}(\hat{\mathbf{k}})|^2$ contains all the details of the gap anisotropy. The ground-state energy is then the sum of the energies of the filled lower band

$$E_g = -2\sum_{\mathbf{k}}\sqrt{(\epsilon_{\mathbf{k}}/2)^2 + V^2_{\hat{\mathbf{k}}}} + N_s E_o\,. \quad (15)$$

Now both λ and Δ_3 are fixed independently of the direction of $\hat{\mathbf{b}}$, so that E_o does not depend on $\hat{\mathbf{b}}$. To see this, write the eigenvalues of the traceless crystal field matrix as $\Delta_{1,2} = (1/\sqrt{6})\Delta \pm \delta$, $\Delta_3 = -(2/\sqrt{6})\Delta$. Since the upper two crystal field states are empty, stationarity with respect to δ requires $\delta = 0$. Since Δ_3 couples directly to the f charge, we obtain $\partial E_g/\partial\Delta = -\sqrt{\frac{2}{3}}\langle n_f\rangle + (\Delta/g) = 0$, so that $\Delta = \sqrt{\frac{3}{2}}g$. Thus both $\lambda = -\Delta_3 - E_f$ and $\underline{\mathbf{\Delta}}_o$ are fixed independently of $\hat{b}$. The selection of the crystal field configuration is thus entirely determined by minimizing the kinetic energy of the electrons.

To examine the dependence of the mean field on $\hat{b}$, we replace the momentum sum in (15) by an energy and angular integral,

$$\sum_{\mathbf{k}} \{\cdots\} \rightarrow N(0) \int_{-D}^{D} d\epsilon \, \frac{d\Omega_{\hat{\mathbf{k}}}}{4\pi} \{\cdots\}, \qquad (16)$$

where $N(0)$ and $2D$ are, respectively, the density of states and bandwidth of the conduction band. Completing the integral, noting that the angular average $\langle \Phi_{\hat{\mathbf{b}}}(\mathbf{k}) \rangle = 1$, we find that the shift in the ground-state energy per site due to the hybridization is

$$\Delta E_g = 2N(0)V^2 \left[\ln\left(\frac{V^2}{eD^2}\right) + F[\hat{b}] \right], \qquad (17)$$

where

$$F[\hat{b}] = \int \frac{d\Omega_{\hat{\mathbf{k}}}}{4\pi} \, \Phi_{\hat{b}}(\hat{\mathbf{k}}) \ln[\Phi_{\hat{b}}(\hat{\mathbf{k}})]. \qquad (18)$$

The weak logarithmic divergence inside $F(\mathbf{b})$ favors states with nodes. Figure 1 shows a contour plot of the mean-field free energy as a function of the two first components of $\hat{b}$. There are three global minima and three local minima with slightly higher free energy. The state where $\hat{b} = \hat{z}$, plus two symmetry equivalents, corresponds to the IM state and has the lowest free energy. The IM state is axially symmetric, with a hybridization node along the $\hat{z}$, $\hat{y}$, or $\hat{x}$ axis. But the theory also identifies a new locally stable state where $\hat{b} = (0, \sqrt{5}/4, \sqrt{11}/4)$, plus its two symmetry equivalents. This state is almost octahedral. Like the IM state, the hybridization drops exactly to zero along the $\hat{z}$ axis. But, in marked difference with the IM state, it almost vanishes along the $(1, 1, 0)$ and $(1, -1, 0)$ directions in the basal plane.

The relative stability of the IM and the octahedral state will, in general, be dependent on the details of our model, such as the detailed conduction electron band structure. For this reason, both possibilities should be considered as candidates for the nodal semimetallic states of CeNiSn and CeRhSb. The inset in Fig. 2 shows the density of states predicted by these two possibilities. Although both are

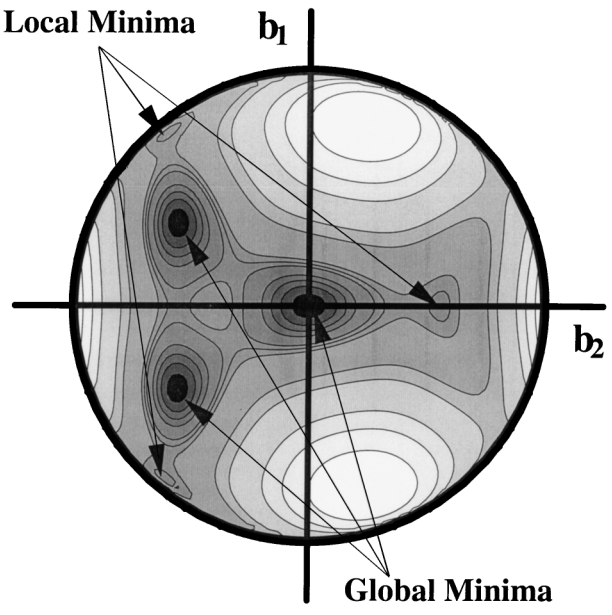

FIG. 1. Contour plot of the ground-state energy in mean-field theory as a function of the two first components of the unit vector $\hat{b}$ (the third one is taken as positive). The darkest regions correspond to the lowest values of the free energy. Arrows point to the three global and three local minima.

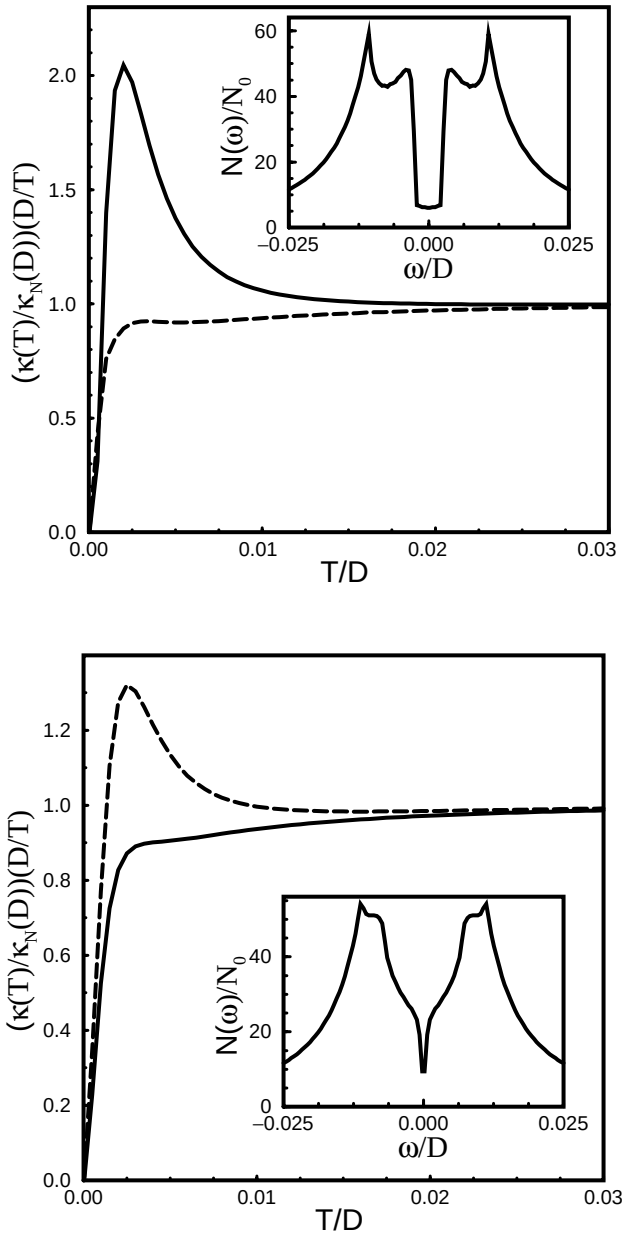

FIG. 2. Normalized thermal conductivity versus temperature along the z axis (solid lines) and in the basal plane (dashed lines). Top: for the Ikeda-Miyake state. Bottom: for the quasioctahedral scenario. The insets show the density of states as a function of the energy. The adjustable parameters have been chosen as $V/D = 0.08$ and an impurity scattering phase shift of $\pi/2$.

gapless, the V-shaped pseudogap of the quasioctahedral state is far more pronounced than in the axial state, and is closer in character to the observed tunneling density of states [18]. A more direct probe of the anisotropy is provided by the thermal conductivity [19] which, unlike the resistivity, does not show a strong sample dependence in these compounds.

To compute and compare the theoretical thermal conductivity with experiments, we compute the thermal current correlator [20],

$$\kappa^{ij} = \frac{1}{2T}\int_{-\infty}^{\infty} d\omega\,\omega^2\Big(-\frac{\partial f}{\partial \omega}\Big)\frac{N(\omega)}{\Gamma(\omega)}\langle \vec{\mathcal{V}}^i\vec{\mathcal{V}}^j\rangle_\omega\,, \quad (19)$$

where f is the Fermi function, $\Gamma(\omega)$ is the quasiparticle scattering rate, and

$$N(\omega)\langle \vec{\mathcal{V}}^i\vec{\mathcal{V}}^j\rangle_\omega = \sum_{\vec{k}} \vec{\mathcal{V}}^i_{\vec{k}}\vec{\mathcal{V}}^j_{\vec{k}}\,\delta(\omega - \vec{E}_{\vec{k}}) \quad (20)$$

describes the quasiparticle velocity distribution, where $\vec{\mathcal{V}}_{\vec{k}} = \vec{\nabla}_{\vec{k}}E_{\vec{k}}$ and $E_{\vec{k}}$ is given by Eq. (14). For our calculation, we have considered quasiparticle scattering off a small, but finite, density of unitarily scattering impurities or "Kondo holes" [21]. We use a self-consistent T-matrix approximation, following the lines of earlier calculations except for one key difference. In these calculations, which depend critically on the anisotropy, it is essential to include the momentum dependence of the hybridization potential in the evaluation of the quasiparticle current. Previous calculations [12] underestimated the anisotropy by neglecting these contributions [20].

The single node in the IM state leads to a pronounced enhancement of the low-temperature thermal conductivity along the nodal $\hat{z}$ axis. By contrast, in the quasioctahedral state the distribution of minima in the gap give rise to a modest enhancement of the thermal conductivity in the basal plane. Experimental measurements [19] tend to favor the latter scenario, showing an enhancement in thermal conductivity that is much more pronounced in κ_x than in κ_z or κ_y.

Three aspects of our theory deserve more extensive examination. Nodal gap formation is apparently unique to CeNiSn and CeRhSb; the other Kondo insulators SmB_6, $Ce_3Bi_4Pt_3$ and YbB_{12} display a well-formed gap. Curiously, these materials are cubic, leading us to speculate that their higher symmetry prevents the dynamically generated contribution to the crystal field from exploring the region of parameter space where a node can develop. At present, we have not included the effect of a magnetic field, which is known to suppress the gap nodes [6]. There appears to be an interesting possibility that an applied field will actually modify the dynamically generated crystal field to eliminate the nodes. Finally, we note that since the spin-fluctuation spectrum will reflect the nodal structure, future neutron scattering experiments [22] should, in principle, be able to resolve the axial or octahedral symmetry of the low energy excitations.

In conclusion, we have proposed a mechanism for the dynamical generation of a hybridization gap with nodes in the Kondo insulating materials CeNiSn and CeRhSb. We have found that Hund's interactions acting on the virtual $4f^2$ configurations of the cerium ions generate a Weiss field which acts to cooperatively select a semimetal with nodal anisotropy. Our theory predicts two stable states, one axial and the other quasioctahedral in symmetry. The quasioctahedral solution appears to be the most promising candidate explanation of the various transport and thermal properties of the narrow-gap Kondo insulators.

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