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Interaction effects in mixed-valent Kondo insulators

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Abstract

We study theoretically the class of mixed-valent Kondo insulators, employing a recently developed local moment approach to heavy Fermion systems using the *asymmetric* periodic Anderson model (PAM). Novel features in spectra and transport, observable experimentally but lying outside the scope of the symmetric PAM or the Kondo lattice model, emerge naturally within the present theory. We argue in particular that a shoulder-like feature in the optical conductivity, that is distinct from the usual mid-infrared or direct gap peak and has been observed experimentally in mixed-valent compounds such as CeOs₄Sb₁₂ and YbAl₃, is of intrinsic origin. Detailed comparison is made between the resultant theory and transport/optical experiments on the filled-skutterudite compound CeOs₄Sb₁₂, and good agreement is obtained.

1. Introduction

Kondo insulator compounds constitute a sub-class of lanthanide/actinide based heavy Fermion materials. Characterised by small spectral and optical gaps, and an activated resistivity at low temperatures, they have been under intense theoretical and experimental investigation for many years (for reviews see [1–7]). From a theoretical perspective, the essential framework for understanding heavy Fermion materials is the periodic Anderson model (PAM), wherein a single correlated f-level in each unit cell of the lattice hybridizes locally with a non-interacting conduction band.

Theories for Kondo insulators (KI) have generally been based on the particle–hole symmetric limit of the PAM [1, 7–13], in which the f-level occupancy (n_f) and the conduction band filling (n_c) are each equal to unity. Although $n_f = 1 = n_c$ indeed satisfies the condition for an insulating ground state, it is not the generic case, which by contrast is $n_f + n_c = 2$ (as shown and discussed in [3, 10, 14]). The strong coupling limit of the PAM is of course the Kondo lattice model with wholly localised f-electrons and hence $n_f = 1$ necessarily, so one naturally expects that if a particular KI is sufficiently strongly correlated then the particle–hole symmetric PAM should provide a sound description of it. And indeed theories based on the

symmetric PAM have been able to describe, even quantitatively, many aspects of a number of these materials (see e.g. [13]).

One cannot however expect such theories to be complete, since the fact that the generic condition for Kondo insulating behaviour is $n_f = 2 - n_c$ [3, 10, 14] itself suggests that KI materials are likely as a rule to be mixed-valent ($n_f \neq 1$); as indeed seems to be the case experimentally [3, 7], and which behaviour lies beyond the scope of the symmetric PAM. A more general treatment of KIs to encompass mixed-valent behaviour is thus clearly desirable, based on the general asymmetric PAM with the constraint $n_f = 2 - n_c \neq 1$. It is this we consider here.

In a previous paper [15], working within the general framework of dynamical mean-field theory (DMFT) [8, 9, 16, 17], we developed a local moment approach (LMA) (see [12, 13, 18–25] for details) to heavy Fermion systems. This encompassed both strong coupling Kondo lattice behaviour ($n_f \rightarrow 1, n_c$ arbitrary), as well as the mixed-valence regime (n_f and n_c arbitrary). The theory was subsequently compared to experiments on several heavy Fermion metals, and excellent quantitative agreement was found [26]. Although comparison was made only to metallic systems, the insulating ground state is just a particular solution of the same basic theory, that may be obtained by restricting the parameter set to the line $n_f + n_c = 2$. In the present paper we treat the generic case by supplementing the theory of [15] with a constraint on the total filling, $n_f + n_c = 2$, but allowing n_f and n_c to deviate from unity. This enables us to capture the mixed-valency along with the insulating nature of these systems.

We begin with a brief overview of the model and formalism used. Theoretical results for spectra and transport are discussed in section 3, followed by a detailed comparison with experiments on the filled skutterudite compound $\text{CeOs}_4\text{Sb}_{12}$, and a brief conclusion in section 4.

2. Model and theory

In standard notation, the Hamiltonian for the PAM is given by:

$$\hat{H} = -t \sum_{(i,j),\sigma} c_{i\sigma}^\dagger c_{j\sigma} + \epsilon_c \sum_{i,\sigma} c_{i\sigma}^\dagger c_{i\sigma} + \sum_{i,\sigma} \left(\epsilon_f + \frac{U}{2} f_{i-\sigma}^\dagger f_{i-\sigma} \right) f_{i\sigma}^\dagger f_{i\sigma} + V \sum_{i,\sigma} (f_{i\sigma}^\dagger c_{i\sigma} + \text{h.c.}). \quad (2.1)$$

The first pair of terms describe the non-interacting conduction (c) band. The first gives the kinetic energy (or ‘free’ conduction band \hat{H}_c^0), with the nearest neighbour hopping $t_{ij} = -t$ scaled as $t_{ij} \propto t^*/\sqrt{Z_c}$ in the large dimensional limit of coordination number $Z_c \rightarrow \infty$ [8, 9, 16, 17], and $t^* \equiv 1$ taken throughout as the unit of energy; while the second gives the c-orbital energy, such that varying ϵ_c simply shifts the centre of gravity of the free conduction band relative to the Fermi level, and as such controls the conduction electron filling n_c . The third term in \hat{H} represents the f-orbital energy (ϵ_f) and the on-site Coulomb repulsion (U) for the localised f-orbitals, and the final term denotes the local hybridization between the c and f-electrons which is responsible for making the otherwise localized f-electrons itinerant.

The free conduction band may be diagonalised, $\hat{H}_c^0 \equiv \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$, with corresponding density of states $\rho_0(\epsilon) = N^{-1} \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}})$. While the basic formalism is valid for any underlying lattice and associated $\rho_0(\epsilon)$, we consider in this paper the specific case of the hypercubic lattice (which is Bloch-decomposable, unlike e.g. a Bethe lattice), for which $\rho_0(\epsilon) = \exp(-\epsilon^2)/\sqrt{\pi}$ is a Gaussian.

Within DMFT, the f-electron self-energy $\Sigma_f(\omega; T)$, representing many-body scattering due to electron interactions, is rendered purely local (i.e. site-diagonal or momentum independent).

The local, site-diagonal Green functions for the conduction- ($G^c(\omega)$) and f-electrons ($G^f(\omega)$) are then given by [8, 9, 14, 16, 17]

$$G^c(\omega) = \int_{-\infty}^{\infty} d\epsilon \frac{\rho_0(\epsilon)}{\omega^+ - \epsilon_c - \frac{V^2}{\omega^+ - \epsilon_f - \Sigma_f(\omega; T)} - \epsilon} \equiv \int_{-\infty}^{\infty} d\epsilon \rho_0(\epsilon) G^c(\epsilon; \omega) \quad (2.2a)$$

$$G^f(\omega) = \frac{1}{\omega^+ - \epsilon_f - \Sigma_f(\omega; T)} \left[1 + \frac{V^2}{\omega^+ - \epsilon_f - \Sigma_f(\omega; T)} G^c(\omega; T) \right] \quad (2.2b)$$

(with $\omega^+ = \omega + i0^+$). Solution of these DMFT equations naturally requires a knowledge—and self-consistent determination—of the f-electron self-energy $\Sigma_f(\omega; T)$, which DMFT by itself does not of course prescribe. For this, we employ the physically transparent local moment approach (LMA) [12–15, 18–26]. This handles non-perturbatively all interaction strengths from weak to strong coupling, and all relevant energy/temperature scales, while at the same time recovering the dictates of Fermi liquid behaviour at low energy/temperature scales. Originally introduced to describe Anderson impurity models [18–25], for which it is found to agree well with e.g. numerical renormalization group calculations and a number of exact results, lattice-based heavy Fermion systems have also been considered within DMFT + LMA [12–15, 26].

Here we sketch in brief only the essential elements of the LMA:

- (i) The starting point is simple *static* mean-field, i.e. unrestricted Hartree-Fock. This has the virtue of recognising local moment formation as the first effect of electron interactions, by introducing the possibility of local moments from the outset. But by itself it is inadequate, for two reasons. First, it results in a (locally doubly-degenerate) symmetry broken mean-field state, which is not perturbatively connected (in U) to the non-interacting limit and in consequence violates Fermi liquid behaviour at low energies. Second, its inherently static nature cannot by construction capture electron correlation effects. It is these signal limitations the LMA overcomes.
- (ii) Electron correlations, embodied in dynamical self-energies, are incorporated within the framework of a spin-rotationally invariant *two-self-energy* description which is an inevitable consequence of the underlying two mean-field saddle points (and from which the conventional single self-energy $\Sigma_f(\omega; T)$ is recovered simply as a byproduct). The resultant dynamical self-energies are built diagrammatically from, and are self-consistently determined functionals of, the underlying mean-field propagators. They include in particular a non-perturbative class of diagrams that capture the spin-flip dynamics central to the physics of the PAM.
- (iii) The third, key element of the LMA is that of *symmetry restoration* [12, 19, 20, 24]: self-consistent restoration of the symmetry broken at pure mean-field level, and hence correct recovery of the low-energy local Fermi liquid behaviour that reflects adiabatic continuity to the non-interacting limit. This is embodied in a single self-consistency condition on the two-self-energies precisely at the Fermi level ($\omega = 0$), which in practice amounts to a self-consistent determination of the local moment (supplanting the simple ‘gap equation’ for such that arises at crude mean-field level).
- (iv) Luttinger’s theorem [2, 27], itself a reflection of perturbative continuity to the non-interacting limit (i.e. $I_L = \text{Im} \int_{-\infty}^0 d\omega (\partial \Sigma_f(\omega; T = 0)/\partial \omega) G^f(\omega) = 0$), is also satisfied by the LMA [14]. We note too that adiabatic continuity to the non-interacting limit is characteristic of *both* the heavy Fermion (metallic) and Kondo insulating states [12, 13].

Full details regarding the structure and implementation of the Local Moment Approach for the generic asymmetric PAM are given in [14, 15], to which the reader is referred for further information.

Since our objective is to study generic Kondo insulators, corresponding to $n_c + n_f = 2$ (for $T = 0$ where the distinction between an insulator and a metal has strict meaning), we now examine the general conditions under which an insulating ground state is obtained. To this end we note that the Luttinger theorem $I_L = 0$ can be expressed as the following exact statement for the Fermi surface of the PAM, as shown in [14]:

$$\frac{1}{2}(n_c + n_f) = \int_{-\infty}^{-\epsilon_c + 1/\tilde{\epsilon}_f^*} \rho_0(\epsilon) d\epsilon + \theta(-\tilde{\epsilon}_f^*) \quad (2.3)$$

(with $\theta(x)$ the unit step function). Here $\tilde{\epsilon}_f^* = \epsilon_f^*/V^2$, and ϵ_f^* is the renormalised or effective f-level given by $\epsilon_f^* = \epsilon_f + \Sigma_f^R(\omega = 0; T = 0)$ (where $\Sigma_f^R = \text{Re}\Sigma_f$).

From this it follows that, for any conduction band $\rho_0(\epsilon)$, the KI filling constraint $n_c + n_f = 2$ is satisfied if $\epsilon_f^* = 0$ (whether $\epsilon_f^* = 0^+$ or 0^-). Moreover for a non-compact bare density of states $\rho_0(\epsilon)$, such as the Gaussian appropriate to the hypercubic lattice we consider, $\epsilon_f^* = 0$ is the only possibility that satisfies $n_c + n_f = 2$. As such, $\epsilon_f^* = 0$ is the general condition for a KI that we seek; with the (particle-hole) symmetric KI ($\epsilon_f = -U/2$ and $\epsilon_c = 0$) simply the particular case for which $n_c = 1 = n_f$.

The condition $\epsilon_f^* = 0$ also leads naturally to a gap at the Fermi level ($\omega = 0$) in the $T = 0$ single-particle spectra $D^c(\omega)$ and $D^f(\omega)$. This is most easily seen from the limiting low-frequency behaviour of equations (2.2a) and (2.2b) for $T = 0$, obtained from a low- ω quasiparticle expansion [14] and given by

$$D^c(\omega) \sim \rho_0 \left(-\epsilon_c - \frac{1}{\tilde{\omega} - \tilde{\epsilon}_f^*} \right) \quad (2.4a)$$

$$V^2 D^f(\omega) \sim \frac{1}{(\tilde{\omega} - \tilde{\epsilon}_f^*)^2} \rho_0 \left(-\epsilon_c - \frac{1}{\tilde{\omega} - \tilde{\epsilon}_f^*} \right) \quad (2.4b)$$

where $\tilde{\omega} = \omega/\omega_L$. Here, $\omega_L = ZV^2/t_*$ is the characteristic low-energy Fermi liquid scale in the problem (with $Z = [1 - (\partial\Sigma_f^R(\omega; T = 0)/\partial\omega)_{\omega=0}]^{-1}$ the usual quasiparticle weight, or inverse mass renormalization factor). From this it is readily seen that with $\epsilon_f^* = 0$, $D^c(\omega = 0) = 0$ (and likewise for the f-spectrum), as one expects for an insulator.

In this paper we implement the filling condition $n_c + n_f = 2$ simply by supplementing the LMA with the $T = 0$ constraint $\epsilon_f^* = \epsilon_f + \Sigma_f^R(\omega = 0; T = 0) = 0$ (which is algorithmically simple), ensuring thereby direct access to the generic Kondo insulating states of interest. The LMA yields directly the local Green functions (G^c and G^f) and self-energies, knowledge of which is well known to be sufficient within DMFT [8, 9, 16, 17] to determine dc transport and optical properties, as detailed e.g. in [13, 15]. In the next section, we discuss our theoretical results.

3. Theoretical results and discussion

The PAM, equation (2.1), is characterised by four ‘bare’ material parameters, U , V , ϵ_c and the f-level asymmetry $\eta = 1 + 2\epsilon_f/U$ (or equivalently ϵ_f itself). The local spectra naturally depend on these parameters, and the ($T = 0$) total filling is given by

$$n_c + n_f = 2 \int_{-\infty}^0 d\omega [D^c(\omega; U, V, \epsilon_c, \eta) + D^f(\omega; U, V, \epsilon_c, \eta)]. \quad (3.1)$$

For a metallic phase, (U, V, ϵ_c, η) are in general independent parameters. But for the Kondo insulating state, the constraint $n_c + n_f = 2$ obviously implies that only 3 of the bare parameters are independent, e.g. $\eta \equiv \eta(U, V, \epsilon_c)$.

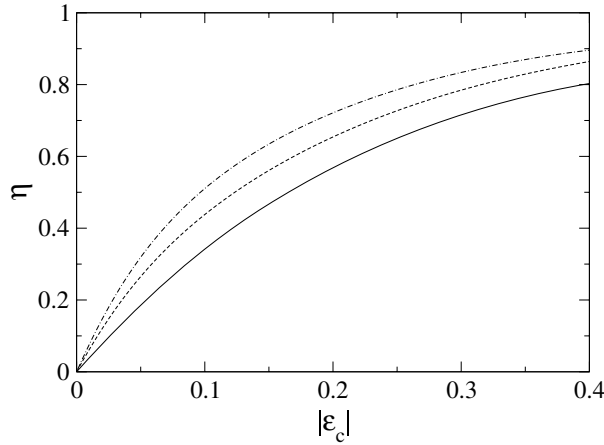


Figure 1. Variation of f-level asymmetry η with $|\epsilon_c|$ ($= -\epsilon_c$) for the Kondo insulating state, for fixed $V^2 = 0.2$ and three different interactions $U = 2.6$ (solid line), 3.8 (dashed line) and 5.2 (point-dash). With increasing $|\epsilon_c|$, the insulator becomes progressively more mixed-valent (the f-electron filling dropping from $n_f = 1$ for $|\epsilon_c| = 0$ to $n_f \simeq 0.63$ for $|\epsilon_c| = 0.4$).

We illustrate this in figure 1, showing the resultant η versus $|\epsilon_c|$ (with $\epsilon_c \leq 0$ and hence $n_c \geq 1$), for a fixed value of the hybridization V and three different interactions U . All curves meet at the origin, this being the symmetric KI ($n_f = 1 = n_c$) for which $\eta = 0 = \epsilon_c$ for *all* U and V , i.e. $\eta(U, V, \epsilon_c = 0) = 0$ is independent of U and V . Away from $\epsilon_c = 0$ however, η depends generically on all of U , V and ϵ_c . On increasing $|\epsilon_c|$ for any given U and V , as in figure 1, the system becomes progressively mixed-valent: η increases (i.e. the f-level moves upwards towards the Fermi level), and n_f steadily diminishes from $n_f = 1$ at $\epsilon_c = 0$, with a concomitant increase in the resultant quasiparticle weight/inverse mass renormalization Z (and hence in the low-energy scale $\omega_L = ZV^2$). In fact over the U -range shown in figure 1, the resultant n_f s for given ϵ_c barely change with U , n_f dropping to $\simeq 0.63$ for $|\epsilon_c| = 0.4$.

To illustrate typical local single-particle dynamics, figure 2 shows the $T = 0$ LMA c- and f-spectra versus $\tilde{\omega} = \omega/\omega_L$ (left and right panels respectively) for a fixed $\epsilon_c = -0.4$, $U = 2$ and a range of different hybridization couplings V as indicated. The associated n_f differs only slightly with V over the range shown, with $n_f \simeq 0.6$ indicating mixed-valent character. The single-particle spectra for this representative asymmetric KI are indeed seen to be gapped at the Fermi level, with magnitude $\sim \omega_L$, and the obvious key point is that the gap is asymmetric about the Fermi level (it is of course strictly soft for a hypercubic lattice, but with exponentially small spectral density in the vicinity of the Fermi level). The four sets of spectra are seen to be quite distinct away from the Fermi level, as one expects. However the limiting low-frequency spectral forms are given (asymptotically exactly) by equations (2.4a), (2.4b) which, with $\epsilon_f^* = 0$ as appropriate to the KI, are seen to depend solely on ϵ_c and $\tilde{\omega}$; i.e. they should be independent of V or U (which we note has nothing *per se* to do with the ‘universal scaling’ of spectra characteristic of the strong coupling limit $n_f \simeq 1$ [12–15]). That the LMA correctly recovers this behaviour is self-evident from the figure.

3.1. Optical conductivity

We consider now the frequency dependence of the optical conductivity $\sigma(\omega; T)$, focusing specifically on $T = 0$ (results at finite- T will be included in the following section). Figure 3

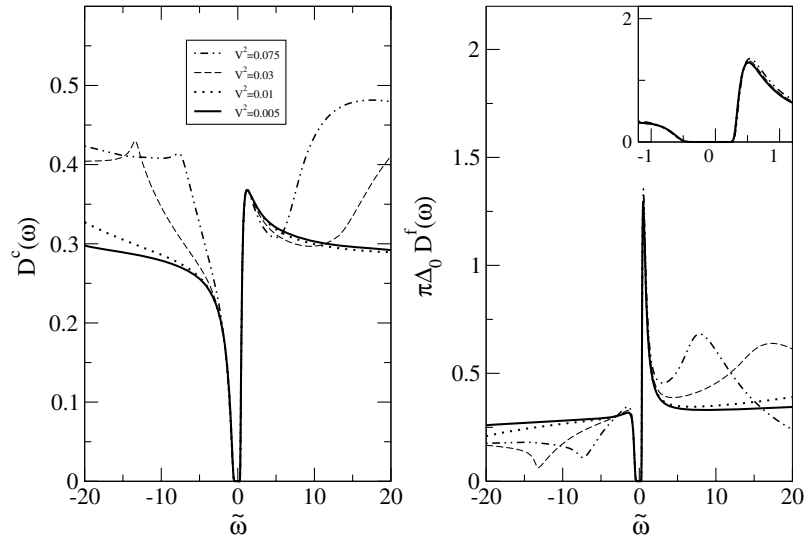


Figure 2. The local conduction electron spectra (left panel) and f-electron spectra (right panel, with the constant $\Delta_0 = \pi V^2 \rho_0(-\epsilon_c)$) are shown versus $\tilde{\omega} = \omega/\omega_L$ for a fixed $U = 2.0$, $\epsilon_c = -0.4$ and varying $V^2 = 0.005$ (solid line), 0.01 (dotted), 0.03 (dashed) 0.075 (double dot-dashed). An asymmetric gap is seen straddling the Fermi level. Inset: magnified view of the low frequency f-spectrum.

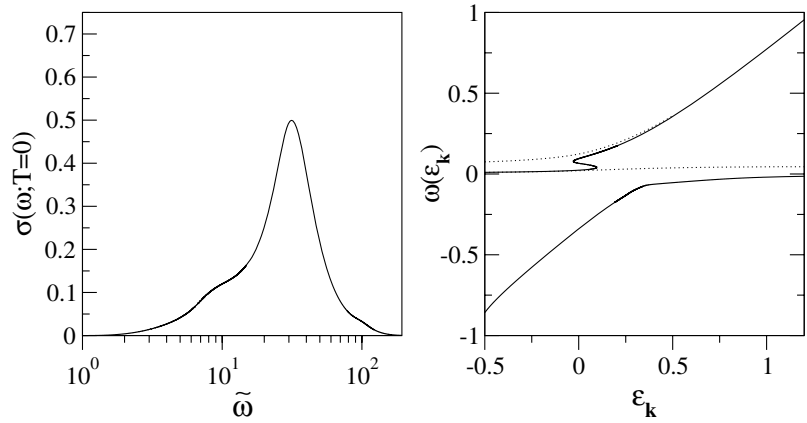


Figure 3. Left panel: Optical conductivity $\sigma(\omega; 0)$ versus $\tilde{\omega} = \omega/\omega_L$ for a representative mixed-valent Kondo insulator ($n_f \simeq 0.73$), with $U = 3.8$, $V^2 = 0.2$, $\epsilon_c = -0.3$ and $\eta = 0.8$. Right panel: the renormalized bandstructure $\omega(\epsilon_{\mathbf{k}})$ versus $\epsilon_{\mathbf{k}}$ (solid lines). For the dotted lines, see discussion in text.

shows the optical conductivity obtained from the LMA for a representative mixed-valent Kondo insulator. The dominant feature in the optics is the usual strong, direct gap absorption (‘mid-infrared peak’). In the absence of scattering due to electron interactions there would be no absorption whatever below the direct gap [13, 15]; but, just as for the (particle-hole) symmetric KI considered in [13], interaction-induced many-body scattering leads as seen to continuous absorption all the way down to the indirect gap scale $\omega = \Delta_{\text{ind}} = 2\omega_L$ (which is why $\sigma(\omega; 0)$

is shown as a function of $\tilde{\omega} = \omega/\omega_L$, figure 3 showing there is indeed negligible absorption below $\tilde{\omega} \simeq 2$).

Figure 3 also shows that the optical conductivity possesses a distinct low-frequency shoulder, lying somewhat above the indirect gap (at $\tilde{\omega} \approx 10$ in the present example). Such a feature occurs neither in the non-interacting limit nor for the interacting symmetric KI [13]. From investigation of a wide range of underlying material parameters however, we find it to be entirely typical of interacting mixed-valent (necessarily asymmetric) Kondo insulators, albeit naturally becoming less pronounced as the symmetric limit is approached. In previous work [15, 26] we have also found such behaviour to be characteristic of correlated intermediate valence metals. We conclude therefore that a low-frequency shoulder should typically exist, as an *intrinsic* optical feature, in interacting mixed-valent systems whether metallic or insulating; and that it arises from a combination of many-body scattering and mixed-valency. Experimentally, such a shoulder has been observed in the optical conductivity of Kondo insulators such as CeOs₄Sb₁₂ [28] as well as in intermediate valence metals such as YbAl₃ [29]. In [26] we considered the case of YbAl₃ in detail, and obtained very good agreement between theory and experiment, including striking reproduction of the low-energy optical shoulder. Analogous comparison for CeOs₄Sb₁₂ will be given in the following section.

First, however, we seek to interrogate the optics in more microscopic detail. In the absence of vertex corrections (as appropriate to DMFT [8, 9, 16, 17]) the $T = 0$ optical conductivity is given by [13, 15]

$$\sigma(\omega; 0) \propto \int_{-\infty}^{\infty} d\epsilon \rho_0(\epsilon) I(\epsilon; \omega) \quad (3.2a)$$

(bar extraneous constants), with

$$I(\epsilon; \omega) = \frac{1}{\omega} \int_{-\omega}^0 d\omega_1 D^c(\epsilon; \omega_1) D^c(\epsilon; \omega_1 + \omega). \quad (3.2b)$$

Here, $D^c(\epsilon; \omega) \equiv D^c(\epsilon_{\mathbf{k}} = \epsilon; \omega)$ is the $\epsilon_{\mathbf{k}}$ -resolved conduction electron spectrum (accessible e.g. via ARPES): $D^c(\epsilon; \omega) = -(1/\pi) \text{Im} G^c(\epsilon; \omega)$, with the \mathbf{k} -space propagator $G^c(\epsilon_{\mathbf{k}}; \omega)$ given by

$$G^c(\epsilon_{\mathbf{k}}; \omega) = [\gamma(\omega) - \epsilon_{\mathbf{k}}]^{-1} \quad (3.3a)$$

where

$$\gamma(\omega) = \omega^+ - \epsilon_c - \frac{V^2}{\omega^+ - \epsilon_f - \Sigma_f(\omega; T)} \quad (3.3b)$$

(such that the local, site-diagonal propagator $G^c(\omega) = N^{-1} \sum_{\mathbf{k}} G^c(\epsilon_{\mathbf{k}}; \omega) \equiv \int d\epsilon \rho_0(\epsilon) G^c(\epsilon; \omega)$ as in equation (2.2a)).

The physical content of equations (3.2) is clear: for given $\epsilon \equiv \epsilon_{\mathbf{k}}$ (as in equation (3.2b)), optical transitions occur from a state below the Fermi level (lying at $\omega_1 < 0$) to a state ω higher in energy that lies above the Fermi level (at $\omega_1 + \omega > 0$); all transitions being ‘direct’ in the sense that absorption occurs for given/fixed $\epsilon_{\mathbf{k}}$. The net optical conductivity at frequency ω is then, as in equation (3.2a), the sum of all such processes over the full range of $\epsilon \equiv \epsilon_{\mathbf{k}}$ (with density $\rho_0(\epsilon) = N^{-1} \sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon)$). This picture is of course wholly familiar at an elementary level in the context of non-interacting electrons (or ‘renormalized’ non-interacting electrons, as considered below). But we emphasise that it is quite general: it applies equally well to the fully interacting case, where the states between which absorptive transitions occur are many-body states. There is of course an obvious difference between the interacting and non-interacting cases, namely the existence of scattering (and hence ‘lifetime’ effects) due to

electron interactions in the former case. That in turn generates a profound difference between optics in the two cases, which we now consider since it also throws light on the optical conductivity shown in figure 3.

The simplest description of the optics is at the level of ‘renormalized bandstructure’ [9]. Here, $\gamma(\omega)$ in equation (3.3a) is taken to be purely real, $\gamma(\omega) \equiv \gamma^R(\omega)$, neglect of $\gamma^I(\omega) = \text{Im} \gamma(\omega)$ meaning from equation (3.3b) that the imaginary part of the f-electron self-energy—the source of all scattering—is completely neglected. In addition, $\gamma^R(\omega)$ is further approximated by its asymptotic low-frequency behaviour, which (from equation (3.3b)) comes from that for $\Sigma_f^R(\omega; 0) \equiv \text{Re} \Sigma_f(\omega; 0)$, namely the simple Taylor expansion $\Sigma_f^R(\omega; 0) \sim \Sigma_f^R(0; 0) - (1/Z - 1) \omega$ (with Z the usual quasiparticle weight). With this approximation $G^c(\epsilon_{\mathbf{k}}; \omega) \simeq [\gamma^R(\omega) - \epsilon_{\mathbf{k}}]^{-1}$ has poles at two frequencies, $\omega = \omega^+(\epsilon_{\mathbf{k}}) > 0$ above the Fermi level and $\omega = \omega^-(\epsilon_{\mathbf{k}}) < 0$ below it. These are given explicitly by

$$\omega^\pm(\epsilon_{\mathbf{k}}) = \frac{1}{2} \left[(\epsilon_c + \epsilon_{\mathbf{k}}) \pm \sqrt{(\epsilon_c + \epsilon_{\mathbf{k}})^2 + 4ZV^2} \right] \quad (3.4a)$$

(where we use the fact that the renormalized level $\epsilon_f^* = \epsilon_f + \Sigma_f^R(0; 0) = 0$ for a generic KI, as discussed in section 2), with a gap between them $\tilde{\Delta}(\epsilon_{\mathbf{k}}) = \omega^+(\epsilon_{\mathbf{k}}) - \omega^-(\epsilon_{\mathbf{k}})$ of

$$\tilde{\Delta}(\epsilon_{\mathbf{k}}) = \sqrt{(\epsilon_c + \epsilon_{\mathbf{k}})^2 + 4ZV^2}. \quad (3.4b)$$

Equation (3.4a) is simply the renormalized bandstructure of the problem (reducing trivially to the non-interacting limit result for $Z = 1$), the two branches $\omega^+(\epsilon_{\mathbf{k}})$ and $\omega^-(\epsilon_{\mathbf{k}})$ reflecting physically the fact that, per unit cell, a single f-level hybridizes locally to a single conduction band. The minimum gap between them, the ‘direct gap’ at this level, occurs for $\epsilon_{\mathbf{k}} = -\epsilon_c$ and is thus $\Delta_{\text{dir}} = \tilde{\Delta}(\epsilon_{\mathbf{k}} = -\epsilon_c) = 2\sqrt{Z}V$.

Since the resultant $D^c(\epsilon_{\mathbf{k}}; \omega') \propto \text{Im} G^c(\epsilon_{\mathbf{k}}; \omega')$ contains two poles, at $\omega' = \omega^+(\epsilon_{\mathbf{k}})$ and $\omega^-(\epsilon_{\mathbf{k}})$, it follows from equation (3.2b) that optical absorption can only arise from transitions between these two δ -peaks—provided of course their separation $\omega^+(\epsilon_{\mathbf{k}}) - \omega^-(\epsilon_{\mathbf{k}})$ coincides with the requisite absorption frequency ω ; and in consequence that there is no absorption at all (i.e. $\sigma(\omega; 0) = 0$) for $\omega \leq \Delta_{\text{dir}} = 2\sqrt{Z}V$. This level of description may be improved, very slightly, by retaining $G^c(\epsilon_{\mathbf{k}}; \omega) \simeq [\gamma^R(\omega) - \epsilon_{\mathbf{k}}]^{-1}$ but with the full LMA $\gamma^R(\omega)$ employed instead of its asymptotic low- ω expansion. The results of such a calculation are shown in figure 3 (right panel, solid lines, where the ‘band branching’ seen over a narrow range around $\epsilon_{\mathbf{k}} = 0$ is simply a consequence of retaining $\gamma^R(\omega)$ but neglecting $\gamma^I(\omega)$).

The above ‘renormalized band’ description, commonly employed though it is, is qualitatively inadequate. The picture changes markedly when interaction-induced scattering is properly retained, as embodied in the imaginary part of the f-electron self-energy and hence a non-vanishing conduction electron scattering rate $\gamma^I(\omega)$. To illustrate this, figure 4 shows the full LMA conduction electron spectra $D^c(\epsilon_{\mathbf{k}}; \omega)$ versus ω for two values of $\epsilon \equiv \epsilon_{\mathbf{k}}$, namely $\epsilon_{\mathbf{k}} = -\epsilon_c = 0.3$ (left panel) and $\epsilon_{\mathbf{k}} = 0.6$ (right panel). At the simplistic level of renormalized bands, as in the right panel to figure 3, each of these spectra would consist of one pole below the Fermi level ($\omega = 0$) and one above it. Reality is clearly different: the spectra are significantly broadened due to interactions and form a continuum (save for the expected gap in the immediate vicinity of the Fermi level). It is for this reason that, in contrast to the renormalized band picture, conduction electron spectra for essentially *any* $\epsilon_{\mathbf{k}}$ contribute to optical absorption for *all* frequencies down to the lowest energy (indirect) gap scale.

In figure 4 we also mark (by solid arrows) the locations in $D^c(\epsilon_{\mathbf{k}}; \omega)$ of the two nominal poles that would arise at the renormalized band level (their positions can be read off from the right panel in figure 3 at the appropriate $\epsilon_{\mathbf{k}}$). These are seen to correspond rather accurately to the position of the dominant peak maxima in $D^c(\epsilon_{\mathbf{k}}; \omega)$. Just above the Fermi level, an additional small peak (marked by an arrow) can also be seen in figure 4. This feature does

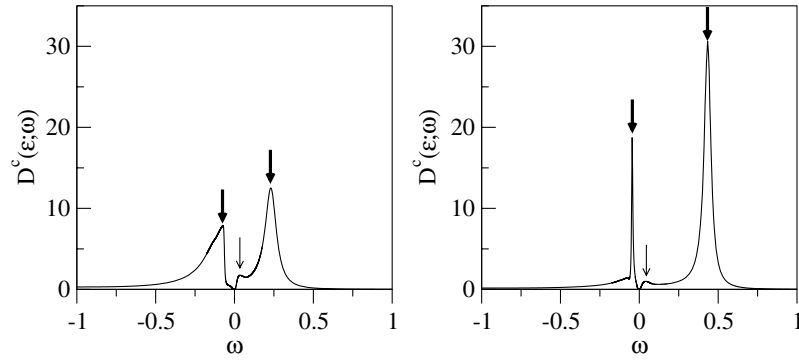


Figure 4. For the same bare parameters as in figure 3. Left panel: $T = 0$ conduction electron spectrum $D^c(\epsilon_{\mathbf{k}}; \omega)$ versus ω , for fixed $\epsilon_{\mathbf{k}} = 0.3 (= -\epsilon_c)$. The solid arrows indicate the location of the pure poles that would arise from a simple renormalized band picture (following from the renormalized bandstructure shown in figure 3, right panel). An additional spectral feature above the Fermi level, arising from interactions, is indicated by a single arrow. Right panel: the same, shown for an $\epsilon_{\mathbf{k}} = 0.6$.

not of course have any counterpart at the renormalized band level, and we find its existence to be characteristic of mixed-valent Kondo insulators (it does not occur in the particle–hole symmetric limit). These spectral features, two peaks above and one below the Fermi level, are found to be characteristic of the conduction spectra $D^c(\epsilon_{\mathbf{k}}; \omega)$ for all $\epsilon_{\mathbf{k}}$. The positions of the two peak maxima above the Fermi level in the full $D^c(\epsilon_{\mathbf{k}}; \omega)$ can be mapped out as a function of $\epsilon_{\mathbf{k}}$, and are shown in figure 3 (right panel, dotted lines). Note in particular that the lower-energy such peak lies close to, but slightly above, the Fermi level for all $\epsilon_{\mathbf{k}}$. We thus expect (see equation (3.2b)) significant optical absorption *to* this peak *from* the dominant spectral peak in $D^c(\epsilon_{\mathbf{k}}; \omega)$ below the Fermi level; particularly at relatively low frequencies where (see figure 3 right panel) for $\epsilon_{\mathbf{k}} \gtrsim 0.3$ or so the latter peak itself lies close to the Fermi level, exhibits only modest dispersion with $\epsilon_{\mathbf{k}}$, and is spectrally sharp (as in figure 4 right panel).

We return now to the optical conductivity $\sigma(\omega; 0)$ given by equations (3.2a), (3.2b), shown in the left panel of figure 3 for the representative bare parameters indicated, and again on a linear- ω scale in figure 5 (solid line). With the preceding comments in mind, our aim is to determine what range of values of $\epsilon \equiv \epsilon_{\mathbf{k}}$ give the primary contribution to $\sigma(\omega; 0)$ in different frequency intervals—in particular, frequencies in the vicinity of (a) the dominant direct gap absorption ($\omega \approx 0.4$ in the present example), (b) the low-frequency shoulder ($\omega \approx 0.1$), and (c) the lowest frequency scales down to the indirect gap ($\omega \approx 0.02$).

To that end, we simply partition the ϵ -integral in equation (3.2a) for $\sigma(\omega; 0)$, into contributions from different ϵ -intervals. This is shown in the left panel to figure 5, where the separate contributions to the total $\sigma(\omega; 0)$ (solid line) from $\epsilon \equiv \epsilon_{\mathbf{k}} > 0.1$ (point–dash line), $0 < \epsilon_{\mathbf{k}} < 0.1$ (dashed) and $\epsilon_{\mathbf{k}} < 0$ (dotted) are shown. From this it is clear that the dominant contribution to $\sigma(\omega; 0)$ in all three ω -regimes of interest arises from $\epsilon_{\mathbf{k}} > 0.1$ (the associated renormalized bandstructure being shown in the right panel of figure 3). To distinguish the ω -regimes, the right panel in figure 5 shows the contribution to $\sigma(\omega; 0)$ from $0.1 < \epsilon_{\mathbf{k}} < 0.5$ (dashed line) and $\epsilon_{\mathbf{k}} > 0.5$ (dotted). From the renormalized band description discussed above, the direct gap occurs at $\epsilon_{\mathbf{k}} = -\epsilon_c (= 0.3$ in the present example); and consistent both with this and the inevitable broadening induced by scattering, the dominant contribution to $\sigma(\omega; 0)$ in the vicinity of the strong direct gap absorption at $\omega \approx 0.4$ is indeed seen to arise from the interval $0.1 < \epsilon_{\mathbf{k}} < 0.5$ —i.e. $\epsilon_{\mathbf{k}} = -\epsilon_c \pm 0.2$. In contrast, as seen in particular from the

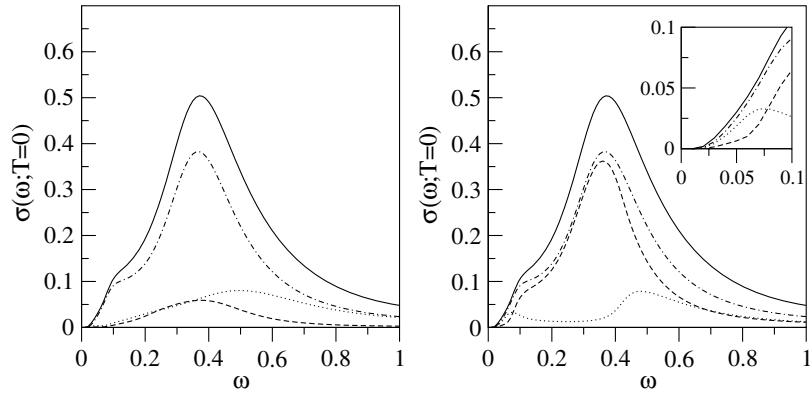


Figure 5. For the same bare parameters as in figure 3. Left panel: the $T = 0$ optical conductivity $\sigma(\omega; 0)$ versus ω (solid line) and the contribution to it arising from $\epsilon \equiv \epsilon_{\mathbf{k}} > 0.1$ (point-dash), $0 < \epsilon_{\mathbf{k}} < 0.1$ (dashed) and $\epsilon_{\mathbf{k}} < 0$ (dotted). Right panel: showing further the contributions to $\sigma(\omega; 0)$ from $0.1 < \epsilon_{\mathbf{k}} < 0.5$ (dashed line) and $\epsilon_{\mathbf{k}} > 0.5$ (dotted). Inset: shown on a lower- ω scale.

right inset to figure 5, absorption on the lowest frequencies down to the order of the indirect gap is controlled by $\epsilon_{\mathbf{k}} \gtrsim 0.5$. This in turn is consistent with the form of $D^c(\epsilon_{\mathbf{k}}; \omega)$ for $\epsilon_{\mathbf{k}}$ s in this range, exemplified by the right panel in figure 4 and discussed above. Finally, the low- ω shoulder in $\sigma(\omega; 0)$ (at $\omega \approx 0.1$) that is typical of the mixed-valent Kondo insulator, is seen to stem mainly from the interval $0.1 < \epsilon_{\mathbf{k}} < 0.5$, its existence reflecting the small spectral feature in $D^c(\epsilon_{\mathbf{k}}; \omega)$ above the Fermi level discussed above, and shown in figure 4.

4. Comparison to transport in $\text{CeOs}_4\text{Sb}_{12}$

The filled-skutterudite compounds RT_4X_{12} (R = rare earth, T = Transition metal and X = pnictide) have attracted much experimental interest, due in part to their possible applications as advanced thermoelectric materials [30]. Recently, several groups have reported investigations of a cerium based filled-skutterudite Kondo insulator, $\text{CeOs}_4\text{Sb}_{12}$. Here we make comparison of the theory outlined in this paper to experimental measurements of dc and optical transport in $\text{CeOs}_4\text{Sb}_{12}$.

We consider first the dc transport. In this compound the phonon contribution to the dc resistivity is quite significant, so for comparison to theory we need to extract the magnetic contribution, $\rho_{\text{mag}}(T)$, from the dc resistivity measured directly. This is achieved by subtracting the phonon contribution—itsself estimated conventionally as the resistivity of $\text{LaOs}_4\text{Sb}_{12}$ [31, 32] (see [26] for a detailed discussion)—from the experimentally measured dc resistivity [33]; and is shown as circles in figure 6. Another experimental group has also reported $\rho_{\text{mag}}(T)$ itself [31]; and although their absolute magnitudes are quite different from those of [33], a simple y-axis rescaling is sufficient to collapse the two sets of data, as indicated by squares and circles in figure 6 (and indicating simply distinct sample geometries in the two cases).

The low temperature ($T \lesssim 30$ K) resistivity can be fitted to a $\exp[(T^*/T)^{1/2}]$ form, suggesting the dominant mechanism of transport in this temperature range to be Efros–Shklovskii type variable range hopping [34] (which extrinsic behaviour is not of course included in the present theory). A shallow maximum is seen in figure 6 at $T \sim 100$ K, beyond which $\rho_{\text{mag}}(T)$ decays monotonically. A rough estimate of the low energy scale

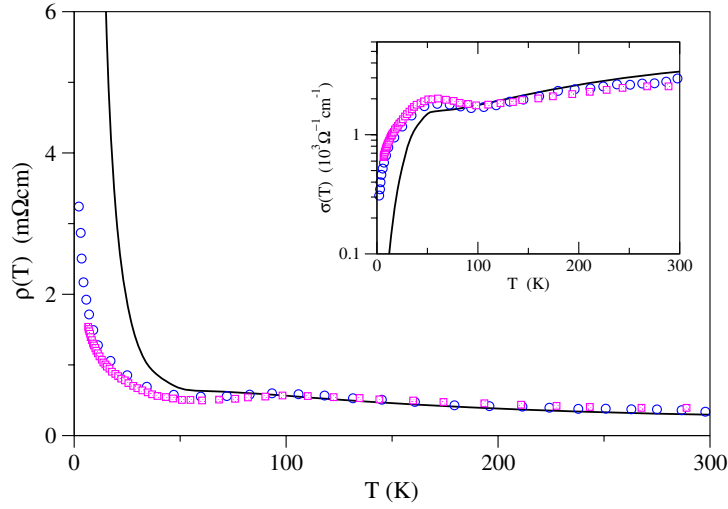


Figure 6. Experimental dc resistivity of $\text{CeOs}_4\text{Sb}_{12}$ with the phonon contribution subtracted (circles [33] and squares [31]) compared to the theoretically determined $\rho(T)$ (solid line), which has been rescaled by $\omega_L = 86$ K and $1/\sigma_0 = 74 \mu\Omega \text{ cm}$. The inset shows the corresponding dc conductivities.

(This figure is in colour only in the electronic version)

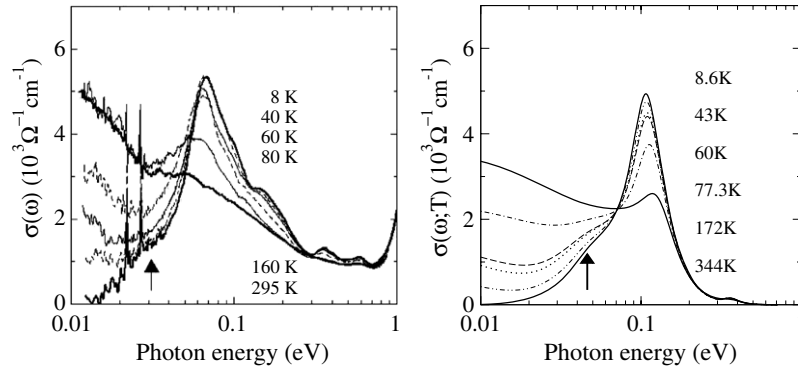


Figure 7. The left panel shows the experimentally measured optical conductivity of $\text{CeOs}_4\text{Sb}_{12}$ [28] for various temperatures. The right panel shows the theoretically determined $\sigma(\omega; T)$ for the same model parameters as in figure 6 and similar temperatures to experiment.

($\omega_L \equiv ZV^2/t_*$) in this system may be obtained through an estimation of the (indirect) gap in the experimental optical conductivity [28], shown in the left panel of figure 7. This yields $\Delta_{\text{ind}} \sim 15 \text{ meV} \simeq 175 \text{ K}$, which thus gives the low energy scale $\omega_L = \Delta_{\text{ind}}/2 \simeq 90 \text{ K}$ (see also the left panel of figure 3 and [13]).

An idea of the parameter regime this system belongs to can be gleaned from two qualitative features evident in the (ω, T) -dependence of the experimental $\sigma_{\text{exp}}(\omega; T)$ [28] shown in figure 7. First, the highest temperature at which $\sigma_{\text{exp}}(\omega; T)$ is measured is 295 K which is $\sim 3\omega_L$, while the optical conductivity at the same temperature is affected up to $\sim 0.3 \text{ eV} \simeq 40\omega_L$. The fact that the thermally induced spectral weight redistribution is over a range of

frequencies much higher than the temperature at which $\sigma_{\text{exp}}(\omega; T)$ is measured is characteristic of relatively weak correlations [13]. Second, a closer look at the low-frequency structure of $\sigma(\omega; T = 8 \text{ K})$ reveals an additional absorption feature at $\omega \sim 30 \text{ meV}$, which in the context of the theoretical results obtained above (see e.g. figure 3), is suggestive of mixed-valence character.

With this in mind, we choose an $\epsilon_c = -0.3$, and for various U, V^2 calculate $\sigma(\omega; T)$. We find that the dc resistivity ($\omega = 0$) and the optical conductivity determined at $U \sim 5.5, V^2 = 0.5$ match best with the experiment, with $\omega_L \sim 86 \text{ K}$. With these parameter values the f-level asymmetry η is found to be 0.9, implying $n_f = 0.75$ and $n_c = 1.25$ consistent with mixed valent behaviour, while the quasiparticle weight $Z \simeq 0.083$ implying a relatively low effective mass ~ 12 consistent with modest correlations. The resultant theoretical dc resistivity is shown in figure 6 (solid line, with the x -axis scaled by $\omega_L = 86 \text{ K}$ and the y -axis by $1/\sigma_0 = 74 \mu\Omega \text{ cm}$). And comparison to experiment is seen to be rather good for $T \gtrsim 30 \text{ K}$ or so (recall as above that transport for $T \lesssim 30 \text{ K}$ is dominated by variable range hopping [34], which is naturally absent from the theory).

The theoretical optical conductivity evaluated for the same model parameters as in figure 6 is shown in the right panel of figure 7, for similar temperatures as the experiment [28] (left panel). An arrow marks the additional absorption seen as a shoulder, which arises at $\omega \sim 40 \text{ meV}$ and thus compares well with the experimental value of $\sim 30 \text{ meV}$. The theoretical direct gap peak appears at $\omega \sim 100 \text{ meV}$, while the corresponding experimental peak position is $\sim 70 \text{ meV}$. The overall theoretical lineshape and its thermal evolution also matches rather well with experiment. We add further that this comparison does not depend crucially on ϵ_c being equal to -0.3 . Varying ϵ_c by ± 0.1 does not change the qualitative picture, although optimal quantitative agreement arises for $\epsilon_c = -0.3, U = 5.5$ and $V^2 = 0.5$ as employed above.

5. Conclusion

We have described in this paper a many-body theory for mixed-valent Kondo insulators, employing a local moment approach to the periodic Anderson model within the framework of dynamical mean field theory. Kondo insulators were argued as a rule to be mixed-valent, with $n_f = 2 - n_c \neq 1$, and which regime of behaviour is not captured by the particle-hole symmetric limit of the PAM ($n_f = 1 = n_c$). To that end we have considered the general asymmetric PAM, together with the constraint $n_f + n_c = 2$ which ensures an insulating gap in the ($T = 0$) single-particle spectrum and related dynamics.

Single-particle spectra, as well as optical and dc conductivities, have been considered, and exhibit features specific to mixed-valent behaviour. The \mathbf{k} -resolved conduction electron spectra are found to contain additional absorption features above the Fermi level, giving rise in turn to an intrinsic shoulder-like absorption in the optical conductivity at frequencies lower than the direct (mid-infrared) gap. We emphasise that such a structure is found to be characteristic of the *interacting mixed-valent* case, and not restricted to either an insulating or metallic ground state. Thus we believe that the shoulder-like feature seen experimentally in the optical conductivity of mixed-valent materials such as the insulator $\text{CeOs}_4\text{Sb}_{12}$ and the metal YbAl_3 , arises intrinsically from a combination of many-body scattering and intermediate valence. A direct comparison between theory and transport/optical experiments on $\text{CeOs}_4\text{Sb}_{12}$ has been given. This yields good quantitative agreement, both reaffirming the view of $\text{CeOs}_4\text{Sb}_{12}$ as a mixed-valent hybridization gap material [33, 34] and showing that the theory described here for generic mixed-valent Kondo insulators can account for the transport/optical properties of these systems.

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