Competition between phase separation and “classical” intermediate valence in an exactly solved model

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(March 24, 2022)

The exact solution of the spin-$\frac{1}{2}$ Falicov-Kimball model on an infinite-coordination Bethe lattice is analyzed in the regime of “classical” intermediate valence. We find (i) either phase separation or a direct metal-insulator transition preclude intermediate valence over a large portion of the phase diagram and (ii) within the intermediate valence phase, only continuous transitions are found as functions of the localized f-electron energy or temperature.

71.28+d, 71.30+h, and 71.10-Hf

Introduction

The phenomenon of intermediate valence (IV) is seen in a number of rare-earth compounds (such as Ce, SmB₆, SmS, YbB₁₂, Eu₃O₄, etc.), where the average f-electron filling per ion becomes nonintegral \[ \begin{it} \cite{1} \end{it} \]. These materials exhibit distinctive anomalies in thermodynamic and transport properties accompanied with either continuous or discontinuous valence transitions as the temperature, pressure, or composition are varied.

IV materials have a localized f-level that lies near the chemical potential for the conduction electrons and is broadened by either hybridization with the conduction band or by electron correlations. This large density of states acts as an electron reservoir and leads to both the IV phenomenon and the thermal and transport anomalies. Theoretical descriptions have focused on two different approaches: (i) the Falicov-Kimball model (FKM) \[ \cite{2} \], where the IV arises from an ensemble average of states with different integral valence (“classical” IV) and the transitions are either discontinuous or continuous, being driven by the strength of the Coulomb interaction between the f-electrons and conduction electrons, or (ii) the periodic Anderson model (PAM) \[ \cite{3} \], where IV arises from a quantum-mechanical mixture of states with different f-occupancy (“quantum-mechanical” IV) and the local moments can be seen in a number of rare-earth compounds (such as Ce, SmB₆, YbB₁₂, Eu₃O₄, etc.). We discovered that the experimentally observed discontinuous transitions arise from an additional coupling of the electrons to the lattice vibrations. A realistic theoretical description should include the physics of both of these approaches, but has proven to be cumbersome to carry out. Here we focus on case (i) to see why few materials can be found that fit into this scenario (likely materials \[ \cite{4} \] include Eu₃O₄, Eu₅S₄, and Sm₃S₄). We discovered that the “classical” IV phase is often precluded by either phase separation or a direct metal-insulator transition, which we believe helps explain why few “classical” IV systems can be found in nature.

It is important to examine the experimental differences between scenario (i) and (ii). The most obvious difference is in the response to a magnetic field. The FKM always possesses full f-moments, so it displays a Curie-like susceptibility proportional to $1/T$. If one includes the additional (superexchange and RKKY) interactions between the moments, then the uniform susceptibility will behave like $1/(T + T^*)$, which will not diverge for positive $T^*$. Such a system will likely order in a spin-density wave at some characteristic temperature, though. The susceptibility never saturates or displays a maximum as $T$ is lowered in the IV phase of the FKM (it does in the metallic phase when f-electrons are not present at low $T$ and become thermally populated at higher $T$ \[ \cite{5} \]). The PAM, on the other hand, displays Curie-like behavior at high $T$ but either saturates, or displays a low-$T$ maximum because of the Kondo effect, and the screening of the local moments by the conduction electrons. RKKY interactions are also present and can lead to magnetic order, which makes a sharp differentiation between the two models more difficult. Most real materials that do not have long-range magnetic order, display a susceptibility that either saturates or has a low-$T$ maximum, indicating that scenario (ii) applies. It is the purpose of this contribution to explain why scenario (i) is so difficult to attain.

Model

The spin-$\frac{1}{2}$ FKM consists of localized f-electronic states and a delocalized conduction band. There is an on-site Coulomb interaction ($U > 0$) between the localized f-electron and the conduction electron. The model neglects the hybridization of the localized f-states with the conduction band, and the valence transitions occur only when the thermodynamic occupation of the different electronic states changes under the variations of external conditions (such as pressure, temperature, etc.). The Hamiltonian of the model is

$$
H = -\sum_{i,j,\sigma} t_{ij} d_{i\sigma}^\dagger d_{j\sigma} + E_f \sum_{i,\sigma} f_{i\sigma}^\dagger f_{i\sigma} + U_{ff} \sum_i f_{i\uparrow}^\dagger f_{i\uparrow} f_{i\downarrow}^\dagger f_{i\downarrow} + U \sum_{i,\sigma,\sigma'} d_{i\sigma}^\dagger d_{i\sigma'} f_{i\sigma'}^\dagger f_{i\sigma} - \mu \sum_{i,\sigma} (d_{i\sigma}^\dagger d_{i\sigma} + f_{i\sigma}^\dagger f_{i\sigma}),
$$

where $d_{i\sigma}^\dagger$ ($d_{i\sigma}$) is the creation (annihilation) operator for a conduction-band electron of spin $\sigma$ at site $i$, $t_{ij}$ is the hopping matrix between lattice sites $i$ and $j$, $f_{i\sigma}^\dagger$
(f_{cr}) is the creation (annihilation) operator for a localized electron with its site energy $E_f$, and $U_{ff}$ is the on-site Coulomb repulsion between f-electrons. $U_{ff}$ is large in real materials, so we choose $U_{ff} \to \infty$, and restrict the number of f-electrons per site to $n_f \leq 1$. We choose the total number of electrons to satisfy $n_{total} = n_d + n_f = 1$ to examine the IV phenomenon where each ion donates one electron to the system. When the f-level lies below the bottom of the conduction band, the system is an insulator ($n_d = 0, n_f = 1$); when the f-level lies above the middle of the conduction band, it becomes a metal ($n_d = 1, n_f = 0$); IV phenomena can only occur when the f-level lies inside the bottom half of the conduction band. In our calculations, we adjust a chemical potential $\mu$ to satisfy the constraint $n_{total} = 1$; $\mu$ is pinned to $E_f$ in the noninteracting IV regime, and the average f-filling becomes nonintegral.

**Methodology** The FKM can be solved in the infinite-coordination-limit, where the local approximation becomes exact, and the momentum independent irreducible self-energy $\Sigma(\omega)$ has a functional form which explicitly depends on $n_f, U$, and the local Green’s function $G(\omega)$.

We examine this model on the Bethe lattice, where the density of states for the noninteracting system becomes semicircular with the band width $4t^* = 4\sqrt{\frac{\mu}{\pi}}$. [We take $t^*$ as our energy unit ($t^* = 1$).] In this case, there is a cubic equation for $G(\omega)$ that determines the interacting density of states $A(\omega) = -\frac{1}{\pi} \text{Im} G(\omega)$ for any given $n_f$.

Therefore, when $n_{total} = 1$, we solve the problem by minimizing the free energy $F[n_f, n_{total} = 1]$ as a function of $n_f$ ($0 \leq n_f \leq 1$):

$$F[n_f, n_{total} = 1] = 2 \int \frac{d\epsilon}{\pi} f(\epsilon) A(\epsilon) + E_f n_f$$

$$+ 2T \int \frac{d\epsilon}{\pi} \{ f(\epsilon) \ln (f(\epsilon) + [1 - f(\epsilon)] \ln [1 - f(\epsilon)]) \} A(\epsilon)$$

$$+ T \{ n_f \ln n_f + (1 - n_f) \ln (1 - n_f) - n_f \ln 2 \},$$

where $f(\epsilon)$ is the Fermi distribution function.

First, we construct the ground-state phase diagram as a function of $E_f$ and $U$ (see Fig. 3). For large enough $U$, there are only two phases: a metal when $E_f > -\frac{t^*}{2}$ and an insulator when $E_f < -\frac{t^*}{2}$. In this limit, the system becomes effectively noninteracting, avoiding the energetically unfavorable double-occupancy of both d and f electrons on the same site, and does not display IV. For $U$ small enough, there is a range of values of $E_f$, lying in the lower half of the conduction band, where the chemical potential is pinned at $E_f$, and the average f-filling is nonintegral. As the system changes from a metal to a homogeneous IV phase, the value of the $n_f$, at which the ground-state energy $F_{gs}[n_f, n_{total} = 1]$ has its minimum, increases continuously from 0. Hence, the boundary between the metal and the homogeneous IV phases may be obtained from the following condition:

$$\frac{\partial F_{gs}}{\partial n_f} \bigg|_{n_f=0, n_{total}=1} = 0,$$  \hfill (3)

which determines when the metallic phase is no longer a local minimum of the free energy. The analytic form of $F_{gs}[n_f \to 0, n_{total} = 1]$ is found from a low-density expansion [1] for $\Sigma(\omega)$ and $G(\omega)$. After some tedious algebra, the boundary equation resulting from Eq. (3) becomes

$$E_f = -\frac{2}{\pi} + \frac{1}{2U} - \frac{U}{2} + \frac{2}{\pi} \left( \frac{1}{U} + U \right)$$

$$\times \left( \text{arctan} \frac{2U}{1-U^2} - \text{arctan} \frac{1+U}{1-U} \right).$$ \hfill (4)

Direct numerical calculations, minimizing the free energy in Eq. (2) shows good agreement with Eq. (4). This result is valid for $U \leq 1.84177$; larger values of $U$ have the direct transition from the metal to the insulator at $E_f = -8/3\pi$, which occurs before the metal becomes locally unstable.

A similar analysis cannot be performed when $n_f \to 1$, because there is a first-order transition between the insulator and a phase-separated state. In order to show this phase separation, we minimize the free energy $F[n_f, n_{total}]$ with respect to $n_f$ for fixed $n_{total}$ and then determine the free-energy curve as a function of $n_{total}$. A Maxwell construction is finally performed to determine the convex hull of $F$ and see whether or not the unit-density case is phase separated. In equations, we compare

$$F_{avg} = \alpha F[n_{total}^A] + (1 - \alpha) F[n_{total}^B],$$ \hfill (5)

with

$$1 = n_{total}^A + (1 - \alpha) n_{total}^B,$$ \hfill (6)

to $F[n_{total} = 1]$, where the superscript $A$ indicates $n_{total}^A < 1$ and $B$ indicates $n_{total}^B > 1$.

**Valence Transitions** We begin at the $U = 0$ limit. In this case, IV phases can be found whenever $-2 \leq E_f \leq 0$ and the chemical potential for the conduction electrons is pinned at $E_f$ yielding $n_d$ conduction electrons ($0 \leq n_d \leq 1$). The remaining electrons $1 - n_d$ are f-electrons, and the average filling per ion will be noninteger. However, because all of the f-electrons share the same energy, the ground-state energy of this configuration is degenerate with any phase-separated mixture of states with different f-electron fillings (such as the integer-valent states $n_f^A = 0$, and $n_{total}^A = n_d$ and $n_f^B = 1$, and $n_{total}^B = n_d + 1$) because the f-electron energy is linear in the f-electron filling. In order to determine what situation is favorable as $U$ increases from zero, we need to expand the ground-state energy in a power series through second order in $U$, and determine whether the homogenous phase, or the phase-separated states are lower in energy. Such an
Infinite temperatures, all of these phases survive, and phase transitions occur between them as a function of temperature. This is, in fact, the best place to look for these first-order transitions experimentally—by measuring the specific heat as a function of $T$ and looking for the large spikes near the first-order transitions. $C_V$ is determined by numerically differentiating the entropy (including averaging for the phase-separated states). Typical results are summarized in Fig. 4, for all different ground-state phases. All of our theoretical results are displayed in the experimental results of Eu$_2$S$_4$[10]: there is a first-order transition at 160K from a homogeneous to an inhomogeneous IV phase (with a sharp peak in the specific heat accompanied by a structural transition) followed by a ferromagnetic transition below 3.7 K (which is expected in any classical IV system which has local moments).

Conclusions We have examined the phenomenon of intermediate valence in the spin-one-half Falicov-Kimball model. This is a model that can only display “classical” IV phenomena, as the microscopic occupation of the $f$-electrons is always exactly zero or one, but IV can occur from ensemble averaging, where the average $f$-filling becomes nonintegral. Such systems should display magnetic susceptibilities that are Curie-like (or Curie-Weiss-like if additional magnetic couplings are added in) which is not what is seen in most IV compounds. Instead most experiments show a susceptibility that either saturates, or has a maximum as $T$ is lowered, which can best be described by the Kondo effect, and models that include the hybridization between $f$-electrons and conduction electrons. We discovered a fundamental reason why “classical” IV materials are more difficult to find experimentally: either phase separation or a direct metal-insulator transition preclude the IV state over a wide range of parameter space. We believe this result helps explain why nearly all observed IV materials require hybridization to describe them. We also found, that the FKM does not support discontinuous IV transitions. All valence changes, within the IV phase, are continuous as functions of $E_f$ or $T$. The only ways to get discontinuous transitions IV is to either couple the electrons to the lattice, or to have a transition to a phase-separated state[10].

ACKNOWLEDGMENTS

We would like to acknowledge stimulating discussions with P. van Dongen and V. Zlatić. This work was supported by the Office of Naval Research Young Investigator Program under the grant ONR N000149610828.
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FIG. 1. Phase diagram of the spin-$\frac{1}{2}$ Falicov-Kimball model when $n_{\text{total}} = 1$ and $T = 0$. The filled-symbols and the solid lines indicate analytic results and the dotted lines are fit to the numerical results (open-symbols). The open circles denote the crossover from maximal phase separation (below the circles) to IV phase separation (above the circles).

FIG. 2. Maxwell construction of the free energy (solid line) as a function of the total electron density, which shows that the system phase separates into an A-phase ($n_{\text{A total}} < 1$, circle) and a B-phase ($n_{\text{B total}} > 1$, square) rather than remaining homogeneous with $n_{\text{total}} = 1$. The dotted line that connects A to B is the convex hull, and the vertical dot-dashed line is a guide to the eye for $n_{\text{total}} = 1$. Here, $U = 1.5$, $E_f = -0.85$ and $T = 0$.

FIG. 3. Electron density for all four ground-state phases at $U = 0.9$ in the ground-state phase diagram. The solid symbols show $n_{\text{total}}$ and the open symbols denote $n_f$ for the phase-separated cases. The dot-dashed line is the average electron density, and the dotted line is the average f-electron density. The system is an insulator for $E_f < -1.265$, phase separates when $-1.265 < E_f < -0.845$. It has IV when $-0.995 < E_f < -0.598$ and becomes a simple metal for $E_f > -0.598$. The dashed line between the maximal and IV phase-separated states marks the approximate location of the smooth crossover.
FIG. 4. Specific heat for the various different values of $E_f$ when $U = 0.9$. The sharp jump as the temperature decreases indicates the first-order transition (the phase separation) at the corresponding critical temperature. The triangles mark phase-separated states.