Competition between Phase Separation and "Classical" Intermediate Valence in an Exactly Solved Model

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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 that (i) either phase separation or a direct metal-insulator transition precludes 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.

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The phenomenon of intermediate valence (IV) is seen in a number of rare-earth compounds (such as Ce, SmB_6, SmS, YbB_{12}, Eu_3O_4, etc.), where the average f-electron filling per ion becomes nonintegral [1]. These materials exhibit distinctive anomalies in thermodynamic and transport properties accompanied with either continuous or discontinuous valence transitions as the temperature, pressure, or composition is 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) [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) [3], where IV arises from a quantum-mechanical mixture of states with different f occupancy ("quantum-mechanical" IV) and the transitions are continuous, being driven by the hybridization between the f electrons and the conduction electrons. Most materials fall into category (ii) and it is believed 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 [1,4] include Eu_3O_4, Eu_3S_4, and Sm_3S_4). 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. Similar work has been performed in one dimension [5].

It is important to examine the experimental differences between scenarios (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 [6]). 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

$$H = -\sum_{ij,\sigma} t_{ij} d^\dagger_{i\sigma} d_{j\sigma} + E_f \sum_{i,\sigma} f^\dagger_{i\sigma} f_{i\sigma} + U_{ff} \sum_i f^\dagger_{i\uparrow} f_{i\uparrow} f^\dagger_{i\downarrow} f_{i\downarrow} + U \sum_{i,\sigma\sigma'} d^\dagger_{i\sigma} d_{i\sigma} f^\dagger_{i\sigma'} f_{i\sigma'} - \mu \sum_{i,\sigma} (d^\dagger_{i\sigma} d_{i\sigma} + f^\dagger_{i\sigma} f_{i\sigma}), \quad (1)$$

where $d^\dagger_{i\sigma}$ ($d_{i\sigma}$) is the creation (annihilation) operator for a conduction-band electron of spin σ at site i, t_{ij} is the hopping matrix between lattice sites i and j, $f^\dagger_{i\sigma}$ ($f_{i\sigma}$) 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 $n_{\text{total}} = n_d + n_f = 1$ 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 occur only when the f level lies inside the bottom half of the conduction band. In our calculations, we adjust a chemical potential μ to satisfy the constraint $n_{\text{total}} = 1$; μ is "pinned" near 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 $G(\omega)$ [6–8]. We examine this model on the Bethe lattice, where the density of states for the noninteracting system becomes semicircular with the bandwidth $4t^* = 4t\sqrt{Z}$. [We take t^* as our energy unit ($t^* = 1$), t is the hopping integral, and Z is the coordination number ($Z \to \infty$).] 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 [9]. Therefore, when $n_{\text{total}} = 1$, we solve the problem by minimizing the free energy [2] $F[n_f, n_{\text{total}} = 1]$ as a function of n_f ($0 \leq n_f \leq 1$):

$$F[n_f, n_{\text{total}} = 1] = 2\int d\epsilon\, \epsilon f(\epsilon) A(\epsilon) + E_f n_f + 2T \int d\epsilon \{f(\epsilon)\ln f(\epsilon) + [1 - f(\epsilon)]\ln[1 - f(\epsilon)]\} A(\epsilon) + T[n_f \ln n_f + (1 - n_f)\ln(1 - n_f) - n_f \ln 2], \quad (2)$$

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. 1). For large enough U [7], there are only two phases: a metal when $E_f > -\frac{8}{3\pi}$ and an insulator when $E_f < -\frac{8}{3\pi}$. In this limit, the system becomes effectively noninteracting 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 near 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 $F_{\text{gs}}[n_f, n_{\text{total}} = 1]$ has its minimum, increases continuously from 0. Hence, the boundary between the metal and the homogeneous IV phases may be obtained from

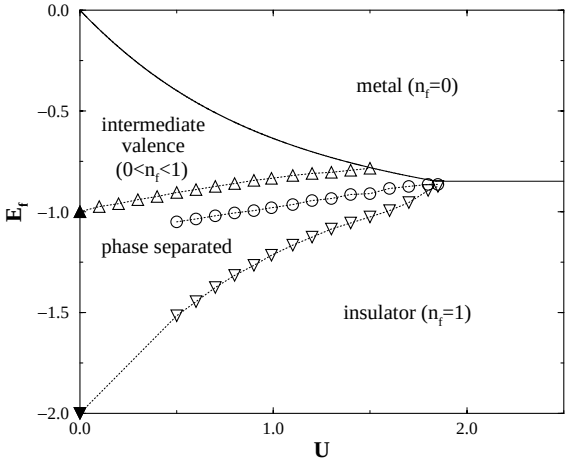

FIG. 1. Phase diagram of the spin-$\frac{1}{2}$ Falicov-Kimball model when $n_{\text{total}} = 1$ and $T = 0$. The filled symbols and the solid lines indicate analytic results and the dotted lines are fit to the numerical results (open symbols). The open circles denote the crossover from maximal phase separation (below the circles) to IV phase separation (above the circles).

$$\left.\frac{\partial F_{\text{gs}}}{\partial n_f}\right|_{n_f=0, n_{\text{total}}=1} = 0, \quad (3)$$

which determines when the metallic phase is no longer a local minimum of the free energy. The analytic form of $F_{\text{gs}}[n_f \to 0, n_{\text{total}} = 1]$ is found from substituting the small-n_f expansion [7] for $A(\omega)$,

$$A(\omega) = \frac{\sqrt{4 - \omega^2}}{2\pi}\left[1 + \frac{n_f U(\omega - 2U)}{(1 - U\omega + U^2)(4 - \omega^2)} + O(n_f^2)\right], \quad (4)$$

into Eq. (2) at $T = 0$. After performing the integral, the boundary equation resulting from Eq. (3) becomes

$$E_f = -\frac{2}{\pi} + \frac{1}{2U} - \frac{U}{2} + \frac{2}{\pi}\left(\frac{1}{U} + U\right) \times \left(\arctan\frac{2U}{1 - U^2} - \arctan\frac{1 + U}{1 - U}\right). \quad (5)$$

Direct numerical calculations, minimizing the free energy in Eq. (2), show good agreement with Eq. (5). This result is valid for $U \leq 1.841\,77$; 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 $F[n_f, n_{\text{total}}]$ 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

$$F_{\text{avg}} = \alpha F[n^A_{\text{total}}] + (1 - \alpha)F[n^B_{\text{total}}], \qquad (6)$$

with

$$1 = \alpha n^A_{\text{total}} + (1 - \alpha)n^B_{\text{total}}, \qquad (7)$$

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

Valence transitions.—We begin at the $U = 0$ limit. In this case, IV phases can be found whenever $-2 \le E_f \le 0$ and the chemical potential for the conduction electrons is pinned at E_f yielding n_d conduction electrons ($0 \le n_d \le 1$). The remaining $1 - n_d$ electrons 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 $n^A_f = 0$, $n^A_{\text{total}} = n_d$, $n^B_f = 1$, and $n^B_{\text{total}} = n_d + 1$) 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. Such an analysis is tedious, but shows that the maximal phase-separated state (where $n^A_f = 0$ and $n^B_f = 1$) is stable whenever $E_f \le -1$. The rest of the phase diagram is determined numerically in Fig. 1. There are four different stable phases as a function of E_f and U: (i) the insulating phase, where all electrons are in the f level, $n_d = 0$ and $n_f = 1$; (ii) the metallic phase, where all the electrons are in the conduction band, $n_d = 1$ and $n_f = 0$; (iii) the phase-separated state, which is maximal when the A and B phases that the system separates into have $n^A_f = 0$ and $n^B_f = 1$, respectively, and is intermediate valent when at least one state has nonintegral f filling; and (iv) the homogeneous intermediate valence state, where n_f is nonintegral. Notice how both phase separation and the direct metal-insulator transition preclude IV behavior over much of the phase diagram. The phase separation is likely to become inhomogeneous charge ordering in a real material, because the long-range Coulomb interaction (ignored in the FKM) will not allow the system to separate into states that have excess charge over a large volume, and it will break up into microscopic domains of the different phases.

We examine this behavior in more detail in Figs. 2 and 3. Figure 2 shows the Maxwell construction for the free energy in a case where phase separation occurs. Notice how the free energy becomes concave near $n_{\text{total}} = 1$ which illustrates how the phase-separated state is stabilized. Figure 3 is a vertical slice through the phase diagram at $U = 0.9$. It displays the characteristics of all different

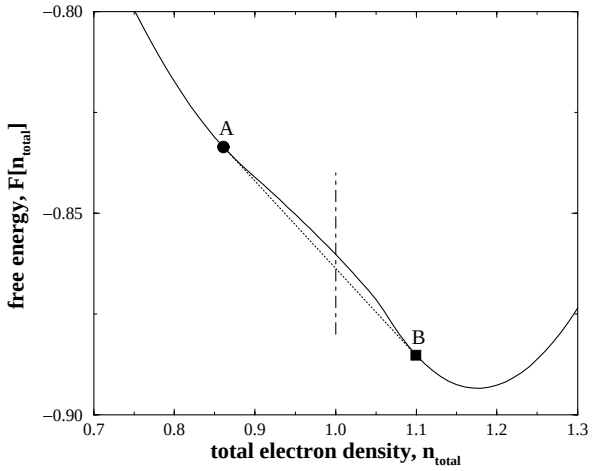

FIG. 2. Maxwell construction of the free energy (solid line) as a function of the total electron density, which shows that the system phase separates into an A phase ($n^A_{\text{total}} < 1$, circle) and a B phase ($n^B_{\text{total}} > 1$, square). The dotted line that connects A to B is the convex 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 $T = 0$.

phases. When $E_f \le -1.265$ the system is an insulator; for $-1.265 \le E_f \le -0.995$ it is a maximal phase-separated state; for $-0.995 \le E_f \le -0.845$ it is IV phase separated; for $-0.845 \le E_f \le -0.598$ it is in the homogeneous IV phase; for $-0.598 \le E_f$ it is a metal. There is no phase transition between the maximal and IV phase-separated states, rather it is a smooth crossover, occurring approximately at the position of the circles in Fig. 1 (our

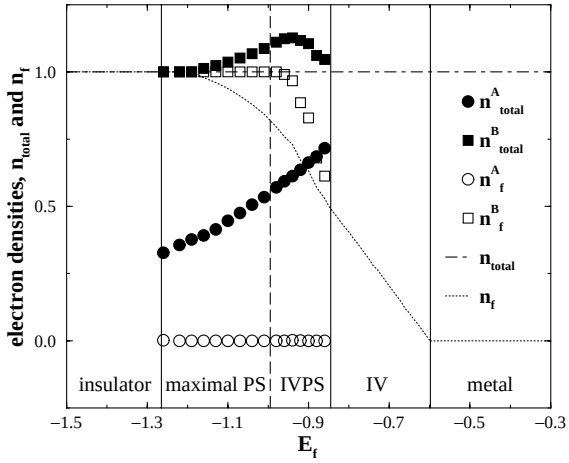

FIG. 3. Electron density at $U = 0.9$ in the ground state. The solid symbols show n_{total} and the open symbols denote n_f for the phase-separated cases. The dot-dashed line is the average electron density, and the dotted line is the average f-electron density. The system is an insulator for $E_f < -1.265$; the 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.

criterion for the crossover is when $n_f^B \leq 0.999$). We found that within the homogeneous IV phase, the valence change as a function of E_f (and of T) was always continuous and exhibited no first-order (discontinuous) transitions. The only first-order transitions occur in the phase-separated states. Hence, the only way to have discontinuous IV transitions arises either from the coupling of the electrons to the lattice, or involves a phase-separation transition rather than a pure IV change. (We should emphasize here that we have not examined all other fillings of the FKM, where some discontinuous transitions could occur.) These results differ from those recently seen in the one-dimensional model [5], where discontinuous IV transitions are also possible (although that calculation has difficulty differentiating from a discontinuous transition and phase separation).

These results summarize the behavior at $T = 0$. At finite 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_3S_4 [4]: there is a first-order transition at 160 K 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).

We have examined the phenomenon of intermediate valence in the spin-$\frac{1}{2}$ Falicov-Kimball model. This is a model that can display only 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 precludes 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].

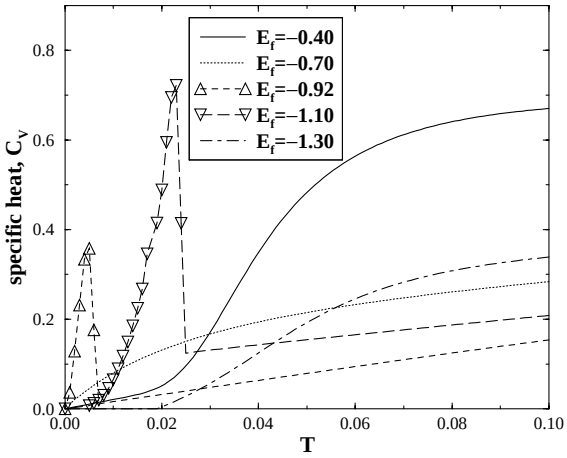

FIG. 4. Specific heat for the various different values of E_f when $U = 0.9$. The sharp jump as the temperature decreases indicates the first-order transition (the phase separation) at the corresponding critical temperature. The triangles mark phase-separated states.

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[1] D. I. Khomskii, Sov. Phys. Usp. **22**, 879 (1979); in *Quantum Theory of Solids*, edited by I. M. Lifshits (Mir, Moscow, 1982).
[2] L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. **22**, 997 (1969); R. Ramirez, L. M. Falicov, and J. C. Kimball, Phys. Rev. B **2**, 3383 (1970).
[3] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[4] O. Massenet, J. M. D. Coey, and F. Holtzberg, J. Phys. (Paris), Colloq. **10**, C4-297 (1976).
[5] P. Farkašovský, Phys. Rev. B **51**, 1507 (1995); **52**, R5463 (1995); **54**, 11 261 (1996); Z. Phys. B **104**, 147 (1997); Phys. Rev. B **60**, 10 776 (1999).
[6] J. K. Freericks and V. Zlatić, Phys. Rev. B **58**, 322 (1998).
[7] Woonki Chung and J. K. Freericks, Phys. Rev. B **57**, 11 955 (1998).
[8] U. Brandt and C. Mielsch, Z. Phys. B **75**, 365 (1989); **79**, 295 (1990); U. Brandt, A. Fledderjohann, and G. Hülsenbeck, Z. Phys. B **81**, 409 (1990); U. Brandt and C. Mielsch, Z. Phys. B **82**, 37 (1991).
[9] P. G. J. van Dongen and C. Leinung, Ann. Phys. (Leipzig) **6**, 45 (1997).
[10] We have not ruled out discontinuous IV transitions at other values of n_{total}. The FKM does have discontinuous metal-insulator transitions at larger values of U [7].