Dimerization Induced by the RKKY Interaction

J. C. Xavier,[1] R. G. Pereira,[1] E. Miranda,[1] and I. Affleck[2]
[1]*Instituto de Física Gleb Wataghin, Unicamp, C.P. 6165, Campinas SP 13083-970, Brazil*
[2]*Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215, USA*
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We report the presence of spin dimerization in the ground state of the one-dimensional Kondo lattice model at quarter filling. The emergence of this new phase of the Kondo lattice can be traced to the form of the RKKY interaction between the localized moments and provides the first example of dimerization induced indirectly by itinerant electrons. We propose this dimer ordering as the driving mechanism of the spin-Peierls phase observed in the quasi-one-dimensional organic compounds $(\mathrm{Per})_2M(\mathrm{mnt})_2$ (M = Pt, Pd). Moreover, this suggests that a richer phase diagram than the Doniach paradigm may be needed to accommodate the physics of heavy fermion materials.

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Our understanding of the physics of heavy fermion materials has been strongly influenced by the paradigm set by Doniach [1]. It proposes that the ground state of the Kondo lattice model exhibits, as a function of the Kondo coupling constant, antiferromagnetic and paramagnetic phases separated by a quantum critical point. A great deal of effort, both experimental and theoretical, has been devoted to the elucidation of the nature of this quantum phase transition (for an overview, see [2]). On the other hand, the variety of behavior observed in real materials suggests that the complete picture is far richer.

We illustrate this richness by identifying a new phase of the one-dimensional Kondo lattice model [3]. Our numerical calculations with the density matrix renormalization group (DMRG) technique show that the ground state of the model has spin dimerization at quarter filling ($n = \frac{1}{2}$). We explain how this previously overlooked state can be understood in terms of the effective spin-spin RKKY [4] interaction mediated by the conduction electrons. Interestingly, the quasi-one-dimensional organic compounds $(\mathrm{Per})_2M(\mathrm{mnt})_2$ (M = Pt, Pd) are *actual realizations of weakly coupled quarter-filled* $S = \frac{1}{2}$ *Kondo chains* [5–8]. We will show, based on our results, that the itinerant-electron-induced dimer order we have found is a viable candidate for the driving mechanism behind the hitherto unexplained dimerization transition observed in these systems.

We consider the one-dimensional $S = \frac{1}{2}$ Kondo lattice Hamiltonian with L sites

$$H = -\sum_{j=1,\sigma}^{L-1} (c_{j,\sigma}^{\dagger} c_{j+1,\sigma} + \mathrm{H.c.}) + J \sum_{j=1}^{L} \mathbf{S}_j \cdot \mathbf{s}_j, \quad (1)$$

where $c_{j\sigma}$ annihilates a conduction electron in site j with spin projection σ, $\mathbf{S}_j$ is a localized spin-$\frac{1}{2}$ operator, and $\mathbf{s}_j = \frac{1}{2}\sum_{\alpha\beta} c_{j,\alpha}^{\dagger} \boldsymbol{\sigma}_{\alpha\beta} c_{j,\beta}$ is the conduction electron spin-density operator. $J > 0$ is the Kondo coupling constant between the conduction electrons and the local moments. We have set the hopping amplitude and the lattice spacing to unity to fix the energy and length scales. We treated the model with the DMRG technique [9,10] with open boundary conditions. We used the finite-size algorithm for sizes up to $L = 120$ keeping up to $m = 800$ states per block. The discarded weight was typically about 10^{-5}–10^{-8} in the final sweep.

Dimerization of the localized spins may be detected through the order parameter $D(j) = \langle \mathbf{S}_j \cdot \mathbf{S}_{j+1} \rangle$. In a uniform system $D(j)$ is j independent, whereas it shows oscillations of period 2 in the presence of dimerization. In Fig. 1(a) we show $D(j)$ at quarter filling ($n = \frac{1}{2}$) for $J = 0.5$ and $L = 120$. There are strong oscillations with amplitude ≈ 0.21 around an average zero value. We have checked that this is not an artifact of a finite system or open boundaries. Indeed, in Fig. 1(b), we show the value of the order parameter at the center of the chain $D(j = L/2 - 1)$ as a function of $1/L$. There is very weak size dependence indicating that the value at $L = 120$ is

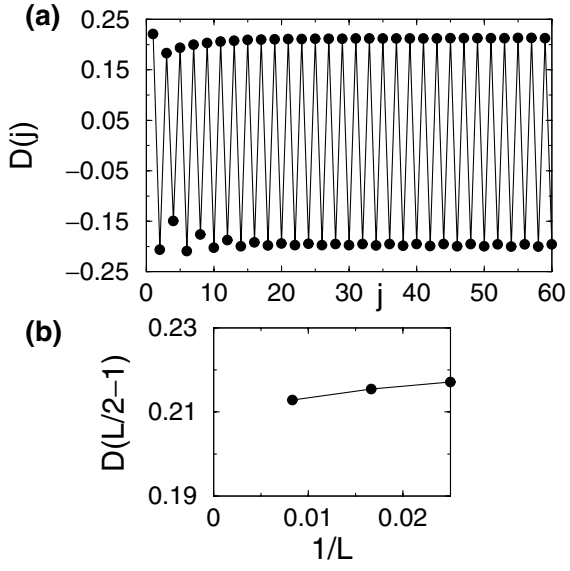

FIG. 1. (a) The dimer order parameter $D(j)$ vs lattice site for $J = 0.5$, $L = 120$, and density $n = 0.5$. Only half the chain is shown. (b) $D(L/2 - 1)$ vs $1/L$ for $J = 0.5$ and $n = 0.5$.

already very close to the thermodynamic limit. This robust result is unambiguous evidence for a dimerized ground state at quarter filling and it is surprising that it has gone unnoticed in such a well-studied model [3]. As far as we know, it is the first example of dimerization induced by an *indirect* spin-spin interaction mediated by itinerant electrons.

It is also instructive to study the Fourier transform of $D(j)$. In order to minimize boundary effects we used a smoothed Fourier transform as suggested in Refs. [11,12]. In Fig. 2(a) we show the smoothed Fourier transform of $D(j)$ for $J = 0.5$, $n = 0.5$, and $L = 120$. The only feature is a noticeable peak at $q = \pi$ reflecting the alternating sign of the order parameter $D(j)$. The critical value of J that separates the paramagnetic phase from the ferromagnetic one is $J_c \sim 1.7$ for $n = 0.5$ [3]. We found that the dimerization occurs only inside the paramagnetic phase. In Fig. 2(b) we show the intensity of the peak of $D(q)$ at $q = \pi$ as a function of the Kondo coupling J for $L = 120$ and $n = 0.5$. As can be seen, the dimerization decreases smoothly as we increase J and disappears in the ferromagnetic phase (within the accuracy of the DMRG).

A very small magnetic field is enough to kill the dimerization. We show in Fig. 3 the magnetization density and the smoothed Fourier transform of the dimer order parameter as a function of magnetic field h for $J = 0.5$ and $n = 0.5$ (making $g\mu_B = 1$ for both localized spins and conduction electrons). Since finite-size effects are negligible, the results here are for $L = 40$. There is a characteristic field $h^* \approx 0.05$, which separates a high susceptibility region at $h \lesssim h^*$ from a low susceptibility one at $h \gtrsim h^*$ (see inset of Fig. 3). Similar results were observed for other densities and Kondo couplings. As h is increased up to h^*, the magnetization density grows linearly up to $M \approx 0.5$. This corresponds to the full polarization of the localized spins. A further increase of h past h^* acts to slowly polarize the conduction electrons (eventually reaching full saturation at $M = 0.75$), which are now effectively decoupled from the local moments. This is confirmed by the value of the slope for $h \gtrsim h^*$, which is very close to the spin susceptibility of the noninteracting one-dimensional electron gas. Thus, the field h^* is the characteristic energy scale of the interaction between the spin lattice and the electron sea. The numerical values of h^* and the ratio of high-field and low-field susceptibilities (≈ 0.008) both suggest the presence of an exponentially small scale, as seen in other studies [3]. This scale also governs the suppression of the dimerization as can be seen in Fig. 3. Since at $h \gtrsim h^*$ the conduction electrons effectively decouple from the localized spins, this is direct evidence that the dimerization is induced by the interaction with the itinerant electrons.

Dimerization at quarter filling is perhaps not too surprising if we consider the RKKY interaction between localized spins a distance j apart. This is appropriate if $J \ll 1$. Using the usual RKKY formula for a one-dimensional tight-binding lattice at quarter filling we can get the first ten couplings $J_{\mathrm{RKKY}}(j)$ as shown in Fig. 4. Focusing initially on the first two neighbors, we see that $J_{\mathrm{RKKY}}(1) < 0$ and $J_{\mathrm{RKKY}}(2) > 0$. It is believed that a spin chain with first and second neighbor interactions J_1 and J_2 is spontaneously dimerized if $J_2 > 0$ and $-4J_2 < J_1 < 0$ [13] and this is satisfied by the RKKY couplings. In fact, even if $J_1 > 0$ dimerization would ensue provided that $J_1 \lesssim 4.15J_2$ [14,15].

Another curious aspect of Fig. 1 is the sign alternation of $D(j)$ with an almost constant amplitude ~ 0.21. A classical localized spin configuration of the type $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\cdots$ would give rise to such an alternation with amplitude 0.25. Interestingly, the further neighbor RKKY couplings

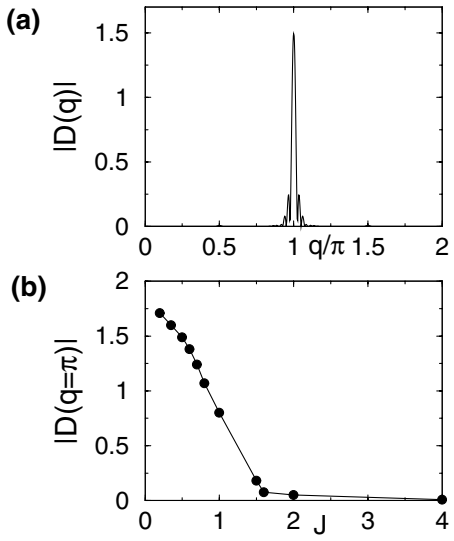

FIG. 2. (a) Modulus of the smoothed Fourier transform $|D(q)|$ vs momentum for $J = 0.5$, $L = 120$, and density $n = 0.5$. (b) $|D(q = \pi)|$ as a function of the Kondo coupling J for $L = 120$ and $n = 0.5$.

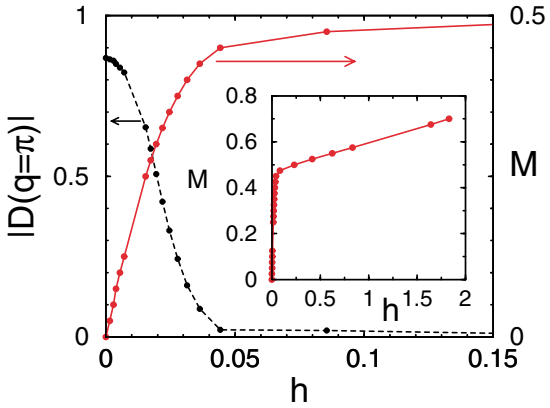

FIG. 3 (color online). Magnetization density M and modulus of the smoothed Fourier transform $|D(q = \pi)|$ as a function of applied magnetic field h, for $L = 40$, $J = 0.5$, and $n = 0.5$. Inset: Magnetization density up to higher fields.

of Fig. 4 favor this classical state [note that $J_{\mathrm{RKKY}}(j) \approx 0$ for odd $j \geq 3$]. Of course, we do not expect this long-range classical order to survive in the singlet ground state, but the fact that $|D(j)| \sim 0.25$ suggests that it may have a very long correlation length.

We have also calculated dimer correlations away from $n = 0.5$. We observed that $D(j)$ no longer oscillates symmetrically around zero. The average actually goes from positive (ferromagnetic) for $n < 0.5$ to negative (antiferromagnetic) for $n > 0.5$. This is consistent with the general trend of the RKKY interaction which is predominantly ferromagnetic at low fillings. However, in contrast to the quarter-filled case, away from $n = 0.5$ $D(j)$ has more than one characteristic wave vector. This is shown in Fig. 5 for the densities $n = 0.4$ and $n = 0.6$ ($L = 120$ and $J = 0.35$). They have $4k_F = 2\pi n \pmod{2\pi}$ as the dominant peak. There are also subdominant peaks at $2k_F^{\mathrm{small}} = \pi n$ or $2k_F^{\mathrm{large}} = \pi(1 - n)$, which are the Fermi sea sizes without and with the localized moments included in the count, respectively [16–18]. However, no clear trend can be discerned. Quantum fluctuations will destroy incommensurate order in one dimension. However, the system may lock onto particular commensurate structures within finite intervals of n. Such long commensurate periods have been discussed in related Kondo lattice models [19] used to describe the pnictide CeSb [20] and in the context of doped Mott insulators [21].

The organic compounds $(\mathrm{Per})_2M(\mathrm{mnt})_2$, where $M = \mathrm{Pt}$ or Pd, "Per" is perylene and "mnt" is maleonitriledithiolate, are realizations of quarter-filled quasi-one-dimensional Kondo lattices [5,7,8]. The localized spins reside in the $M(\mathrm{mnt})_2$ units and the conduction electrons are provided by the perylene groups. These compounds show metal-insulator transitions at $T_{\mathrm{MIT}}(\mathrm{Pt}) = 7$ K and $T_{\mathrm{MIT}}(\mathrm{Pd}) = 28$ K, accompanied by one-dimensional lattice instabilities which indicate the formation of a Peierls-type dimerization. Initial studies [6] had difficulties reconciling the behavior of these systems with conventional electron-phonon (Peierls) or spin-phonon (spin-Peierls) instabilities and the exact nature of these transitions has remained a mystery. On the other hand, there were speculations on the role played by the RKKY interaction [7]. Several uncertainties remained, however, since spin-density wave (SDW) ordering was not observed and the Fermi wave vector of the conduction electrons ($2k_F = \pi/2$) does not match the period of the dimerization.

Our results suggest a possible way out of this quandary. Indeed, the one-dimensional nature of the system suppresses the appearance of a conventional SDW and favors a dimerized state instead. Furthermore, the Fermi wave vector, as explained in connection with Fig. 4, is actually crucial for providing the correct spatial dependence of the RKKY interactions that lead to the dimer order. An estimate of the finite transition temperature (absent in the strictly one-dimensional model) could be obtained from the divergence of the dimer susceptibility as $T \to 0$, along the lines explained in Refs. [22,23]. Our results on the ground state, however, suggest the presence of a (probably exponentially) small energy scale of a size compatible with the transition temperatures (Fig. 3). It is therefore tempting to use this scale as an estimate of T_{MIT}. Moreover, the direct measurement of the magnetic field needed to destroy the dimer order at $T = 0$ showed it to be of the order of $k_B T_{\mathrm{MIT}}/\mu_B$ [8], lending further support to this identification.

Finally, in Fig. 6 we plot the finite-size charge gap for several densities (in the sector of total spin zero) as a function of $1/L$. It is clear that the quarter-filled case has a charge gap, unlike other fillings (see Ref. [12] for a similar case). A mechanism for the opening of this gap can be obtained by bosonization. By analogy with the RKKY interaction, if we integrate out the localized spins an effective interaction between conduction electron spins at sites i and j is generated, which is proportional to $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$. The strong dimer correlations of Fig. 1 lead to a term $\propto \delta_{i,j+1}(-1)^j$. This gives rise to a *staggered* nearest neighbor interaction between conduction electron spins $(-1)^j \mathbf{s}_j \cdot \mathbf{s}_{j+1}$. Bosonizing this *at quarter filling* leads to a

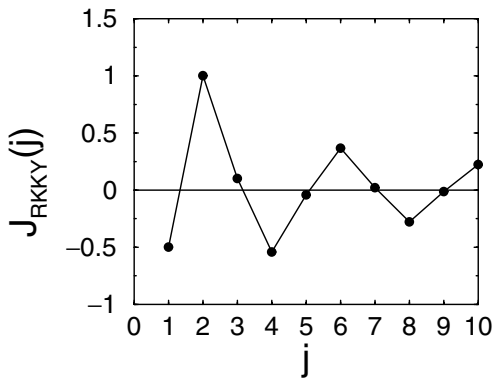

FIG. 4. RKKY coupling constant (in arbitrary units) as a function of the distance between sites.

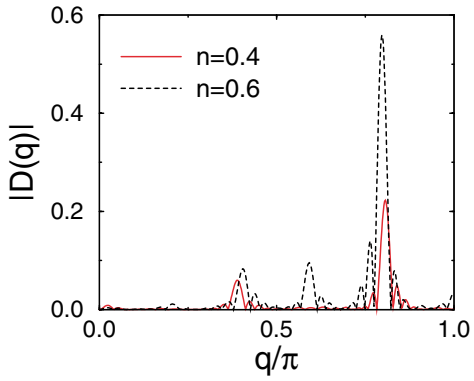

FIG. 5 (color online). Modulus of the smoothed Fourier transform $D(q)$ away from quarter filling ($L = 120$ and $J = 0.35$).

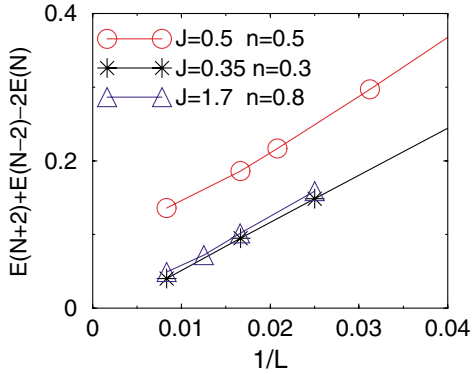

FIG. 6 (color online). Charge gap vs $1/L$ for various fillings. The notation is the same as in Ref. [12]. The accuracy is given by the size of the symbols.

$\cos(\sqrt{8K_\rho}\phi_\rho)$ term, where we follow the notation of Ref. [24]. If $K_\rho < 1$ this term is relevant and opens a gap in the charge sector in close analogy to the umklapp term in the half-filled Hubbard model [24]. This is a very mild condition and is likely to be fulfilled. Indeed, numerical estimates of K_ρ at other fillings indicate that $K_\rho < 1$ [17]. Thus, we propose this RKKY-induced dimerization as the driving mechanism behind the metal-insulator transitions observed in $(\mathrm{Per})_2M(\mathrm{mnt})_2$. Note that a similar term is generated in the spin sector $\cos(\sqrt{8K_\sigma}\phi_\sigma)$. However, $K_\sigma = 1$ due to SU(2) symmetry and this is a *marginal* term. Its relevance and the accompanying spin gap depends on the sign of the coupling constant. We have found no evidence of a spin gap at this filling.

In conclusion, we have found that the Kondo lattice model in one dimension has a novel type of dimerization at quarter conduction electron filling. It can be understood from the structure of the RKKY interaction between localized moments. Furthermore, it provides a simple mechanism for the metal-insulator transition of some quasi-one-dimensional organic compounds. Although confined to one dimension, we believe our results may have implications for the phase diagram of three-dimensional heavy fermion materials.

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