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Can there be "Hidden Order" in transition metals?

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We examine the conditions required to produce a combined spin and orbital density wave state such as that which has been proposed to describe the "Hidden Order" phase of URu_2Si_2. By using an idealized tight-binding model with only nearest-neighbor hopping processes, we search for factors that could stabilize "Hidden Order" phases in transition metals. It is found that strong anisotropy or reduced dimensionality may stabilize "Hidden Order" over spin-density wave phases. This suggests the possibility that the enigmatic pseudogap phases reported for the high-temperature ironpnictide superconductors may also be described by the Hund's rule "Hidden Order" mechanism.

1 Introduction The "Hidden Order" phase of URu_2Si_2 is marked by a large jump in the specific heat and the formation of a pseudogap in the density of states at 17.5 K [1, 2]. Far-infrared reflectance measurements [3] have shown that gaps of the order of 5.6 and 7.5 meV develop below the transition temperature. STM measurements [4] confirmed the evolution of 5 meV gaps in the "Hidden Order" phase, and similar pseudogaps have also been observed by ultrafast optical spectroscopy [5]. Thermodynamic and transport measurements [2, 6] indicate that approximately 40% of the Fermi-surface is gapped in the "Hidden Order" phase. There is evidence that the "Hidden Order" state also has a modified spatial periodicity [7] and involves Fermi-surface nesting [8]. Electronic structure calculations give support for the involvement of Fermi-surface nesting [9, 10]. Initially, the transition was assumed to be due to the formation of a static spin density wave. It is now believed that the "Hidden Order" transition is not due to the formation of a spin density wave although an antiferromagnetic phase does form under pressure [11] and has a transition temperature and a Fermi-surface that are similar to those of the "Hidden Ordered" phase [12]. Since experiments have been unable to identify the nature of the order parameter, the transition has come to be known as a "Hidden-Order" Transition. Recently, it has been discovered that the "Hidden Order" phase has broken spin-rotational invariance [13]. A recent review of the subject has been given in Ref. [14].

It has been suggested [15] that the "Hidden Order" transition occurs in the uranium compound URu_2Si_2 but not in cerium compounds since the uranium f orbitals are occupied by approximately two electrons while cerium only has a single f electron. In the case of multiple occupation, the Hund's rule exchange interaction is expected to have significant effects. It was proposed that the "Hidden Order" state is produced by the Fermi-surface nesting of bands with different orbital characters which become coupled when the spin-rotational invariance of the Hund's rule exchange interaction is spontaneously broken. The formation of a combined spin and orbital density wave lifts the degeneracy of the Fermi-surface, producing gaps across most of the Fermi-surface. Detailed calculations were performed with the underscreened Anderson Model [15], using two degenerate 5f bands. The proposed mechanism should also be operative for transition metal compounds which is in accord with the hypothesis of Tateiwa et al. [16], who suggested that "Hidden Order" of the type found in URu_2Si_2 could also be responsible for the mysterious pseudo-gap phase seen in the high-temperature iron-pnictide superconductors.

2 Tight-binding model The model describes a set of degenerate localized orbitals (labeled by χ) which acquire itinerant character through direct hopping onto neighboring ions. The Hamiltonian is

written as

$$\hat{H} = \hat{H}_{\rm b} + \hat{H}_{\rm int}, \tag{1}$$

where $\hat{H}_{\rm b}$ describes the electronic bands formed by the inter-ionic hopping, and $\hat{H}_{\rm int}$ describes the spin-rotationally Coulomb interaction between the electrons in the localized orbitals on the same atom.

The tight-binding band Hamiltonian can be written as

$$\hat{H}_{\rm b} = \sum_{\underline{k},\sigma,\chi} E^{\chi}(\underline{k})\, d^{\dagger,\chi}_{\underline{k},\sigma}\, d^{\chi}_{\underline{k},\sigma} + \sum_{\underline{k},\sigma,\chi,\chi'} V^{\chi,\chi'}(\underline{k})\, d^{\dagger,\chi}_{\underline{k},\sigma}\, d^{\chi'}_{\underline{k},\sigma}, \tag{2}$$

where the $E^{\chi}(\underline{k})$ and $V^{\chi,\chi'}(\underline{k})$ are calculated for tetragonal structure and are expressed in terms of the Slater–Koster parameters. The Slater–Koster parameters [17] are denoted by $t_{dd\sigma}$, $t_{dd\pi}$ and $t_{dd\delta}$, and their dependence on the inter-nuclear separations R are sketched in Fig. 1. The Slater–Koster parameters were calculated with a spherically symmetric potential and normalized to unity. The canonical 3d band model values of these parameters for a cubic system [18] are in the proportions 6, −4, 1.

The spin-rotationally invariant Coulomb interaction is expressed in the form

$$\hat{H}_{\rm int} = \left(\frac{U-J}{2N}\right) \sum_{\underline{k},\underline{k}',\underline{q},\sigma,\chi\neq\chi'} d^{\dagger,\chi}_{\underline{k}+\underline{q},\sigma}\, d^{\chi}_{\underline{k},\sigma}\, d^{\dagger,\chi'}_{\underline{k}'-\underline{q},\sigma} d^{\chi'}_{\underline{k}',\sigma} + \left(\frac{U}{2N}\right) \sum_{\underline{k},\underline{k}',\underline{q},\sigma,\chi,\chi'} d^{\dagger,\chi}_{\underline{k}+\underline{q},\sigma}\, d^{\chi}_{\underline{k},\sigma}\, d^{\dagger,\chi'}_{\underline{k}'-\underline{q},-\sigma} d^{\chi'}_{\underline{k}',-\sigma} + \left(\frac{J}{2N}\right) \sum_{\underline{k},\underline{k}',\underline{q},\sigma,\chi\neq\chi'} d^{\dagger,\chi}_{\underline{k}+\underline{q},\sigma}\, d^{\chi'}_{\underline{k},\sigma}\, d^{\dagger,\chi'}_{\underline{k}'-\underline{q},-\sigma}\, d^{\chi}_{\underline{k}',-\sigma}. \tag{3}$$

The last line in the interaction of Eq. (3) originates from the spin-flip term of the Hund's rule interaction which is required from considerations of spin-rotational invariance. It is expected that U has a magnitude of about 4 eV and J is the order of an eV.

3 The "Hidden Order" instability The "Hidden Order" instability is assumed [15] to be driven by the Hund's rule interaction J which allows the system to spontaneously break spin-rotational symmetry by selecting a plane in which the spin-flip terms of the Hund's rule exchange are non-zero. This symmetry breaking is characterized by a non-zero expectation value of the spin and momentum-dependent non-Hermitean operator $\hat{z}^{\chi',\chi}_{\underline{q},\sigma}$, defined by

$$\hat{z}^{\chi',\chi}_{\underline{q},\sigma} = \frac{1}{N}\sum_{\underline{k}} d^{\dagger,\chi'}_{\underline{k}+\underline{q},\sigma}\, d^{\chi}_{\underline{k},\sigma}. \tag{4}$$

Within a mean-field approximation [19], this symmetry breaking produces a spin and momentum dependent hybridization between bands with different orbital characters. We shall derive the criterion for instability of the normal phase to the "Hidden Order" state. For the sake of simplicity, we shall assume that the crystal field splitting between the $e_{\rm g}$ and $t_{2\rm g}$ orbitals is sufficiently large so that we may discuss the instabilities of these bands separately.

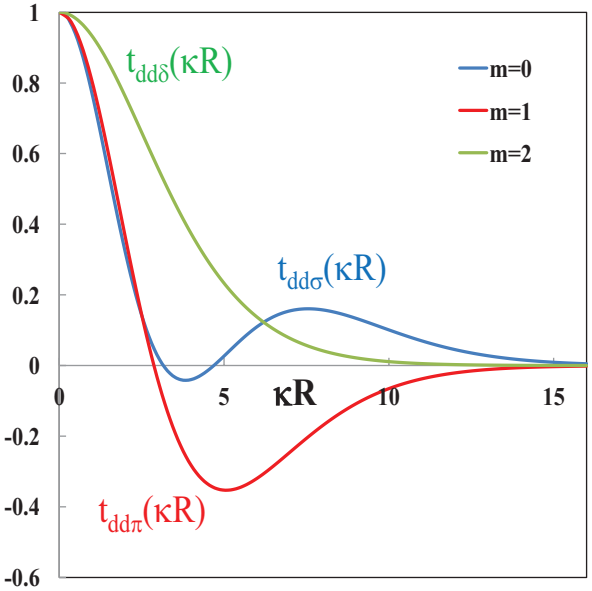

Figure 1 (online color at: www.pss-b.com) The variation of normalized 3d Slater–Koster parameters with internuclear separations R. The parameters were calculated using a spherically symmetric potential.

3.1 The t_{2g} bands For a tetragonal system with nearest neighbor hopping, the three $t_{2\rm g}$ bands have pure (unmixed) orbital characters. We shall examine the spontaneous mixing of the bands that occurs within a mean-field approximation, using a Green's function approach. The time-ordered one-electron Green's functions are defined by

$$G^{\chi,\chi'}_{\sigma}(\underline{k},\underline{k}';t) = -\frac{i}{\hbar}\left\langle \hat{T}\, d^{\chi}_{\underline{k},\sigma}(t)\, d^{\dagger,\chi'}_{\underline{k}',\sigma}(0)\right\rangle, \tag{5}$$

where $\hat{T}$ is Wick's time-ordering operator. The temporal Fourier transform of the Green's functions for the $t_{2\rm g}$ orbitals, defined by

$$G^{\chi,\chi'}_{\sigma}(\underline{k},\underline{k}';\omega) = \int_{-\infty}^{\infty} {\rm d}t\, \exp[\, i\,\omega\, t\,]\, G^{\chi,\chi'}_{\sigma}(\underline{k},\underline{k}';t), \tag{6}$$

satisfy the mean-field equations of motion

$$(\omega - E^{\chi}_{\sigma}(\underline{k}))G^{\chi,\chi'}_{\sigma}(\underline{k},\underline{k}';\omega) - \sum_{\chi''\neq\chi} \kappa^{\chi'',\chi}_{-\underline{Q},\sigma} G^{\chi'',\chi'}_{\sigma}(\underline{k}+\underline{Q},\underline{k}';\omega) = \delta^{\chi,\chi'}\delta^{3}(\underline{k}-\underline{k}'), \tag{7}$$

where

$$\kappa^{\chi',\chi}_{-\underline{Q},\sigma} = J\, z^{\chi',\chi}_{-\underline{Q},-\sigma} - (\,U - J\,)\, z^{\chi',\chi}_{-\underline{Q},\sigma}, \tag{8}$$

and the spin-dependent Hartree–Fock band energies are given by

$$E^{\chi}_{\sigma}(\underline{k}) \;=\; E^{\chi}(\underline{k}) + U\sum_{\chi'}\,\overline{n}^{\chi'}_{-\sigma} \;+ (U-J)\sum_{\chi'\neq\chi}\overline{n}^{\chi'}_{\sigma}, \tag{9}$$

in which $\overline{n}^{\chi}_{\sigma}$ is the average occupation number, per site, of the χ-th orbital for an electron of spin σ. The above set of algebraic equations can be solved for the Green's functions. The occupation numbers $\overline{n}^{\chi}_{\sigma}$ and the expectation values $z^{\chi',\chi}_{\underline{Q},\sigma}$ must be solved self-consistently. The complex off-diagonal expectation values are obtained from the equations

$$z^{\chi',\chi}_{\underline{Q},\sigma} = -\frac{1}{N}\sum_{k}\int_{C}\,\mathrm{d}\omega(2\pi i)f(\omega)G^{\chi,\chi'}_{\sigma}(\underline{k},\underline{k}+\underline{Q};\omega), \tag{10}$$

where the contour C encloses the real axis in a clockwise direction and $\underline{Q}$ is either a commensurate or incommensurate wave vector which results in a modification of the periodicity in the broken-symmetry state.

Close to the "Hidden Order" transition temperature, T_{HO}, Eq. (10) can be linearized in $\kappa^{\chi',\chi}_{-\underline{Q},\sigma}$ to yield the coupled equations

$$z^{\chi',\chi}_{\underline{Q},\sigma}[1-(U-J)\chi^{\chi,\chi'}_{\mathrm{MF},\sigma}(\underline{Q};0)] = -z^{\chi',\chi}_{\underline{Q},-\sigma}J\chi^{\chi,\chi'}_{\mathrm{MF},\sigma}(\underline{Q};0), \tag{11}$$

where $\chi^{\chi,\chi'}_{\mathrm{MF},\sigma}(\underline{Q};0)$ is a static and staggered inter-orbital susceptibility given by

$$\chi^{\chi,\chi'}_{\mathrm{MF},\sigma}(\underline{Q};0) = \frac{1}{N}\sum_{\underline{k}}\left(\frac{f(E^{\chi'}_{\sigma}(\underline{k}+\underline{Q}))-f(E^{\chi}_{\sigma}(\underline{k}))}{E^{\chi}_{\sigma}(\underline{k})-E^{\chi'}_{\sigma}(\underline{k}+\underline{Q})}\right). \tag{12}$$

At $T=T_{\mathrm{HO}}$, the set of equations shown in Eq. (11) allow for a non-trivial solution for which the order parameter is an infinitesimal complex number which is spin-dependent

$$z^{\chi',\chi}_{\underline{Q},\sigma} \;=\; -\,z^{\chi',\chi}_{\underline{Q},-\sigma} \;\neq\; 0, \tag{13}$$

as required if the ordered state is to minimize the Hund's rule interaction energy. The temperature at which the normal state becomes unstable to the "Hidden Ordered" state is given by the largest T_{HO} for all $\underline{Q}$ and all pairs (χ,χ') for which $\chi\neq\chi'$. It is seen that the "Hidden Ordering" is driven by inter-band nesting and the Hund's rule exchange interaction, albeit the instability criterion is enhanced by a Stoner-like enhancement factor involving the direct Coulomb interaction.

3.2 The e_g bands Due to the mixing of the two e_g orbitals, the occurrence of "Hidden Ordering" in the e_g bands is a more complex issue than for the t_{2g} bands. The e_g Bloch bands have mixed characters with amplitudes denoted by $A^{\pm}_{\sigma,\chi}(\underline{k})$ and have Hartree–Fock dispersion relations denoted by $E^{\pm}_{\sigma}(\underline{k})$ that are given by

$$E^{\pm}_{\sigma}(\underline{k}) = \left(\frac{E^{\chi}_{\sigma}(\underline{k})+E^{\chi'}_{\sigma}(\underline{k})}{2}\right) \pm \sqrt{\left(\frac{E^{\chi}_{\sigma}(\underline{k})-E^{\chi'}_{\sigma}(\underline{k})}{2}\right)^{2}+|V^{\chi,\chi'}(\underline{k})|^{2}}. \tag{14}$$

The linearized self-consistency equations reduce to

$$z^{\chi',\chi}_{\underline{Q},\sigma} \;=\; \kappa^{\chi',\chi}_{\underline{Q},\sigma}\;\chi^{\chi,\chi',\chi,\chi'}_{\mathrm{MF},\sigma}(\underline{Q};0) \;+\; \kappa^{*}_{\underline{Q},\sigma}\;\chi^{\chi,\chi',\chi',\chi}_{\mathrm{MF},\sigma}(\underline{Q};0). \tag{15}$$

In the mean-field approximation, the static susceptibilities are given by

$$\chi^{\chi,\chi',\chi'',\chi'''}_{\mathrm{MF},\sigma}(\underline{q};0) = \frac{1}{N}\sum_{\underline{k},\pm,\mp} A^{\pm}_{\sigma,\chi}(\underline{k}+\underline{q})A^{\pm}_{\sigma,\chi''}(\underline{k}+\underline{q})^{*} \times A^{\mp}_{\sigma,\chi'}(\underline{k})^{*}A^{\mp}_{\sigma,\chi'''}(\underline{k}) \times\left(\frac{f(E^{\mp}_{\sigma}(\underline{k}))-f(E^{\pm}_{\sigma}(\underline{k}+\underline{q}))}{E^{\pm}_{\sigma}(\underline{k}+\underline{q})-E^{\mp}_{\sigma}(\underline{k})}\right), \tag{16}$$

where the products of form factors can be expressed in terms of either

$$|A^{\pm}_{\sigma,\chi}(\underline{k})|^{2} = 12\left[1\pm\frac{E^{\chi}_{\sigma}(\underline{k})-E^{\chi'}_{\sigma}(\underline{k})}{\sqrt{(E^{\chi}_{\sigma}(\underline{k})-E^{\chi'}_{\sigma}(\underline{k}))^{2}+4|V^{\chi,\chi'}(\underline{k})|^{2}}}\right], \tag{17}$$

or

$$A^{\pm}_{\sigma,\chi}(\underline{k})^{*}A^{\pm}_{\sigma,\chi'}(\underline{k}) = \pm\frac{V^{\chi,\chi'}(\underline{k})}{\sqrt{(E^{\chi}_{\sigma}(\underline{k})-E^{\chi'}_{\sigma}(\underline{k}))^{2}+4|V^{\chi,\chi'}(\underline{k})|^{2}}}, \tag{18}$$

in which $\chi'\neq\chi$. Since the sign of the second coefficient in the instability criterion of Eq. (15) depends on whether the inter-orbital nesting occurs within the same band or between different bands, the existence of mixing determines the possible phases of the order parameter.

4 Results and discussion For a cubic system and at half-filling, it is found that all three t_{2g} bands show perfect intra-band nesting with nesting vector $\underline{Q}=(\pi,\pi,\pi)$ which expresses the system's tendency to preferentially form spin $S=\frac{3}{2}$ antiferromagnetic phases [20]. This tendency is diminished under doping, however, even when the t_{2g} bands are doubly occupied, the "Hidden Ordered" phase is still not competitive with the formation of spin density wave phases. The tendency for "Hidden Order" to occur is maximized if $t_{dd\pi}(R)\rightarrow -t_{dd\delta}(R)$, which requires a reduction in the internuclear separation R. This can be achieved by imposing a substantial tetragonal distortion on the cubic crystal. The c/a parameter for this distorted system is estimated as

$\sqrt{3}$, if one requires average electron density to be kept approximately constant. Under this condition, the quasi-two dimensional Fermi-surface shows good inter-band nesting at all occupation numbers. In this case, the concept of an adiabatic continuity between the ''Hidden Ordered'' and spin-density wave phases is lost.

By contrast, the e_g bands shows the strongest tendency for inter-orbital nesting at half-filling which, due to the strong mixed orbital character of the bands, also tends to favor the formation of a spin-density wave. The competition between the two ordered phases for nesting between the same portions of Fermi-surface persists for decreasing band fillings. The identical nesting conditions and the similar magnitudes of the interactions suggest that the concept of adiabatic continuity might be applicable.

Apart from the concept of adiabatic continuity discussed above, ''Hidden Ordering'' in transition metals is expected to differ from that found in URu_2Si_2 in at least two other ways. One difference should be in the magnitude of the specific heat jump or the entropy of the transition. The normal state of URu_2Si_2 is characterized as heavy-fermion metal as evidenced by the large γ term in the specific heat [1] which is attributed to a heavy quasiparticle band that crosses the Fermi-energy. The gapping of these heavy-fermion quasiparticle bands at T_{HO} results in a large entropy loss $\Delta S \sim \gamma T_{HO}$ which is quite close to the experimentally observed value [2]. Since for most transition metal compounds the observed quasiparticle masses are significantly smaller than those of heavy fermion systems, the entropy changes that occur at the transitions in 3d metals are expected to be significantly smaller. Another difference that might be expected to occur relates to the loss of spin-rotational invariance at the transition. In URu_2Si_2, the tetragonal symmetry and the strong spin–orbit coupling leads to an easy-axis single-site anisotropy. Due to the combined single-site easy-axis anisotropy and the easy-plane anisotropy associated with the Hund's rule driven symmetry breaking, a fraction of the $S = 1$ spins are expected to condense into a plane with a normal perpendicular to the c-axis. This observation is in accord with the $a - b$ anisotropy experimentally found by Okazaki et al. [13]. The tendency for breaking spin-rotational symmetry in a 3d metal, in which there is no easy-axis anisotropy, is not expected to follow the same pattern as URu_2Si_2.

To summarize, the Hund's rule mechanism described in Ref. [15] could be expected to be at work in transition metal compounds. ''Hidden Ordering'' is favored by highly anisotropic or quasi two-dimensional structures. Hence, one may speculate that the Hund's rule exchange interaction is responsible for the formation of the enigmatic pseudo-gapped phases found in ironpnictide high-temperature superconductors [21].

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