Development of Magnetism in Strongly Correlated Cerium Systems: Non-Kondo Mechanism for Moment Collapse

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We present an ab initio based method which gives clear insight into the interplay between the hybridization, the coulomb exchange, and the crystal-field interactions, as the degree of 4f localization is varied across a series of strongly correlated cerium systems. The results for the ordered magnetic moments, magnetic structure, and ordering temperatures are in excellent agreement with experiment, including the occurrence of a moment collapse of non-Kondo origin. In contrast, standard ab initio density functional calculations fail to predict, even qualitatively, the trend of the unusual magnetic properties.

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The difficulties and interest in treating strongly correlated electron systems, and the consequences of correlation effects on magnetic behavior in the transitional 4f or 5f localization regime, provide one of the central problems of condensed matter physics.1−3 The transitional regime behavior is neither atomiclike nor itinerant. This gives rise to an extremely interesting range of phenomena, but also causes very great difficulties in treating the theory of these phenomena adequately, especially in a way providing the ability to predict the behavior of specific materials.1−3 An adequate treatment requires treating the interelectronic coulomb interaction, i.e. the correlation effects, as constrained by exchange symmetry.4−6 In this letter, we demonstrate an approach for treating these difficulties in predicting the interesting and complex behavior of an important series of cerium compounds.

The isostructural (rock-salt structure) series of the cerium monopnictides CeX (X = P, As, Sb, Bi) and monochalcogenides (X = S, Se, Te) have become prototype model systems for study, because of their unusual magnetic properties.7−13 This series of strongly correlated electron systems offers the opportunity to vary systematically, through chemical pressure, the lattice constant and the cerium-cerium separation on going down the pnictogen or chalcogen column, and hence tailor the degree of 4f localization from the strongly correlated limit in the heavier systems to the weakly correlated limit in the lighter systems.7−13 The calculated single-impurity Kondo temperature, TK, presented below, is much smaller than the magnetic ordering temperature in these systems, and hence this series lies in the magnetic regime of the Kondo phase diagram.14 Nevertheless, in this work we demonstrate that the sensitivity of the hybridization, coulomb exchange, and crystal-field interactions with the chemical environment gives rise to a variety of unusual and interesting magnetic properties across the series, in agreement with experiment, including the occurrence of a non-Kondo magnetic moment collapse.

This class of cerium systems exhibits large magnetic anisotropy which changes from the <001> direction in the pnictides to the <111> direction in the chalcogenides. The low-temperature ordered magnetic moment increases with increasing lattice constant for the pnictides from 0.80μB in CeP to 2.1μB in CeSb and CeBi,7−8 while it decreases with increasing lattice constant for the chalcogenides from 0.57μB in CeS to 0.3μB in CeTe.7−9 The magnetic moment collapse from CeSb to CeTe, with both systems having about the same lattice constant, is indicative of the sensitivity of the magnetic interactions to chemical environment. The experimentally observed low-temperature structure in CeBi and CeSb is the <001> antiferromagnetic type I (↑↓↓↓), whereas in CeAs and CeP the structure is the <001> antiferromagnetic type I (↑↑↓↓).7,15 The ordering temperature increases from 8K in CeP to 26K in CeBi for the pnictides, whereas it decreases from 8.4K in CeS to an unusually low 2.2K in CeTe.7−11 Another unusual feature of this series of cerium compounds is the large suppression of the crystal field (CF) splitting of the Ce3+ free-ion 4f5/2 multiplet from values expected from the behavior of the heavier isostructural rare-earth pnictides or chalcogenides.16 This can be understood17 as arising from band-f hybridization effects. In both the cerium monopnictides and monochalcogenides, the CF splitting between the Γ7 doublet and the Γ8 quartet decreases with increasing anion size, from 150 K for CeP to 10 K in CeBi and from 130 K for CeS to 30 K for CeTe, and it is about the same for the same row in both series, a rather surprising result in view of the additional valence electron on the chalcogen ion.18 Neutron scattering experiments have shown19 that the Γ7-doublet is the CF ground state in all the cerium pnictides and chalcogenides.

In this paper we present material-predictive results from two ab initio based methods to study the change of magnetic properties across this series of cerium systems. The first, ab initio based, method gives clear insight into the role of the three pertinent interactions: 1)
The band-f hybridization-induced inter-cerium magnetic coupling; 2) the corresponding effects of band-f coulomb exchange; and 3) the crystal-field interaction. This approach allows us also to understand the interplay between these interactions as the degree of 4f localization is varied across the series. The predictive calculations give results for the magnetic moments, magnetic structure, and ordering temperatures in excellent agreement with experiment. Thus, this approach allows to understand and predict a number of key features of observed behavior. First, is the very low moment and low ordering temperature of the antiferromagnetism observed in CeTe, an incipient heavy Fermion system. (For a review of theory and experimental behavior of heavy Fermion systems see references 2,3,20,21.) This ab initio-based method, described below, predicts the magnetic moment and ordering temperature collapse from CeSb to CeTe, both systems having about the same lattice constant but CeTe having an additional p electron. The origin of the moment collapse is of non-Kondo origin. The earlier work of Sheng and Cooper3 showed that this magnetic ordering reduction is accurately predicted without including any crystal-field effects. An erroneous statement appears in the recent review article by Santini et al.22 stating that crystal-field effects played an important role in the calculated results of Sheng and Cooper.3 This is incorrect, since crystal-field effects were not included in these calculations. We show in this paper that including the crystal-field effects modifies this behavior only quantitatively. Second, our results demonstrate that, while the band-f coulomb exchange mediated interatomic 4f-4f interactions dominate the magnetic behavior for the heavier systems, which are more localized because of the larger Ce-Ce separation, the opposite is true for the lighter, more delocalized systems, where the hybridization-mediated coupling dominates the magnetic behavior. This reflects the great sensitivity of the relative importance of hybridization and coulomb exchange effects on magnetic ordering depending on the degree of 4f localization. Third, we show that for the lighter more delocalized systems the crystal-field effects are much larger than the inter-cerium interactions and hence dominate the magnetic behavior. Finally, we predict the experimentally observed change of the ground-state magnetic structure from the < 001 > antiferromagnetic type IA (↑↑↓↓) in CeBi and CeSb to the < 001 > antiferromagnetic type I (↑↓↓↑) in CeAs and CeP. On the other hand, the second ab initio method, based on density functional theory within the local density approximation (LDA),23,24 fails to predict, even qualitatively, the trend of magnetic properties in this series of strongly correlated electron systems.

The first, ab initio based, method employs the degenerate Anderson lattice model which incorporates explicitly the hybridization and the coulomb exchange interactions on an equal footing.4,5

\[ H = \sum_k \epsilon_k c_k^\dagger c_k + \sum_{R,m} \epsilon_m f_m^\dagger (R)f_m (R) \\
\quad + \frac{U}{2} \sum_{R,m \neq m'} n_m (R)n_{m'} (R) \\
\quad + \sum_{k,m,R} [V_{km} e^{-i \mathbf{k} \cdot \mathbf{R}} c_k^+ f_m (R) + H.C.] \\
\quad - \sum_{kk',nn'} J_{mn'} (\mathbf{k}, \mathbf{k'}) e^{-i (\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}} c_k^+ f_m (R) c_{k'} f_{m'} (R). \]

(1)

The parameters entering the model Hamiltonian, i.e., the band energies \( \epsilon_k \), the f-state energy \( \epsilon_m \), the on-site coulomb repulsion \( U \), the hybridization matrix elements, \( V_{km} \), and the band-f coulomb exchange \( J_{mn'} (\mathbf{k}, \mathbf{k'}) \) are evaluated on a wholly ab initio basis from non-spin polarized full potential linear muffin tin orbital (FPLMTO) calculations. Here, \( r_1 \) stands for \( |r_1 - r_2|; \phi_k \) are the non-f basis states of the FPLMTO, and \( \psi_m \) are the localized f states. Because of the size of both the hybridization and coulomb exchange matrix elements are much smaller (~0.1 eV) than the intraatomic coulomb interaction \( U \) (6eV), one can apply perturbation theory and evaluate the anisotropic two-ion 6X6 interaction matrices, which couple the two f-ions. The exchange interactions have three contributions: the wholly band-f coulomb exchange mediated interaction proportional to \( J_{mn'}^2 (\mathbf{k}, \mathbf{k'}) \), the wholly hybridization-mediated exchange interaction proportional to \( V_{km}^4 \), and the cross term proportional to \( V_{km}^2 J_{mn'} (\mathbf{k}, \mathbf{k'}) \). With the two-ion interactions having been determined, the low-temperature magnetic moment and the ordering temperature can be determined by use of a mean field calculation.4,5,8 We have previously applied this ab initio based method to investigate the effect of hybridization-induced cerium-cerium interactions4,17 and the combined effect of both the hybridization and coulomb induced interactions9 on the magnetic properties of the heavier cerium pnictides and chalcogenides (CeBi, CeSb, and CeTe). However, these calculations did not take into account the crystal field interaction and employed a warped muffin-tin LMTO calculation for the parameters entering the model. The excellent agreement found9 with experiment for the low-temperature magnetic moment and ordering temperature is relatively unaffected by the CF interaction, because the CF interaction in the heavier cerium systems is smaller than the two-ion exchange interactions.

The second method employs ab initio spin polarized electronic structure calculations based on the FPLMTO method23 using 1) only spin polarization, with the orbital polarization included only through the spin-orbit coupling, and 2) both the spin and orbital polarization.24 In these calculations the 4f states are treated as band states. The orbital polarization is taken into account by means of an eigenvalue shift24,
\( \Delta V_m = -E^3 L_z m_l \), for the 4f atom. Here, \( L_z \) is the z-component of the cerium total orbital moment, \( m_l \) is the magnetic quantum number, and \( E^3 \) is the Racah parameter evaluated self-consistently at each iteration.

The crystalline field, which was neglected in the previous calculations, is expected to affect the magnetic behavior considerably, if it is large. It is important to emphasize that since in the first method the 4f states are treated as core states, they interact only with the spherical component of the effective one-electron potential. Thus, the interaction of the atomic-like 4f state with the non-spherical components of the potential, giving rise to the CF splitting, \( \Delta_{CF} = \epsilon_{f^3} - \epsilon_{f^1} \), is not included in the calculation of the model Hamiltonian parameters. In this paper, we generalize the first, \( ab\ initio \) based, method to include both the interatomic 4f-4f coupling and the crystal-field interactions on an equal footing and to employ a full potential LMTO evaluation of the model Hamiltonian parameters. While the effect of the full potential on both the hybridization and coulomb exchange interactions is small, including the CF interaction will be shown to play a role as important as the interatomic 4f-4f interactions for understanding and predicting the overall trend in the unusual magnetic properties, as all the chemically tunes the degree of 4f localization across this series of strongly correlated electron systems. The resultant Hamiltonian is\(^{4,5}\)

\[
H = - \sum_{i,j} \sum_{\mu \nu} \xi_{i \mu}^{*}(\theta_{ij})e^{-i(\mu - \nu + s - s)}\phi_{ij} c_{i \mu}^{\dagger} c_{j \nu},
\]

\[+ B_4 \sum_i (O_4^0(i) + 5O_4^1(i)), \tag{2}\]

where the \( \xi_{i \mu}^{*}(\theta_{ij}) \) are the two-ion 4f-4f interaction matrices rotated to a common crystal-lattice axis, and the \( O_4^0 \) and \( O_4^1 \) are the Stevens operators evaluating on the Ce\(^{3+} \) free-ion 4f\(^{5/2} \) multiplet.\(^{25}\) The CF splitting is \( \Delta_{CF} = 360B_4 \); a positive \( B_4 \) value gives the \( \Gamma_7 \) ground state, which is experimentally observed.\(^{19}\) While our work in progress is aimed at evaluating the CF splitting on a wholly \( ab\ initio \) basis, in the absence of an \( ab\ initio \) value of the CF interaction in this class of strongly correlated cerium systems, the \( \Delta_{CF} \) is set to the experimental values listed in Table 3.\(^{10,19}\)

In Table I, we list the values of the \( m = m' = 1/2 \) matrix elements (characteristic matrix elements of the 6X6 exchange interaction matrix) for the first three nearest-neighbor shells for the light (CeP and CeS) and the heavier compounds (CeSb and CeTe). Listed separately in this table are the three contributions to the interatomic 4f-4f interactions arising from band-f hybridization (\( V^4 \)), band-f coulomb exchange (\( J^4 \)), and the cross term. It is important to note that while the coulomb exchange mediated interactions dominate the magnetic behavior for the heavier, more localized, 4f systems, the opposite is true for the lighter, more delocalized, systems where the hybridization mediated interactions dominate the magnetic behavior. This change of behavior of the interatomic 4f-4f interactions is a result of the sensitivity of the hybridization and coulomb exchange to the degree of 4f localization. Equally important, is that while both first and second nearest-neighbor 4f-4f interactions are ferromagnetic for CeSb, there is an interplay between ferromagnetic first nearest-neighbor and antiferromagnetic second nearest-neighbor interactions for CeTe.\(^{27}\) These interactions are mediated via scattering of conduction electrons. This results in a saturated ordered moment for CeSb and in the ordered magnetic moment collapse for CeTe (see Table III).

In order to determine whether the magnetic moment collapse might be of Kondo origin, we have evaluated the single-impurity Kondo temperature,\(^ {26}\) \( k_B T_K \)
TABLE II. Values of the $m = m' = 1/2$ matrix elements (characteristic matrix elements of the 6X6 interatomic 4f-4f interaction matrix $E_{\sigma_{m},m'\sigma}'$), for the first, second, and third nearest-neighbor shells in degrees Kelvin. Listed are the values of the hybridization induced $(E_{V4})$, cross terms $(E_{V2j})$, and pure coulomb exchange $(E_{J2})$ contributions.

|          | CeP       | CeS       | CeSb      | CeTe     |
|----------|-----------|-----------|-----------|----------|
|          | $E_{V4}$  | $E_{V2j}$ | $E_{J2}$  | $E_{V4}$  | $E_{V2j}$ | $E_{J2}$  | $E_{V4}$  | $E_{V2j}$ | $E_{J2}$  |
| $R = (\frac{1}{2} \frac{1}{2} 0)$ | 2.23  | 0.64  | 1.53  | 0.85  | -0.40  | 1.50  | 2.23  | 0.64  | 1.53  | 0.85  | -0.40  | 1.50  |
| $R = (1 0 0)$ | 6.39  | 0.27  | 1.65  | -1.60  | 0.04  | -0.80  | 6.39  | 0.27  | 1.65  | -1.60  | 0.04  | -0.80  |
| $R = (\frac{1}{2} \frac{1}{2} 0)$ | -0.08  | -0.02  | 0.16  | 0.38  | -0.16  | 0.13  | -0.08  | -0.02  | 0.16  | 0.38  | -0.16  | 0.13  |

$\Delta_{CE}$ $\mu_0$ $T_N$

|          | CeS       | CeSe      | CeTe     |
|----------|-----------|-----------|----------|
| $\Delta_{CE}$ | 1.40  | 1.80  | 0.73  | 0.57  | 1.0  | 11.0  | 8.4  |
| $\mu_0$ | 116  | 1.10  | 0.79  | 0.57  | 2.5  | 14.0  | 5.7  |
| $T_N$ | 32  | 0.60  | 0.46  | 0.30  | 8.0  | 5.0  | 2.2  |

TABLE III. Calculated values (from the first ab initio based method) of the zero-temperature ordered moment $\mu$ in $\mu_B$, and the ordering temperature $T_N$ in degrees Kelvin, with and without the crystalline field (CF) interaction across the cerium pnictide and chalcogenides series. Also listed are the experimental values$^{7-11}$ of $\mu$ and $T_N$, and the CF splitting$^{19}$ between the $\Gamma_7$ ground state and the $\Gamma_8$ state in degrees Kelvin.

$\Delta_{CE}$ $\mu_0$ $T_N$

|          | CeS       | CeSe      | CeTe     |
|----------|-----------|-----------|----------|
| $\Delta_{CE}$ | 150  | 2.10  | 0.73  | 0.81  | 14  | 11  | 8  |
| $\mu_0$ | 137  | 2.10  | 0.74  | 0.85  | 16  | 13  | 8  |
| $T_N$ | 37  | 2.10  | 1.80  | 2.06  | 20  | 18  | 17  |
| $\Delta_{CE}$ | 8  | 2.10  | 2.10  | 2.10  | 40  | 40  | 26  |

$\Delta_{CE}$ $\mu_0$ $T_N$

$\Delta_{CE}$ $\mu_0$ $T_N$

$\Delta_{CE}$ $\mu_0$ $T_N$

$\Delta_{CE}$ $\mu_0$ $T_N$
behavior. The first, ab initio based, approach which explicitly takes into account the interplay of the three pertinent interactions, gives results in excellent agreement with experiment for all compounds in the series, including the moment collapse from CeSb to CeTe and the trend of moments and ordering temperatures across the series. The remaining problem of determining on a wholly ab initio basis the suppressed crystal-field interactions in this class of systems poses a theoretical challenge for future theoretical work. On the other hand, the second, fully ab initio LDA, method gives good results for the lighter chalcogenide systems, but it entirely fails to give, even qualitatively, the trend of the unusual magnetic behavior.

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