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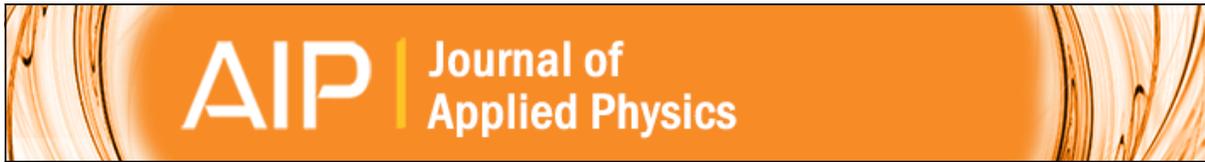
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# Competition of exchange and crystal field interactions in cerium monopnictides and monochalcogenides

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We have applied two *ab initio* based methods to study the dramatic change of magnetic properties across a series of strongly correlated electron systems consisting of cerium monopnictides and monochalcogenides. While, the fully *ab initio* method gives good results for the magnetic moments in the lighter chalcogenides, it entirely fails to give, even qualitatively, the trend of their unusual magnetic behavior. On the other hand, the second approach, which explicitly takes into account the interplay between the hybridization, the Coulomb exchange, and the crystal-field 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. © 2000 American Institute of Physics. [S0021-8979(00)65008-9]

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. This series of strongly correlated electron systems offers the opportunity to vary systematically, through chemical pressure, the lattice constant and the cerium separation on going down the pnictogen or chalcogen column, and hence tailor the degree of  $4f$  localization from the strongly localized limit in the heavier systems to the weakly localized limit in the lighter systems.<sup>1-7</sup> The sensitivity of the hybridization, Coulomb exchange, and crystal-field (CF) interactions to the chemical environment gives rise to a variety of unusual magnetic properties.

This class of systems exhibits strong magnetic anisotropy which changes from the  $\langle 001 \rangle$  direction in the pnictides to the  $\langle 111 \rangle$  direction in the chalcogenides. The low temperature magnetic moment increases with increasing lattice constant for the pnictides from  $0.80 \mu_B$  in CeP to  $2.1 \mu_B$  in CeBi,<sup>1-2</sup> and decreases with increasing lattice constant for the chalcogenides from  $0.57 \mu_B$  in CeS to  $0.3 \mu_B$  in CeTe.<sup>3-5</sup> The *magnetic moment collapse* from CeSb to CeTe, with both systems having about the same lattice constant, is indicative of the sensitivity of the exchange interactions to the chemical environment. The ordering temperature increases from 8 K in CeP to 26 K in CeBi for the pnictides, whereas it decreases from 8.4 K in CeS to an unusually low 2.2 K in CeTe.<sup>1-5</sup>

An unusual feature of the cerium series is the *large suppression* of the CF splitting of the  $Ce^{3+}$  free-ion  $4f_{5/2}$  multiplet from values expected from the behavior of the heavier isostructural rare-earth monopnictides.<sup>8</sup> In both the cerium monopnictides and monochalcogenides, the CF splitting between the  $\Gamma_7$  doublet and the  $\Gamma_8$  quartet decreases with in-

creasing anion size, from 150 K for CeP to 8 K in CeBi and from 140 K for CeS to 32 K for CeTe, and it is about the same in both series, a rather surprising result in view of the additional valence electron on the chalcogen ion.<sup>9</sup> Neutron scattering experiments have shown<sup>10</sup> that the  $\Gamma_7$  doublet is the CF ground state in all the cerium monopnictides and monochalcogenides.

The purpose of this work is to understand the underlying mechanisms responsible for the unusual magnetism in this class of systems and to investigate the interplay of exchange and crystal field interactions. We have employed two *ab initio* based approaches to calculate the magnetic properties of these compounds. First, we have carried out *ab initio* spin polarized electronic structure calculations based on the full potential linear muffin tin orbital (FPLMTO) method<sup>11</sup> using (1) only the spin polarization, with the orbital polarization included only through spin-orbit coupling, and (2) both the spin and orbital polarization correction.<sup>12</sup> Second, we apply an *ab initio* based approach synthesizing (1) a phenomenological theory of *orbitally* driven magnetism based on the Anderson and Kondo lattice model which incorporates explicitly the hybridization induced, the Coulomb exchange, and the crystal field interactions on an equal footing, and (2) FPLMTO electronic structure calculations allowing a first principles evaluation of all the parameters entering the model Hamiltonian, except for the crystal field interaction. To date, our attempts<sup>13</sup> to determine the CF splitting for this class of systems on a fully *ab initio* basis have not proven successful, and thus we use the experimental<sup>10</sup> CF value for each compound. In contrast to the first method, in the FPLMTO evaluation of the parameters entering the model Hamiltonian, the  $4f$  states are treated as *localized, atomic-like*, states and are placed in the core not being allowed to hybridize with the non- $f$  states, in order to be consistent with the treatment of the  $f$  states in the Anderson-Kondo Hamiltonian.<sup>14-16</sup> It should be emphasized that in the second method the band energies, the  $f$ -state energies, the on-site Coulomb repulsion

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$U$ , the hybridization matrix elements,  $V_{km}$ , and the band- $f$  Coulomb exchange  $J_{mm'}(\mathbf{k}, \mathbf{k}') = \langle \phi_{\kappa}^*(r_1) \psi_m^*(r_2) | 1/r_{12} | \psi_{m'}(r_1) \phi_{\kappa'}(r_2) \rangle$  are evaluated from nonspin polarized FPLMTO calculations. Comparison of the two methods tests the limitations of these *ab initio* based calculations as the degree of  $4f$  localization is varied across the series, and reveals the failure of standard *ab initio* electronic structure calculations based on density functional theory within the local density approximation to predict, even qualitatively, the trend of magnetic properties in these strongly correlated electron systems. In the past, we have applied the second method to investigate the effect of hybridization-induced exchange interactions<sup>14,15</sup> and the effect of both the hybridization and Coulomb exchange interactions<sup>16</sup> 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 very good agreement found<sup>16</sup> with experiment for the low-temperature magnetic moment and ordering temperature is due to the fact that the CF interaction in the heavier systems is smaller (about 8 K) than the exchange interactions. We have generalized our *ab initio* based method to include the exchange (both hybridization and Coulomb exchange) and crystal field interactions on an equal footing and to employ a full potential LMTO evaluation of the exchange parameters. While the effect of the full potential on both the hybridization and Coulomb exchange interactions is small, the inclusion of the CF interaction will be shown to play a role as important as the exchange interactions for understanding and predicting the unusual magnetic properties, as one tunes the degree of  $4f$  localization across this series of strongly correlated electron systems. Because the size of both the hybridization and Coulomb exchange matrix elements are much smaller (about 2 meV) than the intra-atomic cerium Coulomb interaction  $U$  (6 eV), one can apply the perturbation theory and evaluate the anisotropic two-ion exchange  $6 \times 6$  matrices.<sup>14–16</sup> The exchange interactions have three contributions: the pure Coulomb exchange interaction term proportional to  $J_{mm'}^2(\mathbf{k}, \mathbf{k}')$ , the hybridization-mediated exchange interaction term proportional to  $V_{km}^4$ , and the cross term proportional to  $V_{km}^2 J_{mm'}(\mathbf{k}, \mathbf{k}')$ .

We next discuss the necessity of including the CF interaction term in the phenomenological Hamiltonian, so we can investigate the interplay of exchange and CF interactions on an equal footing as we *chemically tune* the various pertinent interactions across the series. In the second approach, the  $4f$  states are treated as core states, and as such, they interact only with the spherical component of the effective one-electron potential. Thus, the interaction of the *atomic-like*  $4f$  state with the *nonspherical* components of the potential, giving rise to the CF splitting, is not explicitly included. Thus, the CF interaction is included in the phenomenological theory through the inclusion of the CF interaction,  $H_{CF} = B_4(O_4^0 + 5O_4^4)$  where the  $O_4^0$  and  $O_4^4$  are Stevens equivalence operators.<sup>17</sup> (A positive  $B_4$  value gives the  $\Gamma_7$  ground state, experimentally observed.) In the absence of an *ab initio* value of the CF interaction in this class of strongly cor-

TABLE I. Values of the calculated and experimental (Refs. 1–4) magnetic moments for the cerium chalcogenides and pnictides in units of  $\mu_B$ . Listed are the LMTO values for the spin moment  $\mu_S$ , the orbital moment  $\mu_L$ , and total moment  $\mu$ , for the spin polarized only calculation and for the calculation with spin polarization and orbital polarization correction.

	FP+SP			FP+SP+OP			EXPT
	$\mu_S$	$\mu_L$	$\mu$	$\mu_S$	$\mu_L$	$\mu$	$\mu$
CeS	-1.00	0.91	-0.09	-1.24	1.99	0.75	0.57
CeSe	-1.08	1.02	-0.06	-1.26	2.07	0.81	0.57
CeTe	-1.15	1.28	0.07	-1.31	2.29	0.98	0.30
CeP	-0.80	0.55	-0.25	-0.85	1.27	0.43	0.80
CeAs	-0.84	0.64	-0.20	-0.85	1.42	0.57	0.80
CeSb	-0.86	0.74	-0.12	-0.91	1.61	0.70	2.06
CeBi	-0.86	0.74	-0.12	-0.95	1.69	0.74	2.10

related electron systems,<sup>13</sup> the CF splitting,  $\Delta_{CF} = 360B_4$ , is set to the experimental values, listed in Table III.<sup>10</sup> With the two-ion interactions having been determined, the low-temperature magnetic moment and the ordering temperature can be determined by means of a mean field calculation.

In Table I we present the calculated values of the zero-temperature cerium magnetic moment from the FPLMTO electronic structure calculations. Listed in the table are values both with and without the orbital polarization correction taken into account. Note, the importance of including the orbital polarization in these  $4f$  correlated electron systems. In all cases, the orbital polarization is found to be opposite to the spin polarization, as expected. Comparison of the total energies gives that the magnetic anisotropy changes from the  $\langle 001 \rangle$  direction in the pnictides to the  $\langle 111 \rangle$  in the chalcogenides, in agreement with experiment. On the other hand, except perhaps for the lighter chalcogenides (CeS and CeSe), comparison of the *ab initio* and experimental values for the magnetic moment indicates the *failure* of the local density approximation (LDA) calculations to treat properly the correlation effects of the  $4f$  states (treated as band states) in this series of strongly correlated electron systems. Furthermore, the pure *ab initio* calculations fail to predict the large *moment collapse* from CeSb to CeTe, the latter being described as an incipient heavy Fermion system.

In Table II, listed are values of the  $m = m' = 1/2$  matrix elements (characteristic matrix elements of the  $6 \times 6$  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 exchange interaction from hybridization ( $V^4$ ), Coulomb exchange ( $J^2$ ), and the cross term. It is important to note that while the Coulomb exchange 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 exchange interactions dominate the magnetic behavior. This change of behavior of the exchange interactions is a result of the sensitivity of the hybridization and Coulomb exchange on the degree of  $4f$  localization. Equally important, is that while all nearest-neighbor exchange interactions are ferromagnetic for CeSb, there is an interplay between ferromagnetic and antiferromagnetic interactions for CeTe,

TABLE II. Listed below are characteristic matrix elements of the  $6 \times 6$  two-ion interaction matrix  $[E_{m_a m_b}^{m_b m_a}(\mathbf{R}_b - \mathbf{R}_a)]$  of the  $f$  electrons for a cross section of the cerium compounds. Values of the hybridization induced ( $E_{V^4}$ ), cross terms ( $E_{V^2J}$ ), and pure Coulomb exchange ( $E_{J^2}$ ) interactions are listed for the first, second, and third nearest cerium neighbors in units of K. the listed elements are the  $m = m' = \pm 1/2$ .

	CeP			CeS		
	$E_{V^4}$	$E_{V^2J}$	$E_{J^2}$	$E_{V^4}$	$E_{V^2J}$	$E_{J^2}$
$R=(\frac{1}{2} \frac{1}{2} 0)$	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
$R=(1 \frac{1}{2} \frac{1}{2})$	-0.08	-0.02	0.16	0.38	-0.16	0.13
	CeSb			CeTe		
	$E_{V^4}$	$E_{V^2J}$	$E_{J^2}$	$E_{V^4}$	$E_{V^2J}$	$E_{J^2}$
$R=(\frac{1}{2} \frac{1}{2} 0)$	0.70	0.34	7.30	0.17	-0.19	2.90
$R=(1 0 0)$	2.07	0.07	10.21	-0.19	0.04	-1.69
$R=(1 \frac{1}{2} \frac{1}{2})$	-0.02	-0.03	0.04	0.04	-0.06	-0.01

mediated from the scattering of conduction electrons, giving rise to the saturated moment for CeSb and the *magnetic moment* collapse from CeSb to CeTe (see Table III).

Listed in Table III are the calculated zero-temperature moment and ordering temperature,  $T_N$ , from the second *ab initio* based method, with and without the CF interaction. It is clear that for the heavier systems (CeBi, CeSb, CeTe) the effect of the CF interaction on the magnetic moments is small and slightly more pronounced on the ordering temperatures. This is due to the fact that for the more localized systems the CF interaction is smaller than the exchange in-

TABLE III. Calculated (from the model Hamiltonian) values of the zero-temperature ordered moments ( $\mu_o$ ) and ordering temperatures, Néel temperature ( $T_N$ ) both without (no CF) and with the crystal field splittng term (CF), and the corresponding experimental values for the cerium compounds. The experimental values of the crystal field splitting ( $\Delta_{CF}$ ) are also listed. All moments are given in units of  $\mu_B$ , the temperatures and the crystal field splitting are given in units of Kelvin.

	$\Delta_{CF}$	$\mu_o$			$T_N$		
		No CF	CF	exp	No CF	CF	exp
CeS	140	1.80	0.73	0.57	1.0	11.0	8.4
CeSe	116	1.10	0.79	0.57	2.5	14.0	5.7
CeTe	32	0.60	0.46	0.30	8.0	5.0	2.2
CeP	150	2.10	0.73	0.81	14	11	8
CeAs	137	2.10	0.74	0.85	16	13	8
CeSb	37	2.10	1.80	2.06	20	18	17
CeBi	8	2.10	2.10	2.10	40	40	26

teractions. This is the reason that previous calculations, neglecting the CF interaction, gave results in very good agreement with experiment. On the other hand, for the lighter more delocalized systems the CF interactions are much larger than the exchange interactions and hence dominate the magnetic behavior. The overall decrease of the magnetic moments in the presence of the CF interaction in all systems arises from the mixing of the off-diagonal angular momentum states  $|\pm 5/2\rangle$  and  $|\mp 3/2\rangle$  states from the CF interaction with  $\Gamma_7$  ground state. Overall, we find an excellent agreement with experiment for both the zero-temperature moment and the ordered temperature (a more stringent test for the theory) using the second *ab initio* based approach with all three pertinent interactions (hybridization, Coulomb exchange, and CF interactions) treated on an equal footing.

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