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Mechanism for existence of nonmagnetic cerium sites in magnetically ordered cerium compounds

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Hybridization of moderately delocalized f electrons with band electrons gives rise to a highly anisotropic two-ion interaction, which, as Siemann and Cooper first showed, accounts well for the unusual magnetic behavior of CeBi. In the present paper it is shown that the even more unusual magnetic behavior of CeSb with a succession of magnetic structures in which the higher-temperature structures (AFP) involve a periodic stacking of nonmagnetic {001} planes alternating with magnetically ordered {001} planes of [001] moment alignment can be understood on the basis of the same hybridization-mediated interionic interaction in the presence of a cubic crystal field (CF) of comparable strength. The tendency to form nonmagnetic planes, which are indeed paramagnetic in nature (Kramers doublets), is found to increase with increasing CF strength, and the stability of the AFP phases at high temperatures is shown to arise from the reconciliation of the magnetic ordering with the CF interactions. The calculations yield first-order phase transitions from a low-temperature type I antiferromagnetic phase to two high-temperature AFP phases. The possibility of a fully nonmagnetic singlet ground state, which, however, is not Kondo-like, also occurs and will be discussed.

I. INTRODUCTION

At zero field, CeSb orders with a first-order transition at $T_N \approx 16.2$ K and undergoes six additional first-order phase transitions. The high-temperature (> 8.5 K) phases (AFP) are commensurate with the lattice and correspond to a periodic stacking of nonmagnetic (P) and ferromagnetic (M) {001} planes with an up or down [001] magnetization.² Below 8.5 K the nonmagnetic planes disappear, giving a type IA ($\uparrow\uparrow\uparrow\uparrow$) phase. The octahedral crystal field (CF) splits the Ce^{3+} free-ion $^2F_{5/2}$ multiplet into a Γ_7 doublet and a Γ_8 quartet, with a crystal-field splitting of about 37 K in the paramagnetic phase.³ Recent magnetization and neutron scattering measurements⁴ on CeSb have clearly established that the CF ground state in the paramagnetic phase is the Γ_7 doublet, and that the nonmagnetic planes are indeed paramagnetic in nature with the same level structure (Kramers doublet) as in the paramagnetic phase and a CF splitting of about 43 K.

The magnetic equilibrium and excitation behavior of CeBi was successfully explained^{5,6} on the basis of a highly anisotropic hybridization-mediated two-ion interaction, originally introduced by Coqblin and Schrieffer⁷ (CS) for dilute cerium alloys. This interaction arises from hybridization of moderately delocalized f electrons with band electrons. The purpose of this paper is to illustrate that the central feature of the magnetic equilibrium behavior in CeSb, i.e., the coexistence of magnetic and nonmagnetic layers at higher temperatures, can be understood equally well within the previously developed model,^{5,6} in terms of the competing effects of the CF and hybridization-mediated two-ion interactions, without having to invoke a third proposed⁸ mechanism, i.e., the effective suppression of the Ce^{3+}

magnetic moment due to Kondo spin compensation. The question of whether the presence of sufficiently strong CF interactions could yield a ground state which is fully nonmagnetic, but not Kondo-like, is also investigated.

The hybridization-mediated two-ion Hamiltonian is^{5,6}

$$\mathcal{H}_{\text{CS}} = - \sum_n E_n \sum_{\substack{\mu, \nu \\ \epsilon, \sigma}} B_{\mu\nu}^{\epsilon\sigma}(\theta_n) e^{i(\mu - \nu + \epsilon - \sigma)\phi_n} L_{\mu\nu}^{(\sigma)} L_{\epsilon\sigma}^{(n)}, \quad (1)$$

where σ and n label Ce^{3+} sites, θ_n and ϕ_n are the angular coordinates of the interionic axis $\mathbf{R}_n$ with respect to the [001] axis, $\mu, \nu, \epsilon, \sigma$ label the single-ion states of J^z for [001] quantization, $L_{\mu\nu} = |\mu\rangle\langle\nu|$, and $B_{\mu\nu}^{\epsilon\sigma}(\theta_n)$ gives the angular dependence of the matrix elements of the interaction as transformed to crystal axis quantization. The interaction strength E_n to each of the n th nearest neighbors (with $n \leq 3$) and the CF parameter B_4 ($\Delta_{\text{CF}} = 360B_4$) are treated phenomenologically.^{5,6}

II. RESULTS FOR COEXISTENCE OF MAGNETIC AND NONMAGNETIC PLANES

The effect of the hybridization-mediated two-ion interaction on the formation of Kramers doublets at the paramagnetic site in the AFP1 ($\uparrow\downarrow P$) structure in the absence of a crystal field, can be understood in terms of the dominant diagonal matrix elements of $\mathcal{H}_{\text{CS}}$. The contribution to $\langle 5/2 | \mathcal{H}_{\text{CS}} | 5/2 \rangle$ at the parasite, from a pair of n th nearest-neighbor (NN) equivalent ordered sites with saturated $\uparrow$ and $\downarrow$ moments ($\langle L_{\pm 5/2 \pm 5/2} \rangle = 1$), respectively, is $B_{5/2 5/2}^{5/2 5/2}(\theta) + B_{5/2 5/2}^{-5/2 -5/2}(\theta)$. For general values of θ this matrix element does not vanish because of the strong asymmetry of $B_{5/2 5/2}^{5/2 5/2}$ and $B_{5/2 5/2}^{-5/2 -5/2}$, which follows^{5,6} from the fact that the magnetic quantum numbers of the band and f electrons are exchanged in the scattering involved in the hybridization-mediated mechanism. Moreover, due to the moment

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reversal symmetry of the interaction, for a given pair of equivalent sites $\langle -5/2 | \mathcal{H}_{CS} | -5/2 \rangle = \langle 5/2 | \mathcal{H}_{CS} | 5/2 \rangle$, and hence the up and down moment states at the parasite are doubly degenerate. All of the other matrix elements behave similarly, and thus the parasite develops three Kramers doublets, with a ground state energy below the free-ion (six-fold degenerate) energy ($E = 0$) and higher by a factor of about 3.5 than that of the ordered site. As the temperature increases, the free energy of the parasite decreases less rapidly than that of the free ion, which has a clear entropy advantage, eventually crossing the free-ion energy at the Néel temperature. On the other hand, for an ordered site with an up moment for example, upon decreasing E_3 , the AFP1 structure is less favorable than the AF-I ($\uparrow\uparrow$) structure, but more favorable than the AF-IA structure, and thus the AFP1 structure can never become the ground state of the system. For $T \neq 0$, even though the formation of Kramers doublets have a clear entropy advantage, the AFP1 structure becomes disordered before it has the chance to cross the AF-I structure.

We next investigate the role of the CF interaction in helping to stabilize the AFP structures in the high-temperature regime. From all the six low-field AFP structures experimentally observed^{1,2,4} we consider for simplicity those two with the smallest periods, namely the AFP3 ($\uparrow\uparrow P \uparrow\uparrow\uparrow$) and AFP1 structures, which occur in the temperature range of 12.2–14.8 K and 15.4–16.2 K, respectively. The effect of the “bare” CF interaction, of a sign ($B_4 > 0$) having the Γ_7 doublet below the Γ_8 quartet (favoring a $\langle 111 \rangle$ easy axis⁶), is to increase the diagonal $|\pm 5/2\rangle$ and $|\pm 1/2\rangle$ matrix elements of the Hamiltonian, to decrease the diagonal $|\pm 3/2\rangle$ matrix elements, and to introduce additional off-diagonal mixing between the $|\pm 5/2\rangle$ and $|\mp 3/2\rangle$ states of J^z , which in turn reduces both the $T = 0$ moment and the quadrupolar moment. In the low Δ_{CF}/E_1 region ($\Delta_{CF} < E_1$), the dominant hybridization-mediated two-ion interactions “dress” the “bare” ground state Γ_7 doublet at the parasite so that it becomes Γ_8 -like, and the ground-state energy decreases with B_4 at a slower rate ($\sim -180B_4$) relative to that of the “bare” Γ_7 ground-state energy ($\sim -240B_4$) in the high Δ_{CF}/E_1 region ($\Delta_{CF} > E_1$). The effect of the CF interaction on the ordered site in the low Δ_{CF}/E_1 region is to raise its ground-state energy due to the increment of the dominant $\langle \pm 5/2 | \pm 5/2 \rangle$ matrix element. However, in the high Δ_{CF}/E_1 region ($E_1 < \Delta_{CF} < 3E_1$), the $\langle \pm 3/2 | \pm 3/2 \rangle$ matrix elements become comparable in size with the $\langle \pm 5/2 | \pm 5/2 \rangle$, and decrease more rapidly with Δ_{CF} than $\langle \pm 5/2 | \pm 5/2 \rangle$ increases. The net effect is the lowering of the ordered site ground-state energy with Δ_{CF} for $E_1 < \Delta_{CF} < 3E_1$, but at a rate of about 1.6 slower than that of the parasite. Thus, the presence of CF interactions tends to favor predominantly the parasites. Furthermore, we find that upon increasing Δ_{CF}/E_1 , the relative spacing between the two excited Kramers doublets decreases (approaching the Γ_8 quartet behavior for large enough CF interaction), thus enhancing the entropy advantage of the parasites at high temperatures.

The temperature variation of the average free energy of the AF-I, AF-IA, AFP1, and AFP3 structures is shown in

FIG. 1. Variation of free energy with temperature for the AF-I ($\uparrow\uparrow$), AF-IA ($\uparrow\uparrow\uparrow$), AFP1 ($\uparrow\uparrow P$), and AFP3 ($\uparrow\uparrow P \uparrow\uparrow\uparrow$) magnetic structures of Ce^{3+} systems, with $E_2 = 0.4E_1$, $E_3 = -0.28E_1$, and $\Delta_{CF} = 3E_1$. Also shown is the temperature variation of the free energies of the paramagnetic (P) and ordered (M) sites for the AFP1 structure.

Fig. 1 with $E_2 = 0.4E_1$, $E_3 = -0.28E_1$, and $\Delta_{CF} = 3E_1$. Also plotted in Fig. 1 is the temperature variation of the free energy of the para and ordered planes in the AFP1 structure. For $k_B T < 0.8E_1$, due to the predominance of the exchange interactions, the free energy of the parasite is substantially higher than that of the ordered site, and thus the AF-I and AF-IA structures are more favorable than the AFP1 or AFP3 structures, and the AFP3 structure, containing one paralaier every seven layers, is more favorable than the AFP1 structure which contains one paralaier every three layers. Note that because of the large antiferromagnetic E_3 value the AF-IA structure, which is the experimentally observed^{1,4} low-temperature phase, is less favorable than the AF-I structure over the whole temperature range. However, the low-temperature phase is strongly sample dependent.⁴ With increasing temperature, the free energy of the parasite decreases more rapidly than that of the ordered site because of entropy advantage, and thus, the AF-I structure crosses the AFP3 structure at $T_1 = 1.089E_1$, the latter in turn crossing the AFP1 phase at $T_2 = 1.104E_1$, which finally becomes paramagnetic at $T_N = 1.12E_1$ with a first-order transition.

The molecular-field energy levels at $T = 0$ (in units of E_1) for the AF-I, AF-IA, and AFP1 structures are displayed in Fig. 2, with $E_2 = 0.4E_1$, $E_3 = -0.28E_1$, and $\Delta_{CF} = 3E_1$. For such a large CF splitting, the ordered site ground-state energies in all three magnetic structures are almost identical ($\sim -2.9E_1$) and not much lower than the energy ($\sim -2.1E_1$) of the parasite. Such a situation cannot occur in CeBi, where the CF splitting (~ 8 K) is much smaller³ than the Néel temperature (~ 25 K) which scales directly with E_1 . In particular, for the same E_2 and E_3 values and for $\Delta_{CF} = 0$, the

FIG. 2. Molecular-field energy level schemes at $T=0$ for AF-I, AF-IA, and AFI magnetic structures of Ce^{3+} systems, with $E_2=0.4E_1$, $E_3=-0.28E_1$, and $\Delta_{\text{CF}}=3E_1$; all structures are labeled as in Fig. 1.

ordered site ground-state energies of the AF-I, AF-IA, and AFP1 structures are $-2E_1$, $-1.7E_1$, and $-1.87E_1$, respectively, compared to the rather high paramagnetic site ground-state energy of $-0.43E_1$, showing that the CF interaction favors predominantly the parasites. However, because of the large Δ_{CF}/E_1 value, the $T=0$ moments of the AF-I, AF-IA, and AFP1 structures are greatly suppressed from the almost saturated value ($5/2$) to the values of 1.04, 0.28, and 0.60, respectively. This reduction of the moment can be restored by introducing a small distortional term in the Hamiltonian which increases the diagonal matrix elements.

III. FULLY NONMAGNETIC GROUND STATE

The success of our results, which came out of our investigation into the role that the CF interactions plays on helping to stabilize the coexistence of magnetic and paramagnetic sites in the high-temperature region, motivated us to address the following question: Can the presence of sufficiently strong CF interaction relative to the hybridization-mediated two-ion interaction give rise to a new type of a ground state which is fully paramagnetic (Kramers doublet), which however is not Kondo-like. Since the rate of decrease of the $T = 0$ energy of the ordered site with B_4 is lower by a factor of 1.6 relative to that of the parasite for $E_1 < \Delta_{\text{CF}} \leq 3E_1$, we felt that it is conceivable that for a still larger Δ_{CF}/E_1 , the parasite energy would eventually cross that of the ordered site, provided that both variation rates do not change appreciably. However, as it turns out, the rate of

decrease of the ordered site energy increases and becomes equal to that of the parasite ($-240B_4$) for $\Delta_{CF} > 3E_1$, and thus the ordered site remains always more favorable than the parasite at $T = 0$.

In the process of investigating the possibility of a totally paramagnetic ground state we encountered another peculiar but interesting physical situation. Upon increasing Δ_{CF}/E_1 ($B_4 > 0$), the expectation value $\langle L_{\pm 5/2 \pm 5/2} \rangle$ decreases, $\langle L_{\pm 3/2 \pm 3/2} \rangle$ increases, while $\langle L_{\pm 1/2 \pm 1/2} \rangle$ is vanishingly small, and the $T = 0$ component of the moment along the modulation [001] direction decreases ($\langle J^z \rangle = 5/2 \langle L_{5/2 5/2} \rangle - 3/2 \langle L_{-3/2 -3/2} \rangle$ for an $\uparrow$ site), whereas the components transverse to the modulation direction increase due to the off-diagonal mixing. For the case of $E_2/E_1 = 1$ and $E_3 = -0.3E_1$, and upon increasing Δ_{CF}/E_1 , we find the AF-I and AF-IA structures to be the ground state for $0 < \Delta_{\text{CF}} < 3.12E_1$ and $\Delta_{\text{CF}} > 3.12E_1$, respectively. It turns out that the longitudinal component of the moment in the AF-IA phase decreases so rapidly with Δ_{CF} , that at the point ($\Delta_{\text{CF}} = 3.12E_1$) at which the AF-IA structure becomes the ground state, its [001] moment is zero, yielding a totally nonmagnetic (singlet) state. Moreover, in the presence of such a large Δ_{CF} value, the transversely polarized [110] AF-IA structure with the rather large moment components (~ 0.77) has the same free energy as the longitudinally polarized state over a wide temperature range ($k_B T < 0.4E_1$). Thus, even though the high-moment transversely polarized state has the lowest free energy for $k_B T > 0.4E_1$, one encounters a peculiar low-temperature physical phenomenon where the system fluctuates between two differently polarized states of equal free energies, one of which is a singlet state. This suggests a different possible explanation for the nonmagnetic (singlet) ground state in materials such as CeAl_3 , which has been thought as the prototype of nonmagnetic Kondo lattices.

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