Hybridization-mediated interaction and the equilibrium magnetic behavior in uranium monopnictides

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We present the results of calculations for the equilibrium magnetic behavior of a fcc lattice of $U^{3+}(f^3, J=\frac{9}{2})$ ions coupled by the hybridization-mediated two-ion interaction. The calculations are for L-S intraionic coupling, and have been performed both with and without crystal-field interactions being present. We relate our results to the equilibrium magnetic behavior and thermal phase transitions in UP, UAs, and USb.

I. INTRODUCTION

The monopnictides of uranium (UAs, UP, USb) show[1] noncollinear magnetic structures and interesting phase transitions from noncollinear to collinear structures. For example, UP orders in a double-**k** type-I antiferromagnetic structure at $T=0$ K and undergoes a transition at about 23 K to a single-**k** type-I structure; the Néel temperature is 125 K. In the presence of a magnetic field UP shows further interesting ferrimagnetic structures. UAs also orders at about 125 K in a single-**k** type-I structure, and undergoes a phase transition to a double-**k** type-IA structure at about half the Néel temperature. The thermal transitions between the different structures in both UP and UAs are first order and are accompanied by a change in the magnitude of the ordered moment. USb is thought to order in a triple-**k** structure at all temperatures below the Néel temperature of 214 K.

We believe that the peculiar magnetic behavior in the uranium compounds originates from the hybridization between the moderately delocalized f electrons and the band electrons. The interaction between ions is mediated by the band electrons as in the Ruderman-Kittel-Kasuya-Yosida (KKKY) interaction. A theory based on the hybridization-mediated interaction in the heavier monopnictides of cerium[2,3] has been able to account for their equilibrium and excitation behavior. The theory which is based on the Coqblin-Schrieffer[4] (CS) model of the hybridization has been extended[5] by us for the case of ions with more than one f electron, and successfully applied[5,6] in the case of PuSb [$Pu^{3+}(f^5, J=\frac{5}{2})$]. The interaction derived from our theory depends on the number of f electrons and on the intraionic coupling. In the uranium monopnictides the U^{3+} ion is very close to being an L-S—coupled f^3 system. Here we show the results of calculations for the f^3 L-S—coupled case, and relate the behavior to that of UAs, UP, and USb. The results so obtained are grouped into two classes: (i) without crystal-field interactions, and (ii) with crystal-field interactions.

II. MAGNETIC ORDERING FOR A LATTICE OF U^{3+} IONS

The Hamiltonian arising from the hybridization-mediated two-ion interaction can be written as[5]

$$\mathcal{H}=-\sum_{i,j}E_{ij}\sum_{\substack{\mu,\nu,\\ \epsilon,\sigma}}J^{\epsilon\sigma}_{\mu\nu}(\theta,\phi)_{ij}L^{(i)}_{\mu\nu}L^{(j)}_{\epsilon\sigma}\ , \tag{1}$$

where μ, ν, ϵ, and σ are the magnetic quantum numbers of the ionic states, and these serve to identify the states. $L^{(i)}_{\mu\nu}=|\mu\rangle\langle\nu|$ is a transition operator at site i which projects the ion from the state $|\nu\rangle$ to the state $|\mu\rangle$. $J(\theta,\phi)$ is the interaction function which depends on the angle $(\theta,\phi)_{ij}$ between the quantization axis and the interionic axis joining sites i and j. The angular dependence of the interaction is calculated from the theory,[5] and it depends on the number of f electrons in the ion, the intraionic coupling, and the hybridization strength at a single site. The interaction range functions E_{ij} are treated as phenomenological parameters; and the interaction strength to the nth nearest neighbor is then denoted by E_n.

To study the equilibrium behavior of a system with the Hamiltonian given in Eq. (1), we performed a mean-field calculation for a fcc lattice of U^{3+} ions. The free energies of the different magnetic structures were determined by feeding in trial wave functions for the ions on different sublattices for a given structure and iterating numerically until a stable solution was reached. In addition to the hybridization-mediated two-ion (CS) interaction, small isotropic interactions H_n [the isotropic Hamiltonian used was $\sum_{i,j}(H_{ij}/S^2)\mathbf{J}_i\cdot\mathbf{J}_j$] were sometimes used to stabilize the required magnetic structure. The parameters in the calculations were the anisotropic hybridization-mediated interaction constants E_n, the isotropic interaction constants H_n, and the crystal-field interaction parameters.

A. Without crystal field

The f^3 behavior was investigated for increasing range of the two-ion interactions. The predominant interactions were the hybridization-mediated interactions, with strength to the nth near-neighbor denoted by E_n. A ferromagnetic E_1 stabilizes a ferromagnetic state with moment along the face diagonal as the ground state, with a moment of about $3.46g$ (saturated moment is $4.5g$, and the g value for L-S-coupled f^3 is $\frac{8}{11}$). No type-I antiferromagnetic states are obtained as having local minima of the free energy at $T=0$. For $E_1=E_2=|E_1|$, a fer-

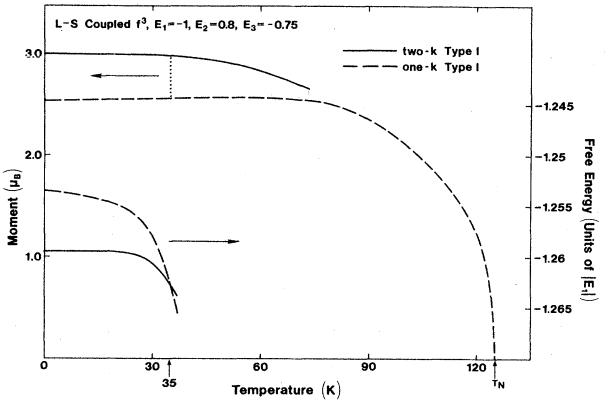

FIG. 1. Temperature variation of moments and the free energies of the two-**k** (noncollinear) type-I and the collinear type-I antiferromagnetic structures for an fcc lattice of U^{3+} ions having L-S intraionic coupling, with the two-ion interaction parameters $E_1=-1$, $E_2=0.8$, and $E_3=-0.75$. A phase transition from the two-**k** type-I to the collinear type-I antiferromagnetic structure takes place at about one-quarter the Néel temperature. [The absolute scale of temperature shown has been obtained by choosing E_1 in K to match T_N of UP ($E_1=-147$ K).]

romagnet with moment along ⟨001⟩ is the ground state, with a moment of $4.35g$. An antiferromagnetic E_1 produces a type-I antiferromagnet as the ground state.

A three-**k** type-I phase can be stabilized as the ground state, at all temperatures, as in USb, for the parameters $E_1=1$, $H_1=-0.12$, with a moment of about $3.0\mu_B$, which is close to the experimental moment.

A behavior similar to that of UP can be obtained for $E_1=-1$, $E_2=0.8$, and $E_3=-0.75$. The temperature dependence of moments and the magnetically ordered structures that are obtained are shown in Fig. 1. The zero-temperature moment is about $3\mu_B$ while the experimental moment[7] of UP is about $2.0\mu_B$. The model predicts a two-**k** type-I to one-**k** type-I transition at about one-quarter of the Néel temperature, while the experimental situation[1] is that the two-**k** to one-**k** transition occurs at about 23 K while $T_N=125$ K. However, there is no intrinsic difficulty in reproducing the correct transition temperature, and this can be achieved by a slight (of the order of a few percent) adjustment of the E_3 interaction parameter already mentioned. The resulting model should be very similar to Fig. 1 in the temperature variation of the moments in the two- and the one-**k** type-I phases.

No two-**k** type-IA structures are found as having local free-energy minima. Hence a behavior as in UAs which orders in a two-**k** type-IA structure at $T=0$ cannot be reproduced. However, the addition of a cubic crystal field can stabilize a two-**k** type-IA structure, and this will be discussed below.

B. With crystal field

Experimental evidence exists for having a crystal-field (CF) splitting in the paramagnetic phase for the compounds of interest. The crystal-field parameters deduced from their behavior are

UP and UAs (Ref. 8): $V_4\sim 3200$ K, $V_6\sim 30$ K,

USb (Ref. 9): $V_4\sim -300$ K, $V_6\sim -15$ K.

(The large value for the V_4 for UP and UAs found in Ref. 8 would give rise to J mixing, but we omit this complication in our model calculations.) We shall follow the notation of Lea, Leask, and Wolf (LLW)[10] and specify the crystal field through use of their parameters W and x. For $U^{3+}(f_3)$ these are related to V_4 and V_6 through the relations

$$V_4=-57.552Wx\ , \tag{2a}$$

$$V_6=-10.446W(1-|x|)\ . \tag{2b}$$

Since the experimental values of V_6 are much less than V_4, we neglect V_6 and take $x=1$ in our model calculations. When $x=1$ and W is negative, the CF states obtained in order of increasing energy are a double Γ_6, a quartet $\Gamma_8^{(2)}$, and a quartet $\Gamma_8^{(1)}$. The overall crystal field splitting is about $0.8V_4$. The splitting is directly proportional to the strength W, and for a given W, its dependence on x for $J=\frac{9}{2}$ is shown in Fig. 8 of Ref. 10.

USb can be modeled by the parameters $E_1=1$, $H_1=-0.12$, $W=0.005$, and $x=1$. The variation of moment for the three-**k** structure with temperature is shown in Fig. 2. The zero-temperature moment is $3.05\mu_B$ compared to the experimental moment of $2.82\mu_B$. Matching the scale of energies given by E_1 to a Néel temperature of 214 K, the value of V_4 which corresponds to this model is -278 K, close to the experimentally deduced value of -300 K. The value of the CF strength here is of the same order as the Néel temperature, and the presence of the crystal field does not affect the existence of the three-**k** type-I state as the ground state, nor its moment in any important way.

In the presence of a crystal field of the experimental[8]

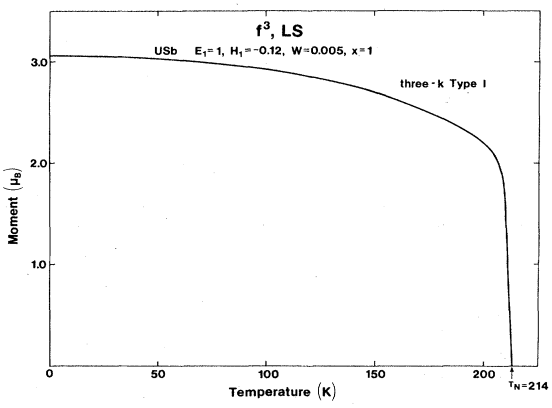

FIG. 2. Temperature variation of the ordered moment for the three-**k** type-I antiferromagnet obtained as the ground state of an fcc lattice of U^{3+} ions having L-S intraionic coupling, when the relative sizes of the interaction parameters E_1 and H_1, and of the crystal-field parameter W (for $x=1$) are given by $E_1=1$, $H_1=-0.12$, and $W=0.005$. [The absolute scale of temperature shown has been obtained by choosing E_1 in K to match the Néel temperature of USb ($E_1=977$ K).]

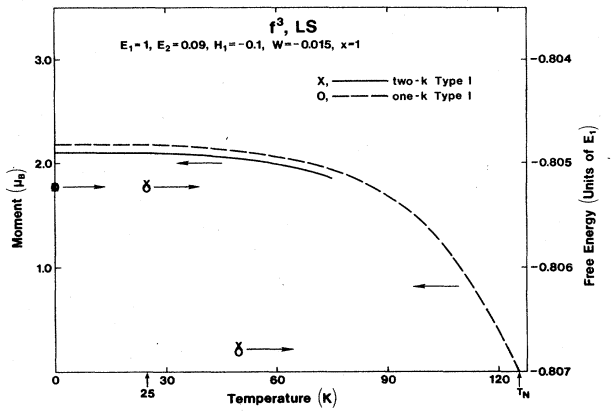

FIG. 3. Temperature dependence of the moments and the free energies of two-**k** type-I and the one-**k** type-I magnetic structures, with the interaction parameters $E_1=1$, $E_2=0.09$, $H_1=-0.1$, and the crystal-field parameters $W=-0.015$, $x=1$. [The absolute scale of temperature has been obtained by choosing the scale of energy given by E_1 to match the T_N of UP ($E_1=500$ K).]

sign, to obtain behavior similar to UP needs drastic modification of the two-ion parameters from those in the absence of CF interactions. Keeping the two-ion parameters the same as in the case without crystal field, and adding a negative W (as is required to have a positive V_4) stabilizes the one-**k** type-I structure as the ground state and increases the free energy of the two-**k** type-I state. Furthermore, the one-**k** type-I state with moments perpendicular to the propagation axis has a lower free energy than the type-I state with moments along the propagation axis.

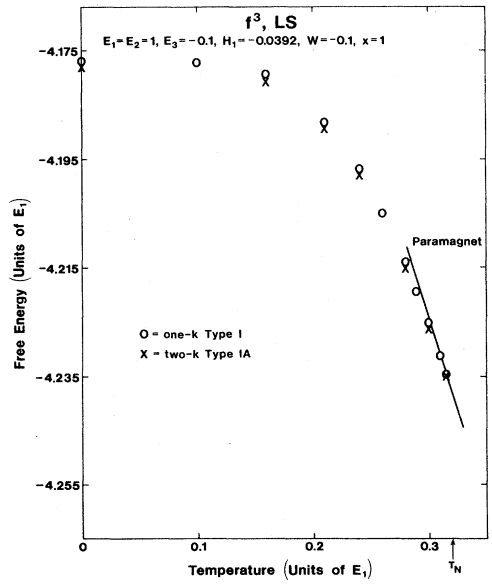

FIG. 4. Temperature dependence of free energies of the two-**k** type-IA and the collinear type-I antiferromagnetic structures for $E_1=E_2=1$, $E_3=-0.1$, $H_1=-0.0392$, $W=-0.1$, and $x=1$.

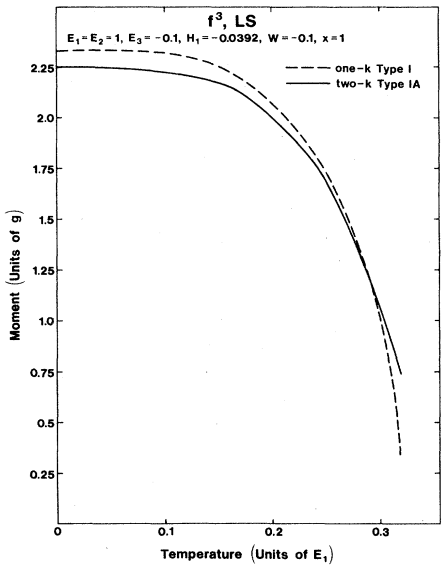

FIG. 5. Temperature dependence of moments of the two-**k** type-IA and the type-I antiferromagnetic structures for $E_1=E_2=1$, $E_3=-0.1$, $H_1=-0.0392$, $W=-0.1$, and $x=1$.

For a set of model parameters $E_1=1$, $E_2=0.09$, $H_1=-0.1$, $W=-0.015$, and $x=1$, a behavior as close to that of UP as we have been able to reproduce can be found. The temperature dependence of moments for the two- and one-**k** states are shown in Fig. 3. The ordered moment at zero temperature is about $2.1\mu_B$, close to the experimental moment. Matching to a Néel temperature of 125 K, in the temperature range between 0 and 25 K, the two- and one-**k** type-I states have very nearly equal (within 0.01%) free energies. At $T=25$ K, the one-**k** state is stabilized as the ground state. The CF parameter V_4 is about 432 K, while the experimental value deduced by Troc and Lam[8] is about 3200 K. The important thing here is that a behavior similar to UP is obtained using a V_4 of the experimental sign, even if the magnitude is off almost by an order of magnitude. Increasing the CF parameter much further in our model destroys the (two-**k** type-I)-to-(one-**k** type-I) transition, as in this case the CF strength is large compared to the two-ion interaction, and the mean-field energy levels for all the magnetically ordered structures obtained are nearly equal; this makes obtaining a thermal transition between structures difficult.

In the presence of a crystal field of strength large compared to the two-ion CS interactions, a two-**k** type-IA state can be obtained as having a local free-energy minimum at zero temperature. For example, such a structure can be stabilized for the parameters $E_1=E_2=1$, other smaller two-ion interactions, and $W=-0.05$ (the V_4 then is over 1000 K). But the crystal field then is large enough to preclude the possibility of a transition to another magnetically ordered state. For the parameter set $E_1=E_2=1$, $E_3=-0.1$, $H_1=-0.0392$, $W=-0.1$, and $x=1$, the two-**k** type-IA state and the one-**k** type-I state with moments along the propagation direction have nearly equal free energies with the two-**k** type-IA being the

ground state at $T=0$, with a moment of $2.25g$. The crystal-field parameter that is obtained by matching to a Néel temperature of 125 K, gives $V_4=2877$ K, close to the experimental value of about 3200 K. Figure 4 shows the temperature variation of free energies and Fig. 5 shows the temperature variation of moments of these two structures. It is seen from Fig. 4 that even though the free energies of the two-**k** type-IA and the one-**k** type-I antiferromagnetic structures are close at all temperatures, a transition between the two structures does not take place. Thus to obtain UAs two-**k** type-IA behavior at low temperatures, a CF strength large compared to the two-ion hybridization-mediated interaction is needed; but having such a large crystal field precludes the possibility of having the transition to a collinear type-I structure with increasing temperature.

We have been successful in modeling the noncollinear to collinear transition in UP and the noncollinear structure in USb. We have also shown that in the limit of a large crystal-field strength, a two-**k** type-IA structure as obtained in UAs can be stabilized at $T=0$. However, the temperature transition between two-**k** type-IA and one-**k** type-I states is difficult to reproduce. In the limit of such a large CF strength, the modifications introduced in the CF interaction by the hybridization[11] need possibly to be taken into account, and this has not been done in our calculations. It is clear that a better understanding of the role of the crystal field in these compounds, both theoretically and experimentally, is needed.

ACKNOWLEDGMENT

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[1]J. Rossat-Mignod, P. Burlet, S. Quezel, and O. Vogt, Physica (Utrecht) **102B**, 237 (1980).

[2]R. Siemann and B. R. Cooper, Phys. Rev. Lett. **44**, 1015 (1980).

[3]P. Thayamballi, D. Yang, and B. R. Cooper, Phys. Rev. B **29**, 4049 (1984).

[4]B. Coqblin and J. R. Schrieffer, Phys. Rev. **185**, 847 (1969).

[5]P. Thayamballi and B. R. Cooper, J. Appl. Phys. **55**, 1866 (1984).

[6]A. Banerjea, B. R. Cooper, and P. Thayamballi, Phys. Rev. B **30**, 2671 (1984).

[7]G. H. Lander, in *Magnetic Properties of Actinide Systems,* edited by W. D. Corner and B. K. Tanner (IOP, London, 1978), p. 173.

[8]R. Troc and D. J. Lam, Phys. Status Solidi B **65**, 317 (1974).

[9]G. H. Lander, M. H. Mueller, D. M. Sparlin, and O. Vogt, Phys. Rev. B **14**, 5035 (1976).

[10]K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[11]P. Thayamballi and B. R. Cooper, Phys. Rev. B **30**, 2931 (1984).