Similarities in Magnetic Behavior of Cerium and Plutonium Compounds

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The first sizable single crystals have been prepared of plutonium compounds. The field and temperature dependence of magnetization of single-crystal PuSb is highly evocative of that of CeSb or CeBi, and PuSb gives anisotropy and magnetic structural behavior as expected from hybridization-mediated interionic interactions for moderately delocalized *f*-electron systems.

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There is much interest in the magnetic behavior of light actinide (U, Np, and Pu) and cerium compounds because of the opportunity of using different families of compounds to span the full range of behavior as the *f* electrons vary between localized and bonding character.[1] Our previous theoretical work[2,3] on cerium and uranium systems has shown that there are characteristic high-field magnetization anisotropy and magnetic structural peculiarities when there is a modest delocalization of the 4*f* or 5*f* electrons. This occurs because the essential determinant of the nature of magnetic ordering for moderately delocalized *f*-electron systems is a hybridization (with band electrons) -induced anisotropic two-ion interaction; and this interaction serves to define large units within a magnetic structure which can move (magnetically) relative to one another with very little cost to the total energy of the system.

Monopnictides and monochalcogenides are "model" systems for this modest delocalization regime because of the relatively large spacing between *f*-ion sites. (The nitrides are apt to differ qualitatively from the other monopnictides because of smaller lattice spacing.) This has led us to focus our attention on these compounds, and for the monopnictides to make the first sizable single crystals of plutonium compounds. In considering Pu^{3+} (f^5) systems, we have been motivated by a hypothesis that a similarity in magnetic behavior of corresponding Ce^{3+} and Pu^{3+} compounds will arise from a similar degree of delocalization of the *f* electrons of Ce^{3+} and Pu^{3+}, both of which have ground-state multiplets with $J=\frac{5}{2}$. Thus we would expect similar hybridization-induced behavior for the heavier (than nitrides) monopnictides of these two ions. In this context, it is important that the experiments on single-crystal PuSb reported here show behavior remarkably evocative of [4,5] CeSb and CeBi. There is strong anisotropy in the magnetization, favoring alignment along cube-edge directions. The magnetic structure is ferromagnetic at low T with a transition to long-period antiferromagnetism at high T. Such strong anisotropy and ease of transitions between superficially dramatically different magnetic structures characteristically occurs in our theory[2,3] for band-hybridization–mediated interaction[6] in moderately delocalized systems. We present new theory for plutonium systems explaining the PuSb behavior. We will also suggest a key conceptual jump speculating that higher multipolar interactions, derived from the same f-band hybridization effects, could be the cause of the complex lattice structures and transitions in elemental plutonium.[7]

Detailed measurements studying microscopic and/or anisotropic interactions with a variety of techniques require well-characterized single crystals. Accordingly, a collaboration is now in operation combining the single-crystal–growth capabilities previously acquired at the Eidgenössische Technische Hochschule (Zürich) with the unique glove-box and handling facilities at the Transuranium Institute (Karlsruhe). This collaboration has succeeded in developing facilities to grow large single crystals of transuranium systems.[8] This Letter reports the first of a series of measurements to be done on plutonium monopnictide single crystals (>5 mm^3) made, characterized, and encapsulated using these facilities.

The special features of magnetization experiments on compounds of transuranic elements lie in the special difficulties of preparation as described in reports cited under Ref. 8 and in the need to work with samples encapsulated in copper. The reasons for encapsulation are (1) to avoid hazards of toxicity and radioactivity, and (2) to avoid self-heating of the sample. Good thermal contact is essential in the encapsulation in order to avoid the self-heating. It is a simple matter to make the small correction in measured magnetization necessary to take account of the diamagnetism of the copper.

Our single-crystal magnetization measurements on PuSb identify the low-temperature magnetic ordering as ferromagnetic, with a transition to antiferromagnetism at 75 K. The Néel temperature (T_N) is 85 K. Neutron diffraction measurements[9] have subsequently identified the antiferromagnetic phase as long period (about ten layer spacings) with structural propagation vector along $\langle 001\rangle$. As shown in Fig. 1, the magnetization at low temperature is extremely anisotropic, with the moment locked along the $\langle 001\rangle$ direction up to high fields, independent of the direction of applied field. This is identical to the behavior of[4] CeSb and CeBi. However, both CeSb and CeBi are[5] type-IA antiferromagnets at low T, a moderate applied field being required to induce ferromagnetism. It is particularly interesting that PuSb is a true ferromagnetic with this same anisotropy behavior. This is striking in light of our theory[2] for Ce^{3+} systems, predicting that a system with a pure Coqblin-Schrieffer-type, hybridization-induced, two-ion interaction has a ferromagnetic ground state.

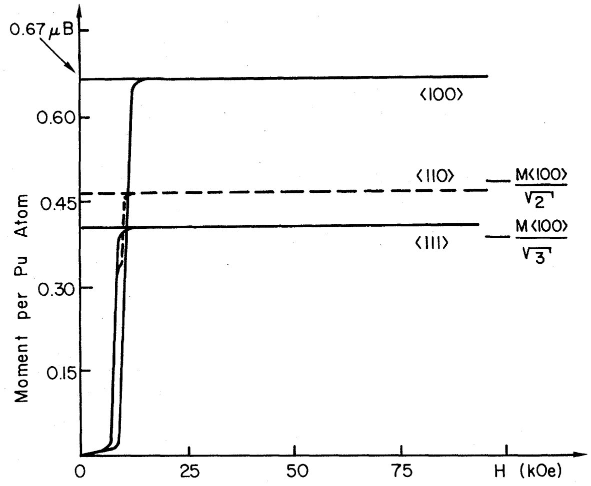

FIG. 1. Magnetization of PuSb vs applied field at 4.2 K. Horizontal bars at right give values of projections of $\langle 100\rangle$ moment along $\langle 110\rangle$ and $\langle 111\rangle$ directions.

For the f^n ($n>1$) systems, our theory for hybridization-mediated interionic interaction is an extension[3,10] of the theory of Siemann and Cooper[2] (which used the Coqblin-Schrieffer[6] approach) for Ce^{3+} systems. The interaction derived in our theory depends on the number of f electrons in the ion and on the nature of intraionic coupling. We have performed calculations for the f^5 system in both the $L-S$ and the $j-j$ limits for the intraionic coupling.[10] For the $j-j$ coupled case, one can prove[10] that the angular dependence of the interaction is the same for f^n and f^{6-n} ions, i.e., the same for Pu^{3+} (f^5) as for Ce^{3+} (f^1). (This results from the electron-hole symmetry between the wave functions of the f^n and f^{6-n} ions in the $j-j$ coupled scheme, with $j=\frac{5}{2}$.) Thus for the $j-j$ coupled case, we can take over the theory for magnetic behavior of Pu^{3+} directly from the previous theory[2] for Ce^{3+}. However, the angular dependence of the two-ion interaction for Pu^{3+} is quite different for L-S from that for $j-j$ intraionic coupling; and so we have also used the two-ion interaction with $L-S$ intraionic coupling to find the free energy of different magnetic structures and alignments for an fcc lattice of Pu^{3+} ions, for varying ratio of next-nearest (E_2) to nearest neighbor (E_1) ferromagnetic interaction. We find that ferromagnetism is very strongly favored over antiferromagnetism for the entire range of E_2/E_1 values between 0 and 1 studied. This favoring of ferromagnetism is much stronger than if the intraionic coupling were $j-j$ (see Fig. 2 of Siemann and Cooper[2]).

Using these results we can relate the experimental behavior of PuSb to the theory for Pu^{3+} systems coupled by hybridization-mediated anisotropic two-ion interactions. We consider the essential results of the magnetization and neutron-diffraction experiments on PuSb to be (1) very strong ⟨001⟩ anisotropy; (2) ferromagnetic ordering between 0 and 75 K with small value of ordered moment (the neutron-diffraction measurements[9] give a moment very close to that from magnetization, indicating little band polarization); (3) antiferromagnetic ordering between 75 and 85 K.

The strong ⟨001⟩ anisotropy follows directly from the anisotropy of the hybridization-mediated two-ion interaction both in the[2] $j-j$ and in the[10] $L-S$ limits for the intraionic coupling. We then consider the temperature dependence of the ordered magnetic moment and the magnetic structures, especially with regard to points (2) and (3) above. In Fig. 2, we compare the experimental temperature dependence of the Pu^{3+} ferromagnetic (remanent) moment in PuSb to the predicted behavior for the $j-j$ and $L-S$ theoretical models. Note that the numbers shown for the theory curves have to be multiplied by a g value to get the actual moment. We now discuss the virtues and failures of the two limiting cases, i.e., $j-j$ or $L-S$ coupling within the Pu^{3+} ion, and recognize that an intermediate (but close to $L-S$) coupling model will probably give excellent agreement with experiment.

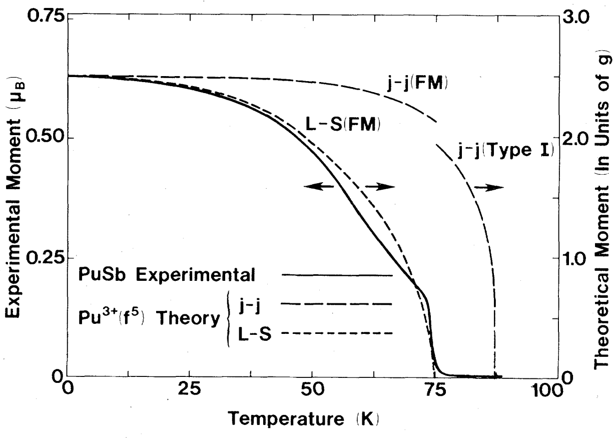

FIG. 2. Comparison of experimental and theoretical behavior for ordered magnetic moment vs temperature of Pu^{3+} in PuSb. (The curve for the $j-j$ theory in the antiferromagnetic phase shows the sublattice moment. The g value for L-S coupling is $\frac{2}{7}$, and g for j-j coupling is $\frac{6}{7}$.)

The $j-j$ model is capable of giving both ⟨001⟩ ferromagnetism and a transition with increasing T to type-I antiferromagnetism. The big problem with the $j-j$ model is that the g value is the same as for Ce^{3+} ($\frac{6}{7}$); and hence the moment is too large, about $2.1\mu_B$. A moment somewhat lower can be obtained; but the lowest obtainable value seems to be about $1.7\mu_B$. A secondary problem is that the temperature dependence of the magnetization is flatter than the experimental behavior. On the other hand, the fact that the transition at T_c is first order is evocative of the experimental behavior.

The magnetization given by the $L-S$ model is in closer agreement with the experimental at all temperatures than that given by the $j-j$ model. The small experimental moment is reproduced since the g value is $\frac{2}{7}$. The decrease of moment with temperature is also much more gradual than in the $j-j$ model. The crucial difficulty with the $L-S$ coupled model is the inability to have an antiferromagnetic transition occur at 75 K as temperature increases.

Thus comparing with experiment, it is seen that the L-S coupling model is very successful in reproducing the experimental behavior in PuSb except for the 75-K transition to antiferromagnetism; the $j-j$ coupling model, on the other hand, does yield that aspect. The coupling in Pu^{3+} is expected to be intermediate between the two simple limits, but closer to the L-S coupling scheme. At present, we have done a crude approximation to an intermediate coupled model, by taking a ground-state wave function for Pu^{3+} that is a mixture of 90% L-S ground-state wave function and 10% $j-j$ ground-state wave function. This calculation did indeed both give a small moment (characteristic of $L-S$ coupling) and bring the type-I states close in energy to the ferromagnetic state (characteristic of $j-j$ coupling), giving the possibility of a ferromagnetic to antiferromagnetic transition as is experimentally observed, while preserving the large ⟨001⟩ anisotropy. A calculation using intermediate coupled wave functions for Pu^{3+} is under way. While such a calculation using intermediate coupling is required to reproduce all the experimental aspects, the signature of the hybridization-mediated interaction is unmistakable from the calculations performed for the two limiting cases.

Thus we feel that the hybridization-mediated two-ion interaction, resulting from modest delocalization of the $5f$ electrons in PuSb, explains all the essential features of the experimental behavior. In a fundamental sense, the significance of the results discussed here is in pointing to the conclusion that, in similar crystallographic environments, the f electrons of Ce^{3+} and Pu^{3+} show a similar degree of delocalization, giving rise to similar consequent properties.

Finally, we speculate on the relationship of these ideas to the unique crystallographic behavior of elemental plutonium,[7] where six allotropes occur in a temperature range of less than 400 K. We hypothesize that the f electron–band electron hybridization provides a directional focusing mechanism for the f-electron charge density. The slight f-electron delocalization leads to a small bonding contribution with peculiar spatial properities. The detailed modification in shape of the f-electron orbital charge cloud caused by the hybridization depends on both the way f charge is sucked out along the interionic axis and the way it is spatially restricted by correlation effects within the Pu^{3+} f^5 ion. This reshaping of the charge cloud by hybridization thus changes the cohesive energy and hence the lattice structure. It should be possible to quantify this picture by developing an effective field theory in which higher multipolar couplings brought about by the hybridization-induced two-ion coupling would cause transitions between the different crystallographic structures, i.e., viewed as a series of distortions of a high-temperature fcc phase. This would be the spatial analog to the magnetic behavior of[5] CeSb where the hybridization-induced two-ion interaction causes the existence of many magnetically ordered phases separated by first-order transitions.

We gratefully acknowledge information and discussion which helped to shape these ideas, and aid received in overcoming the great technical and institutional problems involved in being able to make the plutonium monopnictide single crystals. Contributions from G. H. Lander were invaluable in both these regards. We thank J. Rossat-Mignod and P. Burlet for providing us with their neutron-diffraction results, and discussion thereof, prior to the presentation at the Journees des Actinides. Information and encouragement from A. C. Lawson, J. L. Smith, and P. Wachter helped greatly. We wish to thank J. Rebizant for his work on crystal orientation and encapsulation, and K. Mattenberger, C. Rijkeboer, and L. Scherer for their skilled assistance. This work was supported by U. S. National Science Foundation through Grant No. DMR-82-04261. This work was performed under the auspicies of the U. S. Department of Energy.

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