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Magnetism in transuranics[a] (invited)

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Transuranic materials exhibit all types of magnetic behavior. This behavior is a relatively smooth function of atomic number and of the atomic volume of the atoms in the materials. The systematics are best described in terms of these volumes as a measure of intinerancy, mixed valence, or local moment formation.

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INTRODUCTION

The transuranic elements, and their compounds and alloys, exhibit all the types of magnetic and related phenomena found in other parts of the periodic table. The relatively scant attention given the transuranic magnetic behavior appears to be due to the limited number of laboratories equipped for this kind of work, due to the hazardous and politically sensitive nature of work on radioactive materials.

The taxonomy of transuranic actinide behavior is nowhere near as complete as that of the transition metals and lanthanides. Nevertheless, it is apparent that work on the transuranics has important bearing on controversial issues of current interest for the magnetism of the transition and lanthanides metals. The current intense activity on cerium based materials is a case in point. Plutonium and its neighbors are the only other elements with similar behavior, and which therefore can be used for comparison. It is becoming clear that the transuranics can provide a rich ground on which to test our theories of magnetism.

We shall describe the difficulties associated with work on radioactive materials, the trends in f-electron localization that give rise to the great variety of behavior, and finally some current work that illustrates what can be done.

The most recent comprehensive review of magnetic materials in actinides is by Brodsky [1], and one is in preparation by Fournier and Troć [2]. Our purpose here is to point out the systematics of the transuranics so that their properties are understandable within the usual framework of magnetic materials

RADIOACTIVITY

The first seven transuranics (Np, Pu, Am, Cm, Bk, Cf, and Es) all have long-lived isotopes with half-lives of at least a year. The magnetic properties of these atoms can certainly be determined in condensed matter. The remaining transuranics (Fm, Md, No, and Lw) have no isotopes with half lives beyond a hundred days and clearly only more limited types of measurements of magnetic properties can ever be made. In particular, sufficiently dilute alloys to contain non-interacting moments could be made and measured as a function of time (and hence composition). Reasonable quantities of the more stable isotopes are becoming available. For example the early work on curium was on the 244 isotope with a half-life of 18 years, but now a total of about 100 mg of ^{248}Cm with a half life of 2×10^5 years is available in the U.S. Because of this, low temperature heat capacity measurements are now in progress at Los Alamos by G. R. Stewart and R. G. Haire.

The effects of the radioactivity must be considered in experiments. The reabsorption of radiation within the samples is seen as self-heating, and the higher activity of impurities must be included. Thus ^{248}Cm calculates to about 4 mW/g of heating; the available material shows about twice that rate. Next the effects of radiation damage must be kept in mind.

We recently prepared tiny single crystals of ^{241}AmB$_6$ because the rather large, reported lattice parameter indicated that it would be a mixed valent material. We confirmed the lattice parameter but also found that it increases at a rate of $\Delta a/a_0 = 7.5 \times 10^{-4}/90$ days from self damage. Finally, the daughters that grow into the samples can affect the magnetic properties. For example, americium is usually in a non-magnetic configuration in metallic systems, but its daughter neptunium usually has a magnetic moment. The effects of radioactivity cannot be neglected in the tranuranics.

f-ELECTRON LOCALIZATION

The physical properties of the early elemental actinides are dominated by gradual stabilization of the 5f-electron energy band. It lowers the melting points, induces a large number of low-symmetry, high density crystal structures, but does not form the local moments seen in the corresponding lanthanide elements [3]. The superconductivity that begins with thorium terminates with uranium. Neptunium and plutonium have their f-bands at the Fermi level, leading to spin fluctuations which suppress superconductivity but do not give magnetic moments. Americium is the first element with localized 5f-electrons, and Hund's rules appear to apply. Interestingly, it possesses a non-magnetic f^6 ground state, unlike its 4f-analogue europium which is divalent with the f^7 gadolinium configuration [4]. Because it has localized f-electrons, in a non-magnetic ground state, it is in fact a superconductor [5]. The remaining pure elements are lanthanide-like in that the f-electrons are fully localized. The understanding of their properties requires the same tools used for the lanthanides.

Curium in the hexagonal phase is antiferromagnetic at 65 K and the face-centered-cubic phase is ferrimagnetic at 200 K. There remain difficulties in finding the full moment anticipated for the f^7 configuration [6,7]. Berkelium is antiferromagnetic at 22 K [8], while californium shows no obvious magnetic ordering [9]. These two elements show Curie-Weiss behavior with the full effective moments expected.

The great variety of magnetic behavior occurs where the f-electrons are becoming localized in elements, compounds, and alloys. Similar effects are seen in the analogous regions of the 3d and 4f series in metallic materials. The position of the crossover from d- or f-electron band (or itinerant) behavior to largely magnetic (or localized) behavior in the 3d, 4f, and 5f series occurs at manganese, cerium and plutonium respectively. These elements have the largest numbers of allotropes, and the highest electronic densities of states among the d- and f-electron elements. One can view the magnetism in these series as resulting from decreasing overlap of the d- or f-electron wave function. In compounds and alloys the onset of magnetism occurs more readily because the foreign atoms isolate the potentially magnetic atoms, decreasing wave function overlap. Similarly, applied pressure tends to make materials near this crossover less prone to

magnetism [3].

For the 3d-series, the d-electrons never become fully localized, while in the 4f-series the entire crossover takes place with cerium. The 5f-electron series is in many ways intermediate between 3d and 4f behavior, with its very gradual transition towards localization through enhanced paramagnetism, to band (or itinerant) magnetism to full localization. This is seen both in the pure transuranics and in families of their compounds which have smooth variations in transuranic size.

In the local moment regime, one has a good chance to determine the role of crystal fields and valence fluctuations. In the itinerant magnetism regime, the various effects cannot be separated in any obvious way. This difficulty is most apparent at plutonium where in a number of compounds and alloys, no moment in found although the plutonium atomic size in the materials suggests localized 5f-electrons. In this case, plutonium should have an f^5 configuration, analogous to samarium. The magnetic behavior of samarium itself is complicated by low lying excited state J-multiplets. Samarium seldom shows good Curie-Weiss behavior in its compounds in the most commonly studied temperature range, below 300 K. The effects of crystal field splittings on the samarium 4f-electron levels is especially difficult to determine. All these problems carry over with force to the plutonium situation.

It is implicit in our view of the onset of magnetism in all the magnetic series of elements that what often passes for mixed valent behavior in cerium materials is distinct from mixed valence in heavier rare earths where there are two degenerate valence states. Our view is that the f-electron in cerium can be either localized or de-localized, to varous degrees. For plutonium, this means that the f^5 configuration can also be localized, or de-localized, to various degrees. Actinide workers have known for a long time that cerium alone among the rare earths should be considered an honorary actinide.

VOLUME CONSIDERATIONS

The f-electrons have a large amplitude near the atomic nucleus, and this amplitude depends sensitively on the degree of localization of the f-electrons. This in turn leads to partial screening of part of the nuclear charge, which again is dependent on the degree of localization of the f-electrons. The consequence is a large variation in atomic size with change in the degree of f-localization. Atomic size in the material, therefore, provides a good measure of the extent to which the f-electrons are localized in the transuranics. This idea was used by Hill [10] to determine the minimum interatomic spacing for Ce, U, Np and Pu atoms, in compounds and alloys, necessary for the appearance of magnetism. Once localized, the actinides can be expected to have their tri-valent sizes, as determined by the smooth interpolation of radii between, actinium and americium and the heavier transuranics. For these localized situations, we can apply, as a first approximation, our experience with the corresponding lanthanides.

Some of the difficulties in understanding the magnetism of the transuranics can be traced to two sources. First, the possibility of mixed valence phenomena of the samarium type very probably occurs in a number of situations, and this makes a straightforward interpretation on the basis of changes in atomic size more complicated. Second, for a number of situations involving the transuranics, but especially plutonium, in which a full local moment is expected, the effects of low lying J-multiplets mentioned above, and potentially very large crystal field splittings can make a decision between itinerant versus localized moment magnetism suspect. We believe the following systematics can be useful in this respect.

Actinium and americium metals are clearly trivalent and a plot of the metallic radii of the actinides shows a steady "lanthanide" contraction
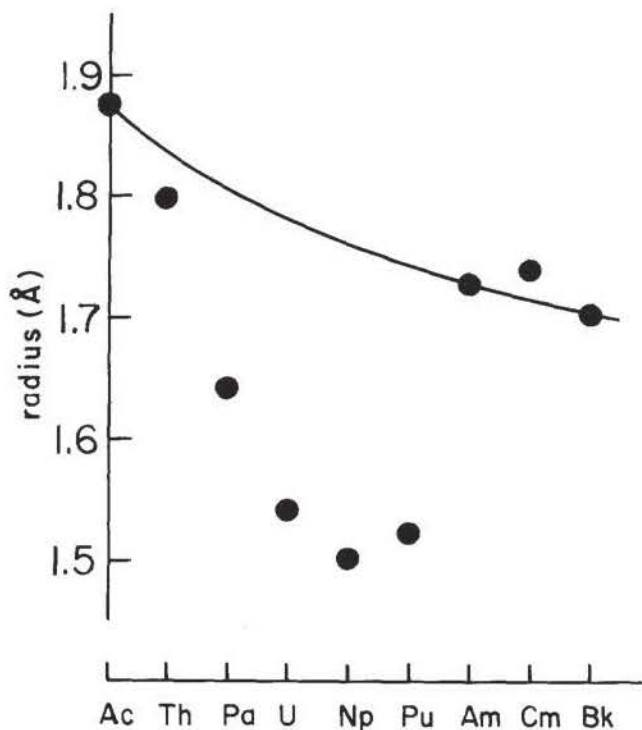

Fig. 1. The known radii of the atomic volumes of the actinide atoms for the room temperature phases of the pure metals. The line shows the assumed actinide contraction (similar to the lanthanides) based upon the radii of Ac, Am, Cm, and Bk. It is the tri-valent size that would occur without f-electron bonding. Curium above the line is the same as for gadolinium in the lanthanides, where the tri-valent line is well-defined.

beyond americium which extrapolates back to actinium (Figure 1). The elements thorium through plutonium, however, fall far below this tri-valent line, but it is possible to estimate a radius appropriate for lanthanide-like tri-valent plutonium which would have a localized $5f^5$ configuration. This radius is $r_m \approx 1.75 Å$, close to the metallic radius of erbium. This is substantially larger than the radius appropriate to fcc δ-phase plutonium ($r_m = 1.64 Å$), its lowest density phase.

Figure 2 shows the similar behavior for intermetallic compounds of three different crystal structures to that shown for the elements in Fig. 1. Again the presence of an f-band causes the depression below the tri-valent line. It has been noted by Damien and de Novion [11] that for the rock-salt structure compounds the tri-valent line is identical for both the lanthanides and actinides. We note that this is more general in that it occurs for essentially all compounds. So although the elemental lanthanide and actinide contractions are different, all f-electron compounds have the same contraction. Then, the formation of an f-band from wave function overlap or hybridization with spd bands results in a smaller size than that of the trivalent line. The fact that the trivalent compound lines are identical is similar to the situation for the 4d and 5d electron elements which also have essentially the same sizes.

Resistivity experiments by Hill and Elliott in the early 70's on plutonium impurities in La, Pr and Zr showed Kondo-type minima at low temperatures, characteristic of localized magnetic virtual bound states [12]. Subsequent magnetic susceptibiltiy measurements on LaPu [13] gave a moment of 0.84 μ_B/Pu, essentially the Russell-Saunders value for the f^5 Hund's Rule ground state. No Curie-Weiss behavior was found in ZrPu [13]. Lattice parameter data on LaPu show that plutonium has essentially the radius expected for tri-

valent plutonium, whereas the plutonium size in ZrPu is approximately that of δ-Pu. So the size considerations make sense of the magnetic data, but the Kondo-type anomaly in ZrPu is unexpected. We note, however, that pure δ-Pu retained to low temperature shows a similar Kondo-like anomaly for which spin fluctuations seem to be the cause [14]. In general plutonium atoms of the δ-size are associated with spin fluctuations.

Size considerations can be similarly applied to compounds by comparing the lattice parameter of a given actinide with the size of the corresponding lanthanide compounds. We give an example from our work. Both plutonium and amercium form the cubic hexaboride phase [15]. In the lanthanide series, erbium appears to be the smallest rare earth which forms this phase (ytterbium is di-valent in YbB_6). We have prepared small single crystals for both PuB_6 and AmB_6 with respective lattice parameters 4.1132 Å and 4.1240 Å. The PuB_6 parameter is identical to that reported for GdB_6, the AmB_6 is even larger. Magnetic susceptibility measurements on PuB_6 show little temperature dependence [16], similar to SmB_6 which is one of the canonical mixed valence materials. The appearance of the crystal (a black sheen) is closer to that of di-valent hexaborides, rather than the deep blue of tri-valent materials. This suggests an unusual electronic situation which we are currently investigating.

The AmB_6 situation is equally strange. Here the lattice parameter is the same as that of NdB_6. Pure americum metal is slightly smaller than lutetium, and should not be expected to form a hexaboraide. This very large size in AmB_6 suggests partial di-valency, which would make AmB_6 the 5f analogue of SmB_6, except here americium would be intermediate between $5f^6$ and $5f^7$. Preliminary resistivity measurements show an increasing resistivity below room temperature, as seen in SmB_6. AmB_6 may provide an interesting material for testing theories of intermediate valence which have been applied to SmB_6.

The compounds U_6Mn, U_6Fe, U_6Co and U_6Ni are all superconductors, with a transition temperature that increases with decreasing lattice parameter [17] in agreement with consideration of 5f wave function overlap [10]. The transuranic compounds Np_6Mn, Np_6Fe, Np_6Co and Pu_6Fe also form, but the neptunium compounds have a relatively large size neptunium atom [18]. Preliminary measurements on these neptunium compounds show that they all possess a small ferromagnetic background at room temperature. The Np_6Mn is more magnetic than the others with one sample showing an anomaly in the magnetization at 200 K, while a second had an anomaly at ∼10 K. In both cases the magnetization reaches a value (unsaturated) of μ ∼0.3 μ_B per formula unit at T = 4 K and H = 5 T. If this is the neptunium moment it is the smallest ever measured, although the moment could reside on the manganese. If this is so, the volume anomaly can be due to the transition metal. Studies of $(U_xNp_{1-x})_6Mn$ could resolve this question and would be a system that goes from a 2.4 K superconductor to a much higher temperature ferromagnet.

An interesting feature of the systematics of the occurrence of magnetism in uranium, neptunium and plutonium compounds is that in many cases a neptunium compound orders magnetically, while the uranium and plutonium analogues do not. Band structure calculations [19] find in the elements, at their observed atomic volumes, approximately 3, 4 and 5 5f-electrons respectively in uranium, neptunium and plutonium. If we suppose that magnetic behavior arises from the localization of these f-electrons in compounds, without changes of occupation number, then one expects an increasing tendency towards magnetism as the nuclear charge Z increases, namely plutonium should order magnetically more often than neptunium.

We suggest a resolution to this question. Lattice parameter systematics point to the plutonium f-configuration in compounds being more localized than that of neptunium. We can imagine, as one goes from uranium to plutonium in a given compound sequence, that
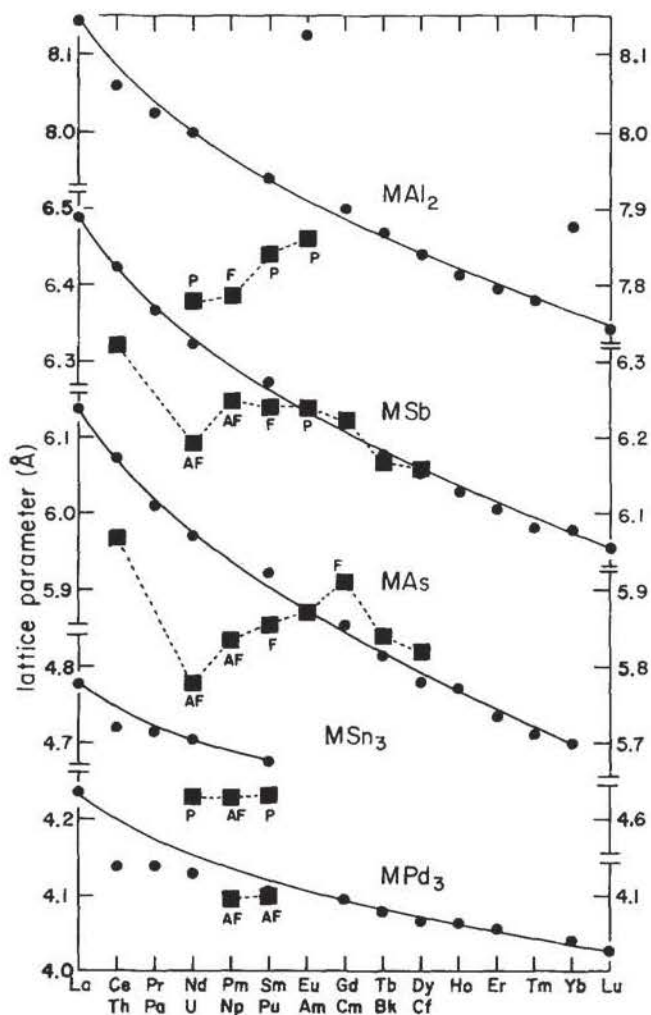

Fig. 2. The lattice parameters for five families of lanthanide (circles) and actinide (squares) compounds. As in the pure elements, the presence of the f-band cause a size depression below the smooth line connecting the lanthanide compounds which is the same line (unlike the pure elements) as for the actinide compounds. Magnetic behavior is indicated by P-paramagnetic, AF-antiferromagnetic, and F-ferromagnetic.

the f-band both narrows and goes through to below the Fermi-level. A narrow magnetic f-band below the Fermi-level could be spin compensated by the spd electrons, forming essentially a concentrated Kondo system. We then would have a competition between the Kondo condensation and magnetic ordering.

Our suggestion then is that neptunium compounds when magnetic are in general itinerant magnets, and that the non-magnetic plutonium analogues of these magnetic neptunium compounds are Kondo compensated. The immediate conclusion from these considerations is that one might be able to drive such plutonium compounds under pressure into a magnetic state, an unusual situation which remains to be tested.

CONCLUSION

Atomic size information is a reliable guide to where interesting physics of magnetism in the transuranics is, but we are still unable to unequivocally interpret it.

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