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EXPERIMENTAL STUDIES OF NARROW BAND EFFECTS IN THE ACTINIDES

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It is the purpose of this paper to present experimental data which emphasize the narrow band behavior of actinides. We will show that phenomena associated with narrow $5f$ -like bands are not rare. The discussion will concentrate on pure actinides and binary cubic intermetallic compounds of the type AnX , AnX_2 , and AnX_3 .

ORIGIN OF f -BANDS

Table 1 summarizes some properties of pure actinide metals.¹ It is seen that their electronic specific heat coefficients,² γ , are large, especially for Np and Pu. No magnetic order is found until the heavy actinides, Cm, Bk, etc., where magnetic moments comparable to heavy rare earths are observed.³ Furthermore, the lighter members of the series, Th, Pa, and U have exhibited superconductivity in at least some of their phases.^{4,5} The low temperature electrical resistivities may be approximated by power law dependences of the temperature, T^n . These change from simple transition metal behavior, T^3 , to what we believe to be spin fluctuation behavior, T^2 , to localized $5f$ electrons (it is believed that Am is trivalent, $5f^6$, with $J = 0$, and therefore nonmagnetic).⁵

The question then arises: where in the light actinides are the properties we expect from f -electrons, viz., magnetism? Part of the answer may be explained by use of Fig. 1. This figure by Freeman and Koelling⁶ shows the radial extent of the $5f$ electron wave functions of various actinides scaled by their interatomic separations in the various allotropic phases. For comparison, the corresponding

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Table 1. Properties of Pure Actinide Metals

	γ $\text{mJ}/(\text{mole-K}^2)$	Magnetic	Supercon.	n $(\rho \propto T^n)$	W (eV)	U (eV)
Th	4.3	No	Yes	3	5	1.5
Pa	-	No	Yes	-	-	1.6
U	9.1	No	Yes	2-3	4	2.3
Np	12.4	No	No	2	3	2.6
Pu	17.0	No	No	2	2	3.5
Am	6.0	No	No	5	0.1	5.0
Cm	-	Yes	No	-	<0.1	-
Bk	-	Yes	No	-	-	-

Fig. 1. Values of $[\langle r^4 \rangle]^{1/4}/R$ for the different phases of the actinide metals; R is the half-internuclear separation (from Ref. 6).

value for iron is also shown. From this figure we see that in the lighter actinides, the $5f$ wave functions overlap each other from site to site. Thus, the wave functions are broadened via direct overlap. This result, which strongly contrasts the localized $4f$ electrons in rare earth metals to the actinide $5f$ electrons, has been pointed out by several authors.^{6,7} Hill observed, also,⁷ that

if the actinide-actinide separations were less than 3.5 Å in uranium compounds and 3.4 Å in neptunium compounds, then the compounds would not become magnetic. This was attributed to the formation of a nonmagnetic 5f electron band. Hill's rule is nearly always obeyed. There are, however, many intermetallic compounds for which the actinide-actinide distance is larger than the minimum values determined by Hill, but which do not order magnetically.³

In the last two columns of Table I we see that the polar state formation energy, U ,⁸ is smaller than the 5f band width, W , determined by APW calculations, at least for Th and uranium.⁶ Since the U given here has not been corrected for screening, these values for U are all too large. Thus, the band model should be appropriate for the light actinides, as $U/W < 1$.

Figure 2 shows the band structure for UIr_3 (ordered AuCu_3 structure) determined by relativistic APW calculations. The U and Ir potentials and the Fermi level have been determined with the aid of deHaas-vanAlphen data.⁹ This band structure successfully predicted the μ frequency due to an orbit centered at X , and the n frequency which exists for a short distance about the (111) direction. It would appear from the band structure that there is little f -character at the Fermi level. There are nearly three f -electrons which may be located at point Γ , and which are strongly hybridized with d electrons to form f - d bands. Yet there is good indication of some f -character at the Fermi level since effective electronic masses as large as 2.5 were measured here and $m^*/m_0 = 5.1$ was measured in isoelectronic URh_3 .¹⁰

Fig. 2. Energy bands for UIr_3 near the Fermi level (from Ref. 9).

In the case of UIr_3 and URh_3 , the existence of hybridized f -bands is well established. Their magnetic susceptibilities are nearly temperature independent and the resistivities follow a T^3 law at low temperatures, typical of d -band behavior.¹¹ The measured γ of URh_3 is only $14.5 \text{ mJ}/(\text{mole-K}^2)$ ¹² which is slightly smaller than the value for a fictitious " RhRh_3 " compound. DeHaas-vanAlphen data and a preliminary band structure are also available for isostructural UGe_3 .⁹ This compound has a T^2 resistivity dependence and $\gamma = 20.4 \text{ mJ}/(\text{mole-K}^2)$.¹³ Thus, in the case of UGe_3 we have made contact with a microscopic measurement and band calculation for an actinide exhibiting a large density of states due to the actinide (γ of UGe_3 - γ of " GeGe_3 " = 12), and probably a spin fluctuation resistivity due to the narrow f -bands. In this compound, the hybridization is presumably of f -s or f -p type.

Returning to Table 1, we can now have further confidence in band calculations for pure actinides with $U/W \lesssim 1$. A very dramatic exhibition of the effects of narrow f -bands on properties is seen in the resistivity-temperature curves of the pure metals, shown in Fig. 3.⁵ Even for uranium there is nonlinearity in the ρ - T curve at room temperature, and the anomalous behavior reaches its peak at plutonium. It has been possible to explain the Np data by a spin fluctuation¹⁴ and narrow band contribution¹⁵ (of course the spin fluctuations rise out of the narrow bands at low temperature). Although similar arguments have been proposed for Pu, they are not totally satisfactory, especially in regards to the resistivity maximum. This is not surprising since $U/W \sim 1$, a very difficult theoretical region.

Apparent spin fluctuation behavior, i.e., $\rho \propto T^2$, is observed fairly often in actinides.¹⁶ There are well over 20 system which exhibit this behavior. The χ - T dependence of the compounds fall into two groupings. For some, e.g., NpIr_2 , etc., there is no temperature dependence of χ . For others, e.g., PuZn_2 , NpRh_3 , etc., χ fits a Curie-Weiss plot, with a temperature-independent contribution, down to some $T \gtrsim T_{SF}$, and then nearly becomes temperature independent. This is similar to what is often termed Kondo-type susceptibility.

Relevance of this behavior to narrow f -bands is seen in Table 2 where γ 's are listed for U and Np AuCu_3 -type and cubic Laves phase (MgCu_2 -type) compounds. The γ 's are given as "excess", i.e., the contribution for the pure X elements have been subtracted away. UIr_3 is the only compound in Table 2 with $\gamma' \geq 10 \text{ mJ}/(\text{mole-K}^2)$ which does not show T^2 resistivity behavior. The same generalization may be made for the pure metals listed in Table 1. Several of the compounds in Table 2 order magnetically and are so indicated. NpSn_3 and NpOs_2 are discussed further below. If the argument of the present paper is valid, viz., narrow f -bands, then in some of the cases listed the bands will contain some very narrow features.

Fig. 3. Electrical resistivity of pure actinide metals (from Ref. 5).

From the discussion given thus far, it could be inferred that the f -character (narrow bands leading to localized f -electrons) generally develops monotonically in the actinide series. Actually this is not the case. In the band calculations of Koelling, the hybridized f -bands change considerably as the f -occupation number is changed.^{9,10} Failure of simple behavior is also seen in the series UAl_2 , $NpAl_2$, and $PuAl_2$. UAl_2 is definitely a spin fluctuation compound^{14,17} (see below), $NpAl_2$ behaves as a local-moment ferromagnet¹⁸ and $PuAl_2$ is probably a spin fluctuation compound.¹⁴ However, in the series $AnRh_3$ there is a gradual change over from itinerant to local $5f$ magnetic behavior.¹¹ The susceptibility data for $ThRh_3$, URh_3 , $NpRh_3$, and $PuRh_3$ are shown in Fig. 4. The corresponding exponents for the temperature dependences of resistivity are T^4 , T^3 , and T^2 for Th , U , and Np , respectively. The systems are described as low density of states transition metal ($ThRh_3$); medium to high density of state transition metal (URh_3); spin fluctuation metal as a consequence of a narrow band [$NpRh_3$, $\gamma = 95 \text{ mJ}/(\text{mole-K}^2)$]¹²; and a local moment antiferromagnet ($PuRh_3$). The local moment character of $PuRh_3$ is seen in the specific heat where the magnetic

Table 2. Excess Electronic Specific Heat Coefficients γ' of Actinide Intermetallic Compounds (a)

<u>mJ/(gram atom of actinide/K²)</u>			
URh ₃	0	NpRh ₃	85
UIr ₃	10	NpSn ₃	237,83 ^(b)
USi ₃	10		
UGe ₃	16		
UAl ₃	38		
UIn ₃	45		
UGa ₃	50		
USn ₃	164		
UIr ₂	53	NpRu ₂	112
UAl ₂	138	NpOs ₂	87,200 ^(b)

^a No corrections have been made for enhancements to γ .

^b The compounds order magnetically. The first value is for the paramagnetic state and the second value is for the ordered state.

Fig. 4. Magnetic susceptibilities of ThRh₃, URh₃, NpRh₃, and PuRh₃ (from Ref. 11).

entropy is $1.0 R \ln 2$. Of course, local moment magnetism may also be observed when the $5f$ electrons are not truly localized.¹⁵

f -BAND MAGNETISM IN ACTINIDES

With such high densities of states at the Fermi energy, it is expected that some f -band compounds will order magnetically. Three examples of magnetic behavior will be given.

UAl₂, a Spin Fluctuation Compound. In addition to a $\rho \propto T^2$ and a χ - T curve not unlike that of "Kondo compounds"^{14,17} the specific heat of UAl₂ clearly shows it to be an f -band spin fluctuation compound. The specific heat data are shown in Fig. 5, where it is seen that the spin fluctuation model of Doniach and Engelsberg¹⁹ fits the low temperature data, but they are not fit by magnetic impurity or crystal field models. Most importantly, the $T^2 \ln T/T_{SF}$ spin fluctuation contribution to γ is only affected by $\sim 1\%$ in an applied field of 43 kOe,¹⁷ in agreement with calculations for spin fluctuations.²⁰ The spin fluctuation contribution to specific heat is seen clearly in this case because $T_{SF} \sim 23K$ is in the right range for this contribution to be observable.

NpOs₂, a Weak Ferromagnet. Mössbauer, magnetization, and neutron diffraction measurements show this to be a ferromagnet with $\mu_0 \approx 0.25 \mu_B$ and $T_C = 7.5K$.¹⁸ Figure 6 shows the specific heat of NpOs₂²¹ plotted as C/T vs T^2 . The peak in C/T occurs at $T_C = 7.9K$. The magnetic entropy is found to be $0.2 R \ln 2$, which indicates an effective moment about $0.6 \mu_B$.

The magnetic moment in NpOs₂ is probably too small to be due to localized $5f$ electron moments. Yet it seems too large to treat in the Stoner-Wohlfarth-Edwards (SWE) model²² for moments $\ll 0.1 \mu_B$, e.g., as in ZrZn₂. Yet it has been shown that the magnetization and thermal data are in fair agreement with the SWE model for weak itinerant ferromagnets.²³ The large values of γ in the paramagnetic and ferromagnetic regimes (Table 2) and the large change in γ at T_C shows that f -bands are strongly involved in the magnetism of NpOs₂.

NpSn₃, an Itinerant Antiferromagnet. Figure 7 shows the electronic specific heat of NpSn₃.^{23,24} The ²³⁷Np Mössbauer effect shows the occurrence of magnetic order at 9K with a small effective moment, $\mu = 0.29 \mu_B/Np$.¹⁸ In this case however, the ordering is antiferromagnetic as shown by the two site character of the ¹¹⁹Sn resonance, and a weakly temperature dependent susceptibility. The magnetic entropy is found to be essentially zero, $-0.007 R \ln 2$. There undoubtedly are f -bands at the Fermi level causing the very large γ 's. The gap-like behavior of the transition, as per Cr, is shown by the large discontinuity at T_N and the near-BCS dependence of the data in Fig. 7.

Fig. 5. C/T vs T^2 for UAl_2 . Fits using data above 3K were made with $C = At + BT^3 + Df(T)$, where $f(T) = 1/T^2$ (dashed curve), $1/T$ (dash-dotted curve), and $T^3 \ln T$ (solid curve). Inset shows the same data over a larger temperature range (from Ref. 17).

VALENCE INSTABILITIES IN ACTINIDES

Since some pure actinides may have $U/W \sim 1$ (see Table 1), it is possible that this is also true for many of the compounds with high densities of states. Thus, it is reasonable to ask (especially at this conference) if valence instabilities occur in actinides. First we must ask if we know the valence in a metallic actinide. Certainly in the materials where the f -electrons are in bands, the concept of valence is misleading. In the rare earth compounds under discussion in most papers at this conference, the hybridization is among ionic states, while in the band picture presented in this paper we are considering one-electron states.^{6,9,10}

Yet, van Daal, et al.,²⁵ have shown that there is a discontinuity in the lattice parameters of $UNi_{5-x}Cu_x$ solid solutions at $x \geq 4$. At this composition, anomalies are found in ρ - T and χ - T curves, and there is an abrupt rise in γ over a narrow range of

Fig. 6. C/T vs T for NpOs_2 . The solid curve is the estimated phonon contribution plus the paramagnetic γ (from Ref. 21).

Fig. 7. Electronic specific heat of NpSn_3 plotted as C_E/T vs T . The solid curve is the mean-field, BCS prediction (from Refs. 23,24).

composition [$\gamma \sim 45$ mJ/(mole-K²) for $x = 4$ and $\gamma = 200$ mJ/(mole-K²) for $x = 5$]. These properties are reminiscent of the valence instability compounds. As of now, we have no microscopic evidence (XPS, Mössbauer effect, neutron diffraction) to prove the proposal.

Arguments such as those of van Daal, et al., based on effective paramagnetic moments and lattice parameters to establish valency assignments are usually misleading in actinides. Chan and Lam²⁶ have pointed out the difficulties associated with valence determinations due to nonobeyance of Russell-Saunders coupling. They have used full j - j manifold mixing in their crystal field calculations and do obtain groupings of effective moments for specific $5f^n$ assignments. However, in the case of PuSb, an example of a compound with apparent local moment magnetism, the crystal field parameters used to fit the magnetization below T_C are unable to fit the paramagnetic susceptibility.²⁶

Zacharisen²⁷ and others have attempted to assign valences based on scaling the actinide contraction with the well documented lanthanide contraction. This approach requires a division of the electrons into valence or f -electrons. As discussed above, the f -band formation (and f -electron participation in bonding) makes this division artificial. Carried to its conclusion, this approach assigns a valence of four to Am and cannot explain the lack of magnetic order in Am. Paper 104 in this conference by Johansson discusses this matter further. However, Johansson also shows that in AmS we might expect a valence instability. Perhaps not all Am compounds are trivalent, $J = 0$, nonmagnetic. It has recently been shown that AmAs is antiferromagnetic²⁸ with $T_N = 13K$ and $\mu_{eff} = 1.36 \mu_B$.

CONCLUSION

In conclusion we have shown that in many actinide metallic systems the f -electrons exhibit band behavior. This is a consequence of direct f - f wave function overlap or hybridization of f -electrons with s -, p -, and d -electrons. The f -bands can be responsible for large electronic densities of states at the Fermi level which may lead to band magnetism of various types. Although the concept of valence instabilities must be approached cautiously especially in the light actinides, it would not be surprising to observe them in the future, especially in Am compounds.

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