correct symmetry requirement at the infinite-temperature limit, namely, $S(\vec{k}, \omega) = S(\vec{k}, -\omega)$. Also in this temperature limit the cluster model $S(\vec{k}, \omega)$ gives the correct second frequency moment as first predicted by de Gennes for a complete Heisenberg system.[10]

*Work supported by Frederick Gardner Cottrell Grant from Research Corp.

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Spin Fluctuations in Plutonium and Other Actinide Metals and Compounds*

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(Received 14 February 1972)

It is proposed that the anomalous behavior of the resistivities of Pu and Np and some actinide intermetallic compounds can be explained on the basis of spin fluctuations in narrow 5*f* bands. An initial T^2 increase is observed in the resistivities of all these systems. From radiation-damage data we conclude that there are two distinct regions of 5*f*-electron behavior: (i) a high-temperature region ($\gtrsim 100$ °K), where the 5*f* electrons occupy virtual bound states and the metal resembles a disordered alloy with magnetic impurities such as Pd(U), and (ii) a low-temperature region, where the 5*f* bands are hybridized and a well-defined Fermi surface is formed. Anomalies observed in several properties of Pu at 60 °K may well reflect the temperature at which well-defined 5*f* bands begin to form.

I. INTRODUCTION

The resistivites of several actinide metals exhibit anomalous behavior which has not been adequately explained.[1] There are maxima in the resistivity-temperature curves for α-neptunium and all of the allotropic phases of plutonium stabilized below room temperature, as well as resistivity minima for stabilized δ-Pu above room temperature. However, the magnetic susceptibilities of these phases are nearly temperature independent. We have now observed qualitatively similar behavior in UAl_2 and $PuAl_2$ which form the $MgCu_2$-type cubic Laves phase. We believe, and will try to show, that in all these materials the primary scattering mechanism is spin-flip scattering from paramagnons in fairly narrow 5*f* bands.

Explanations of the α-Pu properties have been based on (i) a subtle phase change at 60 °K, (ii) interband scattering combined with band-structure effects,[2] and (iii) antiferromagnetic ordering near 60 °K.[3,4] The phase change hypothesis is unlikely because of the lack of diffraction evidence[5] or hystereses in physical properties near 60 °K. Interband scattering proposed by Smoluchowski[2] is probably part of the cause for the rapid increase in the resistivity above ~10 °K. However, the explanation of the negative resistivity-temperature slope at higher temperatures in terms of a particular value for the curvature of the density of states does not seem plausible since very similar values would be required for all three allotropic phases of plutonium (monoclinic α, body-centered-monoclinic β, and face-centered-cubic δ), the intermetallic compounds, and orthorhombic neptunium metal. Also the magnetic susceptibilities fail to show the temperature dependence expected from that band picture.

The nearly magnetic behavior of Pu, as shown by the large magnetic susceptibility, plus the expectation of narrow 5*f* bands caused speculation to center primarily on the existence of antiferromagnetism. A number of studies (specific heat,[6] radiation damage,[7] magnetoresistivity,[1] thermoelectric power,[8] elastic constants,[9] Hall effect[10]) have weakly supported the hypothesis of an antiferromagnetic transition. A detailed discussion of such a transition in α-Pu by Rocher[4] is based on a 5*f*

virtual-bound-state model with a net difference between the population of spin-up and spin-down subbands of 0.1 electron. Although Rocher was able to reconcile the magnitude of the low-temperature resistivity change (due to "spin-disorder scattering") and the thermoelectric power with the model, he failed to explain the negative $d\rho/dT$ above 100 °K, the resistivity minima, or the effects of radiation damage. Moreover, a number of recent microscopic measurements capable of detecting much less than $0.1\mu_B$ (i. e., Mössbauer effect in α- and δ-^{242}Pu,[11] and NMR measurements in Al-stabilized δ-Pu)[12] have failed to find any evidence for localized moments or magnetic order. Neutron-diffraction measurements of α-^{242}Pu, although less sensitive, have also proven negative.[5]

A more coherent model for all the above data is clearly needed. We believe that spin fluctuations offer the best explanation to date, although this model also fails to explain all the details. We must allow the possibility of additional mechanisms to explain all the phenomena. The concept of spin fluctuations in actinide metals and compounds arose from a comparison of Pu data to the results obtained in Pd(U) alloys.[13] In this system, where there is known to be a paramagnon contribution to the specfic heat, Nellis *et al.* observed resistivity maxima and minima together with a temperature-independent susceptibility. The striking similarity between Pd(U) and δ-Pu, and hence the possibility of spin fluctuations in actinide metals, has been pointed out by the authors previously.[14] Doniach's theory of spin fluctuations in narrow-band intermetallic compounds has given support to this possibility and will be used as a basis for arguments in its favor.[15] The existence of narrow, hybridized 5*f* bands in actinides has been proposed previously.[16,17]

II. EXPERIMENTAL RESULTS

Table I presents the best data for the specific heat and room-temperature susceptibilities of various exchange-enhanced metals, alloys and compounds. Clearly Np and Pu are among the metals with large exchange-enhancement factors $S = \chi/\chi_\gamma$ indicating nearly magnetic behavior.

TABLE I. Exchange enhancements of various metals and alloys.

Metal	γ (mJ/g atom °K^2)	$\chi_{300°K}$ (10^{-4} emu/g atom)	S[a]
α-Pu	18[b]	5.12[c]	2.1
α-Np	14[b]	5.50[d]	2.9
Pd–11-at.% U	6.5[e]	1.51[e]	1.7
Pd	9.4[e]	5.11[e]	4.0

[a]Calculated from the room-temperature susceptibilities $S \equiv \chi/\chi_\gamma$.
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[d]Reference 14(c).
[e]Reference 13(a).

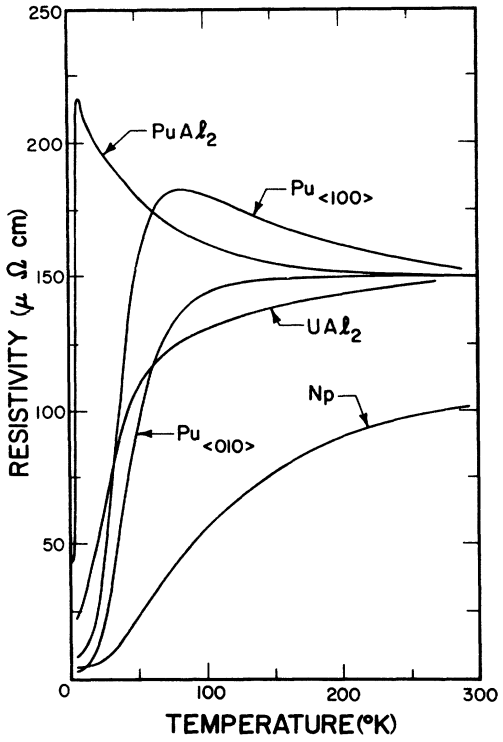

FIG. 1. Resistivity-vs-temperature curves for various actinide metals and compounds. The two Pu curves correspond to current along ⟨100⟩ and ⟨010⟩ directions in a single-crystal specimen. Other specimens were polycrystalline.

Resistivity-vs-temperature curves for α-Np, UAl_2, $PuAl_2$,[18] and two curves for single-crystal monoclinic α-Pu[14(a)] are shown in Fig. 1. $Pu_{\langle 010\rangle}$ (i. e., the current is along ⟨010⟩), UAl_2, and Np have positive slopes up to 300 °K. While no measurements have been made of $Pu_{\langle 010\rangle}$ and UAl_2 above 300 °K, it has been reported that the Np resistivity goes through a maximum at ~ 500 °K.[19] The remaining curves have negative slopes and resistivity maxima below room temperature, with the $PuAl_2$ resistivity strongly resembling that of β-Pu.[10,20] All of the resistivities shown in Fig. 1 vary initially as T^2. This is apparent in Fig. 2. Except for UAl_2, the resistivities then begin to increase faster than T^2, with only the UAl_2 resistivity tending toward a linear behavior. A second T^2 region is observed in α-Np from 20 to 50 °K.

Cubic δ-Pu can be stabilized below room temperature by alloying with a small quantity of a group III or IV metal. For this reason δ-Pu cannot be considered as a pure metal but rather as a con-

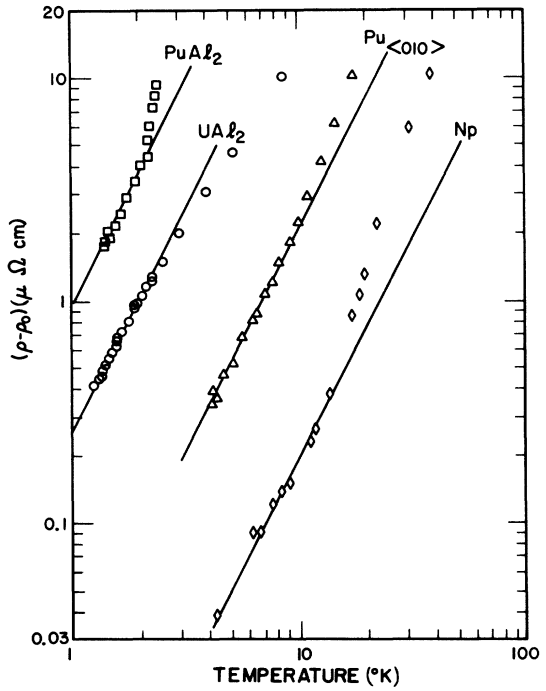

FIG. 2. Log-log plots of $(\rho - \rho_0)$ vs temperature. Slope = 2.0 for the solid lines.

centrated, disordered alloy. Figure 3 shows a typical resistivity-temperature curve obtained using 3.4-at.% Al as the δ retainer.[10] The similarity of this curve to the resistivity of the Pd–11-at.% U alloy is evident in Fig. 3. If α-Pu (and to some extent δ-Pu) is allowed to become disordered by self-radiation damage, the low-temperature resistivity increases to a saturation value equal to the magnitude of the resistivity maximum.[7] The resulting curve again looks very much like the disordered Pd-U alloy shown in Fig. 3. A similar effect is observed in $PuAl_2$ and in Fig. 3 we have plotted the resistivity-temperature curve of $PuAl_2$ self-damaged at room temperature for several months.

The magnetic susceptibilities of α-Pu [14(a)] and δ-Pu,[21] α-Np, and Pd–10-at.% U [13(a)] are nearly temperature independent. UAl_2 and $PuAl_2$ susceptibilities have a Curie-Weiss temperature dependence at high temperatures, and deviate from this at low temperatures as shown in Fig. 4. Curie-Weiss behavior was not found previously for UAl_2.[16] Neutron diffraction,[22] NMR,[16,23] and Mössbauer[11] measurements, however, give no indication of magnetic ordering (despite the sharply peaked resistivity maximum for $PuAl_2$).

III. DISCUSSION

Doniach has postulated the existence of strong spin-fluctuation scattering in narrow-band intermetallic compounds and shows that, as in the dilute alloy case,[24] the resistivity varies as T^2 near $T = 0$ and goes through a region linear in T at slightly elevated temperatures. Unlike the dilute alloy case, the resistivity of an atomically well-ordered intermetallic compound should go to zero at $T = 0$ (aside from small impurity effects) since we do not have individual impurity levels but a coherently hybridized Fermi surface. Because every Wigner-Seitz cell contains magnetic scattering centers the effect on the resistivity can become very large and is likely to dominate in actinide systems. The mean free path of the hybridized f-band electrons can become very short and their energy state very broad compared to the width of the narrow f band. Doniach[15] shows that this limits the scattering from the spin fluctuations and the resistivity no longer increases linearly past T_S (the characteristic spin-fluctuation temperature below which the Curie-Weiss–like susceptibility begins to flatten out) but begins to saturate as T increases beyond T_S and may in fact even drop if T_S begins to increase with T.

The T^2 dependence of the low-temperature resistivities of the atomically well-ordered systems is in agreement with Doniach's model.[15] As the temperature is increased above the T^2 region, only the UAl_2 resistivity tends first toward a linear behavior before there is a knee in the curve at ~ 60 °K, the same temperature at which χ begins to flatten. From Doniach's model $T_S \simeq 60$ °K for UAl_2. For the other materials considered here, ρ begins to increase faster than T^2. The most likely

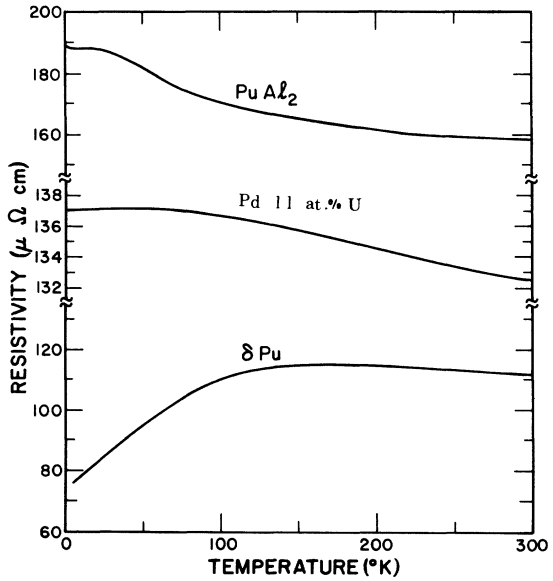

FIG. 3. Resistivity-vs-temperature curves for several disordered actinide alloys and compounds. $PuAl_2$ was allowed to self-damage for 4 months at room temperature.

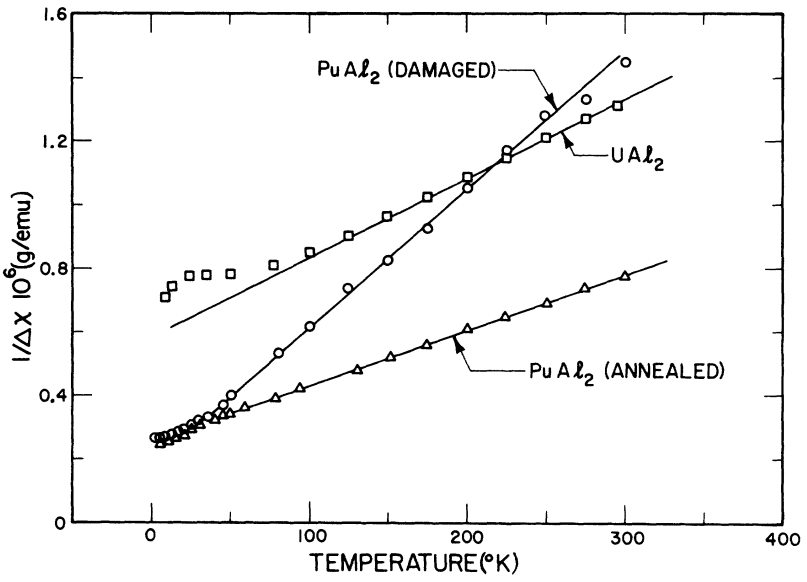

FIG. 4. Plots of $1/(\chi-\chi_\infty)$ vs temperature. The values of the temperature-independent term χ_∞ as determined from best fits to the data are 0, 0.5, and 1.2 for UAl_2 annealed $PuAl_2$ and damaged $PuAl_2$, respectively.

explanation for this behavior is interband scattering.[2] Interband scattering is large in materials having narrow bands, and thus a large density of states at the Fermi level. This scattering can be induced by either phonons or spin fluctuations. We have fitted some of our curves to the equation

$$\rho=\rho_0+AT^2+Be^{-\Theta/T}\ , \qquad (1)$$

where ρ_0 is the residual resistivity, the second term is due to spin-fluctuation scattering, and the third term is due to interband scattering, with Θ being a characteristic temperature and A and B constants. Excellent fits (at temperatures well below the peak or knee of the resistivity-temperature curves) can be obtained using the parameters given in Table II. The T^2 region can thus be extended far above the temperatures shown in Fig. 2. The last column in Table II shows the temperature at which deviations from the above equation are observed. The UAl_2 resistivity cannot be fitted to the above equation, thus probably indicating little or no interband scattering. The large Θ in a α-Np relative to the Debye temperature ($\Theta_D \approx 190$ °K) is consistent with the small contribution to the resistivity from interband scattering.

At temperatures above the peaks or knees in the resistivity-temperature curves we believe that an additional mechanism is operative. The ρ-vs-T curve of damaged $PuAl_2$ in Fig. 3 clearly indicates that radiation damage results in only small changes in ρ at high temperatures but very dramatic changes at low temperatures. This has been observed also in the case of α-Pu but never quite as clearly as in $PuAl_2$, which apparently does not anneal itself at room temperature. Even in δ-Pu the continued additions of a δ retainer results primarily in changes in the shape of the resistivity curve at low temperatures (i. e., the maximum slowly disappears).[25] This would indicate that the undamaged (or atomically well-ordered) systems behave much like disordered systems above ~ 100 °K. Our model then is as follows: At low temperatures the undamaged materials have well-hybridized 5*f* bands and a distinct Fermi surface. Thus ρ tends towards zero, apart from a residual resistivity. The initial rise in resistivity is proportional to T^2 because of spin fluctuations in the narrow bands. At high temperatures the 5*f* bands are no longer completely hybridized but become partially localized leading to a behavior similar to that of disordered systems with spin fluctuations due to virtual bound states, of which the Pd-11-at.% U curve is a prime example. Between the two regions the ρ-vs-T curve is unpredictable and would probably depend to a large extent on the purity and the state of damage of the specimen. Thus, previous researchers have observed power laws in α-Pu varying from $T^{0.9}$ to $T^{2.5}$ at intermediate temperatures (i. e., ~ 10 °K– ~ 50 °K).[26]

The negative slopes at high temperatures observed in some actinide systems can have two possible explanations within the spin-fluctuation model.

TABLE II. Fits of resistivity-temperature data to Eq. (1).

Specimen	ρ_0 ($\mu\Omega$ cm)	A ($\mu\Omega$ cm/°K^2)	B ($\mu\Omega$ cm)	Θ (°K)	Upper limit of fit (°K)
α-Pu$_{(010)}$	2.55	0.021	2.0×10^2	72	44
α-Np	1.12	0.002	2.0×10^2	113	25
$PuAl_2$	41.2	0.94	7.8×10^5	30	3.3

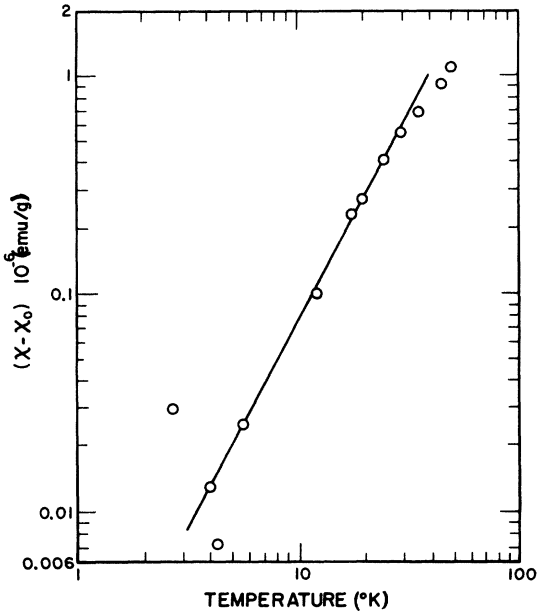

FIG. 5. $(\chi - \chi_0)$ vs temperature for damaged $PuAl_2$; χ_0 is here defined as the value of χ at $T = 0$.

One is that postulated by Doniach, i. e., a softening of the spin-fluctuation spectrum leading to a decrease of magnetic scattering.[15] There is some evidence, however, that at least in $PuAl_2$ the explanation is more complex. Kaiser and Doniach[24] have shown that in dilute, nearly magnetic alloys (disordered), ρ either increases as T^2 or decreases as $(1 - CT^2)$ depending on whether the nearly magnetic ions are off resonance for the former case, or near resonance for the latter (i. e., the scattering phase shift $\delta \approx \frac{1}{2}\pi$). Similarly, below T_S the magnetic susceptibility either levels off for the off-resonant case or varies as $(1 - DT^2)$ in the resonant case. Disordered $PuAl_2$ qualitatively fits the resonant scattering picture. Between ~ 3 and ~ 30 °K we have $\chi \propto (1 - DT^{2.0})$ as shown in Fig. 5 and $\rho \propto (1 - CT^{2.4})$. Since disordered $PuAl_2$ is analogous to a concentrated alloy rather than a dilute alloy, additional factors like Fermi smearing or an increasing T_S with T would decrease the spin-fluctuation scattering, causing the deviation from $(1 - CT^2)$. In this picture $T_S \approx 30$–40 °K and $T_S/T_{max} \approx 5$, where T_{max} corresponds to the resistivity peak. If this explanation is correct, then the peak in the ρ-T curve for atomically ordered $PuAl_2$ and the subsequent dramatic drop at low temperatures merely represent the change from partially localized 5*f* virtual bound states to hybridized 5*f* bands. Interband scattering, of course, contributes significantly to the sharp decrease in resistivity.

One is tempted to use the same argument in the case of α-Pu. But while the resistivity varies in a qualitatively similar manner, no corroborating evidence is observed in χ. By analogy with Pd(U) alloys the flat χ above 80 °K would indicate $T_S > 300$ °K. Since $T_{max} = 80$ °K for $Pu_{(100)}$ we also get $T_S \approx 400$ °K by analogy with $PuAl_2$. The large T_S may obscure the T^2 dependence in the susceptibility. This certainly must be the case in α-Np where a resistivity maximum is also observed at ~ 500 °K and χ is temperature independent. By analogy with $PuAl_2$, $T_S \approx 2500$ for α-Np.

Recent highly detailed measurements by Blaise and Furnier[27] clearly show that the flat χ in α-Pu begins to decrease at 80 °K, goes through a shallow minimum at 40 °K, and has a Curie-Weiss behavior with $p_{eff} = 0.2\mu_B$ below 40 °K. Their conclusion that a shift in the Fermi level causes a localization of 0.2 5*f* electrons is probably not correct in view of the experiments cited previously.[11,14(a)] Furthermore, it is difficult to explain how the sudden appearance of a magnetic moment could result in such a dramatic drop in resistivity. Instead we believe this may be a manifestation of the cross over from virtual bound states to narrow well-defined hybridized 5*f* bands. On this basis, it is likely that many of the property measurements which have indicated magnetic behavior near 60 °K [1,6–10] may be due to this cross over. We must also point out that what we have called interband scattering could be a further manifestation of the decoupling of 5*f* bands. Resistivity is expected to increase as the virtual bound states are formed, but at this time it is not known if this increase is proportional to $e^{-\Theta/T}$.

In summation, the anomalous resistivity-temperature behavior of 5*f* metals and their intermetallic compounds can be explained on the basis of spin fluctuations in narrow-band compounds. The 5*f* bands which are well defined at low temperatures probably become partially localized virtual bound states at high temperatures, where the behavior of atomically well-ordered materials is indistinguishable from disordered metals or alloys. The negative slope in the $PuAl_2$ resistivity is consistent with resonant magnetic scattering, while the picture in α-Pu and α-Np is somewhat less clear, probably because of the large T_S needed for consistency.

ACKNOWLEDGMENTS

The authors wish to thank S. Doniach and F. Y. Fradin for many stimulating discussions during this work. Thanks are also due to S. Doniach for making his unpublished work available to the authors, and for critically reading the manuscript. The experimental assistance of W. Cann, R. J. Friddle, N. J. Griffin, R. Parks, G. J. Schlehman, and C. H. Sowers is deeply appreciated.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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PHYSICAL REVIEW B VOLUME 5, NUMBER 11 1 JUNE 1972

Rare-Earth Impurities in Metals: The Configurational Transition of Ho in Liquid AgAl Solvents*

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(Received 13 December 1971)

We report measurements of the Knight shifts K and susceptibilities χ introduced by Ho impurities in liquid AlAg alloys at 1100 °C. The susceptibilities correspond to values of μ_{eff} in good accordance with those predicted by Van Vleck's theory for free ions. The value of $\Gamma = K^{-1}\,\partial K/\partial c$ caused by Ho impurities exhibits an abrupt transition, as a function of solvent composition, very similar to that previously observed by Blodgett and Flynn for Gd in AgAl and CuAl liquid-alloy solvents. An analysis of these data and the Ho solubility indicates that the rare earths undergo a transition in which the impurities thermally populate two available many-electron configurations that vary in relative energy with solvent composition. It appears probable that the large Γ in Al-rich solutions originate in a degenerate mixing of impurity and orbitals with host band states near E_F; this conclusion cannot, however, be reached with complete certainty. Similar results for intermetallic compounds containing rare-earth components are also discussed.

I. INTRODUCTION

Recent studies of the magnetic properties of impurities in metals have begun to clarify our understanding of the way in which electron-electron interactions cause particular impurity configurations to be preferred.[1] Early theoretical investigations of 3*d*-transitional impurities in simple-