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ELECTRON LOCALIZATION IN THE ACTINIDES

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NUCLEAR MAGNETIC RESONANCE AND THE QUESTION OF 5f ELECTRON LOCALIZATION
IN THE ACTINIDES*

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SUMMARY

Nuclear magnetic resonance results are presented for a number of NaCl-type compounds and cubic Laves-phase type compounds of uranium, neptunium, and plutonium. Special emphasis is placed on the Knight shift and spin-lattice relaxation time measurements and their interpretation in terms of localized or itinerant pictures of the 5f electrons.

The nuclear magnetic resonance parameters of interest for studying the 5f electron magnetism in actinide compounds are the Knight shift and the nuclear spin-lattice relaxation time T_1 . This paper will discuss results on nonactinide nuclei in either metallic or semi-metallic compounds in the paramagnetic state. In these compounds the Knight shift can be represented as

$$K = (H_{\text{hfs}}/2\mu_B) \langle s_z(o) \rangle / H \quad (1)$$

where H_{hfs} is the hyperfine field at the nucleus, μ_B is the Bohr magneton, $\langle s_z(o) \rangle$ is the uniform static spin-polarization of the conduction electrons along the direction of the applied field, and H is the magnetic field. The Knight shift can be seen to be proportional to the uniform spin-polarization of the conduction electrons. In the case where the actinide moment is localized, it can be described by crystal-field theory; the Knight shift can be rewritten as [1]

$$K = K_0 + H_{\text{eff}} \langle S_z \rangle / H \quad (2)$$

where K_0 is a temperature independent Knight shift that would exist in the absence of 5f electron moments and H_{eff} is the effective exchange field at the nonactinide nucleus per Bohr magneton. S_z is the Z component of the spin projection of the actinide moment given by

$$\langle S_z \rangle / H = \mu_B / Z \left[\frac{1}{k_B T} \sum_{\Gamma} e^{-E_{\Gamma} / k_B T} \sum_{\Gamma^1} \langle \Gamma | \mu_z | \Gamma^1 \rangle \langle \Gamma^1 | S_z | \Gamma \rangle + \sum_{\Gamma} \sum_{\Gamma^1} \langle \Gamma | \mu_z | \Gamma^1 \rangle \langle \Gamma^1 | S_z | \Gamma \rangle \frac{e^{-E_{\Gamma} / k_B T} - e^{-E_{\Gamma^1} / k_B T}}{E_{\Gamma} - E_{\Gamma^1}} \right] \quad (3)$$

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where Z is the partition function, μ_z is the dipole moment operator, and S_z is the spin-operator of the localized $5f$ electrons; the first term sums the low frequency components, i.e., $E_{\Gamma_1} = E_{\Gamma}$, and the second term sums the high frequency terms with $E_{\Gamma_1} \neq E_{\Gamma}$.

In Figure 1 we show a calculation [2] appropriate for the $5f^5$ configuration of Pu^{3+} in octahedral symmetry. In this figure we have plotted $\langle S_z \rangle$ versus the susceptibility χ or equivalently the Knight shift versus the susceptibility for a number of values of the fourth order crystal field parameter. The sixth order crystal field parameter, appropriate for the octahedral symmetry of the plutonium ion, is held at a value of 10% of the fourth order parameter. The straight line shown without points is the Hund's rule value, which is appropriate when J is a good quantum number as in the rare-earth systems. It should be noted that with increasing crystal-field interaction strength, the relationship between the Knight shift and the susceptibility can become nonlinear and can in fact change sign. Based on the results of Knight shift, susceptibility, and neutron form factor measurements for plutonium phosphide, the value of the fourth order parameter appears to be $\sim 500 \text{ cm}^{-1}$ yielding effectively a linear $K\chi$ relationship. However there are many examples in actinide systems where a linear $K\chi$ relationship is not found, and we emphasize that this alone should not be taken as evidence of nonlocal character for the $5f$ electron magnetization.

In Figure 2 we show the Knight-shift versus susceptibility [3] for neptunium phosphide, as an example to illustrate when a linear $K\chi$ relationship is not found. In fact, as shown in Figure 3, the reciprocal Knight-shift of ^{237}Np in neptunium phosphide is a linear function of temperature; the nonlinearity in K versus χ arises principally from the deviations of the susceptibility from Curie Weiss-like behavior.

A more direct means of examining the localized versus itinerant character of the $5f$ electrons in metallic actinide compounds is from nuclear spin-lattice relaxation time measurements. As shown in Eq. (4) the relaxation rate in metallic compounds is related to the conduction electron spin-spin correlation function [1],

$$1/T_1 \sim \gamma_n^2 H_{\text{hfs}}^2 \int_{-\infty}^{\infty} \langle s^+(t) s^-(0) \rangle e^{-i\omega_n t} dt \quad (4)$$

where γ_n is the nuclear gyromagnetic ratio, $s^+(s^-)$ is the raising (lowering) operator for the conduction electron spin, and ω_n is the nuclear Larmor frequency. Using the fluctuation dissipation theorem, $1/T_1$ can be related as shown in Eq. (5) to the imaginary part of the spin-flip susceptibility,

$$\frac{1}{T_1} \sim \gamma_n^2 H_{\text{hfs}}^2 T \sum_q \text{Im} \chi^{+-}(q, \omega_n) / \omega_n \quad (5)$$

where $\chi^{+-}(q, \omega_n)$ is the spin-flip part of the generalized dynamic susceptibility for wave vector q and frequency ω_n . This expression takes on quite different forms when the $5f$ magnetism is described in the local picture or in the itinerant picture. We first indicate some of the experimental results in the sodium chloride-type compounds, which we believe are well described by a localized picture. In Figure 4 we give an example of the relaxation data, plotted as $T_1 T$ versus temperature for neptunium phosphide [3]; except quite close to the magnetic transition at ~ 125 K, $T_1 T$ is found to be a linear function of temperature. This same behavior has been found for plutonium phosphide [4], uranium phosphide [5], as well as uranium [6], and plutonium [7] hydrides. In general, the intercept on the temperature axis is different from the Curie Weiss temperature found from the paramagnetic susceptibility. This point will be discussed further.

For a simple metallic system, the relaxation is given by the Korringa expression

$$\frac{1}{T_{1K}} = \pi \gamma_n^2 \hbar k_B T H_{\text{hfs}}^2 N(0)^2 \quad (6)$$

where $N(0)$ is the conduction electron density of states at the Fermi level per spin direction. However, in the presence of localized moments it has been shown that the relaxation rate can be written in the following form [8]:

$$\frac{1}{T_1} = \frac{1}{T_{1K}} \left[1 + 4N(0) |J_{\text{sf}}(q)|^2 \int dt \langle S_z(q_m, t) S_z(-q_m, 0) \rangle \right] \quad (7)$$

where $J_{\text{sf}}(q)$ is the q -dependent s - f exchange interaction constant. We see that in addition to the Korringa term, proportional to T , there is another term involving the spin-spin correlation of the local moment. When J is a good quantum number, this takes on a particularly simple form given by Eq. (8),

$$\frac{1}{T_1} = \frac{1}{T_{1K}} \left[1 + 4N(0) |J_{sf}(q_m)|^2 (g_J - 1)^2 \frac{J(J+1)}{3k_B [T - \theta(q_m)]} \right] \quad (8)$$

where g_J is the Lande' g-factor, J is the total angular momentum quantum number, and $\theta(q_m)$ is an effective interaction constant appropriate for a molecular field treatment of $\langle S_z(q_m) S_z(-q_m) \rangle$, where q_m is the wave vector at the maximum of the correlation. Thus, we can see that in addition to the Korringa term, there is another term, which would give a functional form of $T_1 T \sim T - \theta(q_m)$. Eq. (8) has been written for the case when J is a good quantum number; since in general this is not expected to hold for actinide systems, we have to calculate the spin-spin correlation function of Eq. (7) based on the strong crystal-field formulation. This is given by Eq. (9) where we have used a molecular field approximation for the spin-spin coupling [1,3],

$$\int dt \langle S_z(q_m, t) S_z(-q_m, 0) \rangle = \frac{G_0^{ZZ}(0)}{1 + \lambda(q)_m G_0^{ZZ}(0)} \quad (9)$$

where

$$G_0^{ZZ}(0) = \frac{2}{Z} \frac{1}{k_B T} \sum_{\Gamma} e^{-E_{\Gamma}/k_B T} \sum_{\Gamma^1} |\langle \Gamma | S_z | \Gamma^1 \rangle|^2 + \sum_{\Gamma} \sum_{\Gamma^1} |\langle \Gamma | S_z | \Gamma^1 \rangle|^2 \frac{e^{-E_{\Gamma}/k_B T} - e^{-E_{\Gamma^1}/k_B T}}{E_{\Gamma^1} - E_{\Gamma}}$$

and $\lambda(q)$ is the wave-vector-dependent molecular field constant. This type of relationship should hold when mean-field behavior is expected, that is, not too close to an ordering transition. We find that the temperature intercept is not given, as for the susceptibility, by the uniform term in the magnetization, but is given by the term in which $\chi^{+-}(q)$ is maximized; so, in general, we expect the intercept on a plot of $T_1 T$ versus temperature to be either equal to or higher than the paramagnetic Curie Weiss temperature. That is, for ferromagnetic systems we expect the intercept to be quite similar to the paramagnetic Curie Weiss temperature; whereas for systems that order in a more complicated manner, i.e., where $\chi(q)$ peaks away from $q = 0$, we expect the intercept to occur at higher temperature than the Curie Weiss temperature. In contrast to the relaxation rate behavior for the nonactinide nucleus in local moment systems, which has a strong temperature dependence, or that for simple metals in which $T_1 T$ is a constant, Moriya [9]

has developed theoretical expressions for the nuclear relaxation rate in itinerant nearly ferromagnetic and nearly anti-ferromagnetic systems where spin-fluctuations (paramagnons) are expected to play a strong role. He finds that for nearly ferromagnetic systems $1/T_1$ should be proportional to the susceptibility, whereas for nearly anti-ferromagnetic systems, $1/T_1$ should be proportional roughly to the square root of the sublattice susceptibility.

UAl_2 is perhaps the classic spin-fluctuation system [10]. The similar compound $PuAl_2$, also having the cubic Laves phase structure, has a number of anomalous electronic properties that suggests the importance of spin fluctuations. In Figure 5 we show $(T_1 T)^{-1}$ normalized to the room temperature value for UAl_2 and $PuAl_2$; we see a moderately strong temperature dependent relaxation rate [11]. We have recently further studied UAl_2 on a sample which was cut from a specific heat button that has the $T^2 \log T$ behavior associated with spin fluctuations. The results of the relaxation time measurements carried out at 60 kG are shown in Figure 6; the measurements were performed between 1.7 and 4.3 K. We see a T^2 behavior to the relaxation rate; a T^2 behavior is also found for the susceptibility of UAl_2 between 3 and 10 K. This is consistent with the predictions of Moriya for a nearly ferromagnetic spin fluctuation system; that is, the spectrum of conduction electron spin-spin correlations affecting the relaxation rate is that expected for an itinerant nearly ferromagnetic system. We find based on this data, a spin fluctuation temperature roughly given by 30 ± 5 K, which is consistent with that found in the specific heat, susceptibility, and resistivity experiments.

We would like to summarize, in Table I, a number of results found for non-actinide nuclear resonances [12] in actinide alloys and compounds. In addition to the Knight shift and relaxation rate, the field and temperature dependence of the linewidth of the NMR spectrum is of importance in describing the microscopic inhomogeneity of the internal magnetic fields. Thus, the linewidth can answer questions concerning the existence of paramagnetic impurities. We begin with the nearly pure actinide metals δ -plutonium doped with 4% aluminum and α -uranium doped with 1% vanadium. For these systems the susceptibilities are nearly temperature independent as are the Knight shifts and $(T_1 T)^{-1}$. In addition, the linewidths are found to be independent of temperature and magnetic field. All of these results taken together indicate that these systems can be described as having itinerant $5f$ electrons with no localized magnetic moments.

At the other extreme of behavior are the compounds such as the sodium chloride-type phosphides, the hydrides of uranium and plutonium, and NpAl_2 . These systems have localized $5f$ electrons indicated by very strong temperature dependent Knight shifts and very strong temperature dependent $(T_1T)^{-1}$; although as we pointed out earlier, the Knight shift is not always found to be linear in the susceptibility. In addition for those compounds that are well ordered, and relatively defect free, the resonance linewidth is found to be independent of temperature and magnetic field, thus indicating the presence of a well-ordered array of localized moments.

In the middle ground between the band $5f$ electrons and the localized $5f$ electrons are those systems of highly correlated, though itinerant, $5f$ electrons. Those studied by NMR are listed in Table I. They are generally characterized by moderate temperature dependencies to the Knight shift and $(T_1T)^{-1}$. However, the linewidth, which indicates magnetic field inhomogeneities on a microscopic scale, varies from totally independent of temperature and field for the case of UAl_2 to strong functions of $1/T$ and of H for compounds such as PuAl_2 , USn_3 , etc. The results for UAl_2 are in complete agreement with spin fluctuation models. The results for the other compounds either do not fit present spin fluctuation models, as in the case of T_1T for PuAl_2 , or are not very accurate due to the presence of such strongly broadened resonances. The indication, however, of magnetically broadened resonance lines in supposedly well-ordered compounds, such as in PuAl_2 , is suggestive of the existence of nearly static, itinerant, anti-ferromagnetic correlations of the spin system. The alternative explanation for the linewidth would require a distribution of paramagnetic impurities but this has not been verified by other measurements.

In conclusion, we find that NMR measurements on nonactinide nuclei in metallic actinide alloys and compounds can yield important information about the degree of localization and the strength of the spin-spin correlations in these compounds. Particularly important is the temperature and field dependence of the nuclear spin-lattice relaxation rate. More work, especially in temperature regimes very close to suspected itinerant magnetic transitions, should be done.

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TABLE I. Summary of NMR results in Metallic Actinide Systems

<u>Itinerant 5f Electrons</u>	
δ -Pu-4%Al ²⁷ α -U-1%V ⁵¹	$K, (T_1 T)^{-1} \neq f(T)$ $\Delta H \neq f(T, H)$
UAl ₂ ²⁷ U _{1-x} Pu _x Al ₂ ²⁷ PuAl ₂ ²⁷ USn ₃ ¹¹⁹ NpSn ₃ ¹¹⁹	$K, (T_1 T)^{-1}$ Moderate functions of temperature $\Delta H = f(T, H)$
<u>Localized 5f Electrons</u>	
UP ³¹ NpP ³¹ PuP ³¹ UH ₃ ¹ PuH _{2+x} ¹ NpAl ₂ ²⁷	$K, (T_1 T)^{-1}$ Strong functions of temperature $\Delta H \neq f(T, H)$

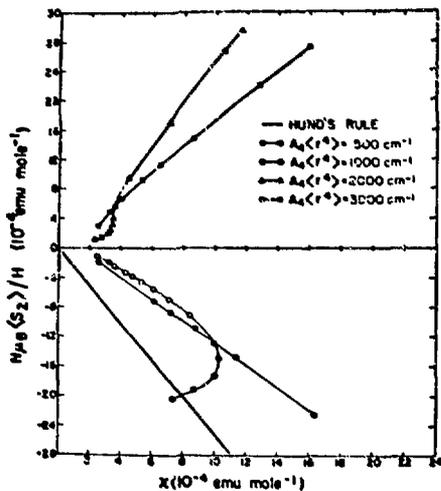


Fig. 1.

Calculated $\langle S_z \rangle$ versus χ for $5f^5$ configuration appropriate for Pu^{3+} with $A_6 \langle r^6 \rangle / A_4 \langle r^4 \rangle = 0.1$.

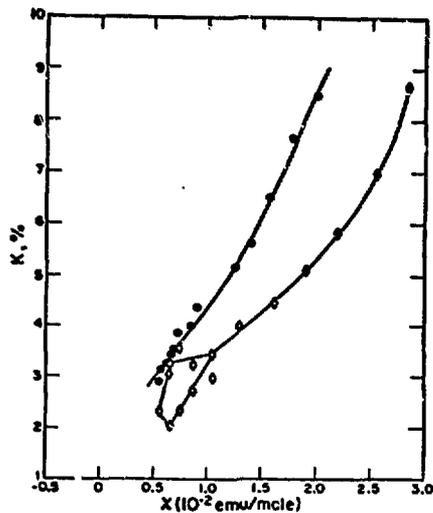


Fig. 2.

^{31}P Knight shift K versus susceptibility χ for NpP. Sample indicated by diamond shaped data points has hysteresis in both K and χ probably indicating a subtle lattice phase transition near 250 K.

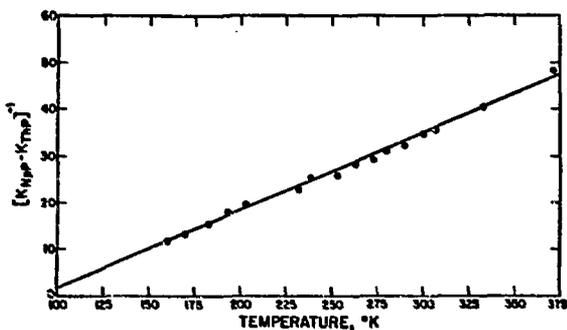


Fig. 3.

Reciprocal Knight shift of NpP corrected for the shift in the nonmagnetic isomorphous compound ThP versus temperature.

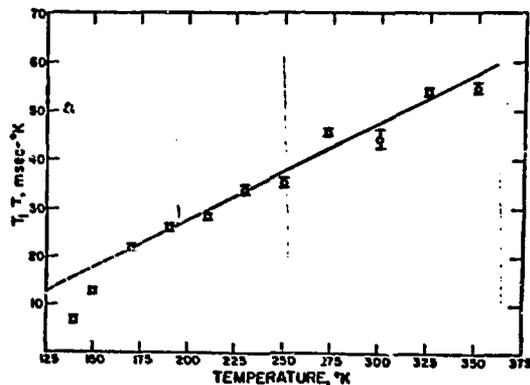


Fig. 4.

$T_1 T$ for ^{31}P in NpP versus temperature.

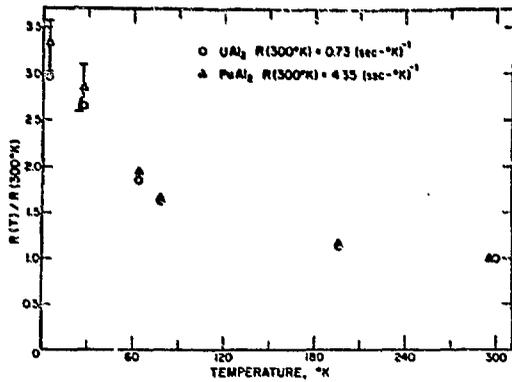


Fig. 5.

$R = (T_1 T)^{-1}$ for ^{27}Al , normalized by 300 K value, for UAl_2 and PuAl_2 as a function of temperature for $H \approx 10$ kOe. Temperature dependence from ~ 4 to ~ 300 K can be due to structure in $N(\epsilon)$ with ~ 100 K degeneracy temperature, which is consistent with $\chi(T)$ and temperature dependent resistivity.

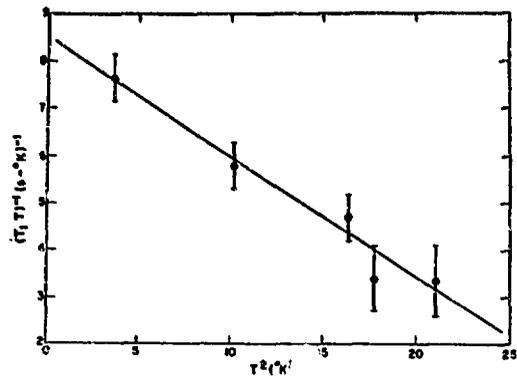


Fig. 6.

$(T_1 T)^{-1}$ for ^{27}Al in UAl_2 between ~ 1.7 and 4.3 K at ~ 60 kOe applied field.