Evidence for Strong Localization of 5f Electrons in Neptunium Intermetallics*

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The correlation between the magnetic hyperfine field H_{hf} and the electronic moment μ at the neptunium site in a number of neptunium conducting compounds is presented. A simple linear relation $H_{hf} = [(1915 \text{ kOe})/\mu_B] \mu$ is found. This behavior is similar to that observed in lanthanide systems and suggests a strong localization of the 5f electrons in these materials. The implications of this result for our understanding of magnetism in the actinides are considered.

The most fundamental uncertainty, and certainly the greatest source of controversy, in discussions of the electronic properties of actinide metallic systems concerns the nature of the 5f electrons. Self-consistent-field calculations for free ions show that the 5f electrons have a substantially larger spatial extent than the 4f electrons of the lanthanide series.[1] As a result, the 5f electrons are less shielded by the outer electrons and more easily removed from the atom. In chemical compounds, this frequently results in a wide range of valencies being found. In the elemental metals, at least for the first half of the series, the large spatial extent and corresponding 5f-5f overlap of neighboring atoms causes a situation which is only properly described by considering the 5f electrons to be itinerant, lying in rather wide conduction bands.[1] In intermetallic compounds, however, the situation is not clear and the primary question in beginning any treatment of the electronic properties of the actinides is whether one should consider the 5f electrons to be localized, itinerant, or in some fashion intermediate. In the first case, one deals with localized magnetism and crystal-field theory,[2] in the second case with band-structure calculations and itinerant-electron magnetism,[1,3] and in the third case with spin-fluctuation theory.[4,5] All these methods have been used and each appears to explain successfully some aspects of observed magnetic phenomena. However in some cases contradictory approaches have been used to treat the same data,[6] and detailed diagnostic information on the state of localization of the 5f electrons is hard to find.

In an effort to focus attention on this challenging problem we present the unexpectedly simple experimental relationship we have found in neptunium compounds between the magnetic hyperfine fields H_{hf} (obtained by the Mössbauer effect in ^{237}Np) and the electronic magnetic moment μ

(obtained by neutron diffraction). A comparison between the hyperfine field and magnetic moment is useful for obtaining information on localization since μ provides a measure of the angular momentum state of the ion, and H_{hf} measures a product of the angular momentum with a factor $\langle r^{-3} \rangle$, which is the average value of $1/r^3$ for the open-shell electrons (in this case 5f) in the ion. The hyperfine field consists of a part due to the orbital state of the electrons plus a core-polarization contribution. Considering a single J manifold in the limit of L-S coupling, the orbital term is written[7]

$$H_{orb} = 125.1 \langle J \| N \| J \rangle \langle r^{-3} \rangle \langle J_z \rangle , \qquad (1)$$

where H_{orb} is in kilo-oersteds, $\langle r^{-3} \rangle$ is in atomic units, $\langle J \| N \| J \rangle$ is a reduced matrix element dependent on the electronic configuration of the ion, and $\langle J_z \rangle$ is the average value of the angular momentum. In the first approximation, one generally takes the core polarization proportional to $\langle S_z \rangle$, which, in L-S coupling, gives[8]

$$H_{core} = \chi (g_J - 1)\langle J_z \rangle . \qquad (2)$$

Thus one may write

$$H_{hf} = H_{core} + H_{orb}$$
$$= [125.1 \langle J \| N \| J \rangle \langle r^{-3} \rangle + \chi (g_J - 1)] \mu/g_J , \qquad (3)$$

where $\mu = g_J \langle J_z \rangle$ is the electronic magnetic moment. In the lanthanides, the 4f electrons causing the hyperfine field are strongly localized and can be treated as being in atomic states. Thus, $\langle r^{-3} \rangle$ may be calculated from atomic self-consistent-field approaches to obtain a value which is valid for solids. The principal effect of placing the ion in a material is that crystal-field interactions change $\langle J_z \rangle$, which leads to a change in both H_{hf} and μ. However, since both quantities are linear in $\langle J_z \rangle$, and the interactions in the solid do not substantially change $\langle r^{-3} \rangle$, the pro-
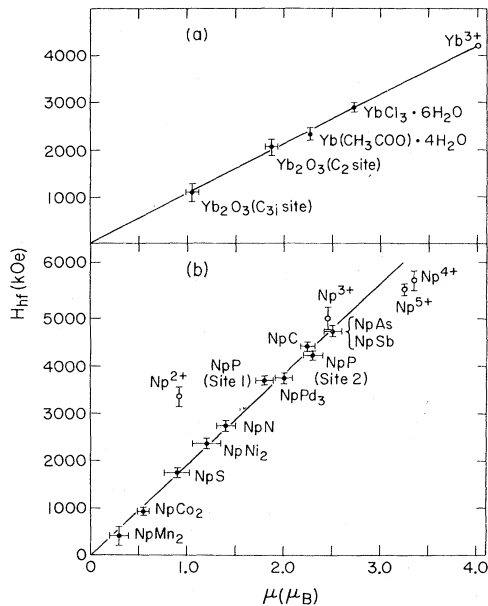
FIG. 1. Comparison between magnetic hyperfine field and electronic magnetic moment for a number of (a) Yb salts and (b) Np intermetallics. Experimental points are shown by solid circles and calculated free-ion values by open circles.

portionality indicated by Eq. (3) is unaltered. Thus, a plot of H_{hf} versus μ will have points lying on a line determined by the origin and the free-ion values. A clear case of this behavior is shown in Fig. 1(a) for a number of Yb^{3+} salts.[9]

In the actinides, a number of cautions must be imposed. It is important to note that (i) relativistic calculations are compulsory to obtain proper values of $\langle r^{-3} \rangle$, (ii) even in the free ion, intermediate-coupling wave functions must be used when calculating g_J and $\langle J_z \rangle$, and (iii) in solids, crystal-field interactions may be very large and result in a certain amount of mixing between different J manifolds. However, with these provisions in mind, the general character of Eq. (3) is unaltered. The value of a comparison between H_{hf} and μ is then to provide information on $\langle r^{-3} \rangle$. If $\langle r^{-3} \rangle$ is constant for several different compounds then H_{hf}/μ will be a constant. In addition, if the electrons are well localized this constant will be determined by the free-ion values. However, if delocalization occurs, the value of $\langle r^{-3} \rangle$ will be reduced, and may have different values for different compounds. Then the simple linear relationship will not be valid.

A comparison of H_{hf} and μ is shown in Fig. 1(b) for a number of neptunium intermetallics.[10] In

all these materials, the neutron-diffraction studies show that the second component does not carry a magnetic moment. The neutron-diffraction experiments measure the product of the electronic magnetic moment and the magnetic form factor $f(\vec{K})$. In deriving the points in Fig. 1(b) we have, of course, had to assume a value for the magnetic form factor, which depends on the electronic structure of the ion. However, in all cases the moments have been obtained from low-angle reflections $[(\sin\theta)/\lambda < 0.30 \text{ Å}^{-1}]$. In this range, the dipole approximation is valid,[11] and the form factor will essentially be the same as that found for a wide variety of uranium compounds.[12] The error bars on μ in Fig. 1(b) allow for uncertainty in $f(\vec{K})$. In obtaining the values of H_{hf} from the hyperfine-splitting data we have used the nuclear-moment assignments of Stone and Pillinger.[13]

Also shown in Fig. 1(b) are points corresponding to several free-ion values calculated with intermediate-coupling wave functions[14] and the relativistic $\langle r^{-3} \rangle$ values of Lewis et al.[15] The principal uncertainty in these calculated values is due to the core-polarization term, which is not well known but is larger than in the lanthanides.[16] The error bars shown on these points reflect that uncertainty.

From the figure one sees an extremely good linear correlation between H_{hf} and μ. A least-squares fit to the data gives

$$H_{hf} = [(1915 \text{ kOe})/\mu_B] \mu. \qquad (4)$$

Of particular interest are the facts that (i) the relation holds over a very wide range of values, (ii) three different crystal structures are represented, and (iii) the straight line extrapolates through the calculated trivalent-Np free-ion value. On the whole, the behavior is remarkably similar to that observed in lanthanide systems. We emphasize that to obtain a hyperfine field of 4800 kOe, such as observed in NpAs and NpSb, a very strong localization must occur to bring into play the large orbital contribution. The fact that H_{hf} comes so near to the free-ion Np^{3+} value suggests an essentially atomic character with this configuration.[17] The proportionality between H_{hf} and μ then shows that the configuration *and* $\langle r^{-3} \rangle$ remain roughly constant and only $\langle J_z \rangle$ is altered in the various materials.

These results indicate that the $5f$ electrons are well localized in a wide range of Np intermetallics. We note, however, that this will not end the controversies concerning actinide magnetism. In fact, for the materials where the moments are

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small, this result itself is surprising. Attempts at applying a crystal-field model with well-localized states, even including J mixing, have not been successful in obtaining moments as small as observed here.[14] In addition, the bulk magnetic properties of materials such as $NpCo_2$ and $NpMn_2$ show some characteristics which are typical of itinerant-electron systems. A narrow-band model might give sufficient spatial localization to reproduce the correlation between μ and H_{hf}, but development of such theories is at present inadequate. This is because all such model calculations are concerned primarily with the energy distribution of electrons, rather than with the spatial distribution. With a few exceptions, this is also true in more detailed band-structure calculations. We suggest that a calculation of the spatial distribution of $5f$ electrons should be an important part of theoretical approaches to the electronic structure of the actinides, and that the data of Fig. 1(b) will provide an important test for those theories.

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