Localization and Relaxation of 5f Electrons in Isolated Np Ions Implanted into Lead

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The loss of nuclear alignment and the precession of the $\frac{5}{2}^-$ state of ^{237}Np nuclei (H_{ext} = 1.3 T), recoil implanted into Pb at various temperatures, have been measured by the α-γ time differential perturbed angular correlation technique. It was deduced that the implanted ^{237}Np ion is in a +6 state with its 5f electron in a localized state and that the loss of nuclear alignment is caused by a pure paramagnetic relaxation with an average atomic correlation time of 2.3×10^{-13} s. Lead was found to offer a quadrupole-perturbation—free environment for the Np implants.

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The nature and behavior of 5f electrons in solids are of great importance for the understanding of the electric and magnetic properties of the actinides. In particular the question whether the 5f electrons in actinides are localized or itinerant is of basic interest.[1] However, the sparse existing experimental information on this point pertains only to the actinide metals[2] or their compounds.[3] To the best of our knowledge nothing has been reported in the literature concerning the localization of 5f electrons in *isolated* actinide atoms in solids. Further, an important still open question relates to the interaction between an actinide ion and its environment in terms of the relaxation of the 5f electrons. No experimental information appears to exist concerning these relaxation times in actinides; data for an isolated lanthanide ion (Ce) has been reported only most recently.[4]

In the present work we deduce information related to 5f electron behavior for the system of Np in Pb from time differential perturbed angular correlation (TDPAC) experiments. We show that (i) Np ions, when implanted into Pb, assume a stable +6 ionization state in which the 5f electron is localized; (ii) the atomic spin-relaxation rate is 4.3×10^{12} s^{-1} and is nearly temperature independent; and (iii) lead is a quadrupole-perturbation—free environment for implanted Np nuclei, and can thus be used as a host material for actinide nuclei in angular-correlation and g-factor measurements. Some questions about this point have recently been raised in connection with such data for fission isomers.[5]

Measurements of the α-γ TDPAC were performed on excited ^{237}Np nuclei recoil implanted into Pb. Ultra thin (<100 Å) ^{241}Am sources were electroplated[6] on Ni foils and were coated by vacuum evaporation with a layer of pure Pb. The sources were mounted on a holder whose tem-

perature could be controlled with the Ni side facing a surface-barrier silicon detector. The excited ^{237}Np nuclei associated with the detected α particles ($E_\alpha = 5.48$ MeV) were implanted into the Pb backing by the 91 keV recoil energy they received as a result of the α emission and stopped within 10^{-13} s at a depth of about 300 Å. The 59.5 keV γ's from the decay of the $\frac{5}{2}^-$ excited state in ^{237}Np ($t_{1/2} = 68$ ns, $g = 0.67$) were detected at angles of 90° and 180° with respect to the α detector. An external magnetic field of 1.3 T could be applied to the samples perpendicular to the plane of the detectors and the temperature could be varied between 120 and 550 K. The α-γ coincidence rates $W(\theta, t)$ were used to form the ratio

$$R(t) = [W(180, t) - W(90, t)]/[W(180, t) + W(90, t)] \quad (1)$$

from which the hyperfine interactions acting on the excited ^{237}Np nuclei were deduced.[7]

In the absence of a magnetic field the $R(t)$ spectra exhibit an exponential decay which was shown to be due only to paramagnetic relaxation.[8] $R(t)$ in such a case is given by[7]

$$R(t) \approx \tfrac{3}{4} A_2 \exp(-\lambda_2 t). \quad (2)$$

When an external field is applied, $R(t)$ is modulated by the Larmor precession of the magnetic moment of the nuclei in the hyperfine field so that for $\omega_L \tau_c \ll 1$,[7]

$$R(t) = \frac{-3A_2 \exp(-\lambda_2 t) \cos(2\omega_L t)}{4 + A_2 \exp(-\lambda_2 t)}. \quad (3)$$

A_2 is the initial anisotropy in the angular correlation; ω_L is the Larmor precession frequency given by

$$\omega_L = -(g\mu/\hbar)\beta(T) H_{ext}; \quad (4)$$

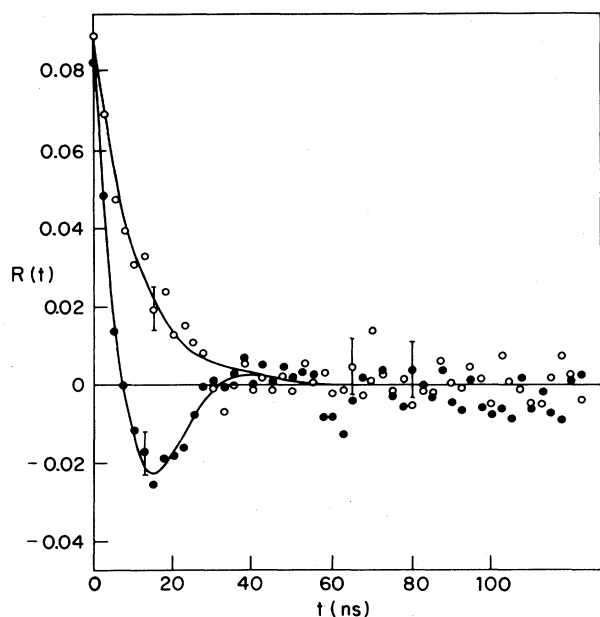λ_2 is the decay constant of the nuclear alignment

FIG. 1. Examples of $R(t)$ spectra obtained at room temperature with and without an external magnetic field (full and open circles, respectively). The lines are the results of the best fits of Eq. (2) and Eq. (3) to the data points.

which, for the case of paramagnetic relaxation, is given by[7]

$$\lambda_2 = \frac{2(J+1)}{J} \left(\frac{g\mu_n}{\hbar} \right)^2 H_{int}^2(0)\tau_c \; ; \tag{5}$$

$H_{int}(0)$ is the hyperfine magnetic field (at $T = 0$); $\beta(T)$ is the temperature-dependent paramagnetic correction factor; τ_c is the average correlation time of the atomic spin relaxation.

In Fig. 1 we present the $R(t)$ spectra obtained at room temperature with and without an applied magnetic field (full and open circles, respectively). The solid lines are the results of least-

square fits of Eq. (2) and Eq. (3) to the data. The parameters obtained for all the measurements together with the experimental conditions are given in Table I. The constancy of the values of λ_2 extracted from all the data should be noted.

The ω_L results presented in Table I can be interpreted in terms of the electronic state of the Np ion, and the λ_2 values in terms of the correlation time τ_c. The β values for different temperatures were calculated from ω_L with use of Eq. (4) (see Table I). They can, in turn, be correlated with the ionization state and with the degree of the localization of the 5f electrons by comparing the experimental results with theoretical calculations. Under the assumption that the 5f electrons are in an atomic ground state with no crystal field it was shown that[9]

$$\beta(T) = 1 + \frac{g_J \mu_B (J+1)}{3kT} H_{int}(0) . \tag{6}$$

The values of $H_{int}(0)$ and $\beta(T)$ for all plausible ionization states of the actinides were calculated with use of wave function and radial distribution functions of localized 5f electrons, and are tabulated in Ref. 10. In Fig. 2, we present the results of these calculations for various ionization states of Np, together with the present experimental data. The good agreement (no parameters adjusted) of the data with the line calculated for Np^{+6} indicates that the assumptions on which the calculations were based are probably correct, the most important of these being the assumption of the localization of the 5f electrons. The possibility that the agreement between the data and the calculations is fortuitous is unlikely in light of the quality of the fit and of the internal consistency of the data (i.e., all points lie on a straight line which passes through $\beta = 1$ at the limit $T^{-1} \to 0$).

The 5f electrons of the light actinides (lighter

TABLE I. Summary of the experimental conditions and the results obtained from the measurements of TDPAC on ^{237}Np implanted in Pb. β and τ_c values were calculated from ω_L and λ_2, respectively, as explained in the text.

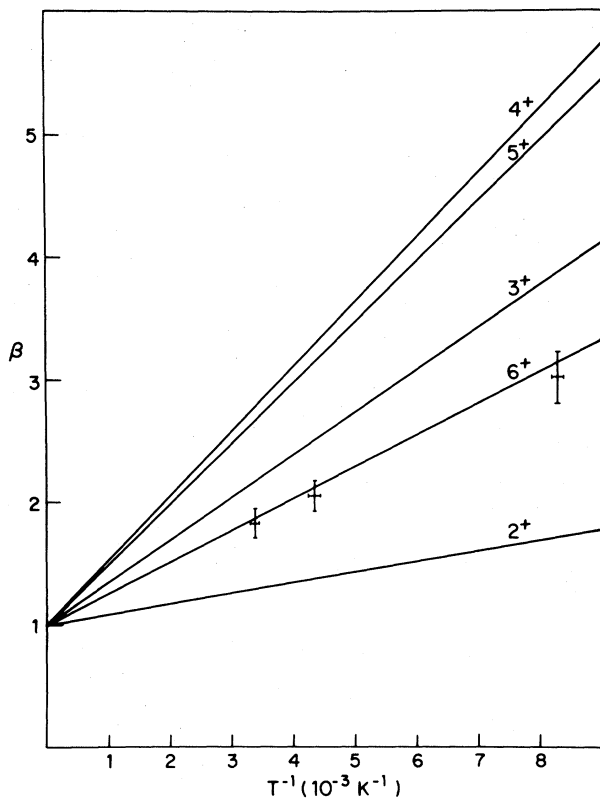| T (K)	H_{ext} (T)	ω_L $(10^7\ s^{-1})$	λ_2 $(10^7\ s^{-1})$	β	τ_c $(10^{-13}\ s)$
300	0	$\cdots$	9.0 ± 1.0	$\cdots$	2.3 ± 0.3
500	0	$\cdots$	9.4 ± 1.5	$\cdots$	2.4 ± 0.4
550	0	$\cdots$	11.1 ± 1.5	$\cdots$	2.8 ± 0.4
300	1.3	7.6 ± 0.5	9.1 ± 1.0	1.82 ± 0.11	2.3 ± 0.3
230	1.3	8.6 ± 0.6	9.0 ± 1.3	2.06 ± 0.14	2.3 ± 0.3
120	1.3	12.6 ± 0.9	6.5 ± 1.6	3.02 ± 0.21	1.7 ± 0.4

FIG. 2. Temperature dependence of β. The lines are calculated values for Np in the ionization states indicated (taken from Ref. 10) and the points are the present experimental results.

than Am) are normally found to be of an itinerant character,[1] the degree of $5f$ localization depending on the overlap of the corresponding $5f$ wave functions with neighboring atoms and on the $5f$-$6d$ hybridization. The conclusions of the present study that for Np in Pb the $5f$ electrons are localized on the actinide atom can be understood in view of the small size of the Np^{+6} ion compared to the lead matrix.

The exponential loss of nuclear alignment, as reflected in the relaxation parameter λ_2, is caused by the random fluctuations of the hyperfine field due to the interaction of the $5f$ electrons with their environment. The average fluctuation time τ_c can be calculated from the measured λ_2 by use of Eq. (5), provided that $H_{int}(0)$ is known. The value of $H_{int}(0)$ was determined from the slope of the β vs T^{-1} curve (Fig. 2) and was found to be $H_{int}^{expt}(0) = 366$ T which, as pointed out above, nearly coincides with the value calculated for the Np^{+6} state $[H_{int}^{calc}(0) = 379$ T]. The τ_c values calculated in this way are presented in

the last column of Table I. As can be seen τ_c is constant, within the experimental errors, over a rather large temperature range, and its mean value is $\tau_c = (2.3 \pm 0.2) \times 10^{-13}$ s. We are not aware of any experimental or theoretical results for τ_c in actinides so that our results cannot be directly compared to others. Barth et al.[4] have, however, published results for τ_c in the case of Ce^{+3} in Pb at 300 and 430 K. A comparison of their results to ours is of relevance since Ce in the $+3$ state is the lanthanide electronic analog of Np in the $+6$ state found in the present work ($4f^1$ and $5f^1$, respectively). The similarity in the relaxation times [$\tau_c = 3.2 \times 10^{-13}$ s for Ce (Ref. 4) and $\tau_c = 2.3 \times 10^{-13}$ s for Np] and the apparent temperature independence found in both cases leads us to believe that the physical mechanisms responsible for those relaxations are the same. As in the Ce case discussed in Ref. 4, we propose that the atomic relaxation of Np in Pb is mainly caused by an exchange interaction of the f electrons with the conduction electrons. Moreover, the similar behavior of τ_c in the lanthanide (Ce^{+3}) and actinide (Np^{+6}) ions further supports the conclusion that the $5f$ electrons in Np^{+6} in lead is in a localized state as are the $4f$ electrons in the lanthanides.

Other than the basic information obtained in the present work on the electronic structure of Np in Pb, our results are of great importance for the planning and interpretation of experiments in which nuclear g factors are deduced from Larmor precession measurements in external fields. For such experiments, environments are required in which the nuclei (mostly isolated, reaction-recoil implanted) are free of quadrupole interactions, and in which the magnetic fields acting on the nuclei are known. Our results show (i) that Pb, in particular when heated to temperatures close to melting, can serve as a quadrupole-perturbation-free environment for implanted Np, and (ii) that the assumptions underlying the calculations of paramagnetic corrections in actinides hold, at least for the case of Np^{+6}. The results of these calculations can thus be used in the extraction of g factors from precession measurements. The paramagnetic relaxation which has caused the rather fast loss of alignment in the present Np case need not necessarily restrict the precession measurements to short times. Since λ_2 is proportional to g^2, nuclear states with g factors smaller than the rather large value of $g(\frac{5}{2}^-) = 0.67$ for the Np case of the present study may preserve the alignment for substantial-

ly longer times. This may have been the case for the precession measurement of the 1.1-μs fission isomer[11] of ^{237}Pu ($g = 0.17$) implanted into lead for which g could be determined.

We have shown in the present work that α-γ recoil-implantation TDPAC experiments can be used to study the electronic properties of actinide ions, as well as to imitate in a simple way the recoil implantation of nuclei following nuclear reactions. For the case of Np in Pb we were able to determine that the Np is in the +6 ionization state, that its $5f$ electron is in a localized state, and that the atomic relaxation rate is 4.3×10^{12} s^{-1}. Lead was shown to offer a good perturbation-free environment for the Np implants. Some of the conclusions of the present work, even though deduced for the specific case of ^{237}Np in Pb, are likely to be valid for other actinides as well.

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Chemisorption-Induced Defects on GaAs(110) Surfaces

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Chemisorption of Ge on GaAs(110) at 320 °C simultaneously introduces acceptor- and donor-type surface states with the same density. The acceptor levels were found to be linked to E_{cs}. Under the assumption of the same behavior for the donor levels, the band bending versus coverage curve was calculated for samples at 20 °C, and very good agreement was found with the experimental data of Spicer *et al.* for metal overlayers on GaAs(110). It is concluded that chemisorption on GaAs(110) surfaces introduces a single type of defect.

In recent years progress has been achieved towards an understanding of metal-semiconductor contacts and semiconductor heterostructures. For example, energy levels of defects formed already in the early stages of metal coverage were proposed to account for the barrier heights in metal–III-V-semiconductor contacts.

The formation of such defects was first considered by Spicer *et al.*[1] They found the band bending at GaAs (110) substrates to saturate at the same value with overlayers of different metals and of oxygen. This "pinning of the Fermi level" occurs at 0.65 and 0.9 eV below the bottom of the conduction band with n- and p-type substrates, respectively, and is completed for coverages larger than 0.1 of a monolayer.[2] These space-charge layers are caused by chemisorption-induced states since clean and well-cleaved GaAs (110) surfaces exhibit no intrinsic surface states[3-5] and therefore have flat bands. Spicer *et al.* concluded that chemisorption-induced donor- and acceptor-type states, respectively, are responsible for the pinning of the Fermi level at the interface, and they correlated these states with *two* different defects.

The formation of Ge:GaAs(110) heterostructures