Experimental Evaluation of the Sternheimer Quadrupole Antishielding Factor γ_∞ for the Tetravalent Neptunium Ion

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Using a point charge model, the lattice contribution to the electric field gradient (EFG) was calculated for the isotypic hydrated neptunium fluorides MNpF$_6$ · 3H$_2$O (M = Mn, Fe, Co, Ni, Zn). The atomic coordinates in these compounds were computed from prescribed interatomic distances using a least squares procedure, the positional parameters in CoNpF$_6$ · 3H$_2$O and the ionic radii differences between the M^{2+} ions. With our structural determinations, calculations of the EFG and the experimental Mössbauer data, we can propose for the Sternheimer antishielding factor γ_∞ (Np^{4+}) the value γ_∞ = −126(13). This result is in good agreement with the calculated value deduced from theoretical considerations. © 1987 Academic Press, Inc.

I. Introduction

For the case of an electric quadrupolar interaction, the hyperfine structure observed by Mössbauer spectrometry can be written as

$$\Delta W_Q = \frac{e^2 qQ}{4}\left[\frac{Q^*}{Q} \cdot K(m^*, I^*) - K(m, I)\right] \tag{1}$$

with

$$K(m^{(*)}, I^{(*)}) = \frac{3m^{(*)2} - I^{(*)}(I^{(*)} + 1)}{I^{(*)}(2I^{(*)} - 1)}$$

where m, I, Q and m^*, I^*, Q^* are the magnetic quantum number, the nuclear spin and the quadrupolar moment of the nucleus in ground and excited state, respectively. The eq parameter is directly connected to the electric field gradient value (EFG).

The complete and coherent calculation of

an EFG remains a difficult problem for several reasons. First of all, there are two contributions to the eq parameter: the eq_{ion} participation of orbital electrons of the resonant nucleus and the eq_{lat} participation of electric charges distributed in the crystal lattice. In addition, there is a coupling between the orbital electrons and the crystal lattice. The EFG due to the crystal lattice polarizes the closed electronic shells of the nucleus which, in turn, induce an EFG, represented by the Sternheimer quadrupole antishielding factor, γ_∞ (*1*). In the same way, a spatial dissymmetry of the orbital electronic charge polarizes the core shells which induce another EFG, represented by the Sternheimer shielding factor, R.

Thus the resulting electric field gradient acting at the nuclear site is given by

$$eq_{tot} = (1 - R)eq_{ion} + (1 - \gamma_\infty)eq_{lat}. \tag{2}$$

For the actinide ions ($90 \leq Z \leq 103$) per-

TABLE I

LATTICE PARAMETERS OF MNpF$_6$ · 3H$_2$O
COMPOUNDS (FROM REF. (3))

MNpF$_6$ · 3H$_2$O	a(Å)	b(Å)	c(Å)	β(°)
Mn	12.351(3)	6.961(2)	8.051(2)	92.84
Fe	12.311(3)	6.933(2)	7.988(2)	92.84
Co	12.119(4)	6.908(3)	7.928(3)	92.84
Ni	12.143(3)	6.895(2)	7.906(2)	92.84
Zn	12.118(3)	6.930(2)	7.930(2)	92.84

turbation-numerical calculations have been performed using nonrelativistic Hartree-Fock-Slater wavefunctions to obtain the Sternheimer antishielding factor (2). But the sparsity of experimental data for eq_{tot} and eq_{lat} prevent the calculation of a γ_∞ value from the experiment.

In this work we have evaluated the antishielding factor in the isostructural series MNpF$_6$ · 3H$_2$O (M = Mn, Fe, Co, Ni, Zn), using the eq_{tot} values from ^{237}Np Mössbauer resonance data (3) and calculated eq_{lat} values. In this series, we have assumed that the $(1 - R)eq_{ion}$ term in Eq. (2) remains constant since all the compounds are isotypic. Therefore, eq_{tot} becomes a linear function of eq_{lat} and then the $(1 - \gamma_\infty)$ term represents the slope of the curve $eq_{tot} = f(eq_{lat})$.

2. Calculation of eq_{lat}

The fluoride compounds MNpF$_6$ · 3H$_2$O (M = Mn, Fe, Co, Ni, Zn) were prepared by hydrothermal synthesis and were crystallized in the monoclinic system (3). The lattice parameters are listed in Table I.

The crystal structure of CoNpF$_6$ · 3H$_2$O has been determined to be in the C_2 space group (4). In this structure, the neptunium ions are in two different sites with similar polyhedra (ninefold coordination: eight F atoms and one H$_2$O molecule). The structure consists of Np polyhedra linked by two

fluorine atoms (F1) and F(2), forming infinite chains parallel to the c axis. Located at $y = 0$ and $y = \frac{1}{2}$, these chains are connected by the Co atoms.

The calculation of the lattice contribution to the EFG requires accurate knowledge of the atomic coordinates. Instead of refining all the crystal structures we have used a crystal structure simulation program DLS-76 (5). In this program, the positional parameters can be computed from prescribed interatomic distances D_j^0 by a least-squares procedure minimizing the residual function:

$$\rho_w = \sum_{\substack{j \\ (m,n)}} w_j^2 [D_j^0 - D_j^{m,n}]^2$$

where $D_j^{m,n}$ is the calculated distance of type j between atoms m and n, and w_j the weight ascribed to the interatomic distance of type j. With the precise interatomic distances in CoNpF$_6$ · 3H$_2$O we have used the differences between ionic radii of M^{2+} ions to evaluate the distances D_j^0 in the other compounds $D_{Np-M'}^0$, $D_{M'-F}^0$ and $D_{M'-H_2O}^0$ (M' = Mn, Fe, Ni, Zn).

We have tested this assumption above with two isotypic compounds for which the crystal structures and then the atomic positions were determined: NaZnTh$_3$F$_{15}$ and NaFeNp$_3$F$_{15}$. The crystal structure of NaFeNp$_3$F$_{15}$ has been refined by Cousson et al. (6) and the atomic positions of NaZnTh$_3$F$_{15}$ given in this paper.

In these two compounds, the heavy atom is located in one crystallographic site and is ninefold coordinated. The $3d$ element transition is at the center of a fluorine octahedron and there is some disorder since the (4d) site is occupied by two Na and two Fe (or Zn) atoms.

Starting with the atomic positions in NaFeNp$_3$F$_{15}$, we have calculated the positions in NaZnTh$_3$F$_{15}$ using the DLS program and compared them to the crystal structure results. Using the differences $r(Th^{4+})$ − $r(Np^{4+})$ = +0.07 Å and $r(Zn^{2+})$ − $r(Fe^{2+})$ =

TABLE II

ATOMIC POSITIONS IN $NaFeNp_3F_{15}$ AND $NaZnTh_3F_{15}$
(1) FROM REF. (6)

		NaFeNp₃F₁₅		NaZnTh₃F₁₅		
		Structure (1)	DLS-76	Structure	DLS-76	Diff (%)
An	x	0.39964	0.39960	0.39821	0.39751	0.2
	y	0.07624	0.07623	0.07514	0.07345	2.3
	z	0.10161	0.10161	0.89838	0.89738	0.1
F1	x	0.11940	0.11941	0.31014	0.30796	0.7
	y	0.31200	0.31199	0.18861	0.18549	1.7
	z	0.01920	0.01918	0.01950	0.01737	12.3
F2	x	0.41430	0.41432	0.53251	0.53258	0
	y	0.53300	0.53304	0.11767	0.11731	0.3
	z	0.05240	0.05239	0.05069	0.05352	5.3
F3	x	0.65930	0.65929	0.17167	0.17046	0.7
	y	0.16910	0.16909	0.51275	0.51063	0.4
	z	0.13660	0.13661	0.13700	0.13581	0.9
F4	x	0.19310	0.19310	0.10490	0.10740	2.3
	y	0.08530	0.08531	0.18873	0.19031	0.8
	z	0.15910	0.15912	0.16364	0.15908	2.9
F5	x	0.13130	0.13122	0.68975	0.69899	1.3
	y	0.44250	0.44249	0.13082	0.13986	6.5
	z	0.21690	0.21688	0.21971	0.21615	1.6
M_{3d}	x	0	0	0	0	—
	y	0	0	0	0	—
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	—
Na	x	0	0	0	0	—
	y	0	0	0	0	—
	z	0	0	0	0	—
NaM^a	x	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	—
	y	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	—
	z	0.15340	0.15343	0.15969	0.15658	2

^{a} Statistical atom on the (4d) site.

-0.025 Å (7) for the calculation of inter-atomic distances in $NaZnTh_3F_{15}$, the obtained atomic positions are in good agreement with those of the structure refinement (Table II). The mean difference between observed and calculated values is around 2%.

In a second step, that we explain in the next paragraph, the calculation of the electric field gradient at the Th site in $NaZnTh_3F_{15}$ with the two sets of positions has shown that V_{zz} (struct. positions) = 0.11650238 Å^{-3} and V_{zz} (calcul. positions) = 0.11414120 Å^{-3}. This leads to a difference of 2.1% between these two values and validates our assumption for the calculation of the distances D_j^o and the EFG.

Atomic Positions in the $MnpF_6 \cdot 3H_2O$ Series

In the structure of $CoNpF_6 \cdot 3H_2O$, there are 13 independent atoms and 30 variable positional parameters. Thirty-five independent interatomic distances have been considered to compute the atomic positions in the $MNpF_6 \cdot 3H_2O$ series. The ionic radii and differences between ionic radii of M^{2+} ions are listed in Table III. The atomic positions are listed in Table IV.

Calculation of the Electric Field Gradient

Since the compounds are ionic, the EFG was calculated using a point charge model for the sites occupied by the tetravalent Np(1) and Np(2) ions. We considered only the monopole contribution due to the ionic charges of the lattice and have neglected the dipole contribution which results from induced dipole moments on the anionic sites. The $EFG_{(mono)}$ can be described by a symmetric second-rank traceless tensor whose components are given by

$$V_{ij} = V_{ji} = \sum_k q_k \frac{3x_{ik}x_{jk} - \delta_{ij}r_k^2}{r_k^5} \qquad (3)$$

where x_{ik} and x_{jk} are the coordinates of the kth atom, q_k the charge on the kth atom located at the distance r_k from the cell origin; δ_{ij} is the Krönecker index ($\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i = j$). The summation

TABLE III

IONIC RADII OF M^{2+} IONS (FROM REF. (7))

M^{2+}	$r(\text{Å})$	$r(Co^{2+}) - r(M^{2+})\text{Å}$
Mn	0.820	-0.085
Fe	0.770	-0.035
Co	0.735	0
Ni	0.700	0.035
Zn	0.745	0.010

TABLE IV

ATOMIC POSITIONS IN MNpF$_6$ · 3H$_2$O COMPOUNDS

		Mn	Fe	Co	Ni	Zn
Np(1)	x	0	0	0	0	0
	y	0	0	0	0	0
	z	0	0	0	0	0
Np(2)	x	0	0	0	0	0
	y	0.03521	0.03332	0.03735	0.03188	0.03298
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
M	x	0.24823	0.24882	0.24969	0.25001	0.25029
	y	0.27011	0.26716	0.26932	0.26470	0.26509
	z	0.23903	0.24075	0.24748	0.24579	0.24734
F(1)	x	0.05986	0.06158	0.06110	0.06409	0.06254
	y	0.15629	0.15615	0.16227	0.15725	0.15813
	z	0.74951	0.74997	0.75174	0.75093	0.75109
F(2)	x	0.16610	0.16570	0.16771	0.16644	0.16744
	y	0.16759	0.16314	0.16416	0.15646	0.15823
	z	0.44654	0.44221	0.44550	0.43777	0.44262
F(3)	x	0.13394	0.13137	0.12530	0.12596	0.12593
	y	0.22192	0.22500	0.23269	0.22978	0.23028
	z	0.05131	0.06359	0.08323	0.08774	0.08477
F(4)	x	0.38179	0.38072	0.38680	0.38316	0.38591
	y	0.31632	0.31498	0.30720	0.30798	0.30457
	z	0.40895	0.41050	0.41080	0.41150	0.41191
F(5)	x	0.33387	0.33310	0.33129	0.33107	0.33135
	y	0.37744	0.37401	0.37157	0.36933	0.37149
	z	0.04511	0.04711	0.05034	0.05105	0.05218
F(6)	x	0.56681	0.56691	0.57456	0.57161	0.57319
	y	0.39191	0.38504	0.39321	0.38316	0.38880
	z	0.26097	0.26098	0.26202	0.26114	0.26123
H$_2$O(1)	x	0.17922	0.18332	0.18428	0.19007	0.18742
	y	0.47847	0.47813	0.48578	0.47936	0.47975
	z	0.81220	0.80799	0.80958	0.80130	0.80529
H$_2$O(2)	x	0.31488	0.31523	0.31840	0.31817	0.31855
	y	0.03632	0.02719	0.02894	0.01561	0.02085
	z	0.67937	0.67702	0.68424	0.67569	0.68076
H$_2$O(3)	x	0	0	0	0	0
	y	0.39128	0.39066	0.39621	0.39066	0.39046
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
H$_2$O(4)	x	0	0	0	0	0
	y	0.62713	0.62506	0.62291	0.62201	0.62409
	z	0	0	0	0	0

was performed using a parallepiped with edges La, Lb, Lc (a, b, c monoclinic lattice parameters).

The tensor components are in Å^{-3} units and the value of these components were determined using a Neville plot (8), in which the results $V_{ij} = f(2L + 1)^{-2}$ were extrapolated analytically to $L = \infty$. To calculate the V_{ij} components we have used the program

EFGDIR (9) and $L = 3$ (Table V). As the multiplicity of sites (2a) and (2b) is the same, the mean value $\overline{V}_{zz}$ was considered for the evaluation of the antishielding factor γ_∞.

3. Calculation of the Antishielding Factor γ_∞

The experimental quadrupole splitting values in the MNpF$_6$ · 3H$_2$O series are listed in Table VI. They were obtained by the resonant absorption of $E_0 = 59.537$ keV γ rays of ^{237}Np. A shift of the source with a velocity equal to 1 mm · sec^{-1} corresponds, by Döppler effect, to an energy E_0/c, e.g., 1.98457×10^{-7} eV.

$$(e^2qQ)_{\text{tot}} = e^2Qq_{zz}(1 - \gamma_\infty). \quad (4)$$

Taking the above relation into account and using $Q_{\text{Np}} = 4.1(7)b$ (10), a quadrupole splitting equal to 1 mm · sec^{-1} corresponds to an EFG$_{\text{tot}}$ equal to

$$q_{zz}(1 - \gamma_\infty) = 0.34(6) \text{ Å}^{-3}.$$

The e^2qQ experimental values are compared to those calculated in Table V, plotting e^2qQ vs $\overline{V}_{zz}$. A linear least-squares treatment, where the errors in both e^2qQ and V_{zz} are included (11) gives $(1 - \gamma_\infty) = +127(13)$ and $(1 - R)eq_{\text{ion}} = -1(2)$ Å^{-3} (the fitting values were obtained with four data points, the Co-related point being excluded; coefficient correlation $r = 0.9896$).

The calculated Sternheimer antishielding factor γ_∞ is equal to $-126(13)$ and is in good agreement with the theoretical value $-102.17(2)$. The larger error on the Q_{Np} value (17%) leads to important errors on experimental e^2qQ values (~20% in Å^{-3} units). Considering the multiplicative conversion factor (mm · sec^{-1} to Å^{-3} units) without error for a given nuclear quadrupole moment, the fit of e^2qQ vs $\overline{V}_{zz}$ gives $(1 - \gamma_\infty) = +121(14)$ and then $\gamma_\infty = -120(14)$, value which is also near of the theoretical one.

TABLE V

VALUES OF COMPONENTS OF THE EFG ON SITES $(2a)$ (Np(1)) AND $(2b)$ (Np(2))[a]

		Mn	Fe	Co	Ni	Zn
	V_{zz}	−0.16097248	−0.14426152	−0.12697928	−0.12263628	−0.12438657
Np(1)	V_{yy}	0.11229651	0.09632309	0.07761241	0.07868636	0.08017255
	V_{xx}	0.04867378	0.04793927	0.04936485	0.04394974	0.04421288
	V_{zz}	−0.10232475	−0.10911791	−0.09241022	−0.10923927	−0.09636049
Np(2)	V_{yy}	0.08551001	0.08167449	0.05827987	0.06844024	0.05942291
	V_{xx}	0.01681448	0.02744286	0.03512122	0.04080096	0.03693653
$\bar{V}_{zz}(\text{Å}^{-3})$		−0.132(3)	−0.127(3)	−0.110(2)	−0.116(2)	−0.110(2)

[a] The error on the mean value $\bar{V}_{zz}$ is estimated to 2.1% as shown in the EFG calculation in Na MAn_3F_{15} (M = Fe, Zn; An = Np, Th).

TABLE VI

EXPERIMENTAL HYPERFINE PARAMETERS IN MNpF$_6$ · 3H$_2$O AT 4.2 K (FROM REF. (3))

Compound	IS(mm · sec^{-1}) rel. to NpAl$_2$	B_{eff} (kOe)	Γ(mm · sec^{-1})	e^2qQ(mm · sec^{-1})	EFG(Å^{-3})
MnNpF$_6$ · 3H$_2$O	−6.0(4)	3700(11)	4.4(4)	−46(2)	−16(3)
FeNpF$_6$ · 3H$_2$O	−6.2(4)	3685(6)	4.2(2)	−44(2)	−15(3)
CoNpF$_6$ · 3H$_2$O	−6.1(4)	3530(6)	4.2(2)	−42(1)	−14(3)
NiNpF$_6$ · 3H$_2$O	−6.3(4)	3670(6)	4.0(2)	−41(1)	−14(3)
ZnNpF$_6$ · 3H$_2$O	−5.8(4)	100(12)	4.5[a]	−38[a]	−13[a]

[a] Fixed.

4. Conclusion

In this paper we have described the experimental evaluation of the antishielding factor γ_∞ of the tetravalent neptunium ion. The crystallographic calculations in the series of isotypic compounds MNpF$_6$ · 3H$_2$O have also been outlined. The result for γ_∞ was found to be in reasonable agreement with the theoretical considerations.

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