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N. Edelstein, W. Kolbe, and J. E. Bray

March 1979

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Comment on the Electron Paramagnetic Resonance Spectrum of the $\Gamma_8$ Ground State of Np$^{4+}$ Diluted in Cs$_2$ZrCl$_6$

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ABSTRACT

The electron paramagnetic resonance spectrum of Np$^{4+}$ diluted in CsZrCl$_6$ is analyzed in terms of the theory formulated by Belorizky, et al. It is shown that if $g_J$, the Lande g factor, is allowed to vary freely, a satisfactory fit may be obtained which is consistent with optical and epr data obtained earlier on other tetrapositive actinide ions in the same host crystal. It is suggested a better fit between the experimental data and the calculated spectrum may be obtained if the Zeeman mixing between the ground $\Gamma_8$ state and the excited $\Gamma_6$ state is considered.

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Introduction

Optical and electron paramagnetic resonance (epr) spectra of \( \text{Np}^{4+} \) in crystals of \( \text{Cs}_2\text{NpCl}_6 \) and \( \text{Cs}_2\text{ZrCl}_6 \) show the metal ion to be at a site of octahedral symmetry with a \( \Gamma_8 \) ground state.\(^1\) Lea, Leask, and Wolf (LLW),\(^2\) among others, have shown that the measured \( g \) values obtained from the epr spectra of the \( \Gamma_8 \) state for \( J = 9/2 \) are dependent upon the ratio of the fourth and sixth order crystal field parameters. From a qualitative interpretation of the epr spectrum of the \( \Gamma_8 \) state of \( \text{Np}^{4+} \) diluted in \( \text{Cs}_2\text{ZrCl}_6 \), Bray concluded that the LLW parameter \( x \) (a measure of the above ratio) was equal to \(-0.567\) which is in contradiction to the value expected for an octahedral complex and found for other actinide ions (See Table 1). In this paper we reanalyze quantitatively the epr spectrum of \( \text{Np}^{4+} \) diluted in single crystals of \( \text{Cs}_2\text{ZrCl}_6 \) and show that the LLW parameter \( x \) has a positive value as expected for octahedral symmetry.

Review of Theory

The ground term of \( \text{Np}^{4+}(5f^3) \) is nominally \( ^4I_{9/2} \). Although crystal field interactions in the actinide series are larger than in the 4f series, we assume we are dealing with an isolated \( J \) level; that is there is no \( J \) mixing by the crystal field. We later take into account the effects of spin-orbit coupling and other interactions which may change the free ion Lande \( g \) value, \( g_J \), by allowing this parameter to vary. The
representation $D^{9/2}$ reduces under $O_h$ symmetry to two $\Gamma_8$ and one $\Gamma_6$ representations. Since there are two $\Gamma_8$ representations the relative eigenvalues and eigenvectors of these levels depend on the ratio of the fourth and sixth order crystal field parameters. Lea, Leask, and Wolf$^2$ have calculated these eigenvalues and eigenvectors for $J = 1/2$ to $15/2$ as a function of the parameter $x$ (see below).

The crystal field Hamiltonian for $O_h$ symmetry may be written as$^3,4$

$$H = A_4 \langle r^4 \rangle \beta [0_4^0 + 50_4^4] + A_6 \langle r^6 \rangle \gamma [0_6^0 - 210_6^4]$$

where $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ are the fourth and sixth order crystal field parameters respectively, $\beta$ and $\gamma$ are the fourth and sixth order operator equivalent factors, and the $O_k^q$ are the equivalent tensor operators. The matrix elements of the $O_k^q$ and the operator equivalent factors have been tabulated for the ground terms of all $J$ states of the $f^n$ ions. Lea, Leask, and Wolf$^2,4$ defined the parameter $x$ as

$$\frac{x}{1-|x|} = \frac{F(4)A_4 \langle r^4 \rangle \beta}{F(6)A_6 \langle r^6 \rangle \gamma}.$$ 

The relative energy levels and eigenfunctions have been calculated for all ratios of the crystal field parameters as $x$ varies from $x = -1$ to 0 to 1. The constants $F(4)$ and $F(6)$ are tabulated multiplicative factors for particular $J$ states for the matrix elements of the fourth and sixth order
operators. Figure 1 shows the relative energy levels of the
J = 9/2 state for octahedral symmetry as a function of x.
We see that for x ≤ 0.83 the \( \Gamma_{8}^{(2)} \) state will be lowest and for
x ≥ 0.83 the \( \Gamma_{6} \) state will be the ground state.

The eigenvectors of the fourfold degenerate \( \Gamma_{8}^{(2)} \) state
for a J = 9/2 multiplet with the axes chosen as the principal
axes of an octahedron may be divided into two pairs

\[
A : a_{1}|±9/2\rangle + a_{2}|±1/2\rangle + a_{3}|±7/2\rangle
\]

\[
B : b_{1}|±5/2\rangle + b_{2}|±3/2\rangle
\]

where the quantum numbers inside the kets correspond to \( |J_{z}\rangle \)
values for the J = 9/2 state and the \( a_{1} \) and \( b_{1} \) depend on the
value of x. These eigenvectors may also be labeled as
\( |\Gamma_{8}^{(2)}±1/2\rangle \) and \( |\Gamma_{8}^{(2)}±3/2\rangle \) where the ±1/2 and ±3/2 are eigen-
values of an operator \( \tilde{J}_{z} \) where \( \tilde{J}_{z} \) is equal to the usual \( J_{z} \)
operator for the representation J = 3/2 (\( \Gamma_{8} \subset D^{3/2} \)). Ayant,
et al.\(^{5}\) have shown that with the above basis vectors the \( J_{z} \)
submatrix for the fourfold degenerate \( \Gamma_{8} \) states of J = 9/2
may be written as

\[
\tilde{J}_{z} = \begin{bmatrix}
\text{P} & \text{Q} \\
-\text{Q} & -\text{P}
\end{bmatrix}
\]

with \( \text{P} = \langle \Gamma_{8}^{(2)}3/2|J_{z}|\Gamma_{8}^{(2)}3/2\rangle \) and \( \text{Q} = \langle \Gamma_{8}^{(2)}1/2|J_{z}|\Gamma_{8}^{(2)}1/2\rangle \)
where we have now labeled the pairs A and B as
\( |\Gamma_{8}^{(2)}±1/2\rangle \) and \( |\Gamma_{8}^{(2)}±3/2\rangle \).
If we consider the magnetic resonance spectrum with the magnetic field along the 001 direction, then

\[ \hbar \nu = 2g_J P \beta' H \quad \text{and} \quad \hbar \nu = 2g_J Q \beta' H \]

for the two components of the \( \Gamma_8^{(2)} \) state where \( \beta' \) is the Bohr magneton and \( H \) is the magnitude of the applied magnetic field. From the epr data of Bray\(^1\) taken in the 110 plane it is clear that \( H \) will be very large for the 001 direction and therefore \( Q \) must be near zero. Figure 2 shows a plot of the values of \( P \) and \( Q \) for the \( \Gamma_8^{(2)} \) state as a function of \( x \). There are two ranges of \( x \) for which \( Q \) is near zero, \( x \approx -0.60 \) and \( x \approx 0.65 \). Bray chose to fix \( g_J \), the free ion \( g \) value for the \( J = 9/2 \) state, at the value calculated by Menzel and Gruber\(^6\) in their study of the optical spectrum of \( \text{Cs}_2 \text{NpCl}_6 \) and found he qualitatively obtained the best fit at \( x = -0.567 \). We have allowed \( g_J \) to be a free parameter in our fitting procedure and find the epr data can be fitted with a positive \( x \) value in agreement with the optical data of other tetrapositive actinide ions in octahedral host crystals as shown in Table 1. In fact the \( x \) values obtained for \( \text{Pa}^{4+} \) and \( \text{U}^{4+} \) in \( \text{Cs}_2 \text{ZrCl}_6 \) suggest we are near the crossover point for the \( \Gamma_6 \) and \( \Gamma_8^{(2)} \) states. The observation of the \( \Gamma_8^{(2)} \) epr resonances with no indication at \( \approx 1.5^\circ \text{K} \) of an isotropic epr \( \Gamma_6 \) resonance shows that \( x < 0.83 \).

The isotope \( \text{Np}^{237} \) possesses a large nuclear magnetic moment of spin \( I = 5/2 \). The theory of the electron paramagnetic resonance (epr) spectrum of a \( \Gamma_8 \) state with hyperfine
structure has been worked out by Belorizky, Ayant, Decampes, and d'Aubigne to various levels of approximation depending on the relative magnitude of the hyperfine coupling interaction to the Zeeman interaction. In the present case we used the Hamiltonian as given by Belorisky, et al.:

\[ H = \frac{\mathbf{g}_J}{\mathbf{B}} \cdot \mathbf{J} + A \mathbf{I} \cdot \mathbf{J} + B \left[ (\mathbf{J} \cdot \mathbf{J})^2 + 1/2 (\mathbf{J} \cdot \mathbf{J}) - 1/3 (\mathbf{I}^2) \right] , \]

(1)

calculated the matrix elements and diagonalized and the resulting matrix. The first term in the Hamiltonian is the Zeeman interaction, the second term the hyperfine interaction, and the third term the quadrupole interaction. The hyperfine coupling constant \( A \), and the quadrupole coupling constant \( B \), are both in energy units. The above Hamiltonian is similar to that used in atomic spectroscopy for the Zeeman effect in free atoms whose nuclei have spin \( I > 1/2 \). The theory and the necessary matrix elements are given in Ramsey's book.

A computer program was written which calculated the matrix elements of the Hamiltonian of Eq. (1) in the \( |JJ_zI_z\rangle \) representation. This matrix was complex and of rank 24; a fourfold degeneracy arising from the electronic \( \Gamma_8 \) state and a sixfold degeneracy from the nuclear spin, \( I = 5/2 \). The magnetic field can be in an arbitrary but known direction and the vector quantity was broken up into components along the octahedral axes of the crystal.

For a particular magnetic field and a particular set of \( \Gamma_8 \) wavefunctions (corresponding to a unique \( x \) value) the matrix elements of the Hamiltonian were calculated, the matrix
diagonalized, and the parameters, $g_J$, $A$, and $B$ adjusted to obtain the best fit of the energies of the transitions to the microwave frequency. There was no way of adjusting the wavefunctions of the $\Gamma_8$ state except by starting the calculations over with a new set calculated for a different $x$ value. In a separate program we took the parameters obtained in the fitting program and, by an iterative numerical process, obtained the magnetic field values that a set of parameters gave for a particular transition at a particular microwave frequency. These programs are checked by reproducing the data of Berlorizky, et al. for the $\text{Er}^{3+}:\text{MgO}$ ($I = 7/2$) system.

Results and Discussion

Initially, a few sets of data were chosen for various magnetic field orientations and these data were fit with various sets of $\Gamma_8$ wavefunctions corresponding to different $x$ values. For $x < 0$ the best fit was obtained for $x = -0.575$. The data was much less sensitive to the positive values of $x$; almost the same quality fit could be obtained for $0.45 < x < 0.83$. This relative insensitivity to $x$ at $x \sim 0.65$ is shown in Fig. 2 by the slowly varying values of $P$ and $Q$ in this region. It was found that the epr spectrum for a particular magnetic field orientation could be fitted quite satisfactorily. However, if all the data for a particular plane of rotation was fitted, the deviation between the calculated spectrum and the experimental points was quite marked. Figure 3 shows the variation of the fitted parameters $g_J$ and $A$ as a function of $x$ for the high and low field
transitions in the 111 and 110 planes, while Fig. 4 shows the calculated and measured transitions at $x = .50$ for the 110 and 111 planes for a particular set of parameters. For $x > .7$ the empirical parameters from a high-field fit caused a significant shift to lower field for the low field transitions calculated from the high field parameters. Similarly if the low field spectrum was fitted and the high field spectrum calculated, the center of gravity of the calculated high field spectrum was shifted to higher magnetic fields.

These results suggest the magnetic field or Zeeman interaction is causing the $\Gamma_6$ and $\Gamma_8^{(2)}$ states to be mixed. At high magnetic fields more of the $\Gamma_6$ state is admixed into the ground state and the parameters of Eq. (1) are adjusted empirically to reflect this mixing. Since the $g$ value of the $\Gamma_6$ state ($3.667 g_\perp$) should be larger than for the high field $\Gamma_8^{(2)}$ state, this mixing will tend to make the actual $\Gamma_8^{(2)}$ spectrum appear at lower fields than it would if no mixing were present. The empirical parameters of Eq. (1) are adjusted by the least-squares program to reflect this mixing even though there is no allowance for it in the Hamiltonian. When these empirical parameters are used to calculate the low field spectrum (where the Zeeman mixing is much less) they give a calculated spectrum which is shifted to lower field because the high field parameters are overcompensated for the lower field. By a similar argument, the shift is to higher field in the high field spectrum if the fit is done with the low field data. This magnetic field mixing between the $\Gamma_8^{(2)}$ and the $\Gamma_6$ states
is anisotropic, will occur for all \( x \) values, and may be the reason that slightly different parameters are obtained for different magnetic field orientations. Because our present analysis does not take into account this Zeeman mixing we can only determine \( x \) as being in the range \( 0.45 < x < 0.83 \). This range is consistent with the data on \( \text{Pa}^{4+} \) and \( \text{U}^{4+} \) in \( \text{CsZrCl}_6 \).

Some of the empirical parameters of Eq. (1) are shown in Table 2 for various \( x \) values and magnetic field orientations and planes of rotation. As shown in Fig. 3, the parameters \( g_J \) and \( A \) are fairly well determined but \( B \) is subject to a larger variation, and in some case a change of sign. The value of \( g_J \) is much reduced from the value \( g_J = 0.769 \) calculated from the parameters of Gruber and Menzel for the \( J = 9/2 \) ground state. However in an epr study of \( \text{Np(BH}_4)_4 \) diluted in \( \text{Zr(BH}_4)_4 \) for which the \( \Gamma_6 \) state is lowest, a value of \( g_J = 0.515 \) was obtained. The ratio \( \frac{g_J}{A} \) agrees within \( \sim 5\% \) for the two systems. This agreement suggests that the assumption of a pure \( J \) multiplet with no crystal field mixing is reasonable. Furthermore a complete calculation of the eigenvector for the ground crystal field state with the electrostatic, spin-orbit, and crystal field parameters for \( \text{Cs}_2\text{NpCl}_6 \), and then with the crystal field parameters (free ion parameters as before) of \( \text{U}^{4+} \) in \( \text{Cs}_2\text{ZrCl}_6 \) shows that higher \( J \) states contribute less than 5% in the former system and less than 3% in the latter system. The reduction in \( g_J \) value seems much too large for a covalency effect and may be due to some dynamic effect such as spin-phonon interactions or Jahn-Teller coupling.
Further work is underway on the optical spectrum of Np$^{4+}$ in Cs$_2$ZrCl$_6$ and on a more complete analysis of the epr spectrum including the $\Gamma_6$-$\Gamma_8^{(2)}$ interactions.

ACKNOWLEDGEMENT

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Table 1. Values for the crystal field parameters of tetra-positive actinide ions in octahedral symmetry.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$A_4(r^4)$ (cm$^{-1}$)</th>
<th>$A_6(r^6)$ (cm$^{-1}$)</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pa$^{4+}$ in Cs$_2$ZrCl$_6$ $^a$</td>
<td>888</td>
<td>41.9</td>
<td>.794</td>
</tr>
<tr>
<td>U$^{4+}$ in Cs$_2$ZrCl$_6$ $^b$</td>
<td>823</td>
<td>35.4</td>
<td>.810</td>
</tr>
<tr>
<td>Np$^{4+}$ in Cs$_2$NpCl$_6$ $^c$</td>
<td>520</td>
<td>150</td>
<td>.387</td>
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</tbody>
</table>


<table>
<thead>
<tr>
<th>x</th>
<th>Plane of Rotation</th>
<th>Transitions</th>
<th>Frequency (GHz)</th>
<th>( g_J )</th>
<th>( A ) (cm(^{-1}))</th>
<th>( B ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>.50</td>
<td>110</td>
<td>High Field</td>
<td>35.28</td>
<td>.5623</td>
<td>.03332</td>
<td>.271 ( \times 10^{-3} )</td>
</tr>
<tr>
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<td>.5553</td>
<td>.03357</td>
<td>.337 ( \times 10^{-3} )</td>
</tr>
<tr>
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<td>.03440</td>
<td>-.222 ( \times 10^{-3} )</td>
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<td>.5535</td>
<td>.03506</td>
<td>.123 ( \times 10^{-3} )</td>
</tr>
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<td>.03338</td>
<td>.358 ( \times 10^{-3} )</td>
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<td>.04002</td>
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<td>.5482</td>
<td>.03485</td>
<td>.131 ( \times 10^{-3} )</td>
</tr>
</tbody>
</table>
REFERENCES

3. The formulation of this problem is described in Reference 4.
9. R. Banks and N. Edelstein, private communication.
FIGURE CAPTIONS

Figure 1. Energy level diagram for a $J = 9/2$ state in octahedral symmetry as a function of $x$.

Figure 2. Values of $P$ or $Q$ for the $r_{8}^{(2)}$ state as a function of $x$.

Figure 3. Values of $g_{J}$ (left hand side) and $A$ (right hand side) as a function of $x$ derived from a least-square fit.

Figure 4. Fit of the experimental and calculated spectra in the 111 and 110 planes for $x = .50$; $g_{J} = .556$, $A = .0339$ cm$^{-1}$, and $B = .0002$ cm$^{-1}$. The angles shown in the graph for the 111 plane low field experimental data should be multiplied by -1. The crystalline axes from which the angles are measured are the [110] and the [001] for the 111 plane and the 110 plane, respectively.
Lea, Leask, Wolf diagram $J = \frac{9}{2}$

Figure 1
Lea, Leask, Wolf diagram $J = 9/2$

Figure 2.
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