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ABSTRACT

Magnetic susceptibility measurements of Cs₂NpCl₆,
[(C₄H₅)₄N]₂NpCl₆, and [(CH₃)₄N]₂NpCl₆ from 2.5 to 70 K show
that the T₈ ground level of the Np⁺ ion is split by 5-10 cm⁻¹
in the first two compounds because of distortions from octahedral
symmetry in these crystals. The T₈ level in [(CH₃)₄N]₂NpCl₆ is
not split, and the measurements agree well with first-order
theory for x = 0.39 and g₁ = 0.60. The Mössbauer spectra at
4.2 K of [(CH₃)₄N]₂NpCl₆ and [(C₂H₅)₄N]₂NpCl₆ are magnetically
split, with a small quadrupole interaction. The spectrum of
[(CH₃)₄N]₂NpCl₆ shows deviations from isotropic magnetic
splitting that may be caused by interactions within the
degenerate T₈ level. The Mössbauer spectrum of [(C₂H₅)₄N]₂NpCl₆
is consistent with two nonequivalent Np⁺⁺ sites. The Mössbauer
spectrum of Cs₂NpCl₆ is obscured by intermediate relaxation
effects.

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INTRODUCTION

The neptunium(IV) ion in an octahedral field has been studied extensively by optical spectra\textsuperscript{1-4} and electron paramagnetic resonance.\textsuperscript{5,6} The major interest is in the properties of the $\Gamma_8$ quartet ground crystal field level that was identified in earlier work.\textsuperscript{1-6} This paper reports additional information obtained from low-temperature magnetic susceptibilities and Mössbauer spectra on Cs$_2$NpCl$_6$, [(CH$_3$)$_4$N]$_2$NpCl$_6$, and [(C$_2$H$_5$)$_4$N]$_2$NpCl$_6$. The structures of these compounds are inferred from their isostructural uranium and plutonium analogues and the infrared spectral studies.\textsuperscript{7}

The Np$^{4+}$ ion is located at the body center of an octahedron of six Cl$^-$ ions in these three compounds. (TMA)$_2$NpCl$_6$ [TMA refers to (CH$_3$)$_4$N$^+$] has a face-centered cubic cell (O$_h$) with the Np$^{4+}$ ion at a point of full cubic symmetry.\textsuperscript{8} (TEA)$_2$NpCl$_6$ has an orthorhombic (D$_{3d}$) cell that differs from (TMA)$_2$NpCl$_6$ by the greater space occupied by the (C$_2$H$_5$)$_4$N$^+$ cations.\textsuperscript{9} Cs$_2$NpCl$_6$ has a trigonal cell (D$_{3d}$), and the NpCl$_6^{2-}$ octahedron is slightly elongated on one axis.\textsuperscript{8,10} The distortions in the structures of Cs$_2$NpCl$_6$ and (TEA)$_2$NpCl$_6$ may be expected to cause a slight splitting of the $\Gamma_8$ quartet into $\Gamma_6$ and $\Gamma_7$ doublets.\textsuperscript{2,3,7} The splitting can be observed by magnetic measurements.
EXPERIMENTAL

Polycrystalline samples of $\text{R}_2\text{NpCl}_6$ and $\text{R}_2\text{ThCl}_6$ were prepared by an adaptation of the method of Ryan, and the identities of the compounds were confirmed by X-ray powder patterns. Magnetic susceptibilities were measured with a Foner-type vibrating sample magnetometer in a field of 10 kOe over the temperature range of 2.5-70 K, as previously reported in the study of Pu$^{4+}$ analogues. The Mössbauer spectra of the $\text{R}_2\text{NpCl}_6$ compounds were taken at 4.2 K with a constant-temperature spectrometer and from 4.2 to 70 K with a variable-temperature spectrometer. The spectrum of $\text{Cs}_2\text{NpCl}_6$ at 2.5 K was also recorded. Details of the techniques used for Mössbauer spectra have been published.

RESULTS AND DISCUSSION

Magnetic Susceptibilities

The inverse magnetic susceptibilities of $\text{Cs}_2\text{NpCl}_6$, $(\text{TMA})_2\text{NpCl}_6$, and $(\text{TEA})_2\text{NpCl}_6$ are shown graphically in Figs. 1-3. The constants were obtained by fitting the data to the Curie-Weiss expression $\chi = C/(T+\Theta)$ shown in Table 1. The data for $\text{Cs}_2\text{NpCl}_6$ and $(\text{TEA})_2\text{NpCl}_6$ exhibit two regions of Curie-Weiss behavior below 70 K; $(\text{TMA})_2\text{NpCl}_6$ follows a single Curie-Weiss law from 2.5 to 66 K. From group theory, a $\Gamma_8$ quartet must split into two Kramers doublets in any symmetry lower than cubic. Thus, the shapes of the reciprocal susceptibility curves for $\text{Cs}_2\text{NpCl}_6$ and $(\text{TEA})_2\text{NpCl}_6$ are consistent with each having a $\Gamma_8$ ground-level split by a small distortion from octahedral symmetry about the Np$^{4+}$ ion. The
breaks in the curves correspond to splittings of 5-10 cm\(^{-1}\). Additional evidence for splittings of this magnitude is found in the optical\(^3\) and infrared spectra\(^7\) of Cs\(_2\)NpCl\(_6\) and (TEA\(_2\)NpCl\(_6\) and is expected from the noncubic crystal structures. In contrast to this behavior, the reciprocal susceptibility of (TMA\(_2\)NpCl\(_6\) is linear down to 2.5 K, indicating that distortions from octahedral symmetry are very small or absent; this observation is consistent with the cubic crystal structure of the compound and with an \(O\(_h\)\) site symmetry of the Np\(^{4+}\) ion.

(TMA\(_2\)NpCl\(_6\) is inferred to have an unsplit \(\Gamma_8\) ground level, from the general similarity of the NpCl\(_{2-}\) complex in the three compounds.

The low-temperature magnetic properties of the \(^{3/2}\) ground state of Np\(^{4+}\) are determined by the crystal field. For an octahedral field, the magnetic properties can be calculated from the tables of Lea, Leask, and Wolf (LLW)\(^1\)\(^0\) and the analysis of the magnetic properties of \(\Gamma_8\) levels by Bleaney.\(^1\)\(^5\) The crystal field Hamiltonian for cubic point symmetry\(^1\)\(^6\) is

\[
H = A_4 <r^4> \beta (O^2_{\theta} + 5 \cdot O^4_{\theta}) + A_6 <r^6> \gamma (O^{\theta}_0 - 21 \cdot O^{6}_0)
\]

where \(A_4 <r^4>\) and \(A_6 <r^6>\) are the fourth- and sixth-order crystal field parameters; \(\beta\) and \(\gamma\), the fourth- and sixth-order operator equivalent factors; \(<r^n>\), expectation values for the 5f electrons; and \(O^m_n\), the equivalent tensor operators. LLW defines the parameter \(x\) by

- 5 -
where \( F(4) \) and \( F(6) \) are constant factors for the matrix elements of the fourth- and sixth-order operators of each \( J \) state. The parameter \( x \) specifies the ratio of the crystal field parameters, and LLW tabulates eigenvectors for the \( J = \frac{9}{2} \) state of the form

\[
A = a_1|\pm^9/2> + a_2|\pm^1/2> + a_3|\pm^7/2>
\]

\[
B = b_1|\pm^5/2> + b_2|\pm^1/2>
\]

where \( |\pm^L/2> \) specifies the \( |J_z> \) vector and \( a_L \) and \( b_L \) depend upon the value of \( x \). For a particular value of \( x \) (Reference 15),

\[
\mu_{\text{eff}} = [(\frac{5}{6})(A^2+B^2)]^{\frac{1}{2}} g_J
\]

Carrying out this calculation for values of \( x \) from 0 to 1 shows that the square root factor varies only from 3.66 to 3.82. This variation shows that the value of \( x \) has only a minor effect on the magnetic moment. If the free-ion \( g_J \) value of \( \frac{8}{11} \) is assumed, \( \mu_{\text{eff}} \) ranges from 2.7 to 2.8, compared with the experimental value for \((\text{TMA})_2\text{NpCl}_6\) of 2.28 \( \mu_B \).

Edelstein, Kolbe, and Bray,\textsuperscript{6} in their analysis of ESR spectra, allowed \( g_J \) to vary to obtain best-fit values for \( g_J \), which range from 0.55 to 0.60. For this range of \( g_J \), \( \mu_{\text{eff}} \) is calculated to be from 2.0 to 2.3 \( \mu_B \), which agrees well with the experimental \( \mu_{\text{eff}} \).

After a value for \( x \) is selected, the experimental value of \( \mu_{\text{eff}} \) can be used to obtain \( g_J \). Menzel and Gruber\textsuperscript{3} derived
a value of $x = 0.39$ from optical studies. A magnetic study of the Pu$_{4+}$ analogues$^{12,16}$ found $A_4 <r^4> = 3.5 A_6 <r^6>$, which corresponds to $x = 0.34$ for the Np$_{4+}$ ion. (Since the crystal field parameters are determined by the environment of the ion, their variation between analogues Np$_{4+}$ and Pu$_{4+}$ compounds should be small.) If the value $x = 0.39$ is selected, then $g_J$ is 0.60, which agrees well with the value obtained from ESR data.$^6$

Mössbauer Spectra

Mössbauer spectra of Cs$_2$NpCl$_6$, (TMA)$_2$NpCl$_6$, and (TEA)$_2$NpCl$_6$, at 4.2 K, are shown in Fig. 4. The three spectra are markedly different from each other and are characteristic of their respective compounds, as determined by the reproducibility of the spectra from multiple preparations of each compound. The dominant features of the spectra (the spans of the hyperfine patterns and the number of lines) are characteristic of magnetic hyperfine splitting.$^{17}$ The magnetic splitting does not result from a ferromagnetic or antiferromagnetic state, since the susceptibility data show that the compounds are paramagnetic at 4.2 K. Instead, the observed splitting at 4.2 K is attributed to slow paramagnetic relaxation rates. This phenomenon is well known in iron and rare earth Mössbauer spectra$^{18}$ and has been noted previously for other neptunium compounds.$^{19,20}$ The possibility of relaxation effects is confirmed by spectra at higher temperatures where faster relaxation rates are present. For each of the compounds, the magnetic splitting disappears and is replaced by a broadened
single line above 20 K. The very broad, unresolved spectrum of Cs$_2$NpCl$_6$ at 4.2 K is apparently due to an intermediate relaxation rate. For Cs$_2$NpCl$_6$, the spectrum at 2.5 K is practically identical to that at 4.2 K.

The spectrum of (TMA)$_2$NpCl$_6$ can be interpreted as magnetically split, with a small quadrupole interaction. The Mössbauer constants for this spectrum analyzed in this fashion are $\delta = -0.66 \text{ cm/sec}$, $g_0 \mu_B H_{\text{eff}} = 7.83 \text{ cm/sec}$, and $\frac{1}{3} eqQ = 0.091$. However, detailed examination of the spectrum shows deviations from an isotropic magnetic-splitting pattern. The hyperfine pattern expected for pure isotropic splitting$^{17}$ is shown for comparison at the top of Fig. 4. Neither the line spacings nor the intensities of the (TMA)$_2$NpCl$_6$ spectrum are consistent with the isotropic splitting patterns, and the deviations cannot be explained by quadrupole splitting. Bleaney$^{15}$ has shown theoretically that anisotropic magnetic hyperfine splitting and small quadrupole interactions can be expected in a pure $\Gamma_8$ level, particularly when unequal magnetic field splitting occurs. Unequal splitting of the $\Gamma_8$ level in the magnetic field may be the cause of the anomalies in the (TMA)$_2$NpCl$_6$ spectrum.

The Mössbauer spectrum of (TEA)$_2$NpCl$_6$ is quite complex, with about twice the number of lines expected from a magnetically split spectrum. The optical absorption spectrum$^2$ at 4.2 K is interpreted as showing Np$^{4+}$ ions in two nonequivalent sites. This interpretation is consistent with the Mössbauer spectrum,
analyzed in terms of two superposed magnetically split spectra with an appreciable quadrupole contribution. The following Mössbauer constants give the most satisfactory fit to the spectrum:

for one site, $\delta = 0.75 \text{ cm/sec}$, $g_{\text{eff}} = 5.78 \text{ cm/sec}$, and $\frac{1}{4} q = 0.33 \text{ cm/sec}$; for the other site, $\delta = 0.71 \text{ cm/sec}$, $g_{\text{eff}} = 6.26 \text{ cm/sec}$, and $\frac{1}{4} q = 0.27 \text{ cm/sec}$. As with $\text{(TMA)}_2\text{NpCl}_6$, the line spacings and intensities are not consistent with the isotropic splitting pattern assumed in the analysis and, therefore, may be modified by a more detailed analysis. However, the spectrum does confirm the presence of two Np$^{4+}$ sites found by optical spectroscopy.$^2$
REFERENCES

\( g_j^2 (A^2 + B^2) \) is equivalent to Bleaney's \( (5\gamma^2 + 3\delta^2) \).
16. A fortuitous system determines \( x \) directly in the \( R_2PuCl_8 \) study. The analysis of Reference 12, however, assumes a
total ground state splitting of only 145 cm$^{-1}$, probably at least a factor of five too small.


### TABLE 1. Magnetic Constants for R$_2$NpCl$_6$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature Range (K)</th>
<th>$C^\alpha$ (emu/mole)</th>
<th>$\Theta$ (K)$^\alpha$</th>
<th>$\mu_{\text{eff}}$ (\mu_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$NpCl$_6$</td>
<td>2.5 - 8</td>
<td>0.40</td>
<td>0.65</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>6 - 45</td>
<td>0.66</td>
<td>5.1</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>45 - 75</td>
<td>1.18</td>
<td>40</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>95 - 303$^b$</td>
<td>1.14</td>
<td>65</td>
<td>3.02</td>
</tr>
<tr>
<td>(TMA)$_2$NpCl$_6$</td>
<td>2.5 - 65</td>
<td>0.643</td>
<td>0.25</td>
<td>2.28</td>
</tr>
<tr>
<td>(TEA)$_2$NpCl$_6$</td>
<td>2.5 - 15</td>
<td>0.43</td>
<td>1.1</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td>15 - 70</td>
<td>0.73</td>
<td>11</td>
<td>2.41</td>
</tr>
</tbody>
</table>

$^a$ $\chi_m = C/(T + \Theta)$.

FIGURE 1. Inverse Magnetic Susceptibility of $\text{Cs}_2\text{NpCl}_6$
FIGURE 2. Inverse Magnetic Susceptibility of (TMA)$_2$NpCl$_6$
FIGURE 3. Inverse Magnetic Susceptibility of (TEA)$_2$NpCl$_6$
FIGURE 4. Mössbauer Spectra of \( \text{Cs}_2 \text{NpCl}_6 \), \((\text{TMA})_2 \text{NpCl}_6\), and \((\text{TEA})_2 \text{NpCl}_6\)