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MÖSSBAUER SPECTRA AND MAGNETIC PROPERTIES OF Cs_2NpCl_6, $(TMA)_2NpCl_6$, AND $(TEA)_2NpCl_6$

by

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ABSTRACT

The cesium, tetramethylammonium (TMA), and tetraethylammonium (TEA) salts of octahedral $NpCl_6^{2-}$ were studied by ^{237}Np Mössbauer spectra and magnetic susceptibility measurements from 2.5 to 70°K. The data are consistent with the assignment of a Γ_8 quartet as the ground level of Np^{4+} ($J=9/2$) in each compound. From the susceptibilities, the Γ_8 ground levels of Cs_2NpCl_6 and $(TEA)_2NpCl_6$ are slightly distorted with 5 to 10 cm^{-1} splitting; $(TMA)_2NpCl_6$ is not split. The Mössbauer spectra exhibit paramagnetic hyperfine structure at 4.2°K, becoming single lines above 20°K; the spectra at 4.2°K have the following features: Cs_2NpCl_6 -- a very broad, unresolved resonance; $(TMA)_2NpCl_6$ -- anomalous spectrum, possibly reflecting the unusual properties (anisotropic hfs, quadrupole interaction) of Γ_8 levels predicted by Bleaney; $(TEA)_2NpCl_6$ -- magnetic and quadrupole splitting, with nonzero asymmetry parameter, indicating that the Γ_8 distortion is of symmetry lower than trigonal.

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INTRODUCTION

Tetravalent actinides form solid compounds of the type R_2MCl_6, where R is a large univalent cation and M is the actinide ion in an octahedral environment. In this paper, we report low-temperature magnetic susceptibilities and Mössbauer spectra of three neptunium salts: Cs_2NpCl_6, $(TMA)_2NpCl_6$, and $(TEA)_2NpCl_6$. Here, TMA = tetramethylammonium ion, $(CH_3)_4N^+$, and TEA = tetraethylammonium ion $(C_2H_5)_4N^+$. The three compounds have different crystal structures[1,2] (Slide 1), but each is isostructural with the corresponding uranium and plutonium compounds.[3-5] From the crystal structures, the octahedral symmetry of Np^{4+} in Cs_2NpCl_6 should be trigonally distorted, $(TEA)_2NpCl_6$ should have a rhombic distortion, and $(TMA)_2NpCl_6$ is expected to be undistorted. Magnetic data for the analogous plutonium compounds have been reported by Karraker,[6] and for the uranium compounds by Candela, Hutchison, and Lewis.[7] Optical, far-infrared, and Raman spectra of the three neptunium compounds have been measured by Gruber and coworkers.[8-10]

The low-temperature magnetic properties of Np^{4+} ($5f^3$) in its $^4I_{9/2}$ ground state are determined by the crystal-field splitting in the octahedral (or near-octahedral) environment. The crystal-field Hamiltonian for octahedral symmetry is given in tensor-operator formalism by

$$H = B_0^4 \, [C_0^4 + (5/14)^{1/2} \, (C_{-4}^{(4)} + C_4^{(4)})]$$

$$+ B_0^6 \, [C_0^6 - (7/2)^{1/2} \, (C_{-4}^{(4)} + C_4^{(4)})]$$

where the splitting is determined by the two crystal-field parameters, B_0^4 and B_0^6. In octahedral symmetry, a $J=9/2$ state splits into two Γ_8 quartets and a Γ_6 doublet. The pertinent portion of the splitting diagram, adapted from the tables of Lea, Leask, and Wolf,[11] and expressed in terms of the B_0^6/B_0^4 ratio, is shown in Slide 2. The diagram, including intermediate coupling effects[12] in Np^{4+}, shows that the Γ_6 level is lowest for $0<(B_0^6/B_0^4)<0.08$, and that a Γ_8 level is lowest for $(B_0^6/B_0^4)>0.08$. From optical spectra of Cs_2NpCl_6 and $(TEA)_2NpCl_6$, $B_0^6/B_0^4 = 0.58$ and $B_0^4 = 4160$ cm^{-1}, indicating that the ground level is a Γ_8 quartet separated by about 1000 cm^{-1} from the other levels.[8,9] Bleaney[13] has predicted properties of Γ_8 levels not usually associated with cubic symmetry: anisotropic Zeeman and hyperfine splittings, and nonzero quadrupole interaction. Systems with isolated Γ_8 ground levels are relatively rare; thus, the neptunium hexachloro complexes offer an excellent opportunity to study the properties of Γ_8 levels.

EXPERIMENTAL

Polycrystalline samples of the R_2NpCl_6 compounds were prepared by the method of Ryan,[14] and the identities of the compounds were verified by X-ray powder patterns.[1,2] Magnetic susceptibilities were measured with a vibrating-sample magnetometer[15] at an applied field of 10000 Oe, in the temperature range 2.5 to 70°K. Mössbauer spectra of the R_2NpCl_6 compounds, using the 59.54-keV γ-ray of ^{237}Np, were taken at 4.2°K with a constant-temperature spectrometer, and from 4.2 to 70°K with a variable-temperature spectrometer; a spectrum of Cs_2NpCl_6 at 2.5°K also was taken. Details of the measurement techniques for both the susceptibilities[6] and the Mössbauer spectra[16] have been given previously.

RESULTS AND DISCUSSION

The magnetic susceptibilities of Cs_2NpCl_6, $(TMA)_2NpCl_6$, and $(TEA)_2NpCl_6$ measured in this work are shown in Slide 3. Here, reciprocal susceptibility versus temperature is plotted for comparison of the data with the Curie-Weiss law,

$$\chi = C/(T + \theta)$$

where C is the Curie constant and θ is the paramagnetic Curie temperature. The data for Cs_2NpCl_6 and $(TEA)_2NpCl_6$ exhibit two regions of Curie-Weiss behavior below 70°K; $(TMA)_2NpCl_6$ follows a single Curie-Weiss law from 2.5 to 66°K. From group theory, a Γ_8 quartet must split into two Kramers doublets in any symmetry lower than cubic. Thus, the shapes of the reciprocal susceptibility curves for Cs_2NpCl_6 and $(TEA)_2NpCl_6$ are consistent with Γ_8 ground levels split by small distortions from octahedral symmetry about the Np^{4+} ion. The breaks in the curves correspond to splittings of 5 to 10 cm^{-1}. Additional evidence for splittings of this magnitude is found in the optical[8,9] and infrared spectra[10] of Cs_2NpCl_6 and $(TEA)_2NpCl_6$, as well as in their noncubic crystal structures. In contrast to this behavior, the reciprocal susceptibility of $(TMA)_2NpCl_6$ is linear down to 2.5°K, indicating that distortions from octahedral symmetry are very small or absent; this is consistent with the cubic crystal structure of the compound and O_h site symmetry of the Np^{4+} ion. $(TMA)_2NpCl_6$ is inferred to have a Γ_8 ground level also, from the general similarity of the $NpCl_6^{2-}$ complex in the three compounds.

Experimental values of the Curie-Weiss constants and effective moments are given in Slide 4. For comparison, the theoretical moments from a first-order calculation[11] including intermediate coupling[12] are 2.4 μ_B for a Γ_6 level and 2.8-2.9 μ_B for a Γ_8 level[13] (depending on the value of B_0^6/B_0^4). Calculations[17] including J-mixing from the first excited state (J=11/2) have shown an increase of about 10% in the Γ_8 effective moment; the Γ_6 moment is nearly independent of J-mixing. Thus, for Cs_2NpCl_6 and $(TEA)_2NpCl_6$, the observed moments ($\sim$3.1 μ_B) at higher temperatures are in good agreement with the calculated moment for a Γ_8 level. This behavior is expected for temperatures such that the thermal energy is much greater than the splitting due to distortion. For Cs_2NpCl_6, the low-temperature moment may be compared with the result from a theoretical treatment[18] of trigonal distortions of Γ_8 levels; the calculated moment, without J-mixing, is 2.0 μ_B, in fair agreement with the experimental value of 1.8 μ_B. The effective moment of $(TMA)_2NpCl_6$ is anomalous; although considerable evidence exists that Np^{4+} in this compound is in an undistorted site of O_h symmetry with a Γ_8 ground level, the theoretical treatment of Γ_8 levels[13] does not account for the observed moment. In all the compounds, J-mixing by the crystal field is an effect of considerable importance on the ground-level moment.

Mössbauer spectra of Cs_2NpCl_6, $(TMA)_2NpCl_6$, and $(TEA)_2NpCl_6$, at 4.2°K, are shown in Slide 5. 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.[19] The magnetic splitting does not result from a ferromagnetic or antiferromagnetic state, because the susceptibility data show that the compounds are paramagnetic at 4.2°K. However, the observed splitting at 4.2°K can be attributed to slow paramagnetic relaxation rates; this phenomenon is well known in iron and rare earth Mössbauer spectra,[20] and has been noted previously for a few neptunium compounds.[21,22] The possibility of relaxation effects was confirmed by spectra at higher temperatures where faster relaxation rates are present. For each of the compounds the magnetic splitting disappeared and was replaced by a broadened single line above 20°K. The very broad, unresolved spectrum of Cs_2NpCl_6 at 4.2°K is apparently due to an intermediate relaxation rate. For Cs_2NpCl_6, the spectrum at 2.5°K was practically identical to that at 4.2°K.

The spectra of $(TMA)_2NpCl_6$ and $(TEA)_2NpCl_6$ exhibit small quadrupole interactions in addition to the magnetic interaction. However, detailed examination shows that the spectra are of a type not previously encountered in neptunium compounds. Preliminary interpretation of the spectra gives qualitative information about the compounds, even though the spectra are complex and simplifying features are absent. The hyperfine pattern expected for pure isotropic magnetic splitting[19] is shown for comparison (Slide 5, inset). The line spacings and intensities in the $(TMA)_2NpCl_6$ spectrum are not consistent with an isotropic magnetic interaction. Bleaney[13] has shown theoretically that anisotropic magnetic hyperfine splitting and nonzero quadrupole interactions are to be expected in a pure Γ_8 level. Although a detailed interpretation of the $(TMA)_2NpCl_6$ spectrum is not yet available, the observed features may reflect the unusual properties of Γ_8 levels; the spectrum is quite different from that usually associated with cubic symmetry. The spectrum of $(TEA)_2NpCl_6$ shows evidence of a quadrupole interaction with a large asymmetry parameter η; this leads to 36 allowed lines instead of 16 for the pure magnetic case, with intensities markedly altered from the original 16 lines. A nonzero asymmetry parameter implies that no threefold or higher symmetry axis exists in the compound, which is consistent with the D_{2h} site symmetry of $(TEA)_2NpCl_6$.

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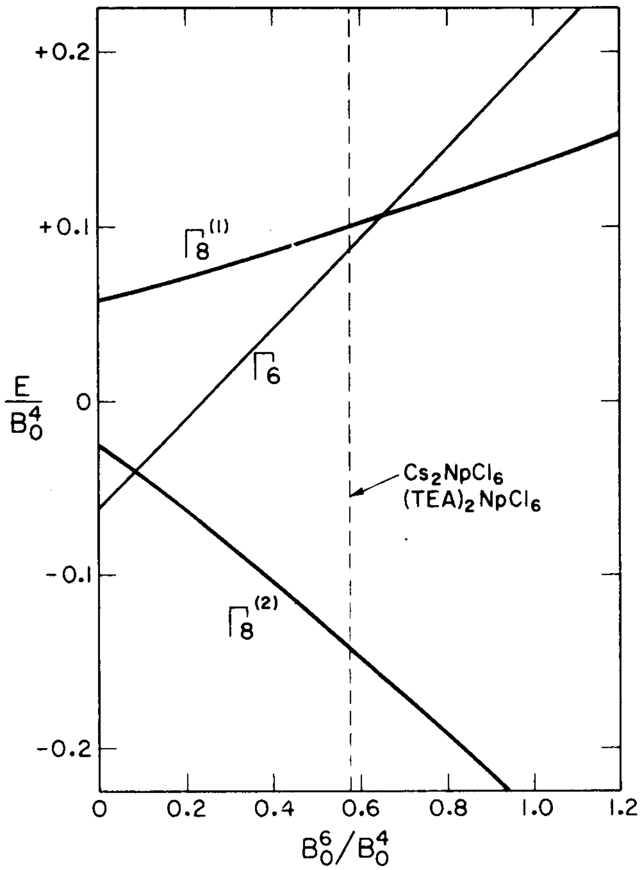
PW:mh

Cs_2NpCl_6	Trigonal	D_{3d}^{3}
$(TMA)_2NpCl_6$	Face-centered cubic	O_h^{5}
$(TEA)_2NpCl_6$	Orthorhombic	D_{2h}^{23}

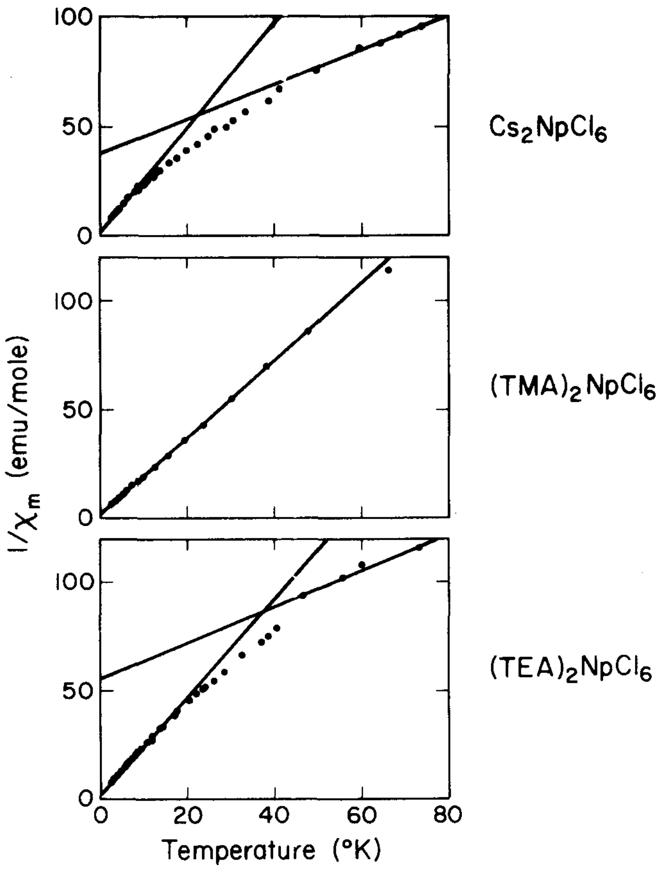
TMA = tetramethylammonium, $(CH_3)_4N^+$

TEA = tetraethylammonium, $(C_2H_5)_4N^+$

SLIDE 1. Crystal structures of $NpCl_6^{2-}$ salts.



SLIDE 2. Octahedral crystal-field splitting of Np^{4+}.



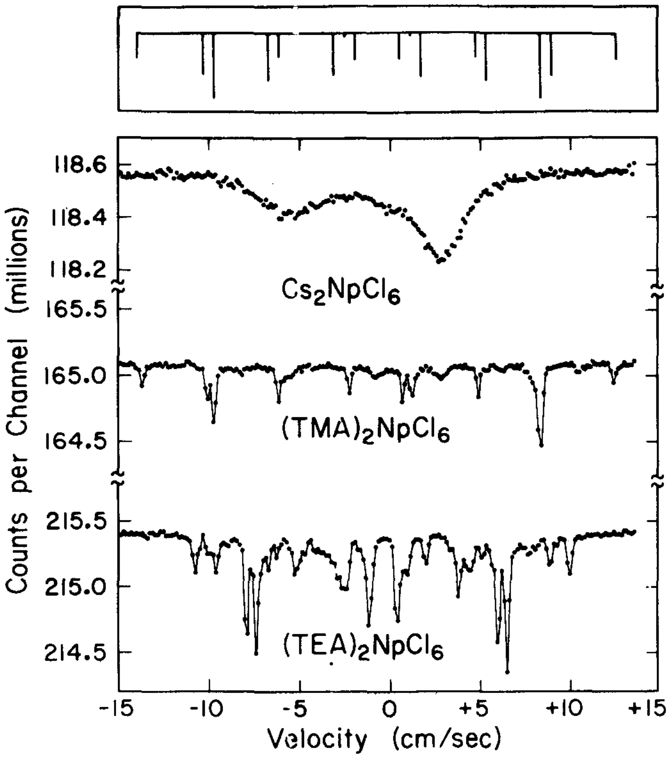
SLIDE 3. Reciprocal molar susceptibilities of R_2NpCl_6 compounds as a function of temperature.

MAGNETIC SUSCEPTIBILITY CONSTANTS

Compound	Temperature Range (°K)	C^a (emu-deg mole^{-1})	θ^a (°K)	μ_{eff} (μ_B)
Cs_2NpCl_6	2.5-7	0.40	0.65	1.80±0.09
	7-50	0.66	5.13	2.30±0.12
	50-73	1.18	39.5	3.07±0.15
$(TMA)_2NpCl_6$	2.5-66	0.55	0.36	2.10±0.10
$(TEA)_2NpCl_6$	2.5-15	0.43	1.10	1.86±0.09
	15-56	0.73	11.3	2.41±0.12
	56-73	1.20	66.6	3.10±0.15

[a] Constants From Curie-Weiss law $\chi = C/(T+\theta)$

SLIDE 4. Magnetic susceptibility constants for R_2NpCl_6 compounds.



SLIDE 5. Mössbauer spectra of R_2NpCl_6 compounds at 4.2° K.