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Analysis of the Optical Spectra and Magnetic Susceptibilities of Li_7UO_6, Ba_3NpO_6, and Li_5PuO_6

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The absorption spectra and magnetic susceptibilities of Li_7UO_6, Ba_3NpO_6, and Li_5PuO_6 obtained from published data are reanalyzed on the basis of an octahedral crystal-field model with/without a small tetragonal distortion. © 1991 Academic Press, Inc.

1. Introduction

Contrary to the situation for the $4f^n$ configurations of rare earths, it is usually impossible to treat the crystal field acting on $5f^n$ configurations of actinide compounds as a small perturbation of atomic levels. In many cases, the crystal-field interaction, spin–orbit coupling interaction, and electronic repulsion interaction are of comparable magnitude, which makes the analysis of the experimental results complicated. However, for the actinide ions having the $[Rn]5f^1$ electronic configuration, the situation is considerably simplified, because there is no electron–electron repulsion interaction.

Kanellakopulos *et al.* (*1*) measured optical spectra and magnetic susceptibilities for a number of uranates (U^{5+}), neptunates (Np^6), and one plutonate (Pu^{7+}) and fitted their data to the theory developed by Eisenstein and Pryce (*2*) with an additional parameter to account for a tetragonal distortion of the crystal field. However, an added empirical temperature-independent paramagnetic susceptibility was necessary in order to obtain a satisfactory fit of the magnetic susceptibility data as a function of temperature. Edelstein and Goffart (*3*) questioned the use of a spin–orbit coupling constant by Kanellakopulos *et al.* which was almost constant for U^{5+}, Np^{6+}, and Pu^{7+} (1800 ~ 1900 cm^{-1}), because the spin–orbit coupling constant is known to increase markedly with higher atomic number and higher charge on the ion (*4*). For some compounds, the orbital reduction factors obtained show the relation $k < k'$, which is an improbable result (*5*) because the orbital reduction factor k is associated with overlap of the t_{2u} orbitals of the $5f$ electrons with p_π electrons on the oxygen; on the other hand the orbital reduction

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factor k' is related to the antibonding of the $5f\delta$ orbitals (t_{1u}) with $2p_\sigma$ electrons on the oxygen atoms. Eisenstein and Pryce pointed out that k should be very nearly unity (*2*).

We focus attention in this paper on the magnetic and optical properties of Li_7UO_6, Ba_3NpO_6, and Li_5UO_6. Although electron paramagnetic resonance (EPR) measurements have not been carried out yet for Ba_3NpO_6 and Li_5PuO_6, we may obtain the ground state g-values from their magnetic susceptibilities, because the susceptibilities are linear against reciprocal temperature over the temperature range from 4.2 to 300 K (*1*).

In this paper, we obtain the crystal-field parameters of Li_7UO_6, Ba_3NpO_3, and Li_5PuO_6 by fitting the calculations not only to the transition energies but also to the ground state g-values, and then calculate the magnetic susceptibilities (including the temperature-independent paramagnetism (TIP)) followed by comparison with the experimental data.

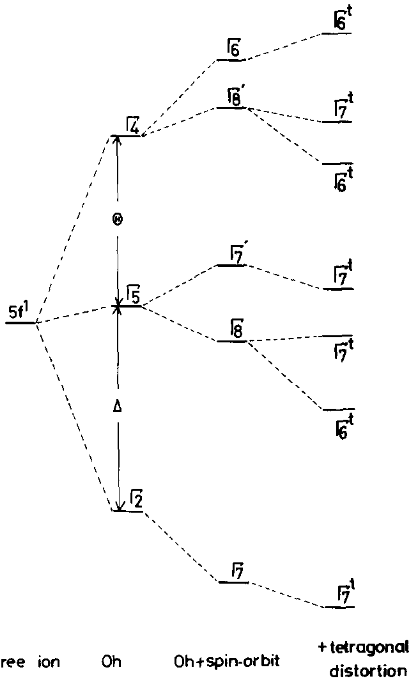

FIG. 1. f^1 orbital energy splitting perturbed by octahedral crystal-field, spin–orbit coupling, and tetragonal crystal-field distortion.

2. Calculation Method

The crystal structure of Ba_3NpO_6 is a cubic perovskite (*6*). Although the optical absorption spectra measured by Kanellakopulos *et al.* are not clear, it is evident that there is no splitting of the Γ_8 quartet level (*1*) (see Fig. 1), which means that the symmetry of the crystal-field coordination around a neptunium ion is still octahedral. Li_5PuO_6 is isomorphous with Li_5ReO_6; this crystallizes in a hexagonal structure (space group: $P3_112$). This compound contains isolated PuO_6 octahedra (*6*). According to Kanellakopulos *et al.* (*1*), the optical spectra of this compound show that the oxygen octahedron is tetragonally distorted. The crystal structure of Li_7UO_6 is hexagonal and of the Li_7SbO_6 type with the distorted octahedral coordination around a uranium ion (*6*). Kanellakopulos *et al.* measured the optical spectra of this compound and reported that although the quartet Γ_8 state splits into two doublets the energy separation of which is 560 cm^{-1}, the splitting of the higher energy quartet Γ_8' state is not observed experimentally (Fig. 1). The distortion from octahedral symmetry seems to be small. We analyze the optical spectra and magnetic susceptibility data by assuming a tetragonal crystal-field distortion on the electronic states of a $5f$ electron in octahedral coordination.

Figure 1 shows the effects of perturbing the f^1 orbital energy levels successively by an octahedral crystal-field, spin–orbit coupling, and tetragonal crystal-field distortion. In an octahedral crystal field, the sevenfold degenerate energy state of the f orbitals is split into Γ_2, Γ_5, and Γ_4 states, where Δ and Θ represent the parameters of the intensity of the crystal field. If spin–orbit coupling is taken into account, the Γ_2 orbital state is transformed into Γ_7, whereas the Γ_5 and Γ_4 states are split into Γ_7^* and Γ_8, and Γ_8^* and Γ_6, respectively. The wave functions for these states are

$$\left\{\begin{aligned}
|\Gamma_7^1\rangle &= \sqrt{\tfrac{1}{2}}|\overset{+}{2}\rangle - \sqrt{\tfrac{1}{2}}|-\overset{+}{2}\rangle\\
|\Gamma_7^2\rangle &= \sqrt{\tfrac{1}{2}}|-\bar{2}\rangle - \sqrt{\tfrac{1}{2}}|\bar{2}\rangle
\end{aligned}\right.$$

$$\left\{\begin{aligned}
|\Gamma_7^{*1}\rangle &= \sqrt{\tfrac{1}{6}}|\overset{+}{2}\rangle + \sqrt{\tfrac{1}{6}}|-\overset{+}{2}\rangle\\
&\qquad - \sqrt{\tfrac{5}{12}}|-\bar{1}\rangle + \tfrac{1}{2}|\bar{3}\rangle\\
|\Gamma_7^{*2}\rangle &= \sqrt{\tfrac{1}{6}}|\bar{2}\rangle + \sqrt{\tfrac{1}{6}}|-\bar{2}\rangle\\
&\qquad - \sqrt{\tfrac{5}{12}}|\overset{+}{1}\rangle + \tfrac{1}{2}|-\overset{+}{3}\rangle\\
|\Gamma_8^1\rangle &= \sqrt{\tfrac{1}{3}}|\overset{+}{2}\rangle + \sqrt{\tfrac{1}{3}}|-\overset{+}{2}\rangle\\
&\qquad + \sqrt{\tfrac{5}{24}}|-\bar{1}\rangle - \sqrt{\tfrac{1}{3}}|\bar{3}\rangle\\
|\Gamma_8^2\rangle &= \sqrt{\tfrac{1}{3}}|\bar{2}\rangle + \sqrt{\tfrac{1}{3}}|-\bar{2}\rangle\\
&\qquad + \sqrt{\tfrac{5}{24}}|\overset{+}{1}\rangle - \sqrt{\tfrac{1}{8}}|-\overset{+}{3}\rangle\\
|\Gamma_8^3\rangle &= \sqrt{\tfrac{3}{8}}|\overset{+}{3}\rangle - \sqrt{\tfrac{5}{8}}|-\overset{+}{1}\rangle\\
|\Gamma_8^4\rangle &= \sqrt{\tfrac{3}{8}}|-\bar{3}\rangle - \sqrt{\tfrac{5}{8}}|\bar{1}\rangle
\end{aligned}\right. \tag{1}$$

$$\left\{\begin{aligned}
|\Gamma_6^1\rangle &= \sqrt{\tfrac{1}{3}}|\bar{0}\rangle + \tfrac{1}{2}|-\overset{+}{1}\rangle + \sqrt{\tfrac{5}{12}}|\overset{+}{3}\rangle\\
|\Gamma_6^2\rangle &= \sqrt{\tfrac{1}{3}}|\overset{+}{0}\rangle + \tfrac{1}{2}|\bar{1}\rangle + \sqrt{\tfrac{5}{12}}|-\bar{3}\rangle\\
|\Gamma_8^{*1}\rangle &= \sqrt{\tfrac{3}{8}}|-\bar{1}\rangle + \sqrt{\tfrac{5}{8}}|\bar{3}\rangle\\
|\Gamma_8^{*2}\rangle &= \sqrt{\tfrac{3}{8}}|\overset{+}{1}\rangle + \sqrt{\tfrac{5}{8}}|-\overset{+}{3}\rangle\\
|\Gamma_8^{*3}\rangle &= -\sqrt{\tfrac{2}{3}}|\bar{0}\rangle + \sqrt{\tfrac{1}{8}}|-\overset{+}{1}\rangle + \sqrt{\tfrac{5}{24}}|\overset{+}{3}\rangle\\
|\Gamma_8^{*4}\rangle &= -\sqrt{\tfrac{2}{3}}|\overset{+}{0}\rangle + \sqrt{\tfrac{1}{8}}|\bar{1}\rangle + \sqrt{\tfrac{5}{24}}|-\bar{3}\rangle.
\end{aligned}\right.$$

The ground state Kramers doublet is the Γ_7 state and is coupled to the excited Γ_7^* state, arising from the Γ_5 orbital, by spin–orbit coupling. The Γ_8 state arising from the Γ_5 orbital state is also coupled to the Γ_8^* state arising from the Γ_4 orbital state by the same spin–orbit coupling interaction. The energy matrices for the Γ_7, Γ_8, and Γ_6 are

$$\Gamma_6\colon\ \left|\Delta + \Theta + \tfrac{3}{2}k_{\Gamma_4\Gamma_4}\zeta\right|$$

$$\Gamma_8\colon\ \begin{vmatrix} \Delta + \tfrac{1}{4}k_{\Gamma_5\Gamma_5}\zeta & \tfrac{3}{4}\sqrt{5}k_{\Gamma_4\Gamma_5}\zeta \\ \tfrac{3}{4}\sqrt{5}k_{\Gamma_5\Gamma_5}\zeta & \Delta + \Theta - \tfrac{3}{4}k_{\Gamma_5\Gamma_5}\zeta \end{vmatrix} \tag{2}$$

$$\Gamma_7\colon\ \begin{vmatrix} 0 & \sqrt{3}k_{\Gamma_2\Gamma_5}\zeta \\ \sqrt{3}k_{\Gamma_2\Gamma_5}\zeta & \Delta - \tfrac{1}{2}k_{\Gamma_5\Gamma_5}\zeta \end{vmatrix}.$$

Here ζ is the spin–orbit coupling constant and $k_{\Gamma_i\Gamma_j}$ are the orbital reduction factors. It does not appear profitable to attempt to interpret the experimental data with so many parameters. Therefore, we assume, as Eisenstein and Pryce (*2*) and Hecht *et al.* (*5*) did, that there are only two orbital reduction parameters k and k', which are characteristic of the Γ_5 and Γ_4 states, respectively. This assumption sets $k_{\Gamma_4\Gamma_4} = k'$, $k_{\Gamma_5\Gamma_5} = k$, $k_{\Gamma_2\Gamma_5} = k^{1/2}$, and $k_{\Gamma_4\Gamma_5} = k^{1/2}k'^{1/2}$ in the above energy matrices. Diagonalization of the Γ_7 matrix produces the ground state Γ_7 and the excited state Γ_7', and the corresponding wavefunctions are written as

$$\begin{aligned}
|\Gamma_7\rangle &= \cos\theta|^2F_{5/2}, \Gamma_7\rangle\\
&\qquad - \sin\theta|^2F_{7/2}, \Gamma_7^*\rangle\\
|\Gamma_7' &= \sin\theta|^2F_{5/2}, \Gamma_7\rangle\\
&\qquad + \sin\theta|^2F_{7/2}, \Gamma_7^*\rangle,
\end{aligned} \tag{3}$$

where θ is the parameter describing the admixture of the Γ_7 levels in the ground state with the relation

$$\tan 2\theta = \frac{2\sqrt{3}k\zeta}{\Delta - \tfrac{1}{2}k\zeta}. \tag{4}$$

Similarly, diagonalization of the Γ_8 matrix produces the two levels Γ_8 and Γ_8', and the corresponding wavefunctions are

$$\begin{aligned}
|\Gamma_8\rangle &= \cos\varphi|^2F_{5/2}, \Gamma_8\rangle\\
&\qquad - \sin\varphi|^2F_{7/2}, \Gamma_8^*\rangle\\
|\Gamma_8'\rangle &= \sin\varphi|^2F_{5/2}, \Gamma_8\rangle\\
&\qquad + \cos\varphi|^2F_{7/2}, \Gamma_8^*\rangle,
\end{aligned} \tag{5}$$

where φ is the parameter describing the admixture of the Γ_8 levels in the excited state, and

$$\tan 2\varphi = \frac{\tfrac{3}{2}\sqrt{5kk'}\,\zeta}{\Theta - \dfrac{k + 3k'}{4}\zeta}. \tag{6}$$

The energies for the Γ_7, Γ_8, Γ_7', Γ_8', Γ_6 (in the order of ascending energies) are

$$\begin{aligned}
E(\Gamma_6) &= \Delta + \Theta + \tfrac{3}{2}k'\zeta \\
E(\Gamma_8') &= \Delta + \tfrac{1}{4}\{k + 3\sqrt{5kk'}\cot\varphi\}\zeta \\
E(\Gamma_7') &= \sqrt{3k}\zeta\cot\theta \\
E(\Gamma_8) &= \Delta + \Theta \\
&\qquad - \tfrac{3}{4}\{k' + \sqrt{5kk'}\cot\varphi\}\zeta \\
E(\Gamma_7) &= \Delta - \tfrac{1}{2}\{k + 2\sqrt{3k}\cot\theta\}\zeta.
\end{aligned} \tag{7}$$

The effect of the tetragonal distortion is that the ground state Γ_7 is transformed into Γ_7^t, whereas the excited states are split or transformed according to $\Gamma_8 \rightarrow \Gamma_6^t + \Gamma_7^t$, $\Gamma_7' \rightarrow \Gamma_7^t$, $\Gamma_8' \rightarrow \Gamma_6^t + \Gamma_7^t$, and $\Gamma_6 \rightarrow \Gamma_6^t$ (Fig. 1). This effect introduces three additional terms into the Hamiltonian in addition to the octahedral terms,

$$V_{\text{tet}} = \tau V_2^0 + \gamma V_4^0 + \delta V_6^0. \tag{8}$$

Here τ, γ, and δ are parameters which depend on the radial functions, and V_2^0, V_4^0, and V_6^0 transform like the spherical harmonics of order 2, 4, and 6, respectively. To reduce the number of parameters, and since the τV_2^0 term is expected to be dominant, we take only this term into account, as do Selbin *et al.* (*7*) and Kanellakopulos *et al.* (*1*). The complete energy matrices for the tetragonal Γ_7 and Γ_6, and the corresponding wavefunctions, are

$$\Gamma_7:\ \begin{array}{c|cccc|}
 & \substack{\Gamma_7^1\\ \Gamma_7^2} & \substack{\Gamma_7^{*1}\\ \Gamma_7^{*2}} & \substack{\Gamma_8^1\\ \Gamma_8^2} & \substack{\Gamma_8^{*1}\\ \Gamma_8^{*2}} \\
 & 0 & \sqrt{3k}\zeta & 0 & 0 \\
 & \sqrt{3k}\zeta & \Delta - \tfrac{1}{2}k\zeta & 0 & \sqrt{10}\tau \\
 & 0 & 0 & \Delta + \tfrac{1}{4}k\zeta & \tfrac{3}{4}\sqrt{5kk'}\zeta + \sqrt{5}\tau \\
 & 0 & \sqrt{10}\tau & \tfrac{3}{4}\sqrt{5kk'}\zeta + \sqrt{5}\tau & \Delta + \Theta - \tfrac{3}{4}k'\zeta - 2\tau
\end{array} \tag{9}$$

$$\Gamma_6:\ \begin{array}{c|ccc|}
 & \substack{\Gamma_8^3\\ \Gamma_8^4} & \substack{\Gamma_8^{*3}\\ \Gamma_8^{*4}} & \substack{\Gamma_6^1\\ \Gamma_6^2} \\
 & \Delta + \tfrac{1}{4}k\zeta & \tfrac{3}{4}\sqrt{5kk'}\zeta - \sqrt{5}\tau & \sqrt{10}\tau \\
 & \tfrac{3}{4}\sqrt{5kk'}\zeta - \sqrt{5}\tau & \Delta + \Theta - \tfrac{3}{4}k'\zeta + 2\tau & 2\sqrt{2}\tau \\
 & \sqrt{10}\tau & 2\sqrt{2}\tau & \Delta + \Theta + \tfrac{1}{2}k'\zeta
\end{array}. \tag{10}$$

Now we can calculate the transition energies by diagonalizing the energy matrices, Eqs. (9) and (10). Although the four Γ_7^t doublets interact with each other through this tetragonal crystal-field term, the transition energy between $\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_7^t(\Gamma_7')$ is nearly unaltered (*7*, *8*).

In the present compounds, no magnetic exchange interaction was found down to 4.2 K. In the paramagnetic temperature range, the magnetic susceptibility of the molecule is given by the equation

$$\chi = \frac{N\beta^2 \sum_i [(E_i^{(1)})^2/kT - 2E_i^{(2)}]\exp(-E_i^0/kT)}{\sum_i \exp(-E_i^0/kT)}, \tag{11}$$

where N is the Avogadro's number, β the Bohr magneton, and E_i the energy of the ith energy level, which can be expected as a power series in the magnetic field, H,

$$E_i = E_i^0 + E_i^{(1)}H + E_i^{(2)}H^2 + . \tag{12}$$

Since the separation of levels within the ground state (when the magnetic field is applied) is much smaller and the energy of the next excited state is much larger compared to kT, the susceptibility is expressed by the form (*9*)

$$\chi = \frac{Ng^2\beta^2}{4kT} + \mathrm{TIP}, \qquad (13)$$

where

$$g = 2\langle\Gamma_7|\ell + 2s|\Gamma_7\rangle$$

$$\mathrm{TIP} = 2N\beta^2 \sum_i \frac{|\langle\Gamma_i|\ell + 2s|\Gamma_7\rangle|^2}{E(\Gamma_i) - E(\Gamma_7)}. \qquad (14)$$

When the symmetry of the crystal field is octahedral, the g-value of the ground Γ_7 state is expressed by the following simple equation after diagonalizing energy matrix (*9*):

$$g = 2\cos^2\theta - 4\sqrt{\frac{k}{3}}\sin 2\theta - \tfrac{2}{3}(1 - k)\sin^2\theta. \qquad (15)$$

For the cases of Li_7UO_6 and Li_5PuO_6 in which the octahedral coordination around an actinide ion is tetragonally distorted, the magnetic susceptibility is no longer isotropic, i.e., both g and TIP are anisotropic. Since the wavefunctions of the ground Γ_7 doublets are written as

$$\begin{aligned} |\Gamma_7\rangle &= C_1|\Gamma_7^1\rangle + C_2|\Gamma_7^{*1}\rangle + C_3|\Gamma_8^1\rangle + C_4|\Gamma_8^{*1}\rangle \\ |\bar{\Gamma}_7\rangle &= C_1|\Gamma_7^2\rangle + C_2|\Gamma_7^{*2}\rangle + C_3|\Gamma_8^2\rangle + C_4|\Gamma_8^{*2}\rangle, \end{aligned} \qquad (16)$$

the $g_\parallel$-value is calculated to be

$$\begin{aligned} g_\parallel &= 2\langle\Gamma_7|\ell_z + 2s_z|\Gamma_7\rangle \\ &= 2\Big\{C_1^2 + \tfrac{1}{3}(k - 1)C_2^2 + (\tfrac{1}{6}k + \tfrac{1}{3})C_3^2 \\ &\quad + (\tfrac{3}{2}k' - 1)C_4^2 + \frac{4}{\sqrt{3}}\sqrt{k}C_1C_2 \\ &\quad + 4\sqrt{\tfrac{2}{3}}\,\sqrt{k}C_1C_3 - \frac{\sqrt{2}}{3}(k - 4)C_2C_3 \\ &\quad + \sqrt{10kk'}C_2C_4 - \sqrt{5kk'}C_3C_4\Big\}. \end{aligned} \qquad (17)$$

Here $|\bar{\Gamma}_7\rangle$ is the Kramers conjugate wavefunction for the ground Γ_7 doublet. If we drop the C_3^2, C_4^2, and C_3C_4 terms because $C_3, C_4 \ll C_1, C_2$, $g_\parallel$ is rewritten as

$$\begin{aligned} g_\parallel &= 2\Big\{C_1^2 + 4\sqrt{\frac{k}{3}}C_1C_2 - \tfrac{1}{3}(1 - k)C_2^2\Big\} \\ &\quad + 2\Big\{4\sqrt{\frac{2k}{3}}C_1C_3 - \frac{\sqrt{2}}{3}(k - 4)C_2C_3 \\ &\quad + \sqrt{10kk'}C_2C_4\Big\} = g_0 + 2\gamma, \end{aligned} \qquad (18)$$

where

$$\begin{aligned} g_0 &= 2\Big\{C_1^2 + 4\sqrt{\frac{k}{3}}C_1C_2 - \tfrac{1}{3}(1 - k)C_2^2\Big\} \\ \gamma &= 4\sqrt{\frac{2k}{3}}C_1C_3 - \frac{\sqrt{2}}{3}(k - 4)C_2C_3 \\ &\quad + \sqrt{10kk'}C_2C_4. \end{aligned} \qquad (19)$$

The equation for g_0 corresponds to the one for the ground Γ_7 state of the $5f^1$ electron in an octahedral symmetry (Eq. (15)). For $g_\perp$, we get the similar equation

$$\begin{aligned} g_\perp &= 2\langle\Gamma_7|\ell_x + 2s_x|\bar{\Gamma}_7\rangle \\ &= g_0 - \gamma. \end{aligned} \qquad (20)$$

As predicted, the g-value becomes anisotropic when the crystal field around an actinide ion is tetragonally distorted. Equations (*18*) and (*20*) are the same with those of $g_\parallel$ and $g_\perp$ for which the octahedral coordination is trigonally distorted (*10*). The average g-value, $\bar{g}$, will be calculated as

$$|\bar{g}| = \sqrt{\tfrac{1}{3}g_\parallel^2 + \tfrac{2}{3}g_\perp^2}. \qquad (21)$$

Since the g-values for Cs_2PaCl_6 and NpF_6 were empirically determined to be negative (*11, 12*), the signs of the g-values for the isoelectronic U^{5+}, Np^{6+}, and Pu^{7+} are all assumed to be negative. Since EPR data are not available, we obtain the g-value for the ground Γ_7 state from the temperature-dependent part of the magnetic susceptibility, as shown in Eq. (13).

3. Results and Discussion

3.1. Li_7UO_6

We have to determine the crystal-field parameters Δ and Θ, the spin–orbit coupling constant ζ, the orbital reduction factors k and k', and the tetragonal distortion parameter τ. Since the splitting of the quartet Γ_8' level is not experimentally observed, the degree of tetragonal distortion is considered to be fairly small, which is elucidated by the following energy level calculation. Thus we first determine approximately the crystal-field parameters by assuming octahedral symmetry around the central uranium ion. We can use Eq. (7) to calculate transition energies. The transition energy for $\Gamma_7 \rightarrow \Gamma_7'$ is expressed by

$$\Delta E(\Gamma_7 \rightarrow \Gamma_7') = \frac{2\sqrt{3}k\zeta}{\sin 2\theta}. \tag{22}$$

From Eqs. (15) and (22), for a given value of ζ, the parameters k and θ are determined (i.e., ζ and k are no longer independent). Through Eq. (4), the crystal-field parameter Δ is obtained. From the transition energy for $\Gamma_7 \rightarrow \Gamma_6$, the crystal-field parameter Θ is obtained for a given k' value. Then from Eq. (6), the admixture parameter of the Γ_8 level, φ, is determined. The calculation to get the crystal-field parameters also can be fitted to the energies of the remaining two transitions, $\Gamma_7 \rightarrow \Gamma_8$ and $\Gamma_7 \rightarrow \Gamma_8'$, so there are no independent parameters; i.e., all the crystal-field parameters are determined definitely by this procedure. Next, we took into account the tetragonal distortion effect, which resulted in the splitting of both quartets, Γ_8 and Γ_8', into Kramers doublets, respectively. The experimental results from the optical absorption spectrum show that the Γ_8 state splits into Γ_6^t and Γ_7^t, the energy difference between them is 560 cm^{-1}, whereas the splitting of the Γ_8' state is not observed (*1*) (Table I). By diagonalizing the energy matrices, Eqs. (9) and (10), we obtained the energies for each level. For six transition energies, the parameters were adjusted. Unfortunately, not all the transitions could be fitted. Since the transition $\Gamma_7 \rightarrow \Gamma_8'$ for octahedral symmetry is known to be broad and since this transition is furthermore broadened due to the tetragonal distortion, we have considered the $\Gamma_7 \rightarrow \Gamma_8'$ transition energy to be the least reliable. The transition energies calculated here, and all the crystal-field parameters and the orbital reduction factors, are listed in Tables I and II, respectively. We obtained Δ = 4604 cm^{-1}, Θ = 6600 cm^{-1}, ζ = 1868 cm^{-1}, and τ = 140 cm^{-1}. The spin–orbit coupling constant (ζ = 1868 cm^{-1}) is considered to be a reasonable value for U^{5+} in solids. This magnitude for the spin–orbit coupling constant has been obtained by others (*1, 7, 13, 14*) and the magnitude is intermediate between those of Pa^{4+} and Np^{6+} compounds (*15*).

Since we have already obtained the wavefunctions for the ground doublets and excited states, the magnetic susceptibility of Li_7UO_6 is easily calculated by Eq. (*13*) as

TABLE I

ELECTRONIC TRANSITION ENERGIES

Compound	Assignment	Transition energies (cm^{-1}): Experiment	Transition energies (cm^{-1}): Calculation
Li_7UO_6	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_6)$	15,468	15,475
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_7^t(\Gamma_8')$	13,871	13,264
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_8')$		13,102
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_7^t(\Gamma_7')$	7,439	7,435
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_7^t(\Gamma_8)$	5,972	5,961
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_8)$	5,416	5,409
Ba_3NpO_6	$\Gamma_7 \rightarrow \Gamma_6$	>16,500	19,077
	$\Gamma_7 \rightarrow \Gamma_8'$	>16,500	17,018
	$\Gamma_7 \rightarrow \Gamma_7'$	9,390	9,390
	$\Gamma_7 \rightarrow \Gamma_8$	7,690	7,580
Li_5PuO_6	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_6)$	18,519	18,511
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_7^t(\Gamma_8')$	15,873	15,758
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_8')$	14,350	14,347
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_7^t(\Gamma_7')$	10,256	10,214
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_7^t(\Gamma_8)$	8,818	8,772
	$\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_8)$	6,623	6,632

TABLE II

CRYSTAL-FIELD PARAMETERS AND ORBITAL REDUCTION FACTORS

Compound	ζ (cm^{-1})	Δ (cm^{-1})	Θ (cm^{-1})	τ (cm^{-1})	k	k'
Li_7UO_6	1868	4604	6600	140	1.0	0.8
Ba_3NpO_6	2378	5695	8800	0	1.0	0.6
Li_5PuO_6	2520	6700	5600	480	1.0	0.6

$$\begin{aligned}\chi &= \tfrac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) \\ &= 0.0256/T + 217 \times 10^{-6}.\end{aligned} \tag{23}$$

The magnetic susceptibility of Li_7UO_6 was measured by several groups, and their reciprocal susceptibilities are drawn vs temperature in Fig. 2. However, the results are not consistent. Kemmler-Sack *et al.* (*16*) measured the susceptibilities at 195, 293, and 373 K and found that the susceptibilities did not obey the Curie–Weiss law but may be represented by $\chi = 0.038/T + 300 \times 10^{-6}$. Keller (*6*) and Kanellakopulos *et al.* (*1*) extended the temperature range of the magnetic susceptibility measurements down to 4.2 K, and reported that the susceptibilities are linear vs $1/T$ with TIP = 238×10^{-6}. From their susceptibility data, the temperature dependence of susceptibility may be represented by $\chi = 0.0253/T + 238 \times 10^{-6}$. Miyake *et al.* (*17*) also reported that when the temperature-independent susceptibility is subtracted from the measured susceptibility, the reciprocal susceptibilities are linear vs temperature and the effective magnetic moment of Li_7UO_6 is 0.64 μ_B. Thus, the susceptibilities measured by them would be represented by $\chi = 0.051/T$ + TIP (the TIP value is not given in Ref. (*17*)). From the comparison of the susceptibility equation obtained by calculation, Eq. (23), with those obtained empirically, both the temperature-dependent and -independent parts of the susceptibility equation for the data measured by Kanellakopulos *et al.* are close to those in Eq. (23). On the other hand, the susceptibility data measured by Kemmler-Sack *et al.* and Miyake *et al.* are found to be far from the calculated values (also see Fig. 2). If we add extra TIP = 15×10^{-6} to Eq. (23), the temperature dependence of magnetic susceptibility measured by Kanellakopulos *et al.* can be well reproduced in the whole temperature range. We consider that some reactant impurities contribute to this excess temperature-independent susceptibility. If the U^{4+} ions of overreduced Li_7UO_{6-x} are octahedrally coordinated by six oxygens, the susceptibility would show temperature-independent paramagnetism over a wide temperature range (*3*) and its magnitude should be much larger than the temperature-independent paramagnetic

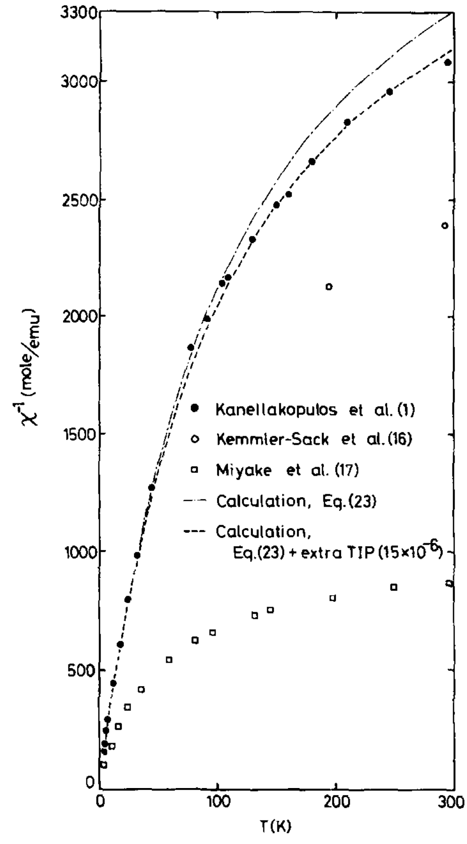

FIG. 2. Reciprocal magnetic susceptibilities of Li_7UO_6 vs temperature.

susceptibility in Eq. (23). Since the temperature-independent part of the susceptibility of UO_2 is large (*18*, *19*), residual UO_2 also would affect the susceptibility of Li_7UO_6.

Miyake *et al.* (*17*) claimed that for pure Li_7UO_6, an EPR spectrum was measured at liquid N_2 temperature. The signal was extremely broad (the linewidth of which was 4000 G) and the *g*-value was ~0.6, although the center of the absorption was obscure. The *g*-value calculated from the temperature-dependent part of the susceptibility ($|g| = 0.52$) is near the value measured by EPR.

3.2. Ba_3NpO_6

Kanellakopulos *et al.* (*1*) measured the optical absorption spectra. Unfortunately, they are not clear. However, it is evident that the absorptions at 7690 and 9390 cm^{-1} correspond to $\Gamma_7 \rightarrow \Gamma_8$ and $\Gamma_7 \rightarrow \Gamma_7'$ transitions, respectively, and that there is no splitting of the Γ_8 quartet state, which is to be expected from the cubic crystal structure of Ba_3NpO_6 (*6*). We do not assign the very weak absorption at 11,760 cm^{-1} and consider that the absorption bands other than the $\Gamma_7 \rightarrow \Gamma_8$ and $\Gamma_7 \rightarrow \Gamma_7'$ transitions lie above 16,500 cm^{-1} (Table I). Since we cannot use many transition energies to determine the crystal-field parameters, we assume the orbital reduction factor *k* is equal to one. The magnetic susceptibilities of Ba_3NpO_6 have been measured by Kanellakopulos *et al.* (*1*, *6*) (Fig. 3) and they are linear vs $1/T$ with TIP = 340×10^{-6} emu/mole. From their susceptibility data, the temperature dependence of the magnetic susceptibility may be represented by $\chi = 0.0279/T + 340 \times 10^{-6}$. Therefore, the ground state *g*-value is calculated to be 0.546. From the transition energies available and the ground state *g*-value, the crystal-field parameters were calculated as shown in Table II. The spin–orbit coupling constant ζ is 2378 cm^{-1}. This value is very close to 2405 cm^{-1} obtained by Eisenstein and Pryce for NpF_6 by assuming $k = 1$ (*2*). Magnetic susceptibilities of Ba_3NpO_6 are calculated and represented by $\chi = 0.0279/T + 155 \times 10^{-6}$. The TIP obtained experimentally is much larger than that calculated. This result suggests that some of the neptunium ions are in the pentavalent state. The electronic configuration of the Np^{5+} ion is $[Rn]5f^2$. If the $5f^2$ ion is octahedrally coordinated by six oxygens, its susceptibility shows a large temperature-independent paramagnetism over a wide temperature range (*3*). The temperature-independent susceptibility needed to obtain a satisfactory fit of the magnetic susceptibility data as a function of temperature is 185 $\times 10^{-6}$ emu/mole.

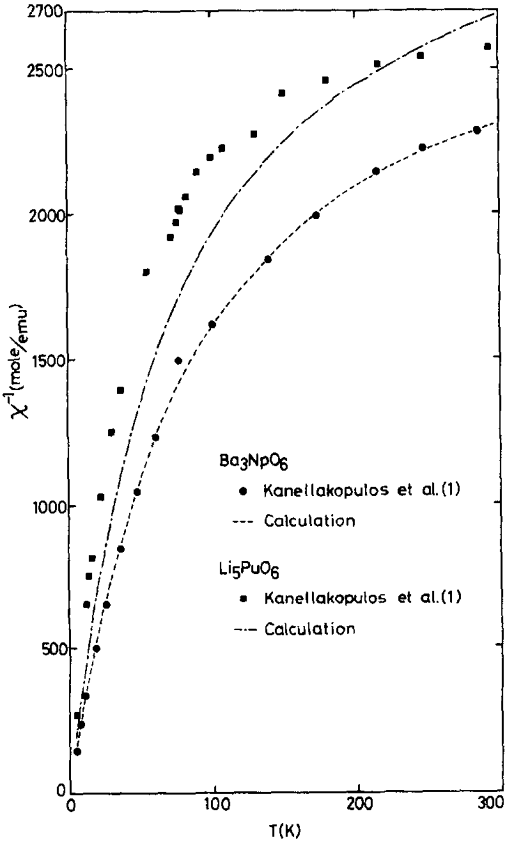

FIG. 3. Reciprocal magnetic susceptibilities of Ba_3NpO_6 and Li_5PuO_6 vs temperature.

3.3. Li_5PuO_6

Li_5PuO_6 crystallizes in a hexagonal structure. This solid compound contains isolated

PuO_6 octahedra (*6*). Kanellakopulos *et al.* (*1*) measured the optical spectra of this compound and reported that the oxygen octahedron is tetragonally distorted. Our calculation model, which indicates that the octahedral crystal-field around the Pu^{7+} ion is a little tetragonally distorted, is based on this result. Kanellakopulos *et al.* have presented the solution spectra measured in 1 *N* $LiOD/D_2O$ as a more reliable spectra than the solid state spectra. Both the Γ_8 and the Γ_8' quartets split greatly due to the tetragonal component of the crystal field around a plutonium ion. Kanellakopulos *et al.* considered that the very weak shoulder absorption at 13,158 cm^{-1} was the transition from Γ_7^t (Γ_7) to $\Gamma_6^t(\Gamma_8')$. If this is the case, the splitting of the Γ_8' quartet is greater than that of the Γ_8 quartet, which contradicts the above-mentioned theoretical consideration that the octahedral coordination around a Pu^{7+} ion is tetragonally distorted. The weak absorptions similar to the one found at 13,158 cm^{-1} are also found at ca. 14,000 and 14,350 cm^{-1}. Considering the $\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_8')$ transition to be the least reliable one, we tried to obtain the crystal-field parameters by fitting the calculations to the other five transitions. The transition energies and crystal-field parameters are listed in Tables I and II, respectively. Table I shows that the transition energies calculated are in good agreement with those obtained experimentally. The transition energy calculated for $\Gamma_7^t(\Gamma_7) \rightarrow \Gamma_6^t(\Gamma_8)$ is 14,350 cm^{-1}, which also has been observed experimentally. The spin–orbit coupling constant calculated for a 5*f* electron of Pu^{7+} is 2520 cm^{-1}, which is larger than the value for Np^{6+}. This trend is constant with the results of the theoretical calculation (*4*). The tetragonal distortion in this compound (τ = 480 cm^{-1}) is much larger than that in Li_7UO_6, as expected from the optical absorption spectra which show the splittings of both quartets Γ_8 and Γ_8' are much larger than those for Li_7UO_6.

From the wavefunctions, the magnetic susceptibility of Li_5PuO_6 is calculated to be $\chi = 0.0218/T + 112 \times 10^{-6}$. Kanellakopulos *et al.* (*1*) measured the magnetic susceptibilities of this compound (Fig. 3) and reported that they are linear vs $1/T$ with TIP = 300×10^{-6}. From their magnetic susceptibility data, the temperature dependence of the magnetic susceptibility may be represented by $\chi = 0.0158/T + 300 \times 10^{-6}$, although this equation is not valid in the whole temperature range. Neither the temperature-dependent nor the temperature-independent part of the susceptibility agrees between experiment and calculation. Even if an extra TIP (188×10^{-6} emu/mole) were added to the susceptibility equation obtained from calculation, it could not reproduce the experimental data (Fig. 3). We believe the reason for this is that some of the Pu^{7+} ions are reduced to the Pu^{6+} state which is much more stable than the Pu^{7+} state. When the Pu^{6+} ion is octahedrally coordinated by six oxygens, its susceptibility shows the large temperature-independent paramagnetism over a wide temperature range (*3*), and if its coordination is tetragonally distorted, the susceptibility becomes temperature-dependent (*20*). The temperature-independent susceptibility obtained experimentally is much larger than that calculated, which is due to the existence of the Pu^{6+} ions in octahedral symmetry. If the number of the Pu^{6+} ions in Li_5PuO_6 were comparable to that of the Np^{5+} ions in Ba_3NpO_6, the TIP value for the former compound should be smaller than that for the latter, because the energy difference between the ground state and the excited state for the former compound is larger than that for the latter. The experimental results show the contrary, i.e., the TIP difference between experiment and calculation for Li_5PuO_6 is comparable to that for Ba_3NpO_6, indicating that the number of $5f^2$ ions in Li_5PuO_6 is much larger than that in Ba_3NpO_6.

The spin–orbit coupling constants obtained for Li_7UO_6, Ba_3NpO_6, and Li_5PuO_6 are all reasonable values for U^{5+}, Np^{6+}, and

Pu^{7+}, and show an increase with atomic number and/or oxidation state, which is consistent with the results of the theoretical calculations (*4*). In this study, we have taken into account the covalency effect in chemical bonding, i.e., introduced the orbital reduction factors in the calculation of energy levels and magnetic susceptibilities. Although the orbital reduction factors determined here (k and k') may not be the unique values for each compound, the results indicate that k' should be much smaller than k, which is consistent with the theoretical view (*2, 5*). To obtain a satisfactory fit of the magnetic susceptibility data as a function of temperature, an added empirical temperature-independent paramagnetic susceptibility was needed for all of the compounds. We suggest the reduced actinide ions with $[Rn]5f^2$ configuration, i.e., U^{4+}, Np^{5+}, and Pu^{6+}, are reasonable for this extra TIP. These ions in an octahedral coordination are known to show a temperature-independent paramagnetism over a wide temperature range. With this hypothesis and from the comparison of the extra TIP between compounds, it was found that a considerable amount of Pu^{6+} ions which are much more stable than Pu^{7+} ions exist in Li_5PuO_6. The crystal-field splitting Δ, which is very sensitive to the magnetic properties of the compounds, increases with atomic number (from U^{5+} to Np^{6+} to Pu^{7+}), as expected.

References

1. B. Kanellakopulos, E. Henrich, C. Keller, F. Baumgärtner, E. König, and V. P. Desai, *Chem. Phys.* **53,** 197 (1980).

2. J. C. Eisenstein and M. H. L. Pryce, *Proc. R. Soc. Ser A* **255,** 181 (1960).

3. N. M. Edelstein and J. Goffart, *in* "The Chemistry of the Actinide Elements" (J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds.), 2nd ed., Chap. 18, Chapman & Hall, London/New York (1986).

4. W. B. Lewis, J. B. Mann, D. A. Liberman, and D. T. Cromer, *J. Chem. Phys.* **53,** 809 (1970).

5. H. G. Hecht, W. B. Lewis, and M. P. Eastman, *Adv. Chem. Phys.* **21,** 351 (1971).

6. C. Keller, *in* "MTP International Review of Science," Vol. 7, "Lanthanides and Actinides" (K. W. Bagnall, Ed.), Series I, p. 47, Butterworths, London (1972).

7. J. Selbin, C. J. Ballhausen, and D. G. Durrett, *Inorg. Chem.* **11,** 510 (1972).

8. Y. Hinatsu and N. Edelstein, submitted for publication.

9. J. H. Van Vleck, "The Theory of Electronic and Magnetic Susceptibilities," Oxford Univ. Press, London (1932).

10. P. Rigny and P. Plurien, *J. Phys. Chem. Solids* **28,** 2589 (1967).

11. J. D. Axe, M. J. Stapleton, and C. D. Jefferies, *Phys. Rev.* **121,** 1630 (1961).

12. C. A. Hutchison, Jr., and B. Weinstock, *J. Chem. Phys.* **32,** 56 (1960).

13. N. Edelstein, D. Brown, and B. Whittaker, *Inorg. Chem.* **13,** 563 (1974).

14. J. Selbin and H. J. Sherrill, *Inorg. Chem.* **13,** 1235 (1974).

15. J. Selbin and J. D. Ortego, *Chem. Rev.* **69,** 657 (1969).

16. S. Kemmler-Sack, E. Stumpp, W. Rüdorff, and H. Erfurth, *Z. Anorg. Allg. Chem.* **292,** 287 (1967).

17. C. Miyake, H. Taniguchi, H. Ohya-Nishiguchi, and S. Imoto, *Phys. Status Solidi A* **74,** 173 (1982).

18. J. K. Dawson and M. W. Lister, *J. Chem. Soc.*, 5041 (1952).

19. S. Nasu, *Jpn. J. Appl. Phys.* **5,** 1001 (1966).

20. T. H. Siddall, III, *in* "Theory and Applications of Molecular Paramagnetism" (E. A. Boudreaux and L. N. Mulay, Eds.), Chap. 6, Wiley–Interscience, New York (1976).