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Semiempirical crystal field calculations for f^N systems IV: Intermediate crystal field effect in $5f^2$ configuration in the $NpO_2Cl_4{}^{3-}$ anion

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Abstract

The crystal field (CF) spectrum of the $5f^2$ configuration of Np(V) in the $NpO_2Cl_4{}^{3-}$ anion was calculated from first principles within the framework of the new many-electron semiempirical method recently developed by us (*Physica Status Solidi B, 169* (1992) 469; *170* (1992) 199). The idealized D_{4h} geometry of the $NpO_2Cl_4{}^{3-}$ anion derived from crystallographic data for $Cs_3NpO_2Cl_4$ and experimental free-ion parameters were used in this calculation. The calculated spectrum is in good agreement with the experimental data. General features of the CF splitting pattern are consistent with a rather intermediate CF effect in the $NpO_2Cl_4{}^{3-}$ anion. The ground electronic state is found to be the $1A_{1g}$ singlet arising from splitting of the lowest $|^3H_4, \pm 4>$ doublet under the influence of the tetragonal component of the CF potential in $NpO_2Cl_4{}^{3-}$. The influence of the energy of splitting Δ on the magnetic properties of $Cs_3NpO_2Cl_4$ is discussed. The calculated splitting energy coincides satisfactorily with the experimental value estimated by analysis of the low-temperature magnetic susceptibility of $Cs_3NpO_2Cl_4$ ($\Delta_{exp} \approx 20$, $\Delta_{calc} = 28$ cm^{-1}).

1. Introduction

The spectroscopic properties of the neptunoyl dioxocation, $NpO_2{}^+$, have been studied extensively both in solids and in solutions. There have been a number of attempts to interpret the electronic spectra of $NpO_2{}^+$ [1–5]. However, to date there has been no satisfactory quantitative interpretation of the crystal field (CF) splitting pattern of the $5f^2$ configuration in $NpO_2{}^+$. The little progress mode in this field may be explained by several reasons, such as lack of single crystals with prominent polarization effects in absorption spectra, the complex vibronic structure of spectra, which makes identification of pure electronic transitions difficult, and problems in theoretical calculations of the level scheme of the $5f^2$ configuration in $NpO_2{}^+$. It is known that there is a specific case of CF pattern in actinyl systems where the magnitude of CF splitting is greater than spin-orbit coupling and is comparable with the Coulomb interaction energy. Thus, energy level calculations in terms of the standard empirical CF model may be unreliable because of the lack of a good initial CF approximation and uncertain assignment of pure electronic transitions.

The aim of this study was to investigate theoretically the CF spectrum of the $5f^2$ configuration of Np(V) in the $NpO_2Cl_4{}^{3-}$ complex anion within the framework of a new many-electron semiempirical method developed recently by us [6, 7]. This method makes it possible to calculate CF energies for f^N configurations of actinide and lanthanide ions in terms of a new many-electron CF formalism from first principles. Earlier we showed that the method gives good results for tetravalent and pentavalent actinide compounds with weak or moderate CF effects [7]. From this point of view, another aim of this paper is to test the validity of this method for f^N systems with strong CF effect, as is the case for the $NpO_2{}^+$ dioxocation.

2. Crystal field calculation procedure

The general CF computation procedure is described in ref. 7. There are two groups of input parameters in the program, corresponding respectively to the $5f^2$ shell of the central ion and to the valence electronic shell of the $NpO_2Cl_4{}^{3-}$ anion. The first group involves free-ion parameters of the $5f^2$ configuration of Np(V) and parametrization of the relativistic $5f_{5/2}$ and $5f_{7/2}$ atomic orbitals of neptunium, while the second involves the geometry of the complex and parameterizations of valent s, p orbitals of ligands and 6d, 7s outer valent orbitals of the central ion.

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The idealized geometry of D_{4h} point symmetry with $R_{Np-O}=1.828$ Å and $R_{Np-Cl}=2.76$ Å was derived for the $NpO_2Cl_4^{3-}$ complex from revised crystallographic data for $Cs_3NpO_2Cl_4$ [8]. Free-ion parameters were taken from the data of Carnall and Crosswhite [9] for the Np^{4+} ion (spin-orbit coupling constant $\zeta=2095$ cm^{-1} and Slater–Condon parameters $F^2=46\,090$, $F^4=42\,000$ and $F^6=27\,180$ cm^{-1}). Parameterizations for the atomic $5f_{5/2}$, $5f_{7/2}$, $6d_{3/2}$, $6d_{5/2}$, and 7s orbitals of neptunium and 2p, 2s orbitals of oxygen were taken from ref. 10, and those for the chlorine 3s and 3p orbitals were taken from refs. 11 and 12. Orbital energies and double-zeta parameters of the radial part of the corresponding orbitals are listed in Table 1. The full basis set containing 91 states was used for diagonalization of the total effective Hamiltonian of the $5f^2$ configuration.

The preliminary calculations result in a divergency in CF energies owing to resonance effects between chlorine 3p (π) orbitals (lying at approximately −13 eV) and neptunium 5f orbitals. The divergency effect was eliminated by a correctional shift of some of the highest occupied molecular orbitals of the $NpO_2Cl_4^{3-}$ complex to the energy of −15 eV. The energies of low-lying levels (below 10 000 cm^{-1}) were found to be insensitive to changes in ligand charges. However, the energies of high-lying levels change considerably with variation of the oxygen charges and change weakly with that of charges on equatorial chlorine atoms in $NpO_2Cl_4^{3-}$ (some energy levels shift to more than 1000 cm^{-1} as the oxygen charge changes from −0.5 to −0.8). Since the relativistic extended Huckel method (REX) [13] used in our CF program as a subroutine poorly reproduces the effective charge on the axial oxygen atoms, we had to input this charge as an empirical parameter. The precise experimental charge on oxygen atoms in NpO_2^+ is not known, so we carried out CF calculations with an empirical charge which was allowed to vary. The best coincidence between calculated CF energies and the experimental 5f–5f transition energies [1] was achieved at the charge value $Q_O=-0.80$ which is in accordance with the available estimations [14, 15], indicating an effective oxygen charge lying within the range −0.5 to −1.0. For the charge on the chlorine atoms, the Mulliken value ($Q_{Cl}=-0.926$) resulting from REX calculations of the valence shell of the $NpO_2Cl_4^{3-}$ complex was assumed.

3. Crystal field spectrum of the $NpO_2Cl_4^{3-}$ complex

Results of calculation of CF energies of the $5f^2$ configuration in $NpO_2Cl_4^{3-}$ are shown in Table 2. Two-electron wavefunctions are presented in the conventional JM-representation (wavefunctions of high-energy levels lying above the last observable level are not shown). It should be noted that the |JM> functions in Table 2 are related to the intermediate coupling scheme (they were calculated by diagonalization of the $5f^2$ shell Hamiltonian without CF terms), not to the LS scheme. The configurational composition of wavefunctions in terms of σ_u, π_u, δ_u and φ_u 5f orbitals is also presented in Table 2 (only the main contributions are shown). One can see that the calculated CF energies are in good agreement with the experimental data for the energies of 5f–5f transitions in the $NpO_2Cl_4^{3-}$ anion in $Cs_3NpO_2Cl_4$ [1].

First, it should be noted that the general character of the CF spectrum in $NpO_2Cl_4^{3-}$ is not compatible with the usual JM-manifold structure of the f^2 configuration because of very strong splitting of 5f levels arising from the influence of the CF potential of axial symmetry. For example, CF splitting for the ground $^3H_4$ manifold exceeds 13 000 cm^{-1} (the highest CF level of the $^3H_4$ manifold corresponds to the $5A_{2g}$ state, see Table 2). We can conclude, therefore, that the CF splitting energy in $NpO_2Cl_4^{3-}$ is larger than the spin-

TABLE 1. Energies and radial functions of atomic orbitals used in CF calculations for the $NpO_2Cl_4^{3-}$ complex

Atom	Orbital	AO energy (cm^{-1})	Double-zeta parameters of radial Slater functions			
			C_1	ζ_1	C_2	ζ_2
Np[a]	$5f_{7/2}$	−9.90	0.594408	5.676028	0.551076	2.839082
	$5f_{5/2}$	−10.80	0.589787	5.814158	0.551561	2.942313
	$6d_{5/2}$	−4.96	0.572180	2.850944	0.584838	1.466449
	$6d_{3/2}$	−5.23	0.576677	2.979870	0.581374	1.528879
	7s	−5.61	0.598932	2.231561	0.522178	1.308015
O[a]	$2p_{3/2}$	−16.75[c]	0.725572	1.627360	0.351630	3.547109
	$2p_{1/2}$	−16.78[c]	0.726163	1.630209	0.351051	3.582122
	2s	−34.08[c]	1	2.225439		
Cl[b]	$3p_{3/2}$	−13.72[c]	0.880909	2.096778	0.190045	0.919955
	$3p_{1/2}$	−13.86[c]	0.879894	2.108155	0.190420	0.930329
	3s	−29.38[c]	1	2.286288		

[a] Ref. 10; [b] ref. 11; [c] ref. 12.

TABLE 2. Energies and wavefunctions of crystal field levels of $5f^2$-configuration of neptunium(V) in $Cs_3NpO_2Cl_4$

State	Energy levels (cm^{-1})		Eigenfunctions	Configurational composition (%)
	Calculated	Experimental [1]		
$1A_{1g}$	0	0	$0.68\{\vert{}^3H_4,4> + \vert{}^3H_4,-4>\} + 0.18\{\vert{}^3H_5,4> - \vert{}^3H_5,-4>\}$	$92[\varphi_u\delta_u]$
$1A_{2g}$	28	20[a]	$0.68\{\vert{}^3H_4,4> - \vert{}^3H_4,-4>\} + 0.18\{\vert{}^3H_5,4> + \vert{}^3H_5,-4>\}$	$92[\varphi_u\delta_u]$
$2A_{1g}$	2578		$0.74\vert{}^3F_2,0> + 0.62\vert{}^3H_4,0> - 0.17\vert{}^3P_0,0> - 0.15\vert{}^3F_4,0>$	$39[\varphi_u^2] + 25[\delta_u^2] + 25[\varphi_u\delta_u]$
$1E_g$	4266		$0.69\vert{}^3F_2,\pm 1> + 0.59\vert{}^3H_4,\pm 1> + 0.29\vert{}^3F_3,\pm 1>$	$61[\varphi_u\delta_u] + 15[\delta_u^2] + 6[\varphi_u^2] + 6[\varphi_u\pi_u]$
$2E_g$	5933	6035	$0.96\vert{}^3H_5,\pm 5> - 0.26\vert{}^3H_6,\pm 5>$	$93[\varphi_u\delta_u]$
$3E_g$	9145	8910	$0.54\vert{}^3H_4,\pm 1> - 0.50\vert{}^3F_3,\pm 1> + 0.34\vert{}^3H_5,\pm 1>$	$40[\varphi_u^2] + 22[\delta_u^2] + 17[\varphi_u\delta_u] + 4[\varphi_u\pi_u]$
$3A_{1g}$	9230	9080	$0.81\vert{}^3F_3,0> - 0.53\vert{}^3H_5,0> + 0.26\vert{}^3P_1,0>$	$93[\varphi_u\delta_u]$
$1B_{1g}$	9961	9758	$0.43\{\vert{}^3F_3,2> - \vert{}^3F_3,-2>\} + 0.28\{\vert{}^3H_4,2> + \vert{}^3H_4,-2>\} - 0.26\{\vert{}^3F_4,2> + \vert{}^3F_4,-2>\} - 0.24\{\vert{}^3H_5,2> - \vert{}^3H_5,-2>\}$	$77[\varphi_u\delta_u] + 12[\varphi_u\pi_u] + 7[\delta_u\pi_u]$
$1B_{2g}$	10043		$0.39\{\vert{}^3F_3,2> + \vert{}^3F_3,-2>\} - 0.28\{\vert{}^3H_5,2> + \vert{}^3H_5,-2>\} - 0.27\{\vert{}^3F_4,2> - \vert{}^3F_4,-2>\} + 0.22\{\vert{}^3H_6,6> + \vert{}^3H_6,-6>\}$	$81[\varphi_u\delta_u] + 10[\varphi_u\pi_u] + 6[\delta_u\pi_u]$
$2B_{2g}$	10477		$-0.65\{\vert{}^3H_6,6> - \vert{}^3H_6,-6>\} + 0.17\{\vert{}^3H_4,2> - \vert{}^3H_4,-2>\}$	$77[\varphi_u\delta_u] + 13[\delta_u^2] + 5[\varphi_u\pi_u]$
$2B_{1g}$	10481		$0.68\{\vert{}^3H_6,6> + \vert{}^3H_6,-6>\} - 0.14\{\vert{}^3H_4,2> + \vert{}^3H_4,-2>\}$	$78[\varphi_u\delta_u] + 14[\varphi_u^2]$
$4E_g$	10589		$0.88\vert{}^3H_4,\pm 3> + 0.25\vert{}^3H_5,\pm 3> - 0.21\vert{}^3F_4,\mp 1>\}$	$71[\varphi_u\pi_u] + 8[\varphi_u\sigma_u] + 7[\delta_u^2] + 3[\delta_u\pi_u]$
$4A_{1g}$	10755	11111	$0.77\vert{}^3F_4,0> - 0.35\vert{}^3H_6,0> - 0.27\vert{}^3F_2,0>$	$64[\varphi_u\delta_u] + 22[\delta_u^2] + 10[\varphi_u^2]$
$3B_{2g}$	12789	12810	$0.60\{\vert{}^3H_4,2> - \vert{}^3H_4,-2>\} + 0.28\{\vert{}^3F_4,2> - \vert{}^3F_4,-2>\}$	$46[\varphi_u\pi_u] + 17[\delta_u\pi_u] + 15[\varphi_u\sigma_u] + 7[\varphi_u\delta_u]$
$5A_{1g}$	13284		$-0.53\{\vert{}^3H_4,0> + 0.46\vert{}^3P_0,0> - 0.28\{\vert{}^3H_5,4> - \vert{}^3H_5,-4>\} - 0.40\vert{}^1D_2,0> + 0.27\vert{}^3F_2,0>$	$30[\varphi_u^2] + 26[\delta_u^2] + 13\text{-}[\delta_u\pi_u] + 11[\varphi_u\pi_u] + 6[\pi_u^2]$
$3B_{1g}$	13633		$0.53\{\vert{}^3H_4,2> + \vert{}^3H_4,-2>\} + 0.33\{\vert{}^3F_4,2> + \vert{}^3F_4,-2>\}$	$56[\varphi_u\pi_u] + 16[\varphi_u\delta_u] + 16[\varphi_u\sigma_u] + 5[\pi_u^2]$
$2A_{2g}$	14862	14931	$-0.54\{\vert{}^3H_5,4> + \vert{}^3H_5,-4>\} + 0.36\{\vert{}^3F_4,4> - \vert{}^3F_4,-4>\}$	$54[\varphi_u\pi_u] + 21[\delta_u^2] + 16[\delta_u\pi_u] + 6[\varphi_u\sigma_u]$
$6A_{1g}$	15175	15278	$0.45\{\vert{}^3H_5,4> - \vert{}^3H_5,-4>\} + 0.36\{\vert{}^3F_4,4> + \vert{}^3F_4,-4>\} + 0.25\vert{}^2D_2,0> - 0.23\vert{}^3P_0,0> + 0.20\vert{}^3H_4,0>$	$34[\varphi_u\pi_u] + 31[\delta_u^2] + 14[\delta_u\pi_u] + 9[\varphi_u^2]$
$4B_{1g}$	15895	15973	$-0.58\{\vert{}^3F_2,2> + \vert{}^3F_2,-2>\} + 0.28\{\vert{}^3H_5,2> - \vert{}^3H_5,-2>\} + 0.22\{\vert{}^3H_4,2> + \vert{}^3H_4,-2>\}$	$81[\delta_u\pi_u] + 9[\varphi_u\pi_u] + 6[\pi_u\sigma_u]$
$4B_{2g}$	16378	16437	$0.59\{\vert{}^3F_2,2> + \vert{}^3F_2,-2>\} + 0.24\{\vert{}^3F_4,2> + \vert{}^3F_4,-2>\}$	$64[\delta_u\pi_u] + 19[\varphi_u\pi_u] + 5[\delta_u\sigma_u] + 3[\varphi_u\sigma_u]$
$5E_g$	16433		$0.55\vert{}^3P_1,\pm 1> + 0.37\vert{}^1D_2,\pm 1> - 0.31\vert{}^1G_4,\pm 1> - 0.30\vert{}^3H_4,\pm 1> + 0.29\vert{}^3H_6,\pm 5> - 0.29\vert{}^3H_5,\pm 1> + 0.24\vert{}^3F_2,\pm 1> - 0.23\vert{}^3H_6,\pm 1>$	$35[\pi_u^2] + 31[\varphi_u\pi_u] + 16[\varphi_u^2] + 4[\varphi_u\delta_u]$
$6E_g$	16572		$0.54\vert{}^3F_4,\pm 1> + 0.47\vert{}^3F_3,\pm 1> - 0.43\vert{}^3H_5,\pm 1> - 0.24\vert{}^1D_2,\pm 1>$	$78[\varphi_u\pi_u] + 11[\varphi_u\delta_u]$
$7A_{1g}$	16690		$0.46\{\vert{}^3F_4,4> + \vert{}^3F_4,-4>\} + 0.31\{\vert{}^3H_5,4> - \vert{}^3H_5,-4>\} + 0.26\{\vert{}^3H_6,4> + \vert{}^3H_6,-4>\} + 0.24\vert{}^1G_4,0> 0.22\vert{}^1D_2,0> + 0.21\{\vert{}^1G_4,4> + \vert{}^1G_4,-4>\}$	$43[\delta_u^2] + 36[\varphi_u\pi_u] + 5[\varphi_u^2]$

(*continued*)

TABLE 2. (*continued*)

State	Energy levels (cm^{-1})		Eigenfunctions	Configurational composition (%)
	Calculated	Experimental [1]		
$3A_{2g}$	16747		$-0.47\{\vert{}^3F_4,4> - \vert{}^3F_4,-4>\} - 0.35\{\vert{}^3G_4,4> - \vert{}^3G_4,-4>\} - 0.29\{\vert{}^3H_6,4> - \vert{}^3H_6,-4>\} - 0.22\{\vert{}^1G_4,4> - \vert{}^1G_4,-4>\}$	$49[\varphi_u\pi_u] + 44[\delta_u^2] + 3[\varphi_u\sigma_4]$
$8A_{1g}$	17435		$-0.69\vert{}^3G_4,0> - 0.36\vert{}^3H_6,0> + 0.29\vert{}^3P_2,0> + 0.26\vert{}^1D_2,0>$	$38[\varphi_u^2] + 34[\delta_u^2] + 9[\varphi_u\pi_u] + 8[\delta_u\pi_u]$
$7E_g$	17646	17830	$0.48\vert{}^3H_4,\pm1> + 0.46\vert{}^1D_2,\pm1> - 0.42\vert{}^3F_2,\pm1> - 0.32\vert{}^3H_6,\pm1> - 0.26\vert{}^1G_4,\pm1> + 0.20\vert{}^1I_6,\pm1>$	$35[\delta_u\pi_u] + 21[\varphi_u\delta_u] + 9[\delta_u\sigma_u] + 5[\varphi_u\pi_u]$
$8E_g$	18096		$0.66\vert{}^3H_5,\pm5> - 0.47\vert{}^1I_6,\pm1> - 0.30\vert{}^3F_2,\pm1> + 0.30\vert{}^3H_4,\pm1>$	$42[\varphi_u\delta_u] + 28[\varphi_u\pi_u]$
$9E_g$	18452	18394	$-0.72\vert{}^3H_5,\pm3> - 0.51\vert{}^3F_4,\pm3> + 0.24\vert{}^1G_4,\pm3> + 0.23\vert{}^3F_3,\pm3>$	$67[\varphi_u\pi_u] + 9[\varphi_u\sigma_u] + 5[\varphi_u\delta_u] + 4[\delta_u\pi_u]$
$5B_{1g}$	18528		$-0.70\{\vert{}^1I_6,6> + \vert{}^1I_6,-6>\}$	$84[\varphi_u^2] + 14[\varphi_u\delta_u]$
$5B_{2g}$	18535		$0.70\{\vert{}^1I_6,6> - \vert{}^1I_6,-6>\}$	$84[\varphi_u^2] + 14[\varphi_u\delta_u]$
$10E_g$	19721		$0.53\vert{}^3F_4,\pm1> - 0.46\vert{}^3P_2,\pm1> - 0.37\vert{}^3F_3,\pm1> 0.26\vert{}^1P_1,\pm1> + 0.22\vert{}^3F_4,\pm1> + 0.20\vert{}^3H_5,\pm1>$	$48[\varphi_u\delta_u]12[\delta_u\pi_u] + 8[\varphi_u\pi_u] + 8[\delta_u^2]$
$11E_g$	20533	20850	$-0.73\vert{}^3F_3,\pm3> - 0.39\vert{}^3H_6,\pm3> - 0.32\vert{}^3H_5,\pm3> + 0.27\vert{}^1G_4,\mp1>$	$52[\delta_u\pi_u] + 11[\pi_u^2] + 8[\varphi_u\pi_u]$
$9A_{1g}$	21854	21480	$-0.78\vert{}^3H_5,0> - 0.49\vert{}^3P_1,0> - 0.35\vert{}^3F_3,0>$	$83[\delta_u\pi_u] + 7[\pi_u\sigma_u] + 6[\varphi_u\delta_u]$
$6B_{1g}$	22423	22309	$-0.55\{\vert{}^3H_5,2> - \vert{}^3H_5,-2>\} - 0.28\{\vert{}^3F_2,2> + \vert{}^3F_2,-2>\}$	$51[\delta_u\pi_u] + 30[\varphi_u\sigma_u] + 6[\pi_u\sigma_u] + 5[\delta_u\sigma_u]$
$10A_{1g}$	22840			
$6B_{2g}$	22849			
$7B_{1g}$	23102			
$7B_{2g}$	23216			
$12E_g$	23497			
$13E_g$	23702			
$11A_{1g}$	24288			
$4A_{2g}$	24290			
$8B_{2g}$	25349			
$8B_{1g}$	26079			
$5A_{2g}$	26121			
$14A_{1g}$	26880			
$15E_g$	27385			
$13A_{1g}$	28514			
$9B_{2g}$	28588			
$9B_{1g}$	29378			
$16E_g$	29575			
$14A_{1g}$	30565			
$6A_{2g}$	30850			
$15A_{1g}$	31031			
$17E_g$	32496			
$18E_g$	32852			
$19E_g$	34185			
$10B_{1g}$	35341			
$10B_{2g}$	35739			
$11B_{1g}$	39327			
$11B_{2g}$	39747			
$16A_{1g}$	40986			
$17A_{1g}$	42149			
$20E_g$	42895			
$12B_{1g}$	46165			
$12B_{2g}$	46428			
$18A_{1g}$	46833			
$21E_g$	47169			
$19A_{1g}$	61997			

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[a] Estimated from data on the low-temperature magnetic susceptibility of $Cs_3NpO_2Cl_4$ [16].

orbit coupling energy and is comparable with the 5f–5f repulsive energy. For this reason there is strong mixing of wavefunctions of different manifolds: in fact, for many CF levels it is meaningless to use the usual ${}^{2S+1}L_J$ labels, *i.e.* the JM structure of the $5f^2$ shell in the $NpO_2Cl_4{}^{3-}$ anion is completely destroyed.

In contrast, it is clearly seen from Table 2 that wavefunctions of many CF levels are represented by mixtures of different two-electron configurations composed of the σ_u, π_u, δ_u and φ_u 5f orbitals. Consequently, the extreme case of the strong CF effect (where every level may be assigned to a single electronic configuration composed of one-electron CF states) does not occur in $NpO_2Cl_4{}^{3-}$. Therefore, the intermediate CF effect takes place in $NpO_2Cl_4{}^{3-}$ (and respectively in $NpO_2{}^+$).

One can see from Table 2 that wavefunctions of low-lying levels (up to 10 000 cm^{-1}) consist mainly of atomic φ_u and δ_u 5f orbitals ($l_z = \pm 3$ and ± 2, respectively). This is due to the non-bonding character of these orbitals with respect to the axial oxygen atoms in the linear dioxocation group and the anti-bonding character of π_u and σ_u 5f orbitals ($l_z = \pm 1$ and 0 respectively). Because of strong CF effect, the π_u and σ_u orbitals lie at a much higher energy level than non-bonding φ_u and δ_u orbitals which have about the same energies. Hence, the CF effect "pushes out" the anti-bonding σ_u and π_u orbitals from the configurational composition of wavefunctions of low-lying levels in $NpO_2{}^+$. Since the electronic density of the φ_u and δ_u orbitals concentrates mainly in the equatorial plane of the $NpO_2Cl_4{}^{3-}$ complex, the energies of these orbitals are less affected by the oxygen charges than those of the σ_u and π_u 5f orbitals whose electronic density concentrates close to the neptunoyl axis. As a consequence, the energies of low-lying CF levels in $NpO_2Cl_4{}^{3-}$ are relatively insensitive to variations in oxygen charge.

The Coulomb contribution to the CF potential was also calculated in order to estimate the role of covalency in the CF effect in the $NpO_2Cl_4{}^{3-}$ anion. Comparing two CF splitting patterns of the $5f^2$ configuration, calculated respectively with and without a covalent contribution, we concluded that covalency dominates the CF effect in the $NpO_2Cl_4{}^{3-}$ anion; the relative covalent contribution is different for different manifolds.

The magnitude of the tetragonal component of the CF potential V_4 arising from four chlorine atoms in the equatorial plane of the $NpO_2Cl_4{}^{3-}$ complex may be evaluated from the splitting energy value of doublet levels with the total angular momentum projection $M = \pm 2$ to the neptunoyl axis. Since the $|J,2>$ and $|J,-2>$ states are directly mixed by the V_4 CF component, the corresponding $|J,\pm 2>$ doublet level splits into two singlet levels, $2^{-1/2}\{|J,2> + |J,-2>\}$ and $2^{-1/2}\{|J,2> + |J,-2>\}$, respectively. The splitting energy ΔE is estimated by

$$\Delta E \approx 2 <J,2|V_4|J,-2> \tag{1}$$

The maximal splitting that is observed for the $|{}^3H_4,\pm 2>$ doublet is about 800 cm^{-1}, the difference in energy between the $3B_{2g}$ and $3B_{1g}$ singlet levels (see Table 2). Therefore, we can estimate

$$V_4 \approx 400\ cm^{-1} \tag{2}$$

i.e. the tetragonal CF component originating from the four equatorial chlorine atoms is much less than the axial CF component ($V_{ax} > 13\,000\ cm^{-1}$) arising from the axial oxygen atoms in the $NpO_2Cl_4{}^{3-}$ complex, and it is comparable in magnitude with CF effects which are usual for trivalent and tetravalent actinide compounds, not containing any dioxocation groups.

These results are in perfect agreement with the well known fact that the CF contribution from the axial oxygen atoms is expected to be much greater than that from the equatorial ligands.

4. Crystal field splitting of the ground electronic state and related magnetic properties of $Cs_3NpO_2Cl_4$

We consider in detail the ground state of the $5f^2$ configuration of the $NpO_2Cl_4{}^{3-}$ anion and related magnetic properties of $Cs_3NpO_2Cl_4$. One can see from Table 2 that the ground state is the $1A_{1g}$ singlet level resulting from splitting of the lowest $|{}^3H_4,\pm 4>$ doublet by the tetragonal CF component V_4. The wavefunction of the ground state is represented by an almost pure [φ_u, δ_u] configuration. The energy of splitting Δ of the $|{}^3H_4,\pm 4>$ doublet into two singlets, $2^{-1/2}\{|{}^3H_4,+4> + |{}^3H_4,-4>\}$ and $2^{-1/2}\{|{}^3H_4,+4> - |{}^3H_4,-4>\}$ respectively, was calculated to be about 28 cm^{-1}. This value is considerably less than the characteristic value $V_4 \approx 400\ cm^{-1}$. It is explained by the fact that the $|{}^3H_4,+4>$ and $|{}^3H_4,-4>$ states are not mixed by the tetragonal CF component directly, but via intermediate excited states with $M = 0$ in the second-order perturbation theory. The main contribution to ground state splitting is found to originate from the first excited singlet level $2A_{1g}$. Thus, the order of magnitude of Δ is given by

$$\Delta \approx \frac{<{}^3H_4,4|V_4|2A_{1g}> <2A_{1g}|V_4|H_4,-4>}{E(|{}^3H_4,\pm 4> \rightarrow |2A_{1g}>)} \tag{3}$$

where the value of the denominator is about the energy of the $2A_{1g}$ level (2578 cm^{-1}, see Table 2). This conclusion is consistent with the experimental data on the low-temperature magnetic susceptibility χ of $Cs_3NpO_2Cl_4$. Karraker and Stone [16] have shown that the magnetic susceptibility (MS) of $Cs_3NpO_2Cl_4$ below 5 K becomes temperature independent while above 20 K it obeys the Curie–Weiss law with $\mu_{eff} = 2.94\mu_B$ and $\theta = +4.5$ K (Fig. 1). This behaviour of MS is related to the above splitting of the $|^3H_4,\pm 4>$ doublet. Taking into the account contributions to MS from the states of the ground doublet only and using the Van Vleck formula, the MS of powdered $Cs_3NpO_2Cl_4$ may be written as

$$\chi(T)=\frac{2M^2}{3\Delta}\,\mathrm{th}(\Delta/2k_BT) \tag{4}$$

where

$M=<{}^3H_4,4|L+2S|{}^3H_4,4>$

At low temperatures $(k_BT\ll\Delta)\chi$ is a constant

$$\chi_0=\frac{2M^2}{3\Delta} \tag{5}$$

while at high temperatures $(k_BT\gg\Delta)$ MS obeys the Curie–Weiss law with $\mu_{eff}=M$

$$\chi(T)=\frac{M^2}{3k_BT} \tag{6}$$

We have found that the experimental temperature dependence of the MS of $Cs_3NpO_2Cl_4$ is reproduced very well by the formula (4) at the splitting energy $\Delta_{exp}\approx 20$ cm^{-1}. This is in satisfactory agreement with the calculated value $\Delta=28$ cm^{-1}.

The calculated effective magnetic moment of the ground $|^2H_4,\pm 4>$ doublet is $3.93\mu_B$. The experimental value $\mu_{eff}=2.94\mu_B$ [16] may be reproduced by taking into account the orbital reduction factor k,

$$M=<{}^3H_4,4|kL+2S|{}^3H_4,4> \tag{7}$$

The calculated value is $k=0.756$. The experimental and calculated temperature variations of the inverse MS of $Cs_3NpO_2Cl_4$ are shown in Fig. 1.

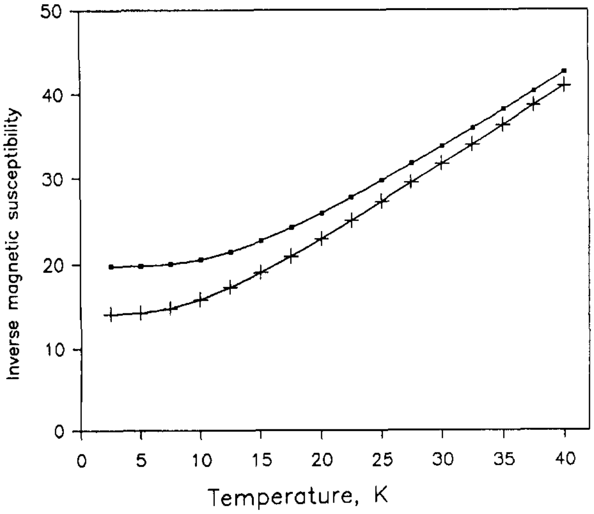

Fig. 1. Calculated (-■-) and experimental [16] (+) variation of the inverse magnetic susceptibility of $Cs_3NpO_2Cl_4$ with temperature.

5. Discussion and conclusion

The above results unambiguously indicate that the semiempirical many-electron method [6, 7] is able to reproduce quantitatively both the CF spectrum and magnetic susceptibility, even for 5f systems with strong CF effect such as the $NpO_2Cl_4{}^{3-}$ anion. We believe that the success of the CF calculations proves the validity of the many-electron CF formalism for many-electron f systems with prominent covalent CF effects.

As far as we know, this CF calculation is the first successful quantitative interpretation of the CF splitting pattern in the $NpO_2{}^+$ dioxocation. However, these results should be considered as preliminary. Further improvement of the agreement between calculated and experimental CF level energies may be achieved by fitting the free-ion parameters and taking into account the higher-order interactions. However, for reliable assignment of electronic f–f transitions in $Cs_3NpO_2Cl_4$, it is highly desirable to have additional experimental information on polarized electronic spectra, the intensity of bands in the absorption spectra, and the Zeeman effect.

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