

Actual and Idealized Crystal Field Parameterizations for the Uranium Ions in UF₄

Z. GAJEK AND J. MULAK

W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, P.O. Box 937, Poland

AND

J. C. KRUPA

Laboratoire de Radiochimie, Institut de Physique Nucléaire, B.P.1, 91406 Orsay, France

Received December 28, 1992; in revised form March 25, 1993; accepted March 26, 1993

The crystal field parameters for the actual coordination symmetries of the uranium ions in UF₄, C₂ and C₁, and for their idealizations to D₂, C_{2v}, D₄, D_{4d}, and the Archimedean antiprism point symmetries are given. They have been calculated by means of both the perturbative ab initio model and the angular overlap model and are referenced to the recent results fitted by Carnall's group. The equivalency of some different sets of parameters has been verified with the standardization procedure. The adequacy of several idealized approaches has been tested by comparison of the corresponding splitting patterns of the ³H₄ ground state. Our results support the parameterization given by Carnall. Furthermore, the parameterization of the crystal field potential and the splitting diagram for the symmetryless uranium ion U(C₁) are given. Having at our disposal the crystal field splittings for the two kinds of uranium ions in UF₄, U(C₂) and U(C₁), we calculate the model plots of the paramagnetic susceptibility $\chi(T)$ and the magnetic entropy associated with the Schottky anomaly $\Delta S(T)$ for UF₄. © 1993 Academic Press, Inc.

1. Introduction

The crystal field effect in the actinide tetrafluorides and especially in UF₄ has eluded effective parameterization for several decades. From the crystallographic data and general characteristics of the absorption spectra of AnF₄, it has been concluded that the degeneracies of the free ion multiplets are completely lifted and that the strength of the effect depends on the position of the fluoride ligand in the spectrochemical series. This corresponds to a splitting on the order of 2000 cm⁻¹ in the case of the ³H₄ ground state of the uranium (4+) ion (1, 2).

The low-temperature paramagnetic behavior and the entropy under the Schottky specific heat anomaly suggest that two

close-lying singlets form the ground state, at least for one type of the uranium ions (3). Despite this analysis, the crystal field patterns of nine singlets originating from the ³H₄ state of the uranium ions remain unknown. Undoubtedly, the exceptionally low coordination symmetries of the uranium ions in this compound have been the main reason for the lack of a crystal field effect interpretation. Of two crystallographic types of uranium ions, one has C₂ symmetry (U(1)) and the second has C₁ symmetry (U(2)), i.e., no symmetry elements at all.

Recently, Carnall *et al.* (4), using results from analysis of the optical spectra of UF₄, NpF₄, and PuF₄ and some theoretical data (5), have achieved effective crystal field fittings within the ground electronic configu-

rations $5f^2$, $5f^3$, and $5f^4$, respectively, and obtained consistent parameterizations of the crystal field potential in these isostructural compounds. Despite the assumption of approximate C_{2v} symmetry, these results are highly reliable and are a good reference for comparison with theoretical values calculated in different models. Unfortunately, the interpretation covers only one-third of the actinide ions (only U(1) ions), although the spectrum of the second type of ion (U(2)) roughly coincides with that for U(1) (4). The most important result of the Carnall interpretation in the case of UF_4 is, apart from the excellent total fitting, the independent confirmation of the pseudodoublet character ($\sim 20 \text{ cm}^{-1}$ gap) of the ground state for one type of uranium ion. Such a pattern was expected, but its disclosure authenticates our explanation of the somewhat mysterious magnetic and heat capacity properties of UF_4 at low temperatures.

In this paper the crystal field parameters for the two types of uranium ions in UF_4 calculated in different models are presented. Two different approaches have been used:

—the perturbative *ab initio* quantum chemical method (6, 7) supplemented by the generalized electrostatic contributions (8), and

—the phenomenological version of the angular overlap model (9, 10).

The calculations have been carried out both for the real coordination symmetries C_1 and C_2 and for several idealized coordinations of D_2 , C_{2v} , D_4 , D_{4d} , and the Archimedean antiprism point symmetry.

Based on the different sets of crystal field parameters, the corresponding energy levels of the ground states, mainly those of 3H_4 origin, are given. This is an instructive test of the adequacy (or inadequacy) of variously idealized models described by a different number of parameters—27 for C_1 , 15 for C_2 , 9 for D_2 and C_{2v} , 5 for D_4 , 3 for D_{4d} , and 2 for the Archimedean antiprism symmetry.

Considering the ambiguity of the crystal field parameterizations in low-symmetry systems, the standardization procedure

given by Rudowicz (11, 12) has been applied.

Finally, the low-temperature paramagnetic susceptibility and the Schottky effect in UF_4 in light of the new crystal field data are briefly discussed.

2. Crystallographic Data and Coordination Symmetry

UF_4 crystallizes in the monoclinic system (13). The unit cell, in the more convenient so-called 1st setting with the z axis unique, has the dimensions $a = 12.73$, $b = 10.75$, $c = 8.43 \text{ \AA}$, and $\gamma = 126^\circ 20'$; space group $C_{2h}^6 - C2/c$. It contains 12 formula units per unit cell (14). UF_4 is isostructural with the whole series of tetrafluorides of Th to Bk (15) as well as with ZrF_4 and HfF_4 (14). It is noteworthy that electron diffraction studies on gaseous UF_4 suggest a C_{2v} symmetry for the molecule with a U–F distance equal to 2.06 \AA (16).

Of the 12 U atoms in the unit cell, four U(1) have C_2 site symmetry, and eight U(2) have C_1 . In both cases the nearest neighborhood of the uranium ion consists of eight fluorine ions arranged in a distorted antiprismatic (D_{4d}) coordination, rather slightly for U(1) (see Table IIa, Fig. 1b) and more seriously for U(2) (see Table IIIb, Fig. 2b).

The exact point group of symmetry of U(1) is the C_2 group with the 2-fold axis directed along the crystallographic c axis (Table Ia, Fig. 1a). The coordinates of the fluorine sites in the initial rectangular coordinate system spanned on the monoclinic unit cell and rotated about the z (c) axis by 39.10° are shown in Table Ia and in Fig. 1a. In this system the coordination polyhedron reveals an approximate D_2 point symmetry (exact 2-fold axis along $z' = z$, two approximate 2-fold axes along the x' and y' directions). The idealized polyhedron may be obtained by averaging the x' , y' , and z' coordinates of the fluorine ligands (1, 2, 7, 8) and (3, 4, 5, 6), respectively (Table Ib). In turn, the rotation around the new y' axis by 90° gives the coordinate system (bis) with

TABLE I

(a) EXACT COORDINATES OF THE U(1) FLUORINE LIGAND IN THE RECTANGULAR SYSTEM ($z \parallel c$) ROTATED IN RELATION TO THE INITIAL (CRYSTALLOGRAPHIC) ONE BY $D(39.10^\circ, 0, 0)$ AND (b) IDEALIZED COORDINATES FOR THE D_2 APPROXIMATION IN THE SAME SYSTEM IN Å, U(1) AT (0, 0, 0)

Ligand number	x'	y'	z'	R
(a)				
1	-1.2729	1.7580	0.9105	2.3537
2	1.2729	-1.7580	0.9105	2.3537
3	-1.2824	0.7439	-1.7211	2.2716
4	1.2824	-0.7439	-1.7211	2.2716
5	-1.1912	-0.6758	1.8232	2.2803
6	1.1912	0.6758	1.8232	2.2803
7	-1.2362	-1.7633	-0.6633	2.2533
8	1.2362	1.7633	-0.6633	2.2533
$\bar{R} = 2.2897$				
(b)				
1	-1.2546	1.7606	0.7869	2.3006
2	1.2546	-1.7606	0.7869	2.3006
3	-1.2368	0.7099	-1.7722	2.2747
4	1.2368	-0.7099	-1.7722	2.2747
5	-1.2368	-0.7099	1.7722	2.2747
6	1.2368	0.7099	1.7722	2.2747
7	-1.2546	-1.7606	-0.7869	2.3006
8	1.2546	1.7606	-0.7869	2.3006
$\bar{R} = 2.2877$				
$(\Delta\mathbf{R}^2)^{1/2} = 0.1037$				
$(\Delta R^2)^{1/2} = 0.0354$				

the z'' axis perpendicular to the c axis and to the plane of Fig. 1b ($x' \rightarrow z''$, $y' \rightarrow y''$, $-z' \rightarrow x''$).

After this transformation, the coordination polyhedron manifests an approximate D_4 or even D_{4d} point symmetry (Fig. 1b). By means of transformation $D(39.10^\circ, 90^\circ, 22.5^\circ)$, where the Euler angles are in parentheses, one may also achieve the system in which the polyhedron in its particular "canonical" position displays approximate C_{2v} point symmetry with the vertical symmetry plane $y'''z'''$ (Table IIa). The idealization requires the averaging of the x''' , y''' , and z'''

coordinates of ligands (1, 3, 5, 7), (2, 8), and (4, 6), respectively (Table IIb).

Assuming the coordination polyhedron to be in the shape of two identical square pyramids of parallel basal planes and twisted one toward the other by an angle α gives a polyhedron of D_4 point symmetry. In the case of U(1) in UF₄, the angle $\alpha \approx 43^\circ$ is close to 45° , as it takes place in the antiprism (D_{4d}). The coordinates of the D_4 polyhedron apexes that differ from those of the D_{4d} antiprism are given in Table IIc in parentheses. The Archimedean antiprism is the extremely idealized U(1) coordination polyhedron (Tables IIa and IIc). This is the twisted cube of the angle $\alpha = 45^\circ$, the height of which is equal to the basal edge.

The adequacy of the given geometrical idealizations is characterized by the mean square deviations of vector \mathbf{R} and scalar R of the apexes of the idealized polyhedrons in relation to the real ones, $(|\Delta\mathbf{R}^2|)^{1/2}$ and $(|\Delta R^2|)^{1/2}$, respectively. The main and common reason for the discrepancies observed in the idealization procedures (Tables I and II, Fig. 1a) is a shift of the uranium ion center by 0.12 Å along the c axis inside the approximate antiprism in relation to its median point. The two basal planes of the antiprism are not strictly parallel and the shift takes place in the direction of their divergence.

The second type of uranium ion, U(2), has no symmetry element at all. There is only an approximate 2-fold axis lying in the xy plane at an angle of $\sim 22.5^\circ$ to the x axis (Fig. 2a). The coordinates of eight ligands of U(2) in the rectangular coordinate system spanned on the crystallographic unit cell and in the system transformed by $D(22.5^\circ, 90^\circ, 17^\circ)$ rotation are presented in Table III. Projections of the coordination polyhedron are shown in Fig. 2. Comparison of the transformed coordinates (Table IIIb) of ligands 1 and 7, 2 and 5, 3 and 4, and 6 and 8 shows the presence of the approximate 2-fold axis. In light of the inadequacy of symmetry idealizations higher than C_{2v} or D_2 in the case of U(1) (4), an analogous approach to U(2)

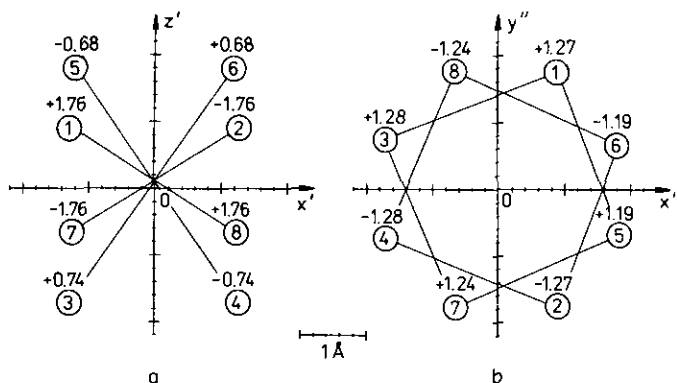


FIG. 1. Projection of the U(1) coordination polyhedron (a) to the $x'z'$ plane of the transformed coordinate system ($D(39.10^\circ, 0, 0)$)—the ligand identification numbers and the y' coordinates (according to Table Ia) are given; (b) to the $x''y''$ plane of the transformed coordinate system ($D(39.10^\circ, 90^\circ, 0)$)—the ligand identification numbers and the z'' coordinates are given.

seems futile. Nevertheless, a roughly approximate coordination antiprism may also be shown for this uranium ion (Fig. 2b). Its approximate 8-fold axis forms in the initial coordinate system the angles $\theta = 73^\circ$ and $\phi = 112.5^\circ$.

3. Crystal Field Parameters

In this work, we follow the standard parameterization of the crystal field potential in tensor notation (17),

$$H_{CF} = \sum_i \sum_{k,q} B_q^k \hat{C}_q^k(\vartheta_i, \phi_i), \quad (1)$$

where i runs over the two $5f$ electrons of the uranium ion and k, q over all effective q components of the spherical tensor operators of rank k .

The B_q^k parameters are, in general, complex,

$$B_q^k = \text{Re } B_q^k + i \text{Im } B_q^k, \quad (2)$$

and from the reality and hermiticity of the potential,

$$\text{Re } B_q^k = \frac{1}{2} (B_q^k + (-1)^q B_{-q}^k) \quad (3)$$

$$\text{Im } B_q^k = \frac{1}{2i} (B_q^k - (-1)^q B_{-q}^k).$$

There are several methods for calculating the crystal field parameters (6–8). In general, they differ in the sets of contributing mechanisms that must be taken into account, as well as in their ways of formulation. One of the generalizations of the naive point charge model which takes into account not only the point charges of the nearest and further neighbors but also their dipole and quadrupole polarizations is the extended electrostatic approach introduced by Faucher and Garcia (8). However, even in the case of markedly ionic compounds, results obtained with this method are far from those expected (8). The essential mechanisms of the metal–ligand interaction that were omitted in the electrostatic model have been taken into account in another approach developed by Newman (6).

The calculations presented are based on a perturbative model (7) derived in a natural way from the general quantum-chemical formulation of the problem (18) which combines both of the above approaches. In this method, in addition to the electrostatic contributions considered by Faucher and Garcia (8) and the space distribution of the electron density effect (Kleiner correction) (19, 20), many other mechanisms are taken into account: the interatomic exchange effect (7); the effects generated by the nonorthogo-

TABLE II

(a) EXACT COORDINATES OF THE U(1) FLUORINE LIGANDS IN THE RECTANGULAR SYSTEM ($z \perp c$) ROTATED IN RELATION TO THE INITIAL (CRYSTALLOGRAPHIC) ONE BY $D(39.10^\circ, 90^\circ, -22.5^\circ)$ AND IDEALIZED COORDINATES FOR (b) C_{2v} , (c) $D_{4d}(D_4)$, AND (d) ARCHIMEDEAN ANTIPRISM APPROXIMATIONS IN THE SAME COORDINATE SYSTEM IN Å, U(1) AT (0, 0, 0)

Ligand number	x'''	y'''	z'''	R
		(a)		
1	1.5140	1.2757	1.2729	2.3537
2	0.1685	-1.9726	-1.2729	2.3537
3	-1.3054	1.3459	1.2824	2.2716
4	-1.8747	-0.0286	-1.2824	2.2716
5	1.4258	-1.3220	1.1912	2.2803
6	1.9430	-0.0734	-1.1912	2.2803
7	-1.2875	-1.3753	1.2362	2.2533
8	0.0620	1.8829	-1.2362	2.2533

$$\bar{R} = 2.2897$$

		(b)		
1	1.3832	1.3297	1.2456	2.2875
2	0	-1.9320	-1.2546	2.3036
3	-1.3832	1.3297	1.2456	2.2875
4	-1.9097	0	-1.2368	2.3036
5	1.3832	-1.3297	1.2456	2.2875
6	1.9097	0	-1.2368	2.3036
7	-1.3832	-1.3297	1.2456	2.2875
8	0	1.9320	1.2546	2.3036

$$\bar{R} = 2.2956$$

$$(\overline{|\Delta R|^2})^{1/2} = 0.1109$$

$$(\overline{|\Delta R|^2})^{1/2} = 0.0395$$

		(c)		
1	1.3584	1.3584	1.2457	2.2897
2	0	-1.9212	-1.2457	2.2897
	(-0.0670)	(-1.9200)		
3	-1.3584	1.3584	1.2457	2.2897
4	-1.9212	0	-1.2457	2.2897
	(-1.9200)	(-0.0670)		
5	1.3584	-1.3584	1.2457	2.2897
6	1.9212	0	-1.2457	2.2897
	(1.9200)	(0.0670)		
7	-1.3584	-1.3584	1.2457	2.2897
8	0	1.9212	-1.2457	2.2897
	(-0.0670)	(1.9200)		

$$\bar{R} = 2.2897$$

$$\left(\overline{|\Delta R|^2} \right)^{1/2} = 0.1127 \quad \left(\overline{|\Delta R|^2} \right)^{1/2} = 0.1084$$

$$\left(\overline{|\Delta R|^2} \right)^{1/2} = 0.0381 \quad \left(\overline{|\Delta R|^2} \right)^{1/2} = 0.0381$$

TABLE II—Continued

Ligand number	x'''	y'''	z'''	R
		(d)		
1	1.3220	1.3220	1.3220	2.2897
2	0	-1.8695	-1.3220	2.2897
3	-1.3220	1.3220	1.3220	2.2897
4	-1.8695	0	-1.3220	2.2897
5	1.3220	-1.3220	1.3220	2.2897
6	1.8695	0	-1.3220	2.2897
7	-1.3220	-1.3220	1.3220	2.2897
8	0	1.8695	-1.3220	2.2897

$$\bar{R} = 2.2897$$

$$(\overline{|\Delta R|^2})^{1/2} = 0.1442$$

$$(\overline{|\Delta R|^2})^{1/2} = 0.0381$$

Note. In part (c) only the different coordinates for the D_4 approximation are given in parentheses.

nality of the central ion and ligand states, i.e., contact covalency or overlap (19), contact shielding (21), and contact polarization (22); and the effects resulting from the main inter- and intraatomic excitations, i.e., the covalency (19) and the shielding (23), respectively. Application of the method has been described previously (7).

The parameters obtained in this way for both U(1) and U(2) ions are presented in Table IV. The calculations for the actual coordination symmetries, C_2 and C_1 for U(1) and U(2), respectively, have been performed in the common coordinate system rotated with respect to the initial system by 39.10° about the crystallographic c axis. In this system the coordination polyhedron of U(1) reveals its approximate D_2 point group symmetry (see Table I).

The results of three different variants of the ab initio calculations of the crystal field parameters for the U(1) ion are presented in Table IV:

—the model values M in which all the above mechanisms have been taken into account except for the polarization effects. The corresponding contributions remain in proportions similar to those from other calculations of this kind (6, 7). Due to the mu-

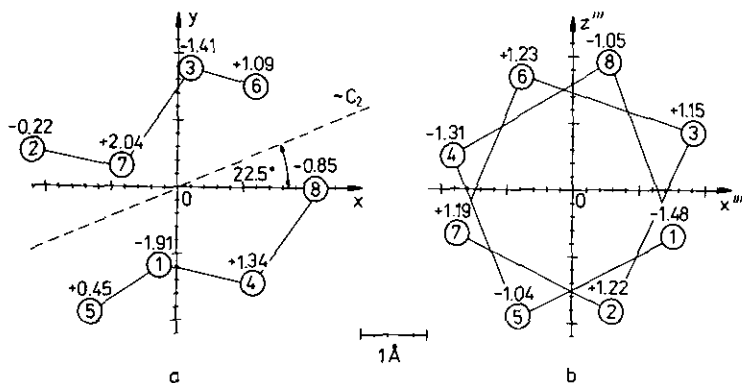


FIG. 2. Projections of the U(2) coordination polyhedron (a) to the xy plane of the initial coordinate system—the ligand identification numbers and the z coordinates (according to Table IIIa) are given and the approximate twofold axis is shown; (b) to the $x''z''$ plane of the transformed coordinate system ($D(22.5^\circ, 90^\circ, 17^\circ)$)—the ligand identification numbers and the y'' coordinates (according to Table IIIb) are given.

TABLE III

(a) EXACT COORDINATES OF THE U(2) FLUORINE LIGANDS IN THE INITIAL RECTANGULAR SYSTEM ($z \parallel c$) AND (b) AFTER ITS ROTATION BY $D(22.5^\circ, 90^\circ, 17^\circ)$ IN Å, U(2) AT (0, 0, 0)

Ligand number	(a)			R
	x	y	z	
1	-0.2626	-1.1497	-1.9146	2.2486
2	-2.1964	0.5480	-0.2172	2.2741
3	0.1800	1.7765	-1.4061	2.2728
4	1.1453	-1.4614	1.3373	2.2882
5	-1.2935	-1.8696	0.4526	2.3181
6	1.2038	1.5260	1.0933	2.2300
7	-0.8458	0.3212	2.0392	2.2310
8	2.0972	-0.0407	-0.8493	2.2630
	$\bar{R} = 2.2657$			
Ligand number	(b)			R
	x''	y''	z''	
1	1.5447	-1.4838	-0.6826	2.2486
2	0.6051	1.2227	-1.8196	2.2741
3	1.8259	1.1464	0.8462	2.2728
4	-1.8057	-1.3139	0.4988	2.2882
5	-0.8002	-1.0437	-1.9106	2.3181
6	-0.7643	1.2296	1.6962	2.2300
7	-1.7651	1.1948	-0.6585	2.2310
8	0.5634	-1.0534	1.9220	2.2630
	$\bar{R} = 2.2657$			

tual cancellation of many of the contributions, the resultant M value comes mainly from the overlap and covalency effects.

—the M values supplemented by the induced dipole contributions, $M + D$.

—the M values supplemented by both the induced dipole and the quadrupole contributions, $M + D + Q$.

The electrostatic contributions have been calculated by the program CHLOE (8, 20, 24). The free ion electronic data have been found by using the ATOM program (25) based on the Dirac-Slater method. In the calculations for the fluorine anion, a stabilizing potential well has been applied. Its depth has been estimated as the mean Madelung potential at a fluorine site in UF_4 , -0.8 a.u., and its radius has been assumed to be equal to the effective ionic radius, 1.3 \AA (26). The dipole and quadrupole polarizability coefficients of the fluorine anion, $\alpha_d = 0.731 \text{ \AA}^3$ and $\alpha_q = 0.631 \text{ \AA}^5$, have been taken from (27). The dipole polarizability of uranium has been estimated by the semiempirical Kirkwood method (28) to be equal to $\alpha_d = 1.5 \text{ \AA}^3$, whereas the quadrupole polarizability coefficient has been assumed to be $\alpha_q = 0.5 \text{ \AA}^5$. The Sternheimer shielding factors have been taken from (29).

The M values have been calculated from the first principles in the purely ab initio

TABLE IV

CRYSTAL FIELD PARAMETERS OF THE U(1) AND U(2) IONS IN UF₄ CALCULATED FOR THE REAL COORDINATION SYMMETRIES IN THE COORDINATE SYSTEM ROTATED IN RELATION TO THE INITIAL SYSTEM ABOUT THE z(c) AXIS BY 39.10°^{a,b}

Parameter $B_q^k = (kq)$	U(1)						U(2)	
	<i>M</i>	<i>M + D</i>	<i>M + D</i> stand	<i>M + D + Q</i>	AOM	exp	<i>M + D</i>	AOM
(20)	1657	1720	-2702	1778	836	1183	1050	526
Re(21)			0				575	251
Im(21)							-484	-160
Re(22)	-838	-760	-295	-891	-366	29	2065	-705
Im(22)	-1272	-1306		-1396	-547		-630	-634
(40)	-3483	-3627	-540	-4792	-2976	-2714	-1453	-924
Re(41)			3949				2990	2498
Im(41)							1419	1290
Re(42)	3546	3635	-5038	4937	2984	3024	-148	-224
Im(42)	1307	1509		1783	982		3082	2567
Re(43)			1027				-687	-627
Im(43)							-4054	-2908
Re(44)	-4480	-4467	566	-6127	-3665	-3791	922	803
Im(44)	1060	1087		1614	784		-2909	-2367
(60)	-1272	-1214	-1817	-2097	-1119	-1433	526	48
Re(61)			-1271				2245	1545
Im(61)							-416	-173
Re(62)	1444	1489	1558	2084	1261	1267	1144	598
Im(62)	-762	-813		-928	-738		-554	-308
Re(63)			-1622				166	-63
Im(63)							-974	-874
Re(64)	-1500	-1477	531	-2256	-1329	-1391	180	113
Im(64)	-133	-26		-241	-117		-55	-5
Re(65)			-642				-1457	-918
Im(65)							935	564
Re(66)	1888	1850	417	2832	1553	1755	-2316	-2377
Im(66)	282	414		383	165		813	9

Note. *M*, main model contributions without polarization effects; *D*, induced dipole contribution; *Q*, induced quadrupole contribution; stand, standardized values—after rotation of the initial coordinate system by *D*(68.97°, 90°, 90°); AOM, phenomenological one-parameter angular overlap model (AOM-I (9) estimation for $e_{\sigma} = 1800 \text{ cm}^{-1}$; exp, Carnall fitting to the U(1) absorption spectrum for *D*₂ idealized coordination symmetry (4).

^a Only for the axial ($q = 0$) and tetragonal ($q = 4$) parameters are the signs determined absolutely.

^b In cm^{-1} .

method, whereas those of *M + D* and *M + D + Q* comprise the polarizability coefficients—empirical macroscopic parameters characteristic of particular ions. Therefore, the approaches are not strictly ab initio. Moreover, in contrast to the quadrupole ones, the dipole polarizabilities are better determined, less lattice dependent, and, in general, much more reliable. What should be noted in comparing the sets of *M*, *M +*

D, and *M + D + Q* parameters is the unexpected role of the quadrupole polarization contributions, especially for the sixth- and fourth-order parameters. From a methodical standpoint, so large a contribution from the quadrupole polarization is even a little striking. One can conclude that switching on the quadrupole part probably leads to overestimated results (a similar feature was observed for some rare earth compounds

(8)) and that the $M + D$ set is the most reliable one.

The above results are compared in Table IV with the parameters estimated within the simple one-parameter version of the angular overlap model (AOM) (9). In this model both the e_σ and e_π parameters are assumed to be simply proportional to the square of the corresponding metal-ligand overlap integrals. The e_δ parameter is neglected. As a consequence, the ratio of e_π/e_σ and the exponents α_σ and α_π in the distance dependencies of e_σ and e_π , respectively, are fixed and the e_σ parameter remains the only free parameter. On the grounds of data gathered for several uranium compounds and their general regularities (9), the e_σ parameter for the U(4+)-F(-) bond should be within the range 1700-1900 cm^{-1} . The values given in Table IV are calculated for $e_\sigma = 1800 \text{ cm}^{-1}$. The remaining fixed parameters are $e_\pi = 625 \text{ cm}^{-1}$, $\alpha_\sigma = 6.78$, and $\alpha_\pi = 7.98$ (9).

It is interesting that this simple AOM estimation turns out to be closer to the experimental values than the theoretical sets including $M + D$ (see Table IV). It is just that the AOM has been applied to simulate the crystal field effect for the idealized coordinations of the U(1) ion considered earlier. On the other hand, using the AOM instead of the $M + D$ model seemed to us to be not so important from the symmetry point of view. In fact, we have verified that the analogous simulation carried out within the $M + D$ model has led to the same conclusions.

Depending on the choice of the main symmetry axis (the z axis) two kinds of symmetry idealizations are possible:

(i) $C_2 \rightarrow D_2$ with the model z axis along the real C_2 axis (Table I) and

(ii) $C_2' \rightarrow C_{2v} \xrightarrow{\quad} D_4 \rightarrow D_{4d} \rightarrow \text{Arch. anti-}$

prism with the main symmetry axis (2-, 4- and $\bar{8}$ -fold respectively) perpendicular to the real C_2 axis (Table II).

It should be noted that the idealization of the C_{2v} type automatically destroys the real C_2 axis lying in the plane perpendicular to the model C_2 axis. Therefore the next step of the idealization is at once D_{4d} symmetry and not D_4 . The crystal field parameters obtained for the coordinations considered here are presented in Table V. In columns C_2 and C_2' , the AOM parameters from Table IV and their transformed set after the $D(0, 90^\circ, 0)$ rotation are given. Their evolution along the idealization process is instructive. The dominant role of parameters that survive the process, i.e., the real ones in the first process and the axial ones in the second, is characteristic. The values of the remaining parameters which vanish for the idealized symmetries can be a measure of deviation of the real coordination symmetry from its idealizations.

A clear agreement between the experimental and the AOM sets in Table V is obvious, given that the symmetry approximation applied by Carnall is of D_2 type and not C_{2v} . Some problem is connected with the B_2^2 parameter. According to the Carnall fitting (4) and his opinion (30), a very small value of B_2^2 is absolutely necessary for obtaining a satisfactory fit. This requirement evidently breaks the ratio B_2^2/B_0^2 , which for the dominating crystal field mechanisms depends only on coordination geometry (9). In addition, as seen in Table IV, no sufficiently strong off-superposition contribution is present (compare the polarization effects). Table V shows that the idealization also does not discriminate the B_2^2 parameter.

For the U(2) ion only the most interesting values, i.e., $M + D$ and AOM, are presented in Table IV. Judging from the U(1) results, the parameters for U(2) should be equally adequate. As expected, they are of the same order as those for U(1). In the coordinate system in which U(1) has an approximate D_2 symmetry, the U(2) parameters are rather uniformly distributed over all k, q values.

TABLE V

EVOLUTION^a OF THE CRYSTAL FIELD PARAMETERS^b OF THE U(1) ION IN UF₄ FOLLOWING THE IDEALIZATION OF ITS COORDINATION SYMMETRY IN THE COORDINATE SYSTEMS (a) ($z \parallel c$) ROTATED IN RELATION TO THE INITIAL SYSTEM BY $D(39.10^\circ, 0, 0)$ ^c AND (b) ($z \perp c$) ROTATED IN RELATION TO THE INITIAL SYSTEM BY $D(39.10^\circ, 90^\circ, -22.5^\circ)$ ^d

Parameter $B_q^k = (kq)$	(a)		exp ^e	(b)				
	C_2	D_2		C_2'	C_{2v}	D_4	D_{4d}	A.a. ^f
(20)	836	952	1183	-866	-873	-876	-873	
Re(21)				209				
Im(21)				-505				
Re(22)	-366	-325	29	232	289			
Im(22)	-547			232				
(40)	-2976	-3224	-2714	-7308	-7264	-7265	-7247	-8013
Re(41)				-148				
Im(41)				357				
Re(42)	2984	2923	3024	173	251			
Im(42)	982			173				
Re(43)				-1105				
Im(43)				458				
Re(44)	-3665	-3584	-3791	0	13	-373		
Im(44)	784			-40				
(60)	-1119	-1010	-1433	3565	3580	3583	3577	2844
Re(61)				-19				
Im(61)				47				
Re(62)	1261	1325	1267	-124	-157			
Im(62)	-738			-124				
Re(63)				-380				
Im(63)				157				
Re(64)	-1329	-1420	-1391	0	11	-351		
Im(64)	-117			-77				
Re(65)				571				
Im(65)				237				
Re(66)	1553	1496	1755	-40	-94			
Im(66)	165			40				

^a Simulation based on the AOM-I.

^b In cm^{-1} .

^c See Table I.

^d See Table II.

^e As in Table IV.

^f Archimedean antiprism.

4. Ambiguous Parameterizations: Standardization of the Low-Symmetry Crystal Field Hamiltonian

In crystallographic systems of lower symmetries: orthorhombic, monoclinic, and triclinic, there is no univocal choice of coordinate system. There may be several apparently different, but in fact equivalent, sets of crystal field parameters. Therefore, the problem of suitable standardization of

the crystal field Hamiltonian arises. An excellent guide in this field are papers on standardization and algebraic symmetry of crystal field Hamiltonians in low-symmetry systems by Rudowicz (11, 12, 31).

The standardization procedure suggested by Rudowicz consists of two steps. In the first, one of the imaginary parameters, namely, $\text{Im } B_2^2$, is removed by appropriate rotation of the coordinate system about the z axis by the angle

$$\phi = \frac{1}{2} \arctan(\text{Im } B_2^2 / \text{Re } B_2^2). \quad (4)$$

The second step is based on a strictly defined transformation of a coordinate system to one of the six possible systems (11), chosen to reduce the ratio of B_2^2/B_0^2 to the range (0, $1/\sqrt{6}$) without changing the number of parameters. The standardization procedure for the orthorhombic and monoclinic systems is in principle the same and gives univocal parameterization. It results from the fact that the orthorhombic parameters transform themselves separately and independently from the monoclinic ones. For the triclinic point groups the ratio can be reduced to the required interval but it is not the unique solution.

In the case of the parameters $M + D$ for U(1) from Table IV, $\phi = 29.87^\circ$ and the new B_2^2 parameter is equal to 1506 cm^{-1} (its sign is immaterial). Hence, the ratio of $B_2^2/B_0^2 = 0.88$; i.e., it lies in the range ($1/\sqrt{6}$, $3/\sqrt{6}$). It denotes that the required transformed system to the range (0, $1/\sqrt{6}$) is S2 in the Rudowicz notation (11). Thus, the second-order parameters after the standardization take the values $B_0^2 = -2702$ and $B_2^2 = -295 \text{ cm}^{-1}$. The fourth- and sixth-orders parameters are transformed similarly according to the conversion relation given in (11, 12). How some actually equivalent parameterizations may apparently differ from each other can be seen by comparing the initial ($M + D$) and standardized ($M + D$ stand) parameters in Table IV.

During the fitting process to any experimental data not all parameters are determinable simultaneously (all but one), and not all the signs of the parameters can be assigned absolutely. For the monoclinic potential, in the case $\text{Im } B_2^2 = 0$, the following information can be determined during fitting (12):

- (i) the magnitudes and the absolute signs of three axial parameters;
- (ii) the magnitudes of 11 (of 12) off-axial parameters, e.g., B_2^2 , $\text{Re}B_q^k$, and $\text{Im}B_q^k$ for $k = 4, 6$ and $q = 2, 4, 6$;
- (iii) the absolute signs of $\text{Re}B_4^4$ and $\text{Re}B_6^6$;
- (iv) the relative signs of $\text{Re}B_2^2$, $\text{Re}B_4^4$, $\text{Re}B_6^6$, and $\text{Re}B_0^2$;

(v) the relative signs of $\text{Im}B_2^4$ and $\text{Im}B_2^6$, as well as $\text{Im}B_4^4$ and $\text{Im}B_4^6$;

(vi) the relative signs of $\text{Im}B_2^4$ and $\text{Im}B_4^4$, as well as $\text{Im}B_4^4$ and $\text{Im}B_6^6$, with respect to the sign of B_2^2 .

The standardization used by Rudowicz has proved the equivalency of many apparently different parameterizations and has demonstrated the incorrectness of some of them, resulting most often from different local minima attained during fitting procedures (11, 12).

The transformation expressions to standardize the crystal field parameters (Table I in Ref. (11) and Table I in Ref. (12)) are formulated for the Stevens operator notation. Therefore, the parameters originating from the tensor notation should be properly transformed (31, 33).

5. Crystal Field Splitting

Based on the crystal field parameters given in Tables IV and V for both real and idealized symmetries and the free ion parameters F^k , ζ_{sf} , α , β , γ , M^k , and P^k used by Carnall *et al.* (4) for U(1) in UF_4 , the simultaneous diagonalization of the standard model Hamiltonian

$$H = \sum_{k=0,2,4,6} F^k f_k + \zeta_{sf} \sum_i \mathbf{l}_i s_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(G_7) + \sum_{k=0,2,4} M^k m_k + \sum_{k=2,4,6} P^k p_k + \sum_{k,q,i} B_q^k C_q^k(i) \quad (5)$$

within the $5f^2$ configuration has been carried out. The operators f_k , \mathbf{l}_i , s_i , $G(G_2)$, $G(G_7)$, m_k , p_k , and C_q^k keep their usual meaning (4, 32). Calculations for C_1 and C_2 crystal fields were performed at Laboratoire des Elements de Transition dans les Solides CNRS, Meudon, Bellevue, France, courtesy of Dr. P. Porcher by means of his newest program BOULI. Calculations for the higher symmetries were performed at Laboratoire de Radiochimie IPN Orsay, France, with the THI program.

The lower portions of the energy spectra corresponding to the $^3\text{H}_4$ manifold splittings

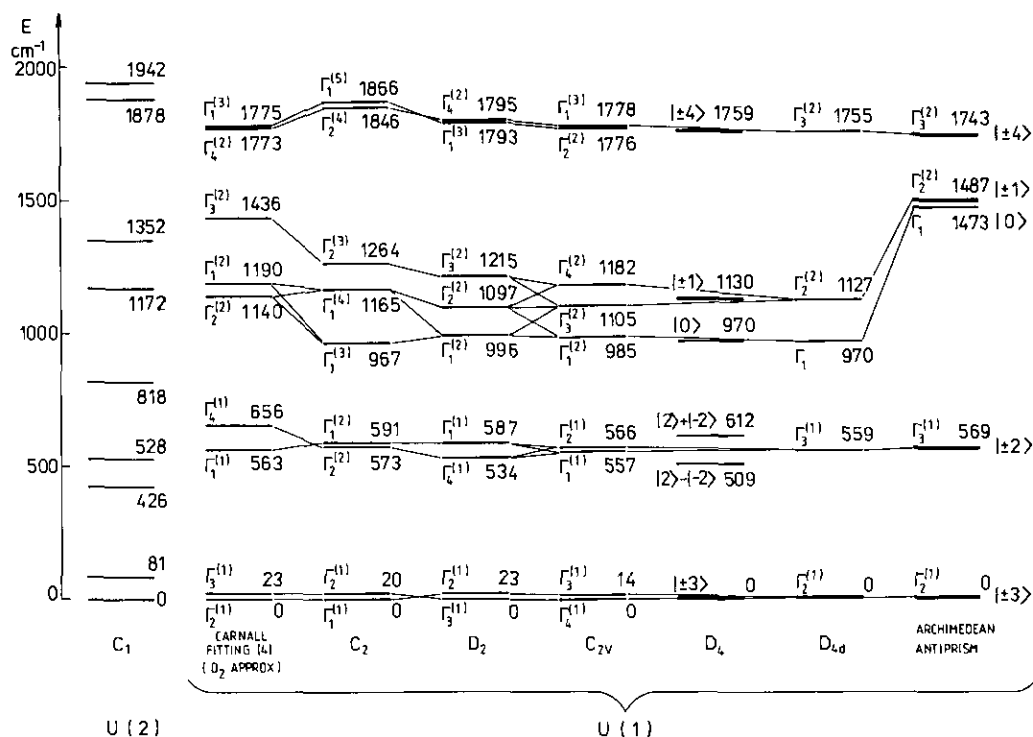


FIG. 3. 3H_4 part of splitting diagrams for U(2) and different approximations of U(1) coordination in UF_4 calculated from the parameters given in Table Vb and VI. Links between the levels reveal their principal genealogy.

are shown in Fig. 3. All patterns including the Carnall fitting diagram are consistent: they reveal a common antiprismatic origin and display a similar total splitting (~ 1800 cm^{-1}). Only the positions of Γ_1 and $\Gamma_2^{(2)}$ levels of $|M_J = 0\rangle$ and $|M_J = \pm 1\rangle$ origin for the Archimedean antiprism symmetry differ distinctly from their lower symmetry counterparts. For the D_2 model pattern which is the best approximation of the experimental one, some downshift of three singlets $\Gamma_1^{(2)}$, $\Gamma_2^{(2)}$, $\Gamma_3^{(2)}$ in D_2 notation, lying between 1000 and 1500 cm^{-1} , by about 150 cm^{-1} and inversion of the sequence in pairs of close lying levels, $\Gamma_3^{(1)} - \Gamma_2^{(1)}$, $\Gamma_4^{(1)} - \Gamma_1^{(1)}$, $\Gamma_1^{(2)} - \Gamma_2^{(2)}$, and $\Gamma_1^{(3)} - \Gamma_4^{(2)}$, should be noted.

As seen in Fig. 3, the doublet of $|M_J = \pm 3\rangle$ origin is the ground state for the $U(4+) - 8F(-)$ antiprismatic coordination.

Similarly, ground states of such origin were previously found in other uranium compounds of $U(4+) - 8O(2-)$ approximately antiprismatic coordinations: $U(SO_4)_2 \cdot 4H_2O$ (34, 35), $U(CH_3COO)_4$ (36), and $U(CH_3COCHCOCH_3)_4$ (34).

The model patterns for U(1) and U(2) are roughly in line, except perhaps for the level at 818 cm^{-1} for U(2) mainly of $|M_J = 0\rangle$ origin. The total splitting in the case of U(2) is somewhat stronger and the antiprismatic character, i.e., the doublet separation, is less pronounced, which is consistent with the smaller mean value of the U-F distance (2.2657 opposed to 2.2897 Å) and lower coordination symmetry.

The coincidence of U(1) and U(2) energy spectra may cause some false assignments of the levels and hence incorrect interpreta-

tion of the optical spectrum. To estimate how the idealization of the coordination symmetry changes the level pattern, the mean square differences of energy of levels $\Delta_{\text{Id.sym}}$ between the idealized $E_i(\text{Id.sym})$ and the real $E_i(C_2)$ symmetries have been calculated by

$$\Delta_{\text{Id.sym}} = \left[\frac{1}{n-1} \sum_{i=2}^n (E_i(\text{Id.sym}) - E_i(C_2))^2 \right]^{1/2}, \quad (6)$$

where n is the number of levels ($(1_2^4) = 91$). Since the energy is measured from the ground singlet, $i = 1$ is excluded. For the ${}^3\text{H}_4$ part of the spectrum, it yields

$$\Delta_{D_2} = 47 \text{ cm}^{-1}, \quad \Delta_{C_{2v}} = 55 \text{ cm}^{-1},$$

$$\Delta_{D_4} = 70 \text{ cm}^{-1}, \quad \Delta_{D_{4d}} = 73 \text{ cm}^{-1}, \quad \text{and}$$

$$\Delta_{\text{Arch.ant}} = 233 \text{ cm}^{-1}.$$

We strongly believe that the numbers are representative of the whole spectrum of the $5f^2$ configuration.

The accuracy of the successive idealizations measured by $\Delta_{\text{Id.sym}}$ is consistently correlated with $(|\Delta\mathbf{R}|^2)^{1/2}$, the mean square deviations of vector \mathbf{R} of the apexes of the idealized coordination polyhedrons in relation to the real ones (Tables I and II). The best approximation is that of D_2 symmetry, whereas the Archimedean antiprism idealization differs markedly from the others.

By analogy, the mean square difference between the energies of the corresponding levels of U(1) and U(2) ions can be found. Taking in both cases the real symmetries C_2 and C_1 , respectively (the third and first patterns in Fig. 3), one obtains $\Delta_{\text{U(1)-U(2)}} = 91 \text{ cm}^{-1}$. This value is comparable with $\Delta_{D_{4d}}$, which means that the error resulting from the D_{4d} idealization is of the same order as that resulting from replacing the U(1) pattern with the U(2) one. For comparison, the mean standard deviation of

TABLE VI

EIGENFUNCTIONS^{a,b} AND ENERGIES OF THE FOUR LOWEST SINGLETS OF URANIUM IONS IN UF_4 : (a) U(1), (b) U(2), AND (c) U(1) ACCORDING TO CARNALL (4, 30)

Energy (cm ⁻¹)	Main components
	(a)
0	0.612 514 ± 2), 0.251 514 ± 4)
20	0.512 514 ± 3), 0.434 514 ± 1)
573	0.624 514 ± 3), 0.218 404 ± 3)
591	0.490 514 ± 4), 0.417 5140)
	(b)
0	0.390 514 ± 2), 0.333 514 ± 3)
81	0.401 514 ± 3), 0.382 5140)
426	0.562 514 ± 1), 0.205 514 ± 2)
528	0.442 514 ± 4), 0.338 514 ± 3)
	(c)
0	0.594 514 ± 2), 0.313 514 ± 4)
23	0.536 514 ± 3), 0.403 514 ± 1)
563	0.559 514 ± 4), 0.289 5140)
656	0.628 514 ± 3), 0.227 404 ± 3)

^a Functions are given in $|LSJM_J\rangle$ notation.

^b The absolute values of the coefficients of only the three or four top components are presented.

the Carnall fitting (calculated from $\sigma = 31 \text{ cm}^{-1}$) is 29 cm^{-1} and is smaller than $\Delta_{D_2} = 47 \text{ cm}^{-1}$, i.e., smaller than the error induced by the idealization of symmetry (!). This fact again suggests the possibility of a "mixed" assignment. Some sets of levels originating from both the U(1) and U(2) ions may better fit the D_2 model than the purely U(1) sets.

The calculated eigenfunctions and eigenenergies of the four lowest singlets of U(1) and U(2) ions in UF_4 for the real coordination symmetry, C_2 and C_1 , respectively, are given in Table VI. Figure 3 and Table VI are good illustrations of the adequacy and usefulness of different symmetry approximations for describing the electronic eigenstates of uranium ions in UF_4 . As can be seen, the idealizations to higher symmetries, especially to D_4 , D_{4d} , and the Archimedean antiprism, are not acceptable when details of the crystal field splitting are essential, as in the case of magnetic or heat capacity properties.

TABLE VII
MOLAR PARAMAGNETIC SUSCEPTIBILITY OF UF₄ UP TO 300 K IN
emu/mol × 10⁶

T	Calculated for			Experimental estimated from (3)
	U(1)	U(2)	$\frac{1}{3}U(1) + \frac{2}{3}U(2)$	
0	48,680	12,090	24,290	24,000
5	48,390	12,090	24,190	21,600
10	43,750	12,090	22,640	17,200
20	30,640	12,030	18,230	12,400
30	22,490	11,650	15,260	
50	14,540	10,170	11,630	
100	7940	6940	7280	6400
150	5660	5240	5380	
200	4480	4240	4320	4200
250	3750	3590	3640	
300	3240	3120	3160	3200

6. Low-Temperature Paramagnetic Susceptibility and the Schottky Effect in Light of the New Crystal Field Data

Having at our disposal the splitting diagrams and the corresponding eigenfunctions for both U(1) and U(2) ions and applying Van Vleck's formula, we can calculate the weighted value (in the ratio 1 : 2) of the paramagnetic susceptibility of UF₄ for any crystallographic direction and within any temperature range. Our calculations relative to powdered material were carried out for all singlets lying below 1000 cm⁻¹, and the high-frequency contributions coming from all those lying below 5000 cm⁻¹ were taken into account. The program BOULI given by Porcher was used.

The calculated susceptibilities together with estimated experimental values (3) are presented in Table VII and Fig. 4. As can be seen, a satisfactory consistency between the calculated and the measured susceptibilities has been obtained. Some discrepancies at low temperatures result from relatively small differences in theoretical and actual energy gaps between the lowest levels.

UF₄ is distinguished by the very short range of temperature-independent paramagnetism (~5 K) and simultaneously a rather

large Curie constant, $C = 1.36$ (37) and 1.18 (38), and Weiss constant, $\theta \approx 100$ K (37, 38). This is an atypical feature for the non-Kramers ion in a low-symmetry crystal field and has been the main problem in interpreting the magnetic properties of the compound. The reason for this is that at the

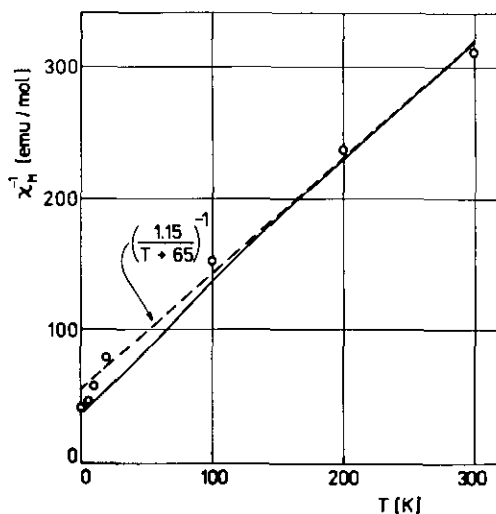


FIG. 4. Calculated χ_M^{-1} versus T plot for UF₄ in the range 0–300 K: (O) estimated experimental values (3); (---) high-temperature Curie-Weiss approximation of the theoretical plot.

TABLE VIII
MOLAR MAGNETIC ENTROPY OF UF₄ ASSOCIATED WITH THE SCHOTTKY
ANOMALY UP TO 300 K, IN R

T	Calculated for			Experimental (39)
	U(1)	U(2)	$\frac{1}{3}U(1) + \frac{2}{3}U(2)$	
10	0.220	0.000	0.073	
20	0.497	0.021	0.180	~0.20
30	0.595	0.100	0.265	
50	0.655	0.301	0.419	
100	0.686	0.565	0.605	
150	0.716	0.707	0.710	
200	0.775	0.842	0.819	
250	0.848	0.966	0.927	
300	0.923	1.072	1.023	~1.10

lowest temperatures the relative contribution of the more abundant species of uranium is distinctly small and only at higher temperatures does it become proportional to its abundance.

In turn, the temperature dependence of the heat capacity shows that the two lowest singlets of U(1) are distant from 15.4 K (10.7 cm⁻¹) (39). The magnetic entropy associated with the Schottky specific heat anomaly was found to be approximately $\frac{1}{3}R \ln 2 = 0.2310R$ at 20 K, i.e., as expected for a two-level system in the U(1) ion, and on the order of $R \ln 3 = 1.0986R$ at 300 K, as expected for an effective population of three singlets (3, 39).

The magnetic entropy associated with the Schottky anomaly for a system of singlets may be expressed in the form

$$\Delta S(T) = R \ln \sum_i \exp(-\delta_i/T) + \frac{R \sum_i \delta_i \exp(-\delta_i/T)}{T \sum_i \exp(-\delta_i/T)}, \quad (7)$$

where i runs over all singlets taken into account, including the ground state for which $\delta_1 = 0$; δ_i are given in K.

The weighted average changes in the entropy for both types of uranium ions, U(1) and U(2),

$$\Delta S = \frac{1}{3}\Delta S(1) + \frac{2}{3}\Delta S(2), \quad (8)$$

calculated in the range 0–300 K for the four lowest singlets of U(1) and the lowest five of U(2) (see Fig. 3) are presented in Table VIII. As can be seen, the calculated ΔS values correspond fairly well to the data given by Burns *et al.* in 1960 (39). Thus, the interpretation of the magnetic and heat capacity properties of UF₄ proposed by Leask, Osborn, and Wolf in 1961 (3) is still up to date and has been independently confirmed in this paper.

Acknowledgments

The authors are grateful to Dr. W. T. Carnall for encouraging inspiration and for sending his unpublished results. We thank Dr. P. Porcher for the low-symmetry diagonalization and paramagnetic susceptibility calculations.

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