

Crystal Field Parameters in USiO₄ from Temperature Dependence of Paramagnetic Susceptibility

J. MULAK

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Pl. Katedralny 1, P.O.B. 937, 50-950 Wrocław, Poland

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Based on the experimentally determined temperature dependence of the paramagnetic susceptibility of tetragonal USiO₄ within the temperature range 2–500°K, the crystal field parameters of D_{2d} symmetry have been estimated (in cm⁻¹): $B_2^0 = -24$, $B_4^0 = -1.25$, $B_4^4 = -12.8$, $B_6^0 = -0.031$, $B_6^4 = 0.51$, and $B_4^4/B_6^4 \approx -25$. The Γ_5 doublet with the approximate composition: $0.78|\pm 1\rangle + 0.63|\mp 3\rangle$ is the ground level of the U⁴⁺ ion. Singlet Γ_1 lying ca. 100 cm⁻¹ above is the first excited level. The total splitting of the ³H₄ term of the U⁴⁺ ion was estimated to be equal to ca. 7500 cm⁻¹.

Introduction

An approximate ab initio calculation of the crystal field parameters is possible for a few compounds whose crystal structure and electronic structure of component ions are known in sufficient detail (1). On the other hand, these parameters can be found by experimental methods by the determination of energy levels of ions, the terms of which are split in the crystal field. One of these methods, involving the ground state of a paramagnetic ion, is based on the analysis of the temperature dependence of its paramagnetic susceptibility.

Formerly we applied this method to a series of uranium(4+) compounds qualitatively or semiquantitatively at most (2–6). In the present paper, uranium orthosilicate, USiO₄, a true paramagnet of strictly tetragonal coordination of uranium by oxygen anions, was selected as the subject of this investigation.

The analysis is based on simplifying assumptions that J is a good quantum number, ³H₄ is the correct ground term of the uranium (4+) ion, and that the crystal field potential may be defined by five independent para-

eters. Such assumptions allow one to estimate the values of the crystal field parameters only approximately. The simultaneous diagonalization of the spin-orbit and crystal-field interactions or J -mixing approaches improve only slightly corresponding eigenfunctions and eigenvalues. The effective values of the crystal field parameters depend also on additional effects such as covalency, overlapping, exchange interactions, etc., which cannot be taken into account within the basis of central-ion eigenfunctions only. However, these contributions can be parameterized in the same way as the electrostatic potential of central-ion surroundings (1). The estimation of the effective crystal field parameters of the uranium(4+) ion in USiO₄ has been carried out in this work.

Uranium orthosilicate is found in nature as coffinite, a black mineral, probably of hydrothermal origin, and in the form of alkaline orthosilicate U(SiO₄)_{1-x}(OH)_{4x}. USiO₄, isomorphous with zircon, thorite, and uranothorite, crystallizes in the D_{4h}^{19} ($I4_1/amd$) space group of the tetragonal system. The unit cell contains four molecules of the compound. The lattice constants and para-

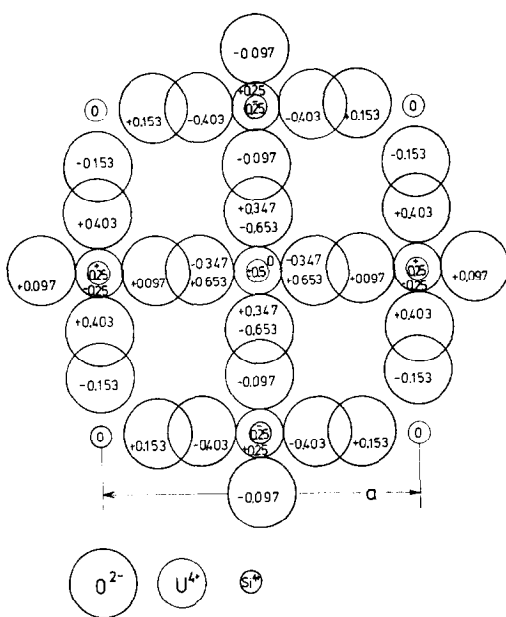


FIG. 1. Uranium(4+) ion surroundings in the USiO_4 crystal lattice. All ions contained within the sphere of the radius of 5 Å are presented (32 O^{2-} , 10 Si^{4+} and 4 U^{4+}). Numbers within the circles are z coordinates in the fractions of the lattice constant c .

meters of the oxygen ion sites are (7): $a = 6.995 \pm 0.004$ Å, $c = 6.263 \pm 0.005$ Å, $u = 0.180 \pm 0.010$, $v = 0.347 \pm 0.010$. For isomorphous ZrSiO_4 , $u = 0.20$ and $v = 0.34$. A larger value of the u parameter in USiO_4 crystal lattice would correspond to a shorter U–O distance within the nearest coordination tetrahedron of the uranium (4+) ion. The scheme of the uranium (4+) ion neighborhood in the USiO_4 crystal lattice is shown in Fig. 1. The symmetry of the uranium(4+) ion surroundings is strictly tetragonal regardless of the values of both u and v parameters. This is typical for orthosilicates. The shortest interionic distances are as follows: U–O = 2.32 Å, U–4O = 2.51 Å, U–2Si = 3.13 Å, U–4U = 3.83 Å and Si–4O = 1.58 Å. The U–O distance in USiO_4 is comparable with those in cubic UO_2 (2.36 Å) and antiprismatic $\text{U}(\text{CH}_3\text{COCHCOCH}_3)_4$ (2.32 Å) coordination polyhedra.

Experimental

USiO_4 was prepared in the form of a gray-bluish microcrystalline powder by means of a hydrothermal reaction from the solution containing equimolar quantities of UCl_4 and Na_2SiO_3 (5 mmole each) at pH 8.3 (NaHCO_3 buffer) in the presence of excess finely powdered vitreous silica. Reagents of analytical degree of purity (p.a.) were used. The reaction was carried out within a glass container inside a stainless steel bomb lined with Teflon at 200–250°C (which corresponds to a pressure of 15–40 atm) for 24–120 hr (7, 8). All operations were performed in an argon atmosphere to prevent oxidation of uranium (4+). After the drying of the product, residual water was removed at 400°C under vacuum. The compound is stable in air but in its finely divided form adsorbs considerable quantities of gases and vapors. At temperatures above 500°C it decomposes into UO_2 and SiO_2 . The content of uranium and SiO_2 were found by chemical analysis (uranium determined as $(\text{UO}_2)_2\text{P}_2\text{O}_7$). The sample used in the magnetic measurements consisted of 80.5% of USiO_4 with the balance of unreacted SiO_2 .

X-ray powder diagrams of USiO_4 were taken with an X-ray diffractometer of the DRON-1.5 type and a Guinier camera. The following values of the lattice constants were obtained: $a = 6.986 \pm 0.002$ Å and $c = 6.268 \pm 0.002$ Å. (hkl) indexes of stronger and characteristic reflections are: (101), (200), (112), and (321). The X-ray diagrams contained no undefined reflections.

The measurements of the paramagnetic susceptibility of USiO_4 over the temperature range 2–500°K were carried out by the Faraday method at a field of 5 kOe using automatic Cahn balance continuous recording. In addition, the dependence of magnetic susceptibility on temperature in the range 4.2–273°K at 50 kOe and the dependence of molar magnetization of USiO_4 on magnetic field intensity in the range 0–50 kOe at 4.2°K were measured by means of a vibrating magnetometer of the PAR-150A type. In the text and figures, only the molar magnetic susceptibility is specified. A molar correction for diamagnetism of USiO_4 equal to $-87 \cdot 10^{-6}$ was assumed.

Basic Formalism

Eigenfunctions and Eigenvalues of Energy Levels of the ³H₄ Term in the Tetragonal Crystal Field of D_{2d} Symmetry

For the complete description of a tetragonal crystal field, it is necessary and sufficient to know 5 or 7 independent parameters according to the point group symmetry of the central ion. For four of seven-point groups of the tetragonal system (D_{2d} , C_{4v} , D_4 and D_{4h}) five real parameters are needed, connected with symmetrical superpositions of spherical harmonics. For the remaining three groups (S_4 , C_4 and C_{4h}), seven parameters including two imaginary ones, connected with antisymmetrical superpositions of tetragonal spherical harmonics, have to be introduced. Our considerations on the potential of D_{2d} symmetry apply to three remaining five-parameter potentials as well. The similar approach for the seven-parameter potentials needs some generalizations due to substantial differences resulting from lack of two-dimensional representations. One should add for sake of exactness that the complete potential of D_{2d} symmetry contains also two antisymmetrical superpositions of spherical harmonics, $1/i(2^{1/2})(Y_3^{2+}-Y_3^{2-})$ and $1/i(2^{1/2})(Y_5^{2+}-Y_5^{2-})$, with imaginary parameters, but they represent the terms of odd degrees and are ineffective except for some configuration interactions.

Consequently, the Hamiltonian of the crystal field of D_{2d} symmetry may in general be expressed in the form:

$$\mathcal{H} = B_2^0 \hat{O}_2^0 + B_4^0 \hat{O}_4^0 + B_4^4 \hat{O}_4^4 + B_6^0 \hat{O}_6^0 + B_6^4 \hat{O}_6^4 \quad (1)$$

where O_k^q 's are the Stevens operators and B_k^q 's are the real parameters with dimension of energy, expressed by: $B_2^0 = A_2^0 \langle r^2 \rangle \alpha$, $B_4^0 = A_4^0 \langle r^4 \rangle \beta$, $B_4^4 = A_4^4 \langle r^4 \rangle \beta$, $B_6^0 = A_6^0 \langle r^6 \rangle \gamma$ and $B_6^4 = A_6^4 \langle r^6 \rangle \gamma$. The A_k^q coefficients are determined by the geometry of the central ion surroundings, $\langle r^k \rangle$ is the mean k th power of the radius of unpaired electrons of the central ion and α , β , and γ are the multiplying factors. The B_k^q parameters defined in the above way should not be confused with the $B_q^{(k)}$ para-

eters coming from expansion of the potential into tensor operators $C_q^{(k)}$, which are related to the $A_q^{(k)}$ parameters otherwise (9).

The tetragonal parameters of the potential (see Eq. (1)) have undefined signs, which means that they may simultaneously be multiplied by -1 without change of the physical sense of the described potential. This corresponds to rotation of the coordinate system around the z axis (axis of quantization) by $\pi/4$.

The potential (Eq. (1)) splits the ninefold degenerate 3H_4 term into two doublets (Γ_5) and five singlets ($2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$). In terms of group theory, this corresponds to reduction of the ninth order matrix to three submatrices (including two identical ones) of second order and one of third order. The eigenfunctions of the seven resultant levels, in $|J_z\rangle$ notation, and their energies, are given in Table I. Bethe symbols of the states are chosen according to the coordinate system with x and y axes lying in the σ_d planes (along the edges of the unit cell of USiO₄).

If the ratios of β/α and γ/ϵ (compositions of the Γ_5 and Γ_1 states) are known, the energies of all the levels are given in the form of linear functions of five crystal field parameters. Of the seven expressions given for the energy levels and the 21 possible equations for energy gaps between different levels, only five are linearly independent. They form a Cramer system of equations, the solution of which gives explicit values of the five crystal field parameters. This means that, knowing the scheme of crystal field splitting (or of its sufficiently large part), one is able to calculate or at least estimate the actual values of the parameters. However, not all arrangements of the levels can occur, particularly, as the coexistence of three ground states of three component submatrices ($\Gamma_5^{(1)}$, $\Gamma_1^{(1)}$ and the lower of the couple Γ_3 , Γ_4) is concerned. Wave functions of these levels are well-known superpositions of the $|J_z\rangle$ functions: $|\pm 3\rangle$ and $|\mp 1\rangle$; $|0\rangle$, $|4\rangle$, and $|\bar{4}\rangle$; $|2\rangle$ and $|\bar{2}\rangle$, respectively. Each of them can be of a double type superposition, with identical (denoted as $(+)$) or mixed $(-)$ signs, depending on the ratio of B_4^4/B_6^4 according to the diagram (Fig. 2). Of 2^3 formally possible sets of signs,

TABLE I
EIGENFUNCTIONS AND EIGENVALUES OF ENERGY LEVELS OF 3H_4 TERM IN TETRAGONAL CRYSTAL FIELD OF D_{2d} SYMMETRY

Irreducible representation	Eigenfunction	Energy
Γ_4	$1/2^{1/2} 2\rangle + 1/2^{1/2} \bar{2}\rangle$	$-8B_0^0 - 660B_2^0 + 27720B_4^0 + 180B_4^4 - 2520B_6^4$
Γ_3	$1/2^{1/2} 2\rangle - 1/2^{1/2} \bar{2}\rangle$	$-8B_0^0 - 660B_2^0 + 27720B_4^0 - 180B_4^4 + 2520B_6^4$
$\Gamma_5^{(1)}$ (lower)	$\alpha \pm 3\rangle + \beta \mp 1\rangle$	$7B_0^0 - 1260B_2^0 - 21420B_4^0 + \beta/\alpha(60(7^{1/2})B_4^4 - 180(7^{1/2})B_6^4)$
$\Gamma_5^{(2)}$ (upper)	$\beta \pm 3\rangle - \alpha \mp 1\rangle$	$-17B_0^0 + 540B_2^0 + 1260B_4^0 - \beta/\alpha(60(7^{1/2})B_4^4 - 180(7^{1/2})B_6^4)$
$\Gamma_1^{(1)}$ (lower)	$\gamma 0\rangle + \epsilon 4\rangle + \epsilon \bar{4}\rangle$	$28B_0^0 + 840B_2^0 + 5040B_4^0 + \gamma/\epsilon(12(70^{1/2})B_4^4 + 360(70^{1/2})B_6^4)$
$\Gamma_1^{(2)}$ (upper)	$\epsilon/2^{1/2} 0\rangle - \gamma/2^{1/2} \bar{4}\rangle - \gamma/2^{1/2} 4\rangle$	$-20B_0^0 + 1080B_2^0 - 25200B_4^0 - \gamma/\epsilon(12(70^{1/2})B_4^4 + 360(70^{1/2})B_6^4)$
Γ_2	$1/2^{1/2} 4\rangle - 1/2^{1/2} \bar{4}\rangle$	$28B_0^0 + 840B_2^0 + 5040B_4^0$

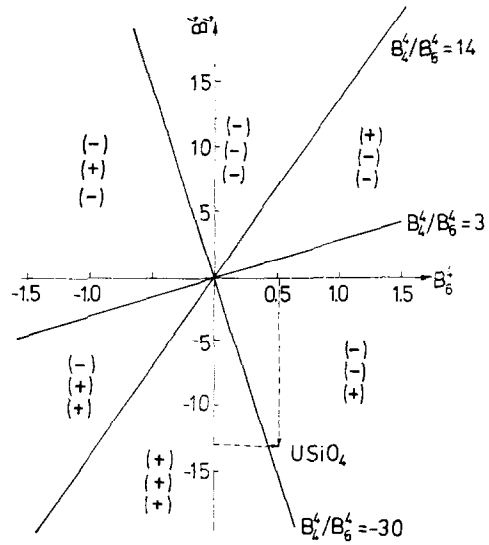


FIG. 2. Diagram of allowed ground eigenstates of the three submatrices spanned on the vectors: $(|2\rangle, |\bar{2}\rangle)$; $(|0\rangle, |4\rangle, |\bar{4}\rangle)$; $(|\pm 1\rangle, |\mp 3\rangle)$, as a function of the B_4^4/B_6^4 ratio. (+) denotes a superposition with identical signs; (-) denotes a mixed sign superposition.

six can be realized; two sets: (+) and (-) can never occur. The values of the β/α and γ/ϵ ratios may be expressed by the B_k^q parameters in the following way:

$$\frac{60(7^{1/2})B_4^4 - 180(7^{1/2})B_6^4}{24B_2^0 - 1800B_4^0 - 22680B_6^0} = \frac{-\beta/\alpha}{(\beta/\alpha)^2 - 1} \quad (2)$$

$$\frac{12(70^{1/2})B_4^4 + 360(70^{1/2})B_6^4}{48B_2^0 - 240B_4^0 + 30240B_6^0} = \frac{-\gamma/\epsilon}{(\gamma/\epsilon)^2 - 2}$$

Two different solutions of each part of Eq. (2) correspond to the two different Γ_5 and Γ_1 states. The left sides of Eq. (2) are ratios of off-diagonal elements to the results of a subtraction of diagonal elements of the appropriate submatrices. Based on the expressions for the energy of the ground levels of three submatrices, one can formulate a general rule saying that the signs of the $|J_2\rangle$ amplitude ratios in the superpositions have to be opposite to the signs of corresponding resultant off-diagonal elements. The change of sign of the tetragonal terms of the potential results in change of sign in the superpositions.

The center of gravity rule in relation to the crystal field splitting is valid for each submatrix separately. In the case of the second-order submatrices, it is obvious; for the third-order submatrices two hints are helpful for discussion of the splitting scheme:

(i) The Γ_2 singlet has to be situated between two Γ_1 singlets, and its energy equal to the $|\pm 4\rangle$ doublet's energy in the axial component of tetragonal field.

(ii) $E(\Gamma_1^{(2)}) - E(\Gamma_2)/E(\Gamma_2) - E(\Gamma_1^{(1)}) = 2(\epsilon/\gamma)^2$.

Paramagnetic Susceptibility of Uranium(4+) Ion in the Tetragonal Crystal Field of D_{2d} Symmetry

With the crystal field splitting of the ground term of magnetic ion known, its temperature dependence of the paramagnetic susceptibility can be expressed with the aid of the Van Vleck equation. Low- and high-frequency terms of the paramagnetic susceptibility of individual levels of the uranium(4+) ion in a tetragonal crystal field are listed in Table II. The algebraic sum of those terms multiplied by their Boltzmann factors is the numerator of the Van Vleck expression, which is to be divided by the partition function to obtain the $\chi(T)$ function. δ denotes the energy gap between interacting levels in K .

Contributions to the susceptibility come from the levels with allowed magnetic dipole transition, which means that matrix elements of the $\hat{J}_z + \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$ operator are nonzero.

Results

The experimental curve of the reciprocal susceptibility of USiO₄ vs temperature within the range 2–500°K and the dependence of its molar magnetization on magnetic field intensity from 0 up to 50 kOe at 4.2°K are presented in Fig. 3.

USiO₄ distinguishes itself by atypically low magnetic susceptibility compared to other uranium(4+) compounds and by atypical, for a non-Kramers ion, temperature dependence of the paramagnetic susceptibility at low temperatures. Its molar paramagnetic susceptibility amounts to $1785 \cdot 10^{-6}$ at 292°K and $8475 \cdot 10^{-6}$ at 4.2°K. Within the low

TABLE II
LOW- AND HIGH-FREQUENCY COMPONENTS OF PARAMAGNETIC SUSCEPTIBILITY OF URANIUM(4+) ION EIGENSTATES IN TETRAGONAL CRYSTAL FIELD^a

	Γ_4	Γ_3	$\Gamma_3^{(1)}$	$\Gamma_3^{(2)}$	$\Gamma_1^{(1)}$	$\Gamma_1^{(2)}$	Γ_2
Γ_4	0	0.64	$(1.06\alpha + 1.20\beta)^2$	$(1.06\beta - 1.20\alpha)^2$	0	0	0
Γ_3	—	—	$(1.06\alpha - 1.20\beta)^2$	$(1.06\beta + 1.20\alpha)^2$	0	0	0
$\Gamma_3^{(1)}$	—	—	$0.16(4x^2 - 1)^2/T$	$5.12x^2\beta^2$	$(1.13\alpha\epsilon + 1.79\beta\gamma)^2$	$(0.80\alpha\gamma - 2.53\beta\epsilon)^2$	$0.64\alpha^2$
$\Gamma_3^{(2)}$	—	—	—	$0.16(4\beta^2 - 1)^2/T$	$(1.13\beta\epsilon - 1.79\alpha\gamma)^2$	$(0.80\beta\gamma + 2.53\alpha\epsilon)^2$	$0.64\beta^2$
$\Gamma_1^{(1)}$	—	—	—	—	0	0	$5.12\epsilon^2$
$\Gamma_1^{(2)}$	—	—	—	—	—	—	$2.56\gamma^2$
Γ_2	—	—	—	—	—	—	0

^a Each off-diagonal value ought to be divided by corresponding δ in K .

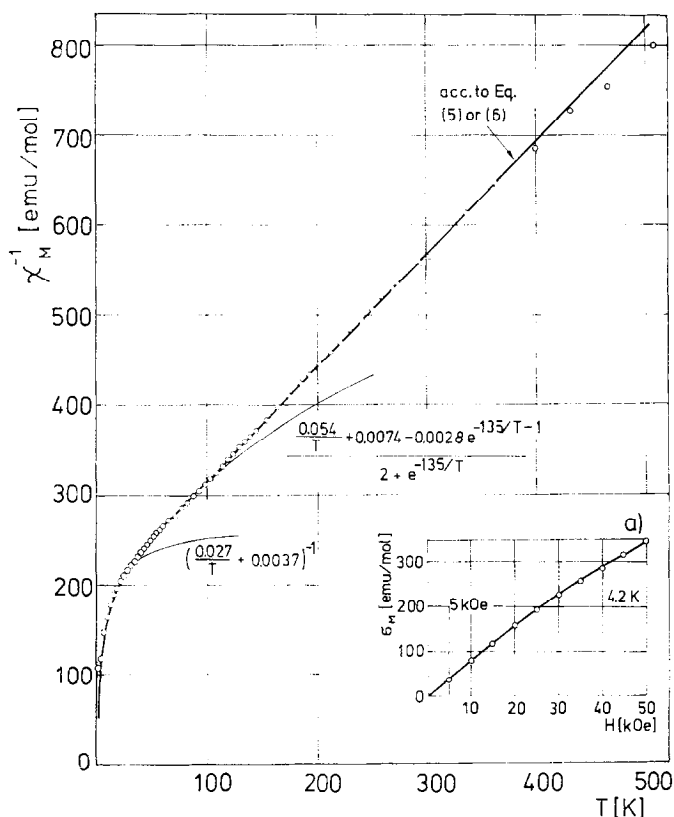


FIG. 3. Reciprocal molar susceptibility of USiO_4 vs temperature within the range 2–500°K. Insert (a): dependence of molar magnetization of USiO_4 on magnetic field intensity within the range 0–50 kOe at 4.2°K.

temperature range, the $\chi(T)$ dependence reflects the degeneracy or pseudo-degeneracy of the ground state. The fact that lowering the temperature from 4.2°K down to 2°K is followed by an increase of the susceptibility only to $9300 \cdot 10^{-6}$ indicates that an unsplit doublet cannot be the ground state. This excludes the origin of the temperature-dependent part of the susceptibility from uranium (5+) ion, and consequently only the tetragonal doublet $\Gamma_5^{(1)}$ subjected to weak “zero splitting” can be the ground state. This fact, rather uncommon among tetragonal uranium(4+) compounds, makes the crystal field parameters obey some restricting conditions. On the other hand, however, the existence of an antiferromagnetic transition below 2°K can not be definitely excluded, although it seems to be not very probable (small magnetic moment of the ground state, fairly large (3.83 Å) U–U distance).

Measurements performed by the magnetometer at $H = 50$ kOe gave a value of the magnetic susceptibility of USiO_4 consistent with that at much lower fields at room temperature ($1850 \cdot 10^{-6}$ at 273°K) but distinctly lower ($7050 \cdot 10^{-6}$) at 4.2°K. This reduction is caused by the apparent paramagnetic saturation effect (Fig. 3a). The $\partial\sigma/\partial H$ derivative at $H = 5$ kOe is equal to ca. $8200 \cdot 10^{-6}$ which is in good agreement with the previous value.

Based on the experimental χ^{-1} vs T curve (Fig. 3), the analytical Van Vleck's form of the $\chi(T)$ function was reconstructed by finding the low- and high-frequency terms of the susceptibility and the energy gaps of the lowest levels subjected to Boltzmann population. The fitting of the parameters to the Van Vleck equation was carried out according to the previously assumed possible pattern of the splitting (number of levels taken into account,

their degeneracy, sequence, etc.). In general, there are many conditions of a physical nature (the total splitting, number and kind of levels, values of high-frequency terms, etc.), which considerably reduce the number of possible variants of the splitting pattern to be verified.

In the case of the tetragonal crystal field in USiO_4 one can suppose that within the range of temperature up to 500°K it is sufficient to take into account two or three excited singlets ($\Gamma_1^{(1)}$, Γ_3 or Γ_4 , Γ_2) apart from the ground doublet $\Gamma_5^{(1)}$. Within the range of lowest temperatures (up to 30°K), under the assumption that the ground doublet $\Gamma_5^{(1)}$ is the only level populated, its temperature dependence of susceptibility should be of the type: $\chi(T) = A/T + B$, where the coefficient A represents the composition of the ground doublet, while B is the sum of polarizing contributions from the upper levels (temperature-independent paramagnetism). From the experimental plot of $\chi(T)$ over the range $10\text{--}30^\circ\text{K}$, the values of A and B coefficients were determined as equal to 0.027 and $3700 \cdot 10^{-6}$, respectively. Since, for the doublet Γ_5 , $\chi = 0.08 M^2/T + B$, where $M = \langle \Gamma_5^{(1)} | \hat{J}_z | \Gamma_5^{(1)} \rangle$, the experimental value of M is equal to ± 0.581 , which leads to two possible compositions of the $\Gamma_5^{(1)}$ doublet:

$$\begin{aligned} \text{(i)} & 0.946|\pm 1\rangle + 0.324|\mp 3\rangle \\ \text{(ii)} & 0.778|\pm 1\rangle + 0.629|\mp 3\rangle \end{aligned} \quad (3)$$

The subject of further analysis is to establish which of the above compositions corresponds to the real ground state. The sign in the superpositions (Eq. (3)) is not determined and it may be assumed as (+). The paramagnetic moment of the ground state amounts to $\mu = 0.8|M|\mu_B = 0.46\mu_B$. Knowing the composition of the ground doublet $\Gamma_5^{(1)}$, one can estimate its "zero splitting" δ_0 , since the temperature dependence of the susceptibility of the pseudo-doublet should approximately fulfil the relation:

$$\chi = \frac{(0.16M^2/\delta_0 + 0.0037) + (-0.16M^2/\delta_0 + 0.0037) \exp(-\delta_0/T)}{1 + \exp(-\delta_0/T)} \quad (4)$$

So the estimated value of the "zero splitting" amounts to ca. 8 K , which corresponds to a maximum value of the molar susceptibility of ca. $10\,500 \cdot 10^{-6}$. The effect of the "zero splitting" produced by a weak lower symmetry distortion will not be discussed in detail.

Undoubtedly, a singlet lying 135°K above with a negative high-frequency term equal to ca. $-2800 \cdot 10^{-6}$ is the first excited level. The fitting of the analytical $\chi(T)$ function to the experimental curve up to 300°K may be attained under the assumption that:

(i) the next excited singlet lies 500°K above the ground doublet and its polarizing term is also negative amounting to ca. $-4300 \cdot 10^{-6}$, so that the magnetic susceptibility has the form (Fig. 3):

$$\chi = \frac{0.054/T + 0.0074 - 0.0028 \times \exp(-135/T) - 0.0043 \exp(-500/T)}{2 + \exp(-135/T) + 2 \exp(-500/T)} \quad (5)$$

(ii) there are two singlets not very distant from each other above the first excited one. Then, with the simplifying assumption of their accidental degeneracy, the magnetic susceptibility would be expressed:

$$\chi = \frac{0.054/T + 0.0074 - 0.0028 \times \exp(-135/T) - 0.0035 \exp(-540/T)}{2 + \exp(-135/T) + 2 \exp(-540/T)} \quad (6)$$

with their energy equal to 540°K and high-frequency term $-3500 \cdot 10^{-6}$.

In spite of some ambiguity of the analytical interpretation of the $\chi(T)$ dependence and its limited accuracy, the basic conclusions concerning the signs, the values of the high-frequency terms and the energy gaps of the levels are in the case of USiO_4 sufficient to estimate the crystal field parameters. For both of the above variants the polarizing terms of the excited levels considered are negative, which gives evidence of their interactions with the ground level. Their sum does not exceed the positive high-frequency term of the ground state.

Discussion and Conclusions

The knowledge of the ground doublet $\Gamma_5^{(1)}$ composition allows one to express the five crystal field parameters as functions of three energy gaps between levels, for example, $\Delta_{15} = E(\Gamma_1^{(1)}) - E(\Gamma_5^{(1)})$, $\Delta_{45} = E(\Gamma_4) - E(\Gamma_5^{(1)})$, and $\Delta_{21} = E(\Gamma_2) - E(\Gamma_1^{(1)})$ (all positive) and the ratio γ/ε . There are five known equations, three for energy differences of the levels (Table I) and two composition relations (Eq. (2)). In addition, the γ/ε ratio may be estimated from the values of high-frequency terms of the susceptibility.

The calculations made for the doublet: $0.946|\pm 1\rangle + 0.324|\mp 3\rangle$ with the ratio $\beta/\alpha = 2.92$ lead to unrealistically large absolute values for the crystal field parameters and to a ratio $B_4^4/B_6^4 \approx -30$, irrespective of the γ/ε value, which corresponds to cancellation of the off-diagonal elements in the third-order submatrix (Fig. 2). This result may be generalized: a Γ_5 doublet rich in the $|\pm 1\rangle$ function cannot practically be the ground level in a tetragonal crystal field.

For the alternative composition of the $\Gamma_5^{(1)}$ doublet: $0.778|\pm 1\rangle + 0.629|\mp 3\rangle$ with the ratio $\beta/\alpha = 1.24$, the similar set of five equations gives for the crystal field parameters the following expressions:

$$\begin{aligned}
 B_2^0 \cdot 10^2 &= -2.21\Delta_{15} - 3.30\Delta_{45} \\
 &+ \frac{1.91(\gamma/\varepsilon)^2 + 1.97\gamma/\varepsilon - 8.24}{(\gamma/\varepsilon)^2} \Delta_{21} \\
 B_4^0 \cdot 10^3 &= -1.28\Delta_{15} - 1.47\Delta_{45} \\
 &+ \frac{0.18(\gamma/\varepsilon)^2 + 0.88\gamma/\varepsilon - 2.92}{(\gamma/\varepsilon)^2} \Delta_{21} \\
 B_4^4 \cdot 10^2 &= -1.62\Delta_{15} - 1.26\Delta_{45} \\
 &- \frac{0.05(\gamma/\varepsilon)^2 - 0.66\gamma/\varepsilon + 3.14}{(\gamma/\varepsilon)^2} \Delta_{21} \\
 B_6^0 \cdot 10^5 &= 2.50\Delta_{15} + 4.00\Delta_{45} \\
 &+ \frac{0.50(\gamma/\varepsilon)^2 - 2.40\gamma/\varepsilon + 3.90}{(\gamma/\varepsilon)^2} \Delta_{21} \\
 B_6^4 \cdot 10^4 &= 5.44\Delta_{15} + 4.19\Delta_{45} \\
 &+ \frac{0.20(\gamma/\varepsilon)^2 - 5.52\gamma/\varepsilon + 10.46}{(\gamma/\varepsilon)^2} \Delta_{21}
 \end{aligned} \tag{7}$$

where B_6^0 's and Δ 's are given in cm^{-1} .

For such a composition of the ground doublet the first excited singlet lying 135°K above can be neither Γ_3 nor Γ_4 , because of their high-frequency terms from the $\Gamma_5^{(1)}$ doublet, amounting to $-0.072/\delta$ and $-2.56/\delta$, respectively. Consequently, the singlet $\Gamma_1^{(1)}$ is the first excited level. Its γ/ε ratio may be estimated from the allowed values of the high-frequency terms (Table II, Eq. (4)–(6)). So, we have:

$$0.0028 < \frac{(1.13\alpha\varepsilon - 1.79\beta\gamma)^2}{\delta} < 0.0040.$$

Substituting $\alpha = 0.629$, $\beta = 0.778$, and $\delta = 135^\circ\text{K}$ one gets two ranges of reconcilable values of γ/ε ratio:

$$0.12 < \gamma/\varepsilon < 0.24 \quad \text{or} \quad -1.65 < \gamma/\varepsilon < -1.39.$$

However, for the first range, the crystal field parameters would have to be unrealistically large, too, as results from Eq. (7).

Based on the experimental $\chi(T)$ plot, four parameters on the right side of Eq. (7) may be estimated as being approximately $\gamma/\varepsilon = -1.6$, $\Delta_{15} = 100 \text{ cm}^{-1}$, $\Delta_{45} = 350 \text{ cm}^{-1}$, and $\Delta_{21} = 400 \text{ cm}^{-1}$. The crystal field parameters corresponding to them are roughly (in cm^{-1}) $B_2^0 = -24$, $B_4^0 = -1.25$, $B_4^4 = -12.8$, $B_6^0 = -0.031$, $B_6^4 = 0.51$, and $B_4^4/B_6^4 \approx -25$. The total splitting of the ${}^3\text{H}_4$ term amounts to ca. 7500 cm^{-1} .

Considering the assumptions made at the beginning and the magnitude of the deduced crystal field splitting, the obtained values should be treated as approximate only. The consistence with the established facts should be similar to that observed for UO_2 under the assumption of $\Gamma_5({}^3\text{H}_4)$ triplet as the ground level and the total splitting of the ${}^3\text{H}_4$ term 5700 cm^{-1} (10). The differences of even a few tenths of a percent between the observed and calculated values of the high-frequency terms of the magnetic susceptibility may occur in similar cases. For instance, the experimental temperature-independent paramagnetic susceptibility of Cs_2UCl_6 , arising mainly from high-frequency interaction between Γ_1 and Γ_4 levels of ${}^3\text{H}_4$ term in the O_h crystal field.

TABLE III
EXPERIMENTAL AND POINT CHARGE CRYSTAL FIELD PARAMETERS OF URANIUM(4+) ION
IN ORTHOSILICATE (IN cm^{-1})

	Ligand point charges	Ligand + distant point charges (up to 5 Å)	According to Mackey <i>et al.</i> (13) U^{4+} in ZrSiO_4	This work
B_2^0	-42.2	67.9	21.0	-24
B_4^0	-0.12	-0.018	-0.183	-1.25
B_6^0	-0.0017	-0.0039	-0.022	-0.031
B_4^4	-3.01	-2.34	-3.93	-12.8
B_6^4	0.0020	-0.0007	-0.018	0.51

is ca. 20% less than the calculated value (11).

The strongly tetragonal character of the crystal field potential in USiO_4 deserves some attention. The axial term of the second degree is not too large and the ratios of the tetragonal to axial terms of both fourth and sixth degrees, respectively, differ essentially from those for a cubic potential.

Because of the comparability of U-O distances in cubic UO_2 and tetragonal USiO_4 , the crystal field splitting of the latter should really be stronger, the more so that the pure electrostatic contribution to the crystal field potential has secondary importance. For UO_2 , the crystal field parameters calculated by Rahman and Runciman (10) are (in cm^{-1}): $B_4^0 = 2.42$, $B_4^4 = 12.11$, $B_6^0 = 0.012$, $B_6^4 = -0.256$, and $B_4^4/B_6^4 = -47.3$. As to absolute values, they resemble the parameters for USiO_4 . The values of the crystal field parameters for isomorphous ZrSiO_4 doped with U^{4+} ions, as determined mainly from absorption spectra, given in previous papers (12, 13), differ considerably from the values deduced in this work from the temperature dependence of the paramagnetic susceptibility. They are distinctly lower (Table III) and the total splitting of the $^3\text{H}_4$ term (ca. 2000 cm^{-1}) is three to four times smaller than the value estimated in this work. This inconsistency is difficult to explain, the more so as the U-O distance in the ZrSiO_4 crystal host is shorter than that in USiO_4 .

Comparison to the Point Charge Model

Two tetrahedra of oxygen anions, 2.32 and 2.51 Å distant from the central uranium ion,

form the first coordination sphere of U^{4+} ion in USiO_4 . The calculated parameters of its point charge electrostatic potential are presented in the first column of Table III. In the second column, the values of the parameters for all ions inside the 5-Å radius sphere are presented. New values of $\langle r^k \rangle$: $\langle r^2 \rangle = 2.042$, $\langle r^4 \rangle = 7.632$, and $\langle r^6 \rangle = 47.774$ (14), which are somewhat greater than those used previously (15), were applied in the calculations. In both point charge models singlet $\Gamma_1^{(1)}$ is the ground state. The point charge crystal parameters are not consistent with those deduced experimentally in this work. Slightly smaller differences are observed when only the ligand point charges are considered. This inadequacy of the model is understood in light of the large ionic charges in the USiO_4 crystal lattice, strong mutual polarization of ions, and covalency effects. On the other hand, the crystallographic data are known with a tolerance which does not allow one to calculate the B_k^q parameters exactly, particularly those of fourth and sixth degrees.

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