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Synthesis, Spectroscopic, and Magnetic Properties of Rubidium Heptachlorodiuranate(III)

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The synthesis of rubidium heptachlorodiuranate(III) together with some of its structural, spectroscopic, and magnetic properties are reported. Unit cell parameters were determined from X-ray powder diffraction data. Uranium(3+) doped single crystals of RbY_2Cl_7 have been grown by the Bridgman–Stockbarger method. The Raman and infrared spectra of RbU_2Cl_7 as well as the electronic absorption spectrum of RbY_2Cl_7: U^{3+} (1%) at 4.2 K have been recorded and are discussed. Magnetic susceptibility measurements were carried out by the Faraday method in the 4.2–300 K range. The Curie–Weiss law is followed in the 210–300 K range with the paramagnetic constants $\mu_{eff} = 3.74\ \mu_B$, $C = 1.750$ emu · K · mole^{-1}, and $\theta = -80$ K.

INTRODUCTION

Rubidium heptachlorodiuranate(III) has been first prepared by reduction of an acetonitrilic solution of uranium tetrachloride with liquid zinc amalgam (1). The formation of this compound was also observed during investigations of binary phase systems containing UCl_3 (2). On the basis of single crystal data of $RbDy_2Cl_7$ (3) Volkov *et al.* (4) have revised the earlier obtained (2) crystal lattice parameters showing that both compounds are isotypic. Except for X-ray powder diffraction data no other properties of the compound have been reported.

EXPERIMENTAL

Synthesis

For the preparation of the compound a well ground mixture of RbCl and $NH_4UCl_4 \cdot 4H_2O$ (5) of a 1:2 molar ratio was first heated in a quartz tube at a nonstatic vacuum of ca. 10^{-6} hPa. In order to convert $NH_4UCl_4 \cdot 4H_2O$ into UCl_3, the temperature of the furnace was slowly increased from 20 to 350°C. Next the tube was sealed off and the mixture was heated for 24 h at 700 and at 850°C. Subsequently the temperature was slowly decreased and the mixture heated at 500°C for 7 days. A brown, fine crystalline powder was obtained. The compound is not resistant to oxidation by air and should be stored under nitrogen in sealed tubes. It is easily soluble in water and a number of more polar organic solvents such as methanol, ethanol, formic acid, and formamide.

Single crystals of RbY_2Cl_7: U^{3+} with a uranium concentration of 0.1 and 1% were grown by the Bridgman–Stockbarger method using RbU_2Cl_7 as the doping substance. Polished plates of RbY_2Cl_7: U^{3+} of 0.52-mm (1%) and 1.0-mm (0.1%) thick were used for electronic absorption measurements in the 4000–13,000 cm^{-1} and 12,000–50,000 cm^{-1} range, respectively.

Analysis

The rubidium, uranium, and chlorine content was determined by the atomic absorption, cerometric, and argentometric method, respectively. Calc. for RbU_2Cl_7: U, 58.79; Rb, 10.56; Cl, 30.65. Found: U, 58.38; Rb, 10.12; Cl, 30.91.

Physical Measurements

An X-ray powder diffraction analysis of RbU_2Cl_7 was carried out at the Institute of Low Temperature and Structure Research in Wrocław on a Stoe automated powder diffractometer using CuKα1 radiation. The unit cell parameters were obtained by least-squares refinement of all 41 observed reflections.

The magnetic susceptibilities were measured by the conventional Faraday method on polycrystalline samples in the 4.2–300 K range with a field of 6 kOe. The values of the magnetic susceptibilities were corrected for diamagnetic increments ($\chi_{dia} = -147.00 \times 10^{-6}$ emu · K · mole^{-1}).

The electronic absorption spectrum was recorded on a Cary-5 UV–Vis–NIR spectrophotometer in the 4000–50,000 cm^{-1} range at 4.2 K. A 1204 Oxford cryostat was used for the low temperature measurements (Figs. 1 and 2).

The infrared transmission measurements were carried out on a Bruker IFS 113v spectrometer in the 60–500 cm^{-1} range at room temperature. The spectrum resolution was 2 cm^{-1} (Fig. 3).

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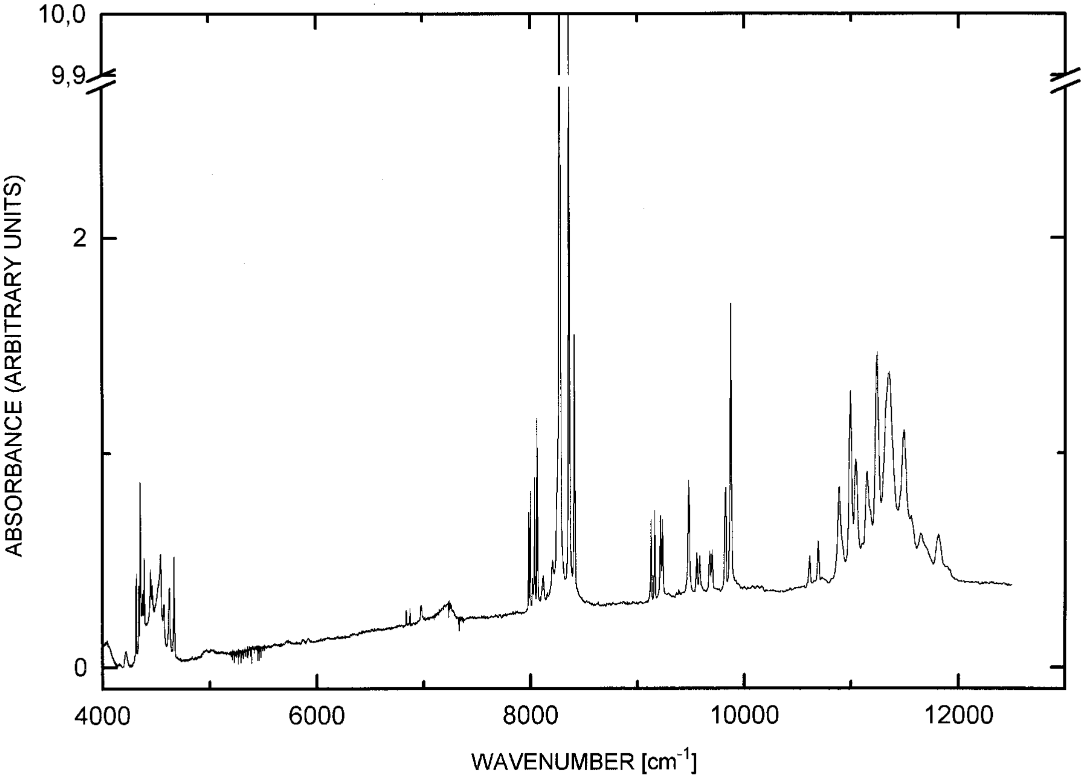

FIG. 1. Absorption spectrum of RbY_2Cl_7:U^{3+}(1%) at 4.2 K.

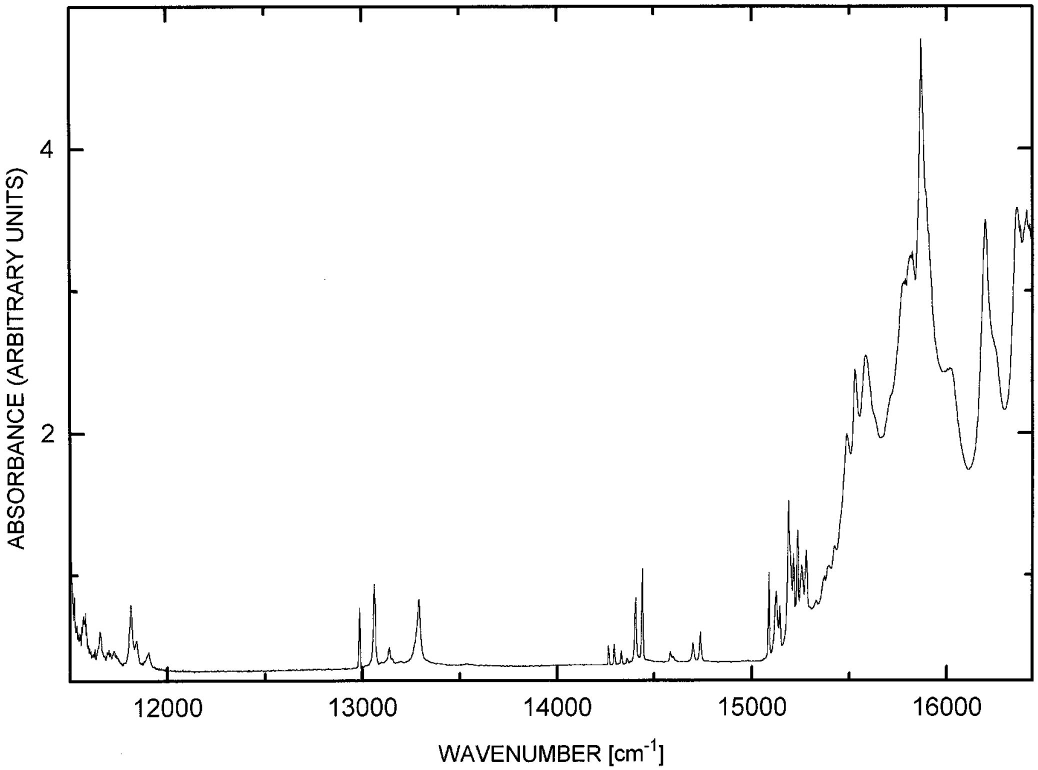

FIG. 2. Absorption spectrum of RbY_2Cl_7:U^{3+}(0.1%) at 4.2 K.

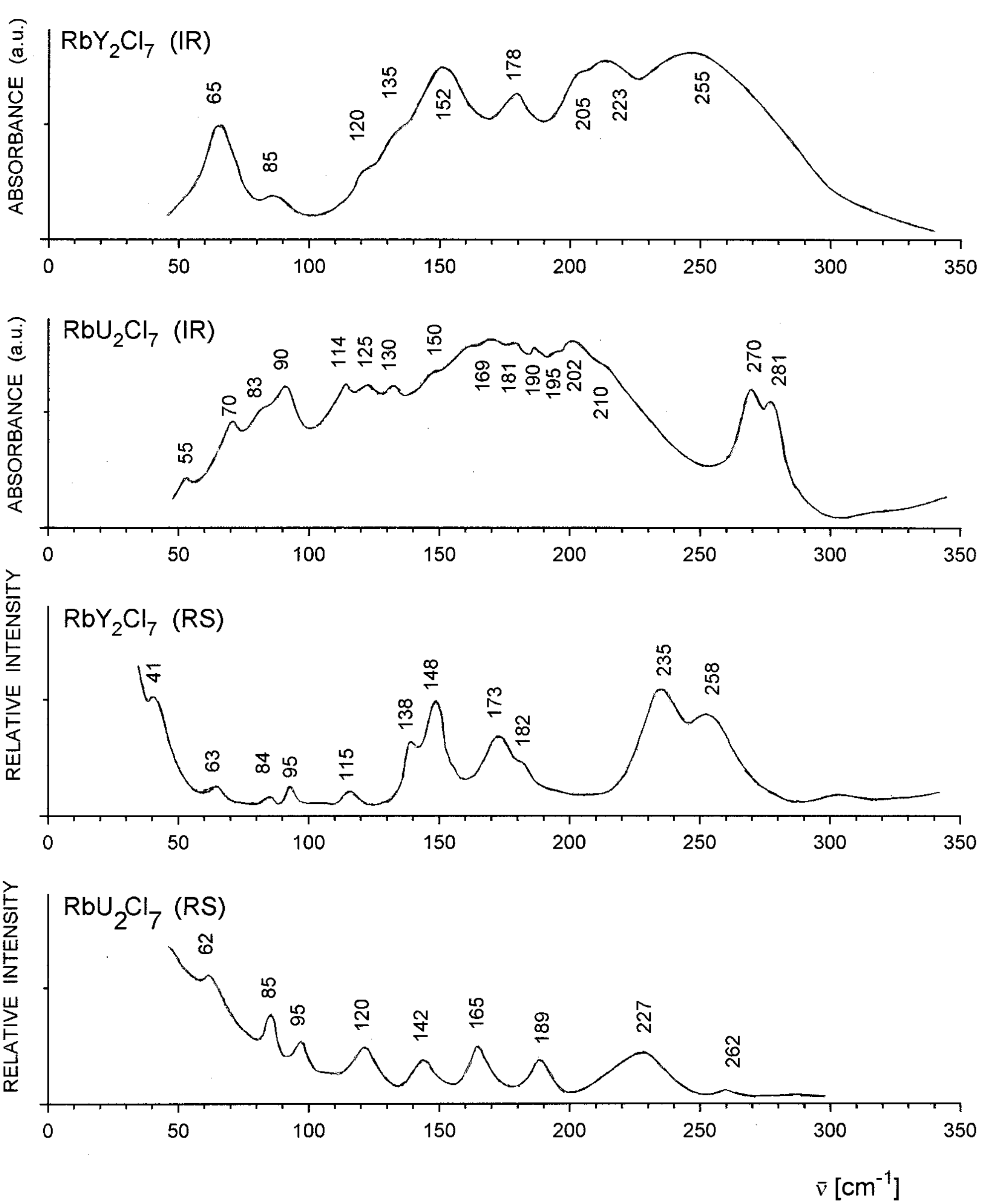

FIG. 3. IR transmission and Raman spectra.

The Raman spectra were recorded at 300 K in the 40–500 cm^{-1} region. The 488- and 514.5-nm lines of an Ar^+ laser were used as the excitation source. A double monochromator DFS 24 manufactured in the LOMO optical works (Russia) and a cooled GaAs photomultiplier with a computer detection of 2 cm^{-1} resolution were applied in the measurements (Fig. 3).

RESULTS AND DISCUSSION

Crystal Structure and Electronic Absorption Spectra

The reflection positions and intensities of the diffraction patterns recorded for RbU_2Cl_7 clearly demonstrate the isotypic crystal structure with $RbDy_2Cl_7$ and RbY_2Cl_7 and are somewhat different from those reported earlier (4). The following lattice parameters have been obtained: a = 12.8458(0.0072) Å, b = 7.0761(0.0038) Å, c = 12.3489 (0.0063) Å, V = 1122.4923 Å, and Z = 4. The calculated and pycnometrically determined densities are 4.79 and 4.71 $g \cdot cm^{-3}$, respectively.

Meyer (3) has shown that $RbDy_2Cl_7$ crystallizes in the orthorhombic space group *Pnma* (D_{2h}) with four molecules per unit cell. The structure consists of monocaped [$DyCl_7$] prisms which are connected via a triangular face with other prisms forming [Dy_2Cl_{11}] groups. These in turn form $^2_\infty[DyCl^f_{3/2}Cl^e_{1/2}]_2$ layers, where f and e denote face and edge

TABLE 1

Level assignment^a	Range encompassing observed groups of crystal field components of the L′S′J′ levels
$^4I_{11/2}$	4313–4663
$^4F_{3/2}$	6839–6991
$^4I_{13/2}$	7979–8409
$^2H_{9/2}$	9125–9497
$^4F_{5/2}$	9556–9874
$^4S_{3/2}$	10607–10840
$^4G_{5/2}$	10884–11061
$4I_{15/2}$, $^4F_{7/2}$	11147–11901
$^4G_{7/2}$	12985–13290
$^4F_{9/2}$	14266–14736
$^2H_{11/2}$	15086–15419
$^4D_{1/2}$, $^2D_{3/2}$	15484–15702

[a] Main component of eigenvector.

connections, respectively. The layers are stacked in the [100] direction and held together by Rb^+ ions. The central metal ions occupy two somewhat different positions Dy(1) and Dy(2) of the same m (C_s) symmetry for which when idealized one may adopt the C_{2v} point symmetry of a monocaped trigonal prism. The Dy–Cl distances in the first polyhedron of Dy(1) are 2 × 2.690, 2 × 2.708, 2 × 2.757, and 2.761 Å which gives a mean value of 2.724 Å, whereas the polyhedron around the Dy(2) site has the Dy–Cl distances ranging from 2.666 to 2.793 Å with the mean value of 2.703 Å (3).

We report in this paper some general properties of the U^{3+} electronic absorption spectrum in the RbY_2Cl_7 host only. A detailed interpretation of the spectrum will be given elsewhere (6). The spectrum was recorded at 4.2 K and is shown in Figs. 1 and 2. In the near infrared and visible ranges, up to ca. 16,000 cm^{-1} one observes very sharp $5f^3 \rightarrow 5f^3$ bands exclusively. Since the U^{3+} ions replace the Y^{3+} ions in the host crystal, they occupy the two optically different sites (1) and (2) of the C_s symmetry, too. As a consequence all the sharp crystal field bands are split into two components, which result from crystal field splittings of the U(1) or U(2) sites, respectively. In this absorption range the spectrum consists almost exclusively of well-separated groups of such bands. It is very interesting to note that for the first time the number of observed crystal field bands in each group is in agreement with that predicted by theory (7) for a corresponding "free-ion" level (L′J′S′ state). Since the intensity of the electric dipole transitions greatly exceeds those of phonon assisted, the vibronic side bands may not be observed. Hence, one may easily assign each of these groups of bands to a particular free-ion level (Table 1) based on earlier reported energy level calculations and assignments of the centers of gravity (L′J′S′ levels) of the observed groups of crystal field bands in the low temperature absorption spectra of $U(HCOO)_3$ (8) and $LaCl_3$: U^{3+} (9).

Above 16,000 cm^{-1} the spectrum consists of broad and very intense bands attributed to Laporte allowed transitions between the $5f^3$ ground state and the crystal field components of the $5f^26d^1$ states, on which the much weaker $5f^3 \rightarrow 5f^3$ transitions are superimposed.

Phonon Properties and Vibrational Spectra

The above described orthorhombic unit cell containing 40 atoms has been taken as a basis for the factor group analysis of the vibrational degrees of freedom. The 120 ($k = 0$) unit cell modes are distributed between $\Gamma_T = B_{1u} + B_{2u} + B_{3u}$ acoustic phonons and $\Gamma_0 = 17A_g + 13B_{1g} + 17B_{2g} + 13B_{3g} + 13A_u + 16B_{1u} + 12B_{2u} + 16B_{3u}$ optic modes. The optic modes can be further subdivided into external and internal vibrations. Table 2 lists these phonons and their symmetries, as well as the selection rules for IR and Raman spectra. The internal vibrations of the

TABLE 2

D_{2h}	United cell modes Γ_N	Acoustic modes Γ_T	Translatory lattice modes $\Gamma_{T'}$	Rotatory lattice modes Γ_R	Internal modes Γ_i	Activity IR	Activity Raman
A_g	17	—	4	1	12	—	x^2, y^2, z^2
B_{1g}	13	—	2	2	9	—	xy
B_{2g}	17	—	4	1	12	—	xz
B_{3g}	13	—	2	2	9	—	yz
A_u	13	—	2	2	9	—	—
B_{1u}	17	1	3	1	12	z	—
B_{2u}	13	1	1	2	9	y	—
B_{3u}	17	1	3	1	12	x	—
Σ	120	3	21	12	84		

TABLE 3

	$M_2Cl_7^-$ ion vibrations C_s symmetry in unit cell	Unit cell vibrations (factor group D_{2h}; Z = 4)
ν(MCl)	$6A'$ (IR, RS)	$6A_g$ (RS) $6B_{2g}$ (RS) $6B_{1u}$ (IR) $6B_{3u}$ (IR)
	$4A''$ (IR, RS)	$4B_{1g}$ (RS) $4B_{3g}$ (RS) $4A_u$ (–) $4B_{2u}$ (IR)
δ(ClMCl)	$6A'$ (IR, RS)	$6A_g$ (RS) $6B_{2g}$ (RS) $6B_{1u}$ (IR) $6B_{3u}$ (IR)
	$5A''$ (IR, RS)	$5B_{1g}$ (RS) $5B_{3g}$ (RS) $5A_u$ (–) $5B_{2u}$ (IR)

$Y_2Cl_7^-$ unit are defined by the correlation diagram presented in Table 3. From this scheme it appears that each of the stretching vibrations and the eleven bending vibrations, described in the point group C_s by the representations $6A' + 4A''$ and $6A' + 5A''$, respectively, are split dynamically into quartets. The components of each multiplet can be observed in the Raman spectra as doublets and in the IR spectra as singlets or doublets. (Tables 2 and 3).

The room temperature IR and Raman spectra of the RbY_2Cl_7 and RbU_2Cl_7 samples are presented in Fig. 3. The observed frequencies and relative intensities of the bands are summarized in Table 4. At a first glance the spectra can be divided into three regions. The first is above 200 cm^{-1} for RbY_2Cl_7 and 150 cm^{-1} for RbU_2Cl_7. The phonon modes in this spectral region originate from stretching vibrations of the Y–Cl and U–Cl bonds. The bending vibrations of these bonds appear in the second range of 120–180 cm^{-1} for the yttrium derivative and 100–150 cm^{-1} for the uranium(3+) heptachloride. In both spectral regions the substitution of yttrium by uranium causes a frequency shift of the observed bands of approximately 12%, which roughly corresponds to the square roots of the appropriate reciprocal values of reduced masses. The lattice vibrations of the compounds appear in the third range, i.e., below 100 cm^{-1}, where translational phonons of Rb/Y and Rb/U are expected. The performed assignment of the vibrational bands to the respective wavenum-

TABLE 4

RbY_2Cl_7		RbU_2Cl_7		
IR (*u* phonons)	RS (*g* phonons)	IR (*u* phonons)	RS (*g* phonons)	Assignment
		281*s*		ν(MCl)
280*sh*	280*sh*			
		271*s*	262*w*	
225*vs*	258*s,b*	210*s*	227*s, b*	
		202*vs*		
		195*sh*		
223*vs*	235*s, b*	190*vs*	189*s*	
		181*vs*		
205*sh*		169*vs*	165*s*	
		150*sh*		
	182*m*			δ(ClMCl)
178*s*				
	173*m*	130*m*	142*m*	
152*vs*	148*s*	125*m*	120*m*	
135*sh*	138*m*	114*m*		
120*sh*	115*w*	90*m*	95*w*	
85*m*	92*w*	83*sh*	85*m*	*T*' (Rb/M)
	84*w*	70*m*		
65*s*	63*w*	55*w*	62*m*	
	41*w*			

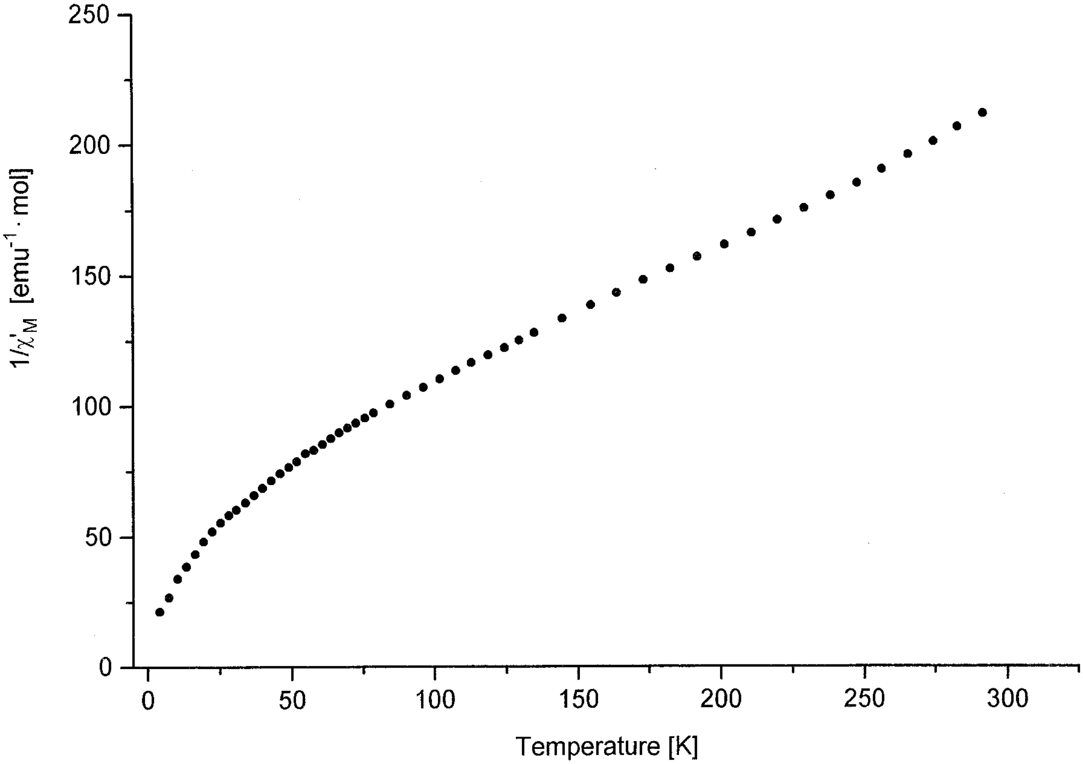

FIG. 4. Inverse magnetic susceptibilities of RbU_2Cl_7.

ber region agrees very well with the normal coordinate analysis performed by Tanner (10) for Cs_2NaUCl_6.

Considering Table 4 one may determine the discrimination between the u and g modes. The difference between the number of modes predicted by FGA (42 Raman and 33 IR singlets) and the number of Raman and IR modes observed is caused by the use of a polycrystalline sample. Nevertheless, the number of observed bands is close to that expected in the static, site symmetry approximation. The broadening of the bands is caused by the polymeric structure of the Y_2Cl_7 and U_2Cl_7 cores in the unit cell.

Magnetic Susceptibility Measurements

The inverse magnetic susceptibility versus temperature plot exhibits above the 210 K range a linear relationship with the paramagnetic constants from the Curie–Weiss law $C = \chi'_M\ (T - \Theta) = 1.750$ emu · K · mole^{-1}, $\Theta = -80$ K, and the effective magnetic moment $\mu_{eff} = 2.84\sqrt{C} = 3.76$ μ_B. At lower temperatures the plot deviates first above and next at ca. 50 K below the Curie–Weiss line, approaching zero (Fig. 4). Such zero-converging character of the plot is typical for lanthanide and actinide ions exhibiting a Kramers doublet in the ground state. Taking into account the presently available intermediate coupling wavefunctions for uranium(3+) compounds (8, 9, 11) one may state that the $^4I_{9/2}$ ground level is about 8% up to 17% admixed with other basis states with $J = 9/2$, which leads to g_J values ranging from 0.744 to 0.762. Hence, the effective magnetic moments calculated from the expression $\mu_{eff} = g_J\sqrt{J(J+1)}$ may range from approximately 3.70 to 3.79 μ_B. So far, this conclusion has been established for uranium(3+) compounds with a ground level splitting not larger than ca. 600 cm^{-1}. From the recently received composition of eigenvectors of the $^4I_{9/2}$ ground level of RbU_2Cl_7 in the intermediate coupling scheme (6) we have calculated the following values: $g_J = 0.752$ and $\mu_{eff} = g_J\sqrt{J(J+1)} = 3.74\ \mu_B$. The last one very closely approaches the experimentally determined effective magnetic moment of 3.76 μ_B. and is close also to those reported for other anhydrous uranium(3+) complex chlorides (11).

SUPPLEMENTARY MATERIAL

The observed and calculated d spacings together with the observed relative intensities are available on request from the authors.

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