

# Line broadening studies for $U^{3+}$ and $U^{4+}$ ions in $RbY_2Cl_7$ single crystals

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## Abstract

Temperature-dependent line broadening measurements of emission and excitation transitions for two intrinsic sites U(1) and U(2) of  $U^{3+}$  ions doped in a  $RbY_2Cl_7$  single crystals as well as of  $U^{4+}$  ions have been performed. Values of the electron phonon (EP) coupling parameter  $\bar{\alpha}$  were determined by a fit of experimentally observed line widths to an equation containing the temperature dependent broadening term due to the Raman two-phonon process. The  $\bar{\alpha}$  parameters for  $U^{3+}$  ions in  $RbY_2Cl_7$  are larger than those determined for this ion in  $LaCl_3$  host crystals. This is due to shorter  $M-Cl$  distances in  $RbY_2Cl_7$  which leads to a stronger interaction of uranium with the chlorine ions and to an increase of covalency. The relatively large  $\bar{\alpha}$  value determined for the  ${}^2H_{2,11/2}$  multiplet of  $U^{3+}$  in  $RbY_2Cl_7$  may result from the proximity of opposite parity  $5f^26d^1$  states. The  $\bar{\alpha}$  parameters obtained for the  $U^{3+}$  ions are larger than those for  $U^{4+}$ . The latter ones are affected by a stronger crystal-field (CF), however the position of the first  $5f^26d^1$  or  $5f^16d^1$  states, which for  $U^{3+}$  is observed at an energy of  $\sim 15,000\text{ cm}^{-1}$  lower than for  $U^{4+}$ , is the dominating one among the factors influencing the EP coupling strength. The EP coupling parameters for all investigated transitions of the  $U^{3+}$  ions are larger for U(2) than for U(1), which results mainly from the larger crystal field strength observed for the U(2) site. The differences in the EP coupling strength of the  $U^{3+}$  ions in the U(1) and U(2) sites are in accordance with decay times observed for emission for both sites from the  ${}^4F_{9/2}$  multiplet.

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## 1. Introduction

Electron–phonon (EP) coupling of lanthanide ions has been a subject of a considerable number of studies (see Ref. [1] and papers cited there). However from among  $5f^N$  ions the EP coupling has been so far studied for  $U^{3+}$  and  $U^{5+}$  ions only. The EP coupling strength of  $U^{3+}$  in  $K_2LaCl_5$  was investigated by performing temperature-dependent line width measurements and has been compared with that obtained for  $Nd^{3+}$  ions in the same crystal [2]. The thermal behavior of the line widths of the infrared levels of  $UCl_5$  single crystals was explained by multiphonon processes [3]. The measurements have also shown large spin–spin interactions between the uranium ions in  $UCl_5$ . Karbowski et al. [1] have investigated the EP coupling strength of  $U^{3+}$  and

$Nd^{3+}$  ions doped in  $LaCl_3$  single crystals on the basis of temperature-dependent line broadening and line shifts and have also presented a comparison of the results obtained for  $U^{3+}$  ions in lanthanum trichloride and tribromide hosts. The authors have noticed, that for  $U^{3+}$  ions, similarly as for the lanthanides, the derived  $\bar{\alpha}$  parameter of the EP coupling strength strongly depends on an individual transition. Both above cited papers also report that the EP coupling strength is about a factor of 2 stronger for  $U^{3+}$  than for  $Nd^{3+}$  ions, and that in the tribromide it is stronger than in the trichloride host. Moreover, a far stronger coupling was observed in the  $K_2LaCl_5$  host crystal than in  $LaCl_3$ .

A less effective shielding of  $5f$  electrons by the filled  $6s^2$  and  $6p^6$  shells as well as a larger spatial extent of  $5f$  orbitals as compared with  $4f$  are the main factors responsible for the observed difference in the EP interaction of  $U^{3+}$  and  $Nd^{3+}$  ions. The differences between the  $K_2LaCl_5$  and  $LaCl_3$  host crystals result mainly from the shorter  $M-Cl$  distances in  $K_2LaCl_5$

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which generate stronger interactions with the chloride ligands and lead to an increase of covalency. Similarly, the stronger EP coupling for  $U^{3+}$  in  $LaBr_3$  as compared with that in the  $LaCl_3$  host is due to a larger covalency of the first one. The position of opposite parity states seems to be of minor importance.

In our previous paper we have reported the results of spectroscopic studies of  $U^{3+}$  ions in  $RbY_2Cl_7$  single crystals [4]. This host crystal contains two slightly inequivalent  $Y^{3+}$  ions of  $C_s$  symmetry [5] and is a unique system to study weak couplings between an  $f$ -element and the chlorine ligands because the two intrinsic sites are almost identical in coordination and symmetry. However, there are small differences in the average metal-chloride distances, which cause a different CF strength (19%) affecting the dopant ions which are replacing the  $Y^{3+}$  ions in the two inequivalent sites labeled as U(1) and U(2) [4]. In this way the relationship between the EP coupling and CF strength can be directly measured in a single compound, independently of any other physical effects.

This paper presents the results of temperature-dependent line width measurements of uranium ions in  $RbY_2Cl_7$  single crystals. For the first time the EP coupling parameters have been compared for  $U^{3+}$  and  $U^{4+}$  ions in the same host crystal.

## 2. Experimental

Single crystals of  $U^{3+}$  (0.05%)  $RbY_2Cl_7$  were grown by the Bridgman–Stockbarger method using  $RbU_2Cl_7$  as a doping material. Due to a partial oxidation of  $U^{3+}$  ions small amounts of  $U^{4+}$  ions appeared in the crystal as impurities. Their concentration was unknown.  $RbU_2Cl_7$  was prepared according to the method described earlier in Ref. [6]. Pieces of  $\sim 5 \times 5 \times 0.5$  mm<sup>3</sup> large single crystals have been cut from a bulk crystal and polished under dry paraffin oil.

Laser-selective excitation and fluorescence spectra were recorded using a Spectra Physics model PDL-3 dye laser pumped by the second-harmonic output of a Spectra Physics model GCR-3 Nd:YAG laser. The dyes LDS 698 and DCM were found appropriate to excite the uranium ions in the 13,900–16,400 cm<sup>-1</sup> range. Fluorescence was analyzed using a Spex model 1403 double-grating monochromator and detected by a thermoelectrically cooled Hamamatsu R943-02 photomultiplier tube. The signal was amplified by a Stanford Research model SR445 fast preamplifier and measured using Stanford Research model SR250 time gated integrator. The temperature of the samples could be varied between 4.2 K and room temperature with an Oxford Instruments cryostat and Lake Shore Autotuning Temperature Controller.

## 3. Results

For the broadening measurements well-isolated lines were chosen. The line widths at 12–14 different temperatures between 4.7 and 110 K for  $U^{3+}$  ions and between 4.7 and 240 K for  $U^{4+}$  ions were determined by fits of the spectral profiles with the Voigt type function (a convolution of the Lorentzian and Gaussian type). At elevated temperatures the lifetimes of both the initial and final level of a transition are shortened due to the phonon-induced relaxation process which results in a larger uncertainty in energy and a broadening of the spectral line [7]. A more detailed description of the theory on line width broadening is given in a number of Refs. e.g., [7–9].

The experimentally observed line width is a sum of the temperature independent inhomogeneous line width  $E^{Inh}$ , which is caused by strains and defects in the lattice, and the temperature-dependent, homogeneous line width,  $E^{Hom}$ :

$$\bar{E}(T) = E^{Inh} + E^{Hom}.$$

For shortening of the lifetime, which contributes to the homogenous line width, various relaxation processes can be responsible. The most important ones are the one-phonon emission and absorption process (the direct process) and the Raman two-phonon process. The contribution of the direct process is relatively large at low temperatures, but at higher temperatures the Raman process dominates.

The negligence of the direct process in the estimation of the EP coupling parameter together with the assumption that the Raman process is the dominant temperature-dependent contribution to the total line width may cause a considerable error [7,10]. However it has been also concluded [7] that even in such case the order of magnitude of the  $\bar{\alpha}$  parameters is retained. Moreover, the evaluation of the direct process is a difficult task due to several one-phonon emissions and absorptions which should have to be taken into account. In the case of the direct and Raman process a fit to an equation which includes a number of unknown parameters could result in an obtainment of less reliable parameter values than those received in a fit to the Raman equation only. Thus, in a study where one intends not to compare the absolute but relative EP coupling strengths the contribution from the direct process may be omitted. The Debye temperature was chosen to be equal to 200 K, the same as for  $K_2LaCl_5$  [2] and  $LaCl_3$  [1] which makes possible a comparison of the  $\bar{\alpha}$  parameter values.

Thus the temperature-dependent FWHM data were then fitted to the simplified below given equation containing the inhomogeneous broadening and temperature-dependent broadening due to the Raman

two-phonon process only [8,11].

$$\begin{aligned}\bar{E}(T) &= E^{\text{Inh}} + E^{\text{R}}(T) \\ &= E^{\text{Inh}} + \bar{\alpha} \left( \frac{T}{T_{\text{D}}} \right)^7 \int_0^{T_{\text{D}}/T} \frac{x^6 e^x}{(e^x - 1)^2} dx,\end{aligned}\quad (1)$$

where  $x = \hbar\omega/kT$ ,  $\omega$  is the phonon frequency and  $\bar{\alpha}$  is the coupling coefficient between the electronic levels of the uranium ion and the lattice phonons. The Debye temperature,  $T_{\text{D}}$ , is equal to  $T_{\text{D}} = \hbar\omega_{\text{cut-off}}/k$  and corresponds to the effective maximum phonon energy. In the Debye approximation the phonon density scales as  $\omega^2$  and then drops to zero at the phonon cut-off frequency  $\omega_{\text{cut-off}}$ .

The measurements were performed for emission or excitation lines corresponding to transitions to the  ${}^4G_{7/2}$ ,  ${}^4F_{9/2}$  and  ${}^2H_{21/2}$  multiplets of the  $\text{U}^{3+}$  ions and to the  ${}^1D_2$  and  ${}^1G_4$  multiplets of the  $\text{U}^{4+}$  ions. The  $\text{U}^{3+}$  ions in the two intrinsic sites, labeled henceforth as U(1) and U(2) as well as the  $\text{U}^{4+}$  ions were excited selectively with a narrow laser excitation. The labels and the assignment of the  $\text{U}^{3+}$  transitions is the same as reported in Ref. [4]. The determination of the line widths could be accomplished in the 4.7–110 and 4.7–240 K temperature range for the  $\text{U}^{3+}$  and  $\text{U}^{4+}$  ions, respectively. Above these temperatures the emission is quenched. For  $\text{U}^{3+}$  ions the line broadening could be investigated on the basis of emission or excitation spectra in a relatively narrow temperature range. This may influence the absolute values of determined  $\bar{\alpha}$  parameters, but should not affect the conclusions drawn from the comparative study. The same transitions have been measured for  $\text{U}^{3+}$  ions in the two intrinsic sites.

Fig. 1 presents excitation spectra of the  ${}^4I_{9/2}(\text{Z}_1) - {}^2H_{21/2}(\text{H}_1)$  transitions for U(1) ( $15,144 \text{ cm}^{-1}$ ) (a) and U(2) ( $15,087 \text{ cm}^{-1}$ ) (b) at 4.7, 35 and 75 K. The full-width at half-maximum (FWHM) for the U(1) ions is equal to 0.9 and  $6.1 \text{ cm}^{-1}$  at 4.7 and 75 K, respectively. For U(2) the corresponding values are equal to 1.3 and  $7.7 \text{ cm}^{-1}$ . Fig. 2 presents the emission spectra recorded for the  ${}^4F_{9/2}(\text{G}_1) - {}^4I_{9/2}(\text{Z}_1)$  transitions of U(1) ( $14,294 \text{ cm}^{-1}$ ) (a) and U(2) ( $14,265 \text{ cm}^{-1}$ ) (b) at 4.7, 55 and 90 K. The FWHM values for the U(1) ions are equal to 0.8 and  $4.0 \text{ cm}^{-1}$  at 4.7 and 90 K respectively. For U(2) these values are equal to 1.1 and  $6.0 \text{ cm}^{-1}$ . Fig. 3 presents the excitation spectra recorded for the  ${}^3H_4 - {}^1G_4$  ( $15543 \text{ cm}^{-1}$ ) transitions of  $\text{U}^{4+}$  at 4.7, 70 and 190 K. The FWHM is equal to  $0.9 \text{ cm}^{-1}$  at 4.7 K and  $20.0$  at 190 K.

As for an actinide ion the widths of lines at low temperatures are relatively small. For all investigated transitions the FWHM for U(1) are smaller than for U(2). The line width at low temperatures is mainly determined by the strains and defects in the  $\text{RbY}_2\text{Cl}_7$  lattices. As one should expect the uranium ions located at sites influenced by stronger crystal-fields are more

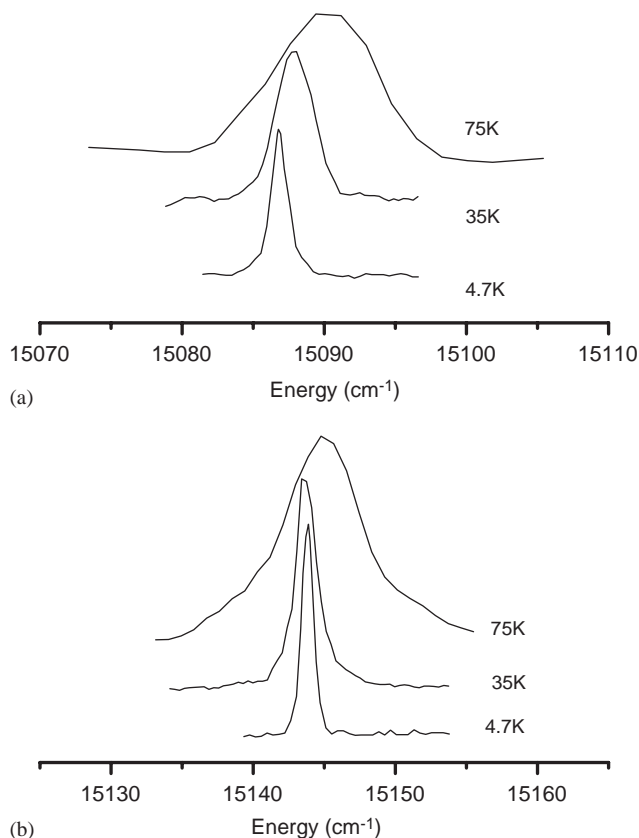


Fig. 1. Excitation spectra of the  ${}^4I_{9/2}(\text{Z}_1) - {}^2H_{21/2}(\text{H}_1)$  transitions for the U(1) site ( $15,144 \text{ cm}^{-1}$ ) (a) and U(2) site ( $15,087 \text{ cm}^{-1}$ ) (b) of the  $\text{U}^{3+}:\text{RbY}_2\text{Cl}_7$  at 4.7, 35 and 75 K. They were recorded while monitoring the  ${}^4F_{9/2}(\text{G}_1) - {}^4I_{9/2}(\text{Z}_1)$  emission line at  $14294$  and  $14,265 \text{ cm}^{-1}$  for U(1) and U(2) respectively.

affected by these factors. With increasing temperature the line widths of the  $\text{U}^{3+}$  and  $\text{U}^{4+}$  ions strongly increases and those for U(2) are larger than for U(1).

The  $\bar{\alpha}$  EP coupling coefficient determined by a least-square adjustment of the experimental and calculated points for  $\text{U}^{3+}$  and  $\text{U}^{4+}$  ions doped in  $\text{RbY}_2\text{Cl}_7$  single crystals as well as the temperature line broadening values ( $\Delta\bar{E}(T)$ ) are presented in Table 1. During the least-square procedure the expression:  $\sum_i [(\bar{E}(T)_{\text{exp}} - \bar{E}(T)_{\text{calc}}) / (\bar{E}(T)_{\text{exp}} + \bar{E}(T)_{\text{calc}})]^2$  has been minimized. Fits and simulations to the temperature-dependent line widths are shown in Figs. 4–6 for the  $\text{U}^{3+}$  (U1),  $\text{U}^{3+}$  (U2) and  $\text{U}^{4+}$  ions, respectively.

#### 4. Discussion

The  $\bar{\alpha}$  parameters strongly depend on a particular transition, what is probably connected with the direct process. A similar observation was made for  $\text{U}^{3+}$  doped  $\text{LaCl}_3$  [1] and  $\text{K}_2\text{LaCl}_5$  [2] single crystals, as well as for  $\text{Ln}^{3+}$  ions [10]. The direct process, in which one phonon is emitted or absorbed, considerably depends on the

energy levels structure and was omitted in our theoretical model. This dependence together with the to some degree arbitrary choice of the Debye temperature, makes the determination of the absolute values of the

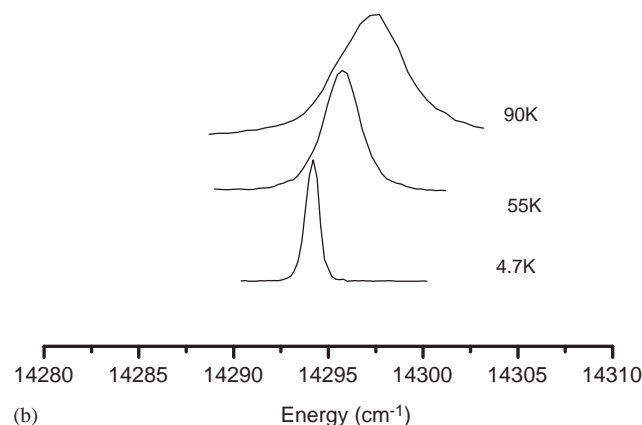
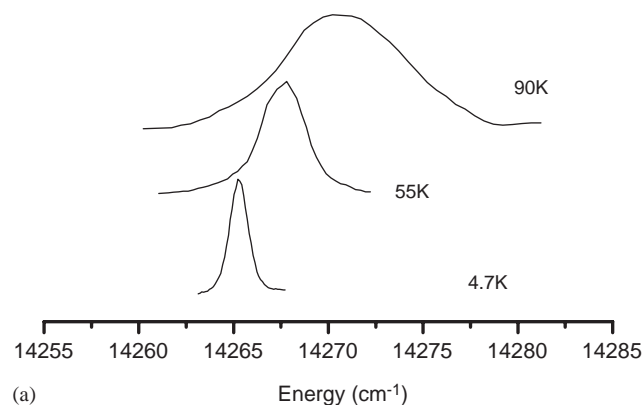


Fig. 2. Emission spectra recorded for the  ${}^4F_{9/2}(G_1) - {}^4I_{9/2}(Z_1)$  transitions for the U(1) site ( $14,294\text{ cm}^{-1}$ ) (a) and the U(2) site ( $14,265\text{ cm}^{-1}$ ) (b) of  $\text{U}^{3+}:\text{RbY}_2\text{Cl}_7$  at 4.7, 55 and 90 K. They were recorded while pumping the  ${}^4I_{9/2}(Z_1) - {}^2H_{21/2}(H_1)$  transition at  $15,144$  and  $15,087\text{ cm}^{-1}$  of U(1) and U(2), respectively.

Table 1

Electron–phonon coupling parameters obtained for various transitions of  $\text{U}^{3+}$  ions in the U(1) and U(2) sites as well as of  $\text{U}^{4+}$  ions, doped in a  $\text{RbY}_2\text{Cl}_7$  single crystal and determined from fits of the experimentally observed temperature induced line broadening to Eq. (1).

Transition <sup>a</sup>	U(1)			U(2)		
	Energy ( $\text{cm}^{-1}$ )	$\Delta\bar{E}$ (T) <sup>b</sup> (K)	$\bar{\alpha}$ ( $\text{cm}^{-1}$ )	Energy ( $\text{cm}^{-1}$ )	$\Delta\bar{E}$ (T) <sup>c</sup> (K)	$\bar{\alpha}$ ( $\text{cm}^{-1}$ )
${}^4G_{7/2}(E_1) \rightarrow {}^4I_{9/2}(Z_2)$	12,892	18.2	373	12,904	13.6	469
${}^4G_{7/2}(E_1) \rightarrow {}^4I_{9/2}(Z_5)$	12,513	9.0	171	12,419	11.0	243
${}^4I_{9/2}(Z_1) \rightarrow {}^4F_{9/2}(G_1)$	14,294	5.3	148	14,265	5.9	222
${}^4F_{9/2}(G_1) \rightarrow {}^4I_{9/2}(Z_1)$	14,294	6.8	165	14,265	6.4	212
${}^4I_{9/2}(Z_1) \rightarrow {}^2H_{21/2}(H_1)$	15,144	15.7	345	15,087	14.3	484
<b>U<sup>4+</sup></b>						
${}^3H_4 - {}^1G_4$	15,543	37.2 <sup>d</sup>	143			
${}^1D_2 - {}^3H_4$	14,590	27.3 <sup>d</sup>	92			

<sup>a</sup> The transition assignments were taken from Ref. [4].

<sup>b</sup> Difference of the line width at 110 K and 4.7 K for  $\text{U}^{3+}$  ions in the U(1) site.

<sup>c</sup> Difference of the line width at 90 K and 4.7 K for  $\text{U}^{3+}$  ions in the U(2) site.

<sup>d</sup> Difference of the line width at 240 K and 4.7 K of the  $\text{U}^{4+}$  ions.

$\bar{\alpha}$  parameter unachievable. Fortunately one may assume that the  $\bar{\alpha}$  parameter, determined even from the simplified equation containing contributions of the Raman two-phonon process only, may for comparison purposes still well serve. The observed constant ratio of the  $\bar{\alpha}$  parameter values determined for various host crystals with a different EP coupling strength justified this conclusion e.g., the ratios obtained for the  ${}^4G_{7/2}$  and  ${}^4F_{9/2}$  multiplets of  $\text{U}^{3+}:\text{LaCl}_3$  and  $\text{U}^{3+}:\text{K}_2\text{LaCl}_5$  are equal to 2.2 and 2.1, respectively.

#### 4.1. Comparison of the results obtained for $\text{U}^{3+}$ in $\text{RbY}_2\text{Cl}_7$ with those in $\text{LaCl}_3$ and $\text{K}_2\text{LaCl}_5$

The obtained  $\bar{\alpha}$  values for  $\text{U}^{3+}$  doped  $\text{RbY}_2\text{Cl}_7$  single crystals are considerably larger than those for the  $\text{LaCl}_3$

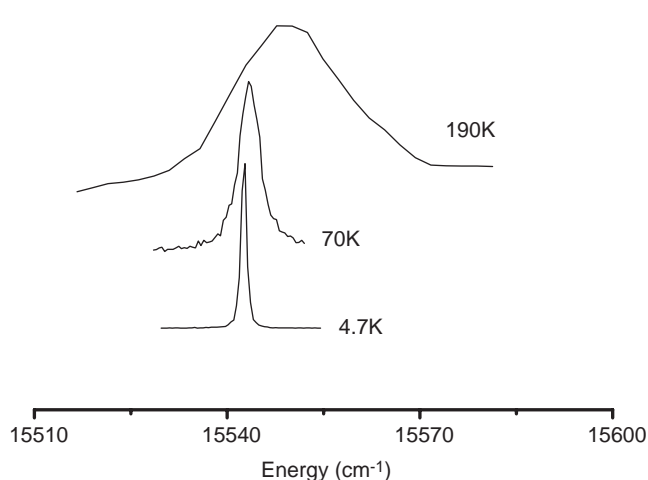


Fig. 3. Excitation spectra recorded at 4.7, 70 and 190 K for the  ${}^3H_4 - {}^1G_4$  ( $15,543\text{ cm}^{-1}$ ) transition of the  $\text{U}^{4+}:\text{RbY}_2\text{Cl}_7$  crystal, while monitoring the  $14,590\text{ cm}^{-1}$  ( ${}^1D_2 - {}^3H_4$ ) emission line.

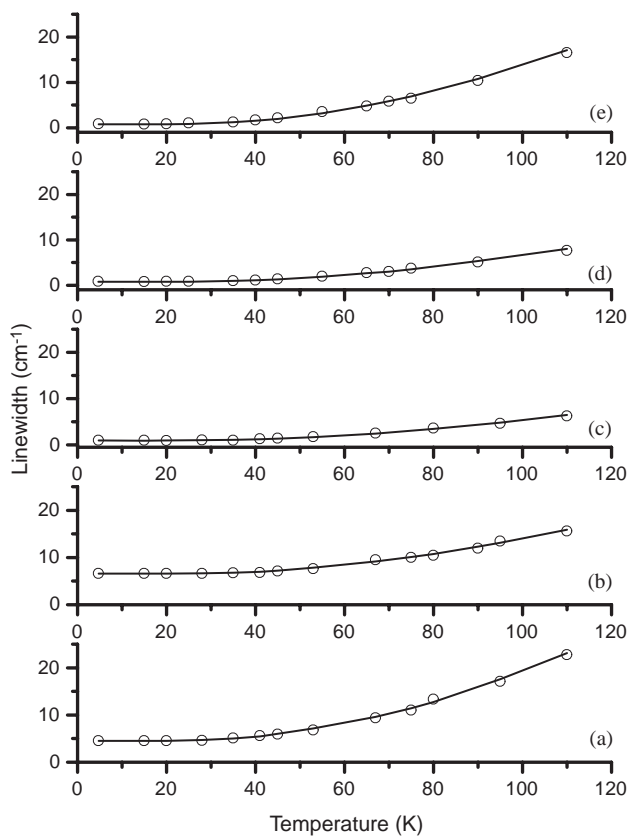


Fig. 4. The line widths of the  ${}^4G_{7/2}(E_1) - {}^4I_{9/2}(Z_2)$  (a),  ${}^4G_{7/2}(E_1) - {}^4I_{9/2}(Z_5)$  (b),  ${}^4I_{9/2}(Z_1) - {}^4F_{9/2}(G_1)$  (c),  ${}^4F_{9/2}(G_1) - {}^4I_{9/2}(Z_1)$  (d) and  ${}^4I_{9/2}(Z_1) - {}^2H_{21/2}(H_1)$  (e) transitions for the U(1) site of the  $U^{3+}:\text{RbY}_2\text{Cl}_7$  crystals as a function of temperature. The circles represent the experimental data and the solid curve is the fit to Eq. (1) for the Raman process.

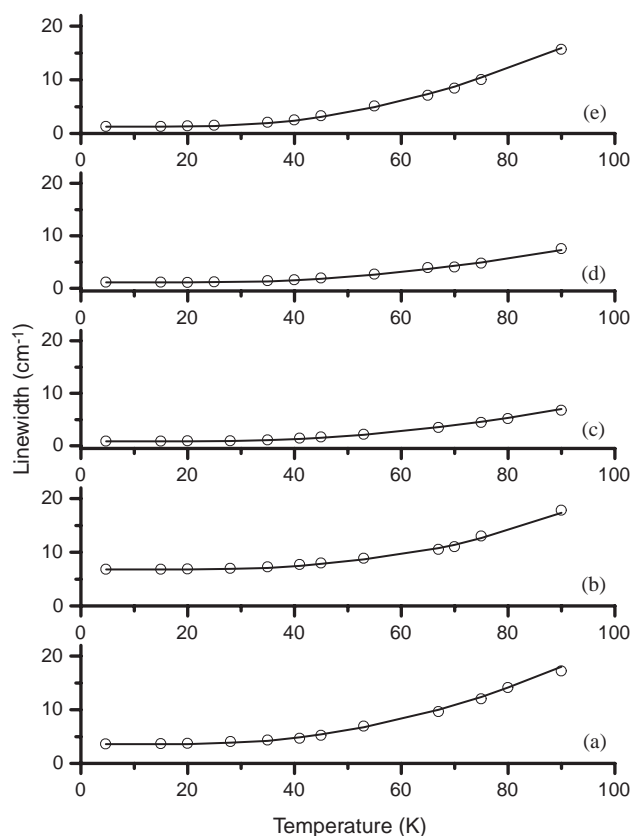


Fig. 5. The line widths of the  ${}^4G_{7/2}(E_1) - {}^4I_{9/2}(Z_2)$  (a),  ${}^4G_{7/2}(E_1) - {}^4I_{9/2}(Z_5)$  (b),  ${}^4I_{9/2}(Z_1) - {}^4F_{9/2}(G_1)$  (c),  ${}^4F_{9/2}(G_1) - {}^4I_{9/2}(Z_1)$  (d) and  ${}^4I_{9/2}(Z_1) - {}^2H_{21/2}(H_1)$  (e) transitions for the U(2) site of the  $U^{3+}:\text{RbY}_2\text{Cl}_7$  crystals as a function of temperature. The circles represent the experimental data and the solid curve is the fit to Eq. (1) of the Raman process.

host. For the last one they stay in  $16\text{--}80\text{ cm}^{-1}$  range [1]. In both host crystals the energies of the highest energy phonons are similar. The main difference is in the U–Cl distances. For  $\text{RbY}_2\text{Cl}_7$  the mean value of the Y–Cl distances is equal to  $\sim 270\text{ pm}$  and is considerably shorter than the mean La–Cl distance in  $\text{LaCl}_3$  ( $\sim 295\text{ pm}$ ). This generates stronger interaction of the uranium ions in the  $\text{RbY}_2\text{Cl}_7$  host with the chlorine ligands and leads to an increase of covalency. The stronger CF affecting the uranium ions in  $\text{RbY}_2\text{Cl}_7$ , may be quantitatively compared by the  $N_v$  scalar parameter [12], characterizing the CF by one single number:

$$N_v = \left[ \sum_{k,q} (B_q^k)^2 \frac{4\pi}{(2k+1)} \right]^{1/2}, \quad (2)$$

where  $B_q^k$  are semi-empirical CF parameters [4].

As one should expect, the  $N_v$  values obtained for U(1) and U(2) in  $\text{RbY}_2\text{Cl}_7$  [4] are equal to 2823 and  $3505\text{ cm}^{-1}$ , respectively and are larger than that for  $U^{3+}:\text{LaCl}_3$  [13] which amounts to  $2144\text{ cm}^{-1}$ . The obtained EP coupling parameters are larger also than

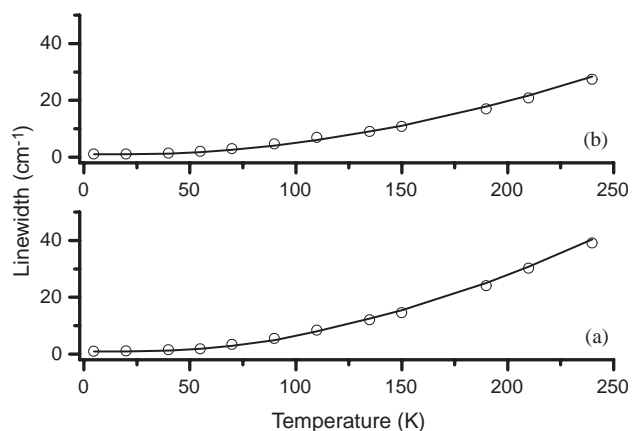


Fig. 6. The line widths of the  ${}^3H_4 - {}^1G_4$  (a) and  ${}^1D_2 - {}^3H_4$  (b) transitions of  $U^{4+}$  ions for the  $U^{3+}(U^{4+}):\text{RbY}_2\text{Cl}_7$  crystals as a function of temperature. The circles represent the experimental data and the solid curve is the fit to Eq. (1) of the Raman process.

those reported for the  $\text{K}_2\text{LaCl}_5$  host [2]. For the last one they stay in  $88\text{--}200\text{ cm}^{-1}$  range. In the  $\text{K}_2\text{LaCl}_5$  crystal the La–Cl distances are in the  $275.2\text{--}285.6\text{ pm}$  range

(average 281.1 pm), while for the U(1) site in the  $\text{RbY}_2\text{Cl}_7$  host crystal they amount to 269.0–276.1 pm (average 272.4 pm). Thus the shorter U–Cl distances cause a stronger overlap between the wave functions of the metal and Cl ligands and, in consequence, a stronger EP coupling is observed for U(1) in  $\text{RbY}_2\text{Cl}_7$ .

The stronger CF and larger covalency, being the result of shorter U–Cl distances causes that the opposite parity states are positioned in  $\text{U}^{3+}:\text{RbY}_2\text{Cl}_7$  or  $\text{U}^{3+}:\text{K}_2\text{LaCl}_5$  at a far lower energy than in  $\text{U}^{3+}:\text{LaCl}_3$ . In the first one the  $f-d$  bands are observed at  $\sim 15,300\text{ cm}^{-1}$ , while in the latter one at  $\sim 21,000\text{ cm}^{-1}$ . The proximity of the  $f-d$  states might enhance the EP coupling [11]. This effect should be larger for levels located closer to the  $f-d$  states. As one may notice in Table 1 a large  $\bar{\alpha}$  value was obtained for transition to the  ${}^2H_{21/2}$  multiplet located close to the  $f-d$  levels. For the next  ${}^4F_{9/2}$  multiplet, located at a lower energy the obtained  $\bar{\alpha}$  value is significantly smaller, however for the next lower positioned  ${}^4G_{7/2}$  multiplet the value of the EP coupling parameter is again almost as large as for the  ${}^2H_{21/2}$  level.

However, as it was already noticed, for a given crystal the value of the EP coupling parameter is not fixed but strongly depends on the individual transition. Thus, in order to evaluate the influence of the position of the  $f-d$  states on the  $\bar{\alpha}$  value the relative ratio of the parameters obtained for the same transitions in different crystals should be compared. The various host crystals will, besides the position of the  $f-d$  states, differ also in CF strength and covalency. Nevertheless, assuming that the increase in covalency and CF strength, being a consequence of the decrease in U–Cl distances, should result in a proportional increase of the  $\bar{\alpha}$  value for all multiplets an extraction of the effect of the  $f-d$  position should be possible. This last one should considerably affect only transitions to multiplets closely located to the  $f-d$  states. Indeed, for  $\text{U}^{3+}:\text{LaCl}_3$ ,  $\text{U}^{3+}:\text{K}_2\text{LaCl}_5$ ,  $\text{U}^{3+}(1):\text{RbY}_2\text{Cl}_7$  and  $\text{U}^{3+}(2):\text{RbY}_2\text{Cl}_7$  the ratios of the obtained  $\bar{\alpha}$  values for the  ${}^4G_{7/2}$  (taking into account the larger value) and  ${}^4F_{9/2}$  multiplet are almost constant and equal to 2.2, 2.1, 2.3 and 2.1, respectively. In contrast, for the  ${}^4G_{7/2}$  and  ${}^2H_{21/2}$  multiplets the ratio of the  $\bar{\alpha}$  values is for  $\text{U}^{3+}:\text{LaCl}_3$  equal to 2.8 but for the two intrinsic sites of  $\text{U}^{3+}$  in  $\text{RbY}_2\text{Cl}_7$  it is significantly different, equal to 1.1 and 0.97, respectively. The observed for the levels of the  ${}^2H_{21/2}$  multiplet large enhance of the EP coupling strength may be ascribed to the proximity of opposite parity states. A strong influence of these states was observed only when the energetic difference between the  $f-f$  transition and the first  $f-d$  transition was sufficiently small. In our case an increase of the EP coupling strength was observed only for the  ${}^2H_{21/2}$  multiplet positioned very closely, at  $\sim 150\text{ cm}^{-1}$  below first  $f-d$  level but for the  ${}^4F_{9/2}$  multiplet, located at  $\sim 1000\text{ cm}^{-1}$  below this level it

could not be noticed. This explains while for the  $\text{K}_2\text{LaCl}_5$  and  $\text{LaCl}_3$  host crystals, where the investigated transitions were observed at a larger distance from the lowest  $f-d$  state, this effect has not been observed. The influence of  $f-d$  states may be related to the extrinsic Raman two-photon process in which one phonon is absorbed and one is simultaneously emitted by means of the first-order term of the EP interaction for the two phonons. The matrix element of the transition probability for this process is inversely proportional to the energy differences between the initial and an intermediate state involved in the phonon absorption and emission. The nearby located  $4f^n(5f^n)$  or  $4f^{n-1}5d^1(5f^{n-1}6d^1)$  states may be in the extrinsic process involved. However, since for a lanthanide (actinide) ion the transition probability for a process involving an opposite parity state is guessed (based on ms ( $\mu\text{s}$ ) vs. ns lifetimes for  $f-f$  and  $f-d$  transitions) to be  $10^6$  ( $10^3$ ) times higher than that for a process involving  $4f(5f)$  states [14] the effect of nearby  $4f^{n-1}5d^1(5f^{n-1}6d^1)$  states will overwhelm those of the  $4f^n(5f^n)$ .

#### 4.2. Comparison of the results obtained for the $\text{U}^{3+}$ and $\text{U}^{4+}$ ions in the $\text{RbY}_2\text{Cl}_7$ single crystal

The obtained  $\bar{\alpha}$  values for  $\text{U}^{4+}$  are considerably smaller than those for  $\text{U}^{3+}$  in the same  $\text{RbY}_2\text{Cl}_7$  host crystal. Again, two factors—the CF strength and the positions of opposite parity  $f-d$  states are expected to have the dominating influence on the EP coupling. A crystal-field analysis for  $\text{U}^{4+}$  ions in  $\text{RbY}_2\text{Cl}_7$  host crystals is not available. However such analysis has been performed for  $\text{U}^{3+}$  and  $\text{U}^{4+}$  ions doped in  $\text{Ba}_2\text{YCl}_7$  single crystals [15,16] in which the ions possess a similar chloride surrounding. In this crystal a far stronger CF is affecting the  $\text{U}^{4+}$  ions, which is expressed by the  $N_v$  parameters equal to 4573 and  $3154\text{ cm}^{-1}$  for  $\text{U}^{4+}$  and  $\text{U}^{3+}$ , respectively. The splitting of the ground level amounts to  $1137\text{ cm}^{-1}$  for  $\text{U}^{4+}$  and  $538\text{ cm}^{-1}$  for  $\text{U}^{3+}$ . In the  $\text{RbY}_2\text{Cl}_7$  crystals a similar value of  $1010\text{ cm}^{-1}$  was determined for  $\text{U}^{4+}$  [17] and of 473 and  $567\text{ cm}^{-1}$  for the U(1) and U(2) sites of the  $\text{U}^{3+}$  ions, respectively [4]. Thus one can assume, that the ratio of the CF strength for the  $\text{U}^{3+}$  and  $\text{U}^{4+}$  ions in  $\text{RbY}_2\text{Cl}_7$  is similar to the one in the  $\text{Ba}_2\text{YCl}_7$  host. The stronger CF should result in a stronger EP coupling for  $\text{U}^{4+}$ , however from our investigations an opposite tendency has been noticed. Thus, the second factor i.e., the proximity of the  $f-d$  states observed at an energy close to  $30,000\text{ cm}^{-1}$ , that is a factor of 2 higher than in the  $\text{U}^{3+}$  spectrum, seems to be the dominating effect. The observed relation between the EP coupling strength for the  $\text{U}^{3+}$  and  $\text{U}^{4+}$  ions is also in accordance with a qualitative statement which means that the intensities of the vibronic sidebands in comparison to those of electronic origin are lower for  $\text{U}^{4+}$  than for  $\text{U}^{3+}$  ions [17].

### 4.3. Comparison of the results obtained for $U^{3+}$ in the two intrinsic sites $U(1)$ and $U(2)$

For all investigated transitions the EP coupling parameters are larger for  $U(2)$  than for  $U(1)$ . The differences range from 28% for the  ${}^4G_{7/2}$  multiplet to 40% for  ${}^2H_{21/2}$ . This results primarily from shorter U–Cl distances in  $U(2)$  (average 270.3 pm) as compared to  $U(1)$  (average 272.4 pm) which generate a stronger CF affecting the uranium ions in the  $U(2)$  site. If one uses for comparison purposes the scalar parameter  $N_v$  (Eq. (2)), the difference in the CF strength is about 19%. As a consequence of this the uranium ions in the  $U(2)$  site interact stronger with the chloride ligands which leads to an increase of covalency. The influence of the second factor has been proved by the larger differences in the values of the EP coupling parameters obtained for the  ${}^2H_{21/2}$  multiplet, which one is being influenced to the largest extent by the position of the opposite parity states (see Section 4.1). The  $5f^3-5f^26d^1$  transitions start for  $U(2)$  at  $\sim 15,300\text{ cm}^{-1}$ , while for  $U(1)$  at  $\sim 15,700\text{ cm}^{-1}$ , and this additional factor, superimposed on the differences in the CF strength, seems to cause the observed 40% increase in the parameter values.

The observed differences in the EP coupling strength are in accordance with the differences in the decay time recorded for emission observed from the  ${}^4F_{9/2}$  multiplet. For the 0.05%  $U^{3+}:\text{RbY}_2\text{Cl}_7$  crystals the decay time measured for the  $U(1)$  site is equal to  $0.94 \pm 0.05\ \mu\text{s}$ , while for the  $U(2)$  site, with a stronger EP coupling, the decay time is considerably shorter and is equal to  $0.23 \pm 0.05\ \mu\text{s}$  [4]. Assuming that the radiation relaxation rate is similar for both sites the differences in the lifetimes are due to a multiphonon relaxation rate to the next lowest  ${}^4G_{7/2}$  multiplet. The minimal energy gaps between these multiplets are very similar for both sites and are equal to 1005 and  $973\text{ cm}^{-1}$  for  $U(1)$  and  $U(2)$ , respectively. Four phonons of the highest energy of  $280\text{ cm}^{-1}$  could bridge the gap in each case and the observed fourfold difference in the non-radiative decay rates cannot be accounted for by the energy-gap law [11].

In our previous paper [4] we have related the observed differences in the lifetime to differences in the crystal-field strength and have shown that the ratio of the measured lifetimes of the  ${}^4F_{9/2}$  level should be roughly equal to the eight power of the ratio of the crystal-field strengths for the two intrinsic sites. More direct differences in the multiphonon relaxation could be related to differences in the U–Cl length or the EP coupling strength. Within the framework of the non-linear relaxation theory proposed by Orlovskii et al. [18] the total  $n$ -phonon relaxation rate,  $W_{\text{MR}}(n)$ , between two rare-earth ion manifolds can be

expressed as

$$W(J \rightarrow J')(n) = \frac{1}{137} (2J + 1)^{-1} \sum_{k=2,4,6} k(\Xi_k)(n) (LSJ || U^{(k)} || L'S'J') \eta^n, \quad (3)$$

where  $\Xi_k(n)$  is the intensity parameter of the  $n$ -phonon transitions,  $U^{(k)}$  are reduced matrix elements and  $\eta$  is a parameter characterizing the electron–phonon coupling. This equation is analogous to the Judd–Ofelt expression [19,20] for line strengths of electric-dipole transition between LSJ states of  $\eta f^N$  ions, and shows that a larger multiphonon relaxation rate is expected for transitions with larger reduced matrix elements,  $U^{(k)}$ , and thus with larger line strengths. Usually  $\eta$  is treated as an empirical parameter, but according to the crude equation in the single frequency approximation of crystal lattice vibrations it can be derived as

$$\eta = \frac{\hbar}{8\pi c \bar{\nu}} \frac{1}{M} \frac{1}{R_0}, \quad (4)$$

where  $M$  is the reduced atomic mass of the ions involved in the vibrations,  $\bar{\nu} = 1/\lambda$  ( $\text{cm}^{-1}$ ) is the frequency of phonons participating in the radiationless transition, and  $R_0$  is the minimal distance between rare-earth ion and the nearest ligands.

Since the reduced matrix elements are insensitive to small changes in the surrounding of the central ion one may assume that the intensity parameters  $\Xi_k(n)$  for  $U^{3+}$  ions in both intrinsic sites are similar. This leads to the ratio  $W(U(2))({}^4F_{9/2} \rightarrow {}^4G_{7/2})(n=4) / W(U(1))({}^4F_{9/2} \rightarrow {}^4G_{7/2})(n=4) = \eta^4(U(2)) / \eta^4(U(1)) = R_0^4(U(1)) / R_0^4(U(2)) = (2.690\ \text{\AA})^4 / (2.666\ \text{\AA})^4 = 1.04$  which significantly differ from the experimentally observed value equal of  $4.1 \pm 1.1$ . However if the  $\eta$  parameters calculated from Eq. (4), which are characterizing the electron–phonon coupling, are replaced by the  $\bar{\alpha}$  values one obtain the ratio:  $\eta^4(U(2)) / \eta^4(U(1)) = \bar{\alpha}^4(U(2)) / \bar{\alpha}^4(U(1)) = 1.39^4 = 3.7$ , which is in accordance with experiment. Hence the determination of the phonon factor, which is governing the multiphonon relaxation rate, on the basis of the shortest distance between the  $\eta f^N$  ion and the nearest ligand may be in many cases a too crude approximation and other factors like the CF strength should be taken into account.

## 5. Summary

For the first time EP coupling parameters have been determined for two slightly different  $U(1)$  and  $U(2)$  intrinsic sites of  $U^{3+}$  ions in a single crystal as well as for  $U^{4+}$  in the same  $\text{RbY}_2\text{Cl}_7$  host crystal. Investigations of temperature induced line broadening were chosen as a method for the determination of the  $\bar{\alpha}$  electron–phonon

coupling parameters. The values of the parameters were determined by a fit of the experimentally observed line widths to an equation containing the temperature dependent broadening due to the Raman two-phonon process. The obtained parameters for the  $U^{3+}$  ions are larger than those determined for the ion in the  $LaCl_3$  and  $K_2LaCl_5$  host crystals. These results from shorter  $M-Cl$  distances in  $RbY_2Cl_7$  which causes stronger interaction with the chloride ligands and leads to an increase of covalency. The position of opposite parity ( $f-d$ ) states results in an increase of the  $\bar{\alpha}$  parameter value determined for the  ${}^2H_{11/2}$  multiplet of  $U^{3+}$ . The same factor is responsible for a weaker EP coupling of the  $U^{4+}$  ions as compared with that of  $U^{3+}$  ions, in spite of a stronger CF affecting the first one. A comparison of the values of the  $\bar{\alpha}$  EP coupling strength parameter for  $U^{3+}$  ions in the two intrinsic sites shows, that they are 28–40% larger for U(2), which is in accordance with the stronger crystal field influencing the ions at this site. The revealed differences of the EP coupling strength are also in accordance with the differences in the decay time recorded for emission observed from the  ${}^4F_{9/2}$  multiplet. However the observed differences in the multiphonon relaxation rate cannot be accounted for by differences in the U–Cl distances of  $U^{3+}$  ions in both sites, but other factors, such as the crystal field strength should be taken into account.

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