

ANALYSIS OF $5f^3 \rightarrow 5f^26d^1$ TRANSITIONS IN THE ABSORPTION SPECTRUM OF U^{3+} IN Cs_2NaYCl_6

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The electronic absorption spectrum of a $Cs_2NaYCl_6:U^{3+}$ single crystal was investigated in the 13000–45000 cm^{-1} spectral range at 300 K. An interpretation of the $5f^3 \rightarrow 5f^26d^1$ transitions on the basis of the $J_i\gamma$ interaction enabled the determination of the energy of the first unresolved level of the $5f^26d^1$ electronic configuration, the distance between the first two levels of the configuration as well as the splitting parameter of the d -electron in the crystal field.

PACS numbers: 78.20.-e, 78.20.Bh, 78.20.We

1. Introduction

The first attempts of an analysis of the $5f^3 \rightarrow 5f^26d^1$ transitions, which occur in uranium(III) absorption spectra, have been reported for solution spectra by Kaminskaya et al. [2, 3] and for solid state by Mazurak et al. [4]. This paper presents a successful interpretation of the $5f^3 \rightarrow 5f^26d^1$ bands observed in the absorption spectrum of a 0.5% U^{3+} doped Cs_2NaYCl_6 single crystal.

2. Experimental

The single crystal of $Cs_2NaYCl_6:U^{3+}$ was grown by the Bridgman–Stockbarger method using Cs_2NaUCl_6 as the doping substance. The crystal had 6 mm in diameter and was grinded to *ca.* 0.5 mm thickness. The uranium concentration was about 0.5%. Some details about the method are given in Ref. [5]. For the preparation of Cs_2NaUCl_6 stoichiometric quantities of $NH_4UCl_4 \cdot 4H_2O$ [6], $CsCl$ and $NaCl$ with an excess of NH_4Cl were heated together for two days in a quartz tube at 400 to 500°C and a vacuum of about 10^{-6} hPa. A deep ink-blue hygroscopic crystalline powder was obtained. X-ray powder diffraction data, taken on a “Stoe Fast Powder Diffractometer” confirmed the O_h^5 ($Fm\bar{3}m$) space group of the crystal. The absorption spectrum was recorded on a Cary-5 NIR-Vis-UV spectrophotometer at 300 K.

3. Results and discussion

The broad and very intense absorption bands observed in the 14000–45000 cm^{-1} spectral range were assigned to the Laporte allowed $5f^3 \rightarrow 5f^26d^1$ transitions. One may distinguish in the spectrum (Fig. 1) five groups of bands

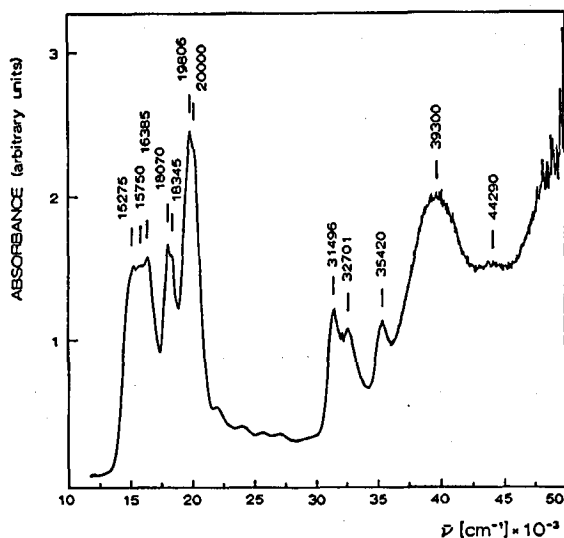


Fig. 1. Absorption spectrum of the U^{3+} doped $\text{Cs}_2\text{NaYCl}_6$ single crystal at 20°C .

with centers of gravity at 15830 cm^{-1} (I), 19055 cm^{-1} (II), 32100 cm^{-1} (III), 35420 cm^{-1} (IV) and 41800 cm^{-1} (V). The interpretation of the transitions is based on the semi-empirical method developed by Johnson and Sandoe [1] for the elucidation of the electronic transitions which gives rise to the broad absorption bands of bivalent rare earth ions substituted in various alkaline earth fluorides and alkali halides of cubic coordination. The $4f^25d^1$ configuration is assumed to behave according to a $J_i\gamma_n$ coupling scheme, where J_i is the total angular momentum of a Russell–Saunders term derived for the $4f^{n-1}$ core and $J_i\gamma_n$ is a state of the $5d$ electron in the crystal field. The observed f – d bands correspond to $4f^n \rightarrow J_i\gamma_n$ transitions with Δ — the separation between γ_3 and γ_5 in an O_h crystal field.

Hence, one may assume with good approximation that the energies of the $5f^3 \rightarrow 5f^26d^1$ bands observed in the absorption spectrum of $\text{Cs}_2\text{NaYCl}_6:\text{U}^{3+}$ arise from transitions between the ground state of the $5f^3$ configuration and the d -crystal-field components of the $5f^26d^1$ states. The observed centers of gravity (I–V) fit very good to the Sm^{2+} type of energy level scheme [1] according to which the separation between the III and I and IV and II bands should be alike. These values are indicated in the energy level diagram (Fig. 2) by the parameters Δ and Δ' and were found to be equal to 16270 and 16365 cm^{-1} , respectively.

On this basis the excitation energy, $E_{fd} = 22338 \text{ cm}^{-1}$, uncorrected for nephelauxetic effects was determined together with the separation,

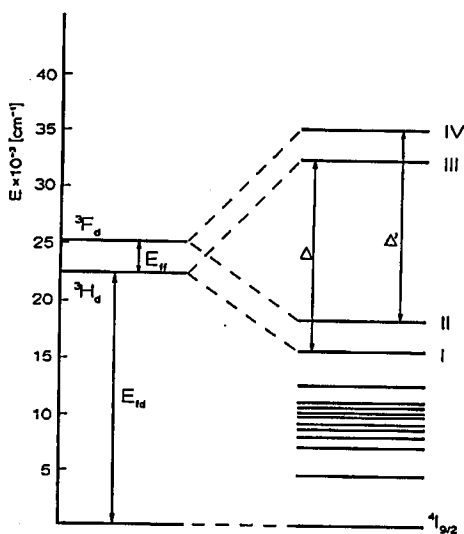


Fig. 2. Energy level diagram for U^{3+} in Cs_2NaYCl_6 .

$E_{ff} = 3263 \text{ cm}^{-1}$, of the first two terms of the $5f^26d^1$ configuration. The positions of the original $5f^26d^1$ levels were calculated by the barycenter rule. As one should expect, the decrease in uranium-chlorine bond lengths in the compound [7] causes a shift of the position of the first $5f^3 \rightarrow 5f^26d^1$ band as well as the excitation energy, E_{fd} , towards lower energies as compared with other uranium(3+) chloro-compounds [2, 3, 7]. The excellent agreement with theory received in this investigations confirmed the possibility of an analysis of the $5f^3 \rightarrow 5f^26d^1$ transitions in actinide compounds by means of the $J_i\gamma$ scheme of interactions.

Acknowledgments

This work was supported by the Committee for Scientific Research within project 0424/P3/92/03 which is gratefully acknowledged.

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