

OPTICAL SPECTRA OF NEODYMIUM AND EUROPIUM TUNGSTATES AND MOLYBDATES

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Absorption and excitation spectra of lanthanides molybdates and tungstates were measured and analyzed. Probabilities of electronic transitions were analysed on the basis of the Judd-Ofelt theory. The significant differences of intensities were observed. Those differences could result from the symmetry changes, cooperative effects and electron-phonon interaction. The elucidation of intensities given by separate mechanisms needs further investigation.

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1. Introduction

Recently a big effort was made to explain the nature of optical properties of lanthanides tungstates and molybdates. The main interest of these investigations concerns the energy transfer and energy migration in one-, two- and three-dimensional systems; with one and more site symmetry positions [1-3].

The single crystals of neodymium tungstates and molybdates of types $\text{KLn}(\text{WO}_4)_2$ and $\text{KLn}(\text{MoO}_4)_2$ and doped $\text{KY}(\text{MoO}_4)_2:\text{Ln}$ are especially interesting for the reason of their applications [4]. Numerous studies have been made on vibronic transition associated with $4f-4f$ transitions of rare earth ions in crystals. The vibronic transitions observed in optical spectra reflect electron-lattice interaction, which also causes variations of nonradiative transitions types [5]. These studies can explain what types of phonons are coupled in the vibronic transitions and what sort of mechanism can explain their intensities [6].

On the other hand, the dimensionality of the systems is an important parameter of the relaxation dynamics of metal ions in solids which imposes the restriction on ion-ion interaction. These types of investigations are the newest and of great importance in explanation of both the concentration dependence of intensities of optical lines and the structure of optical lines [7].

In this paper we would like to explain: (a) the differences in electronic transition intensities of neodymium tungstates and molybdates on the basis of absorption spectra and (b) the differences in vibronic structures of optical bands in both the types of crystals, basing on the excitation spectra at 77 K and absorption spectra at 5 K.

2. Experimental

The single crystals of $\text{KLn}(\text{MoO}_4)_2$ and $\text{KLn}(\text{WO}_4)_2$ were grown from using the method described by Klevtsova et al. [8].

The absorption spectra at 300 and 5 K were measured using Cary-Varian 5 spectrophotometer. The intensity analysis was performed according to the procedure described in Ref. [9].

Excitation spectra were detected by SPF-500 SOPRA spectrofluorometer. The analysis of vibronic sidebands was performed on the basis of IR and Raman spectra [10].

3. Results and discussion

Figures 1-3 show the absorption spectra of neodymium tungstate and molybdate at 300 and 5 K and excitation spectra of europium single crystals at 77 K. In both the cases the complex structure of the bands is remarkable, as well as the significant differences in their intensities mainly for transitions observed in absorption spectra. Besides main electronic lines, rich vibronic structure of bands is observed.

Crystallographic data for monoclinic tungstates and molybdates indicate complex polymeric structure of the investigated single crystals. From X-ray analysis and IR and Raman spectra Klevtsova and Volkova concluded that two main classes were presented in the case of tungstates [11]. In the former europium compound crystallized creating dimeric subunits of W_2O_{10} types, while in the latter one, neodymium formed subunits of $\text{W}_4\text{O}_{16}^{8-}$ type with two nonequivalent W sites. In this way the sandwich layer structure is composed of periodical LnO_8 and KO_{12} repeated polyhedra. Those differences in the crystal structure are reflected in IR and Raman spectra [10, 12].

In the case of molybdates of series of lanthanides some small differences can be found. Neodymium molybdate plays an intermediate role in this series, the probable structure containing separate tetrahedra of MO_4 units exists, while europium seems to crystallize in dimeric type structure. In both types of structures LnO_8 polyhedra are formed with only little differences in their symmetry distortion.

What effect, if any, of these polymeric structures is observed in the electron spectroscopy of the systems under investigation? In Table I there are compiled the oscillator strength values and the Judd-Ofelt parameters for $\text{KNd}(\text{MoO}_4)_2$ and $\text{KLn}(\text{WO}_4)_2$ single crystals. The significant differences are observed in the values of oscillator strengths and τ_λ parameters for neodymium tungstate and molybdate. On the other hand, all the oscillator strength values are drastically

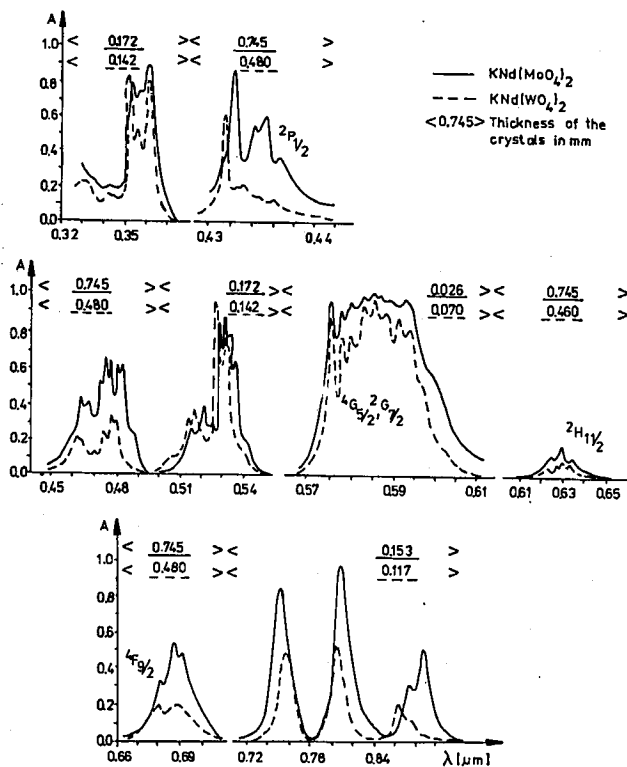


Fig. 1. Absorption spectra of neodymium tungstate and molybdate at 300 K.

increased compared to those observed in the spectra of lanthanide aquoion and other lanthanide compounds with dimeric or polymeric structure [13].

What are the factors which can affect the intensities of electronic transition for the same ion? They are: symmetry, polarizability and, connected with covalency, vibronic coupling and ion-pairs interaction. Judging from the available X-ray and IR data for two types of compounds of tungstates and molybdates, the site symmetry of Nd³⁺ ion changes from C_2 for the former to C_1 for the latter. Such changes of symmetry cannot explain the drastical changes in intensities.

Similar changes of symmetry for the set of lanthanide polymeric carboxylates did not follow the drastical differences in intensities [13]. Moreover, the intensities of carboxylates are four or three times lower. Let us consider the Ln-O bonding lengths. In dimeric carboxylates Nd₂Ala₂(H₂O)₄ they are equal to 2.491 for Nd-O_{WO₄}²⁻ ≈ 2.48 whereas P_{exp} for $4I_{9/2} \rightarrow 4G_{5/2}, 2G_{7/2}$ are equal to 1237×10^{-8} and 3885×10^{-8} , respectively (Table I). The intensities of $4I_{9/2} \rightarrow 4G_{5/2}, 2G_{7/2}$ transitions in the neodymium tungstate spectra are comparable to those observed in DMF solution of lanthanide nitrates [9], explained by polarizability mechanism of Mason [14], and are little higher than those found for lanthanide nitrate [15].

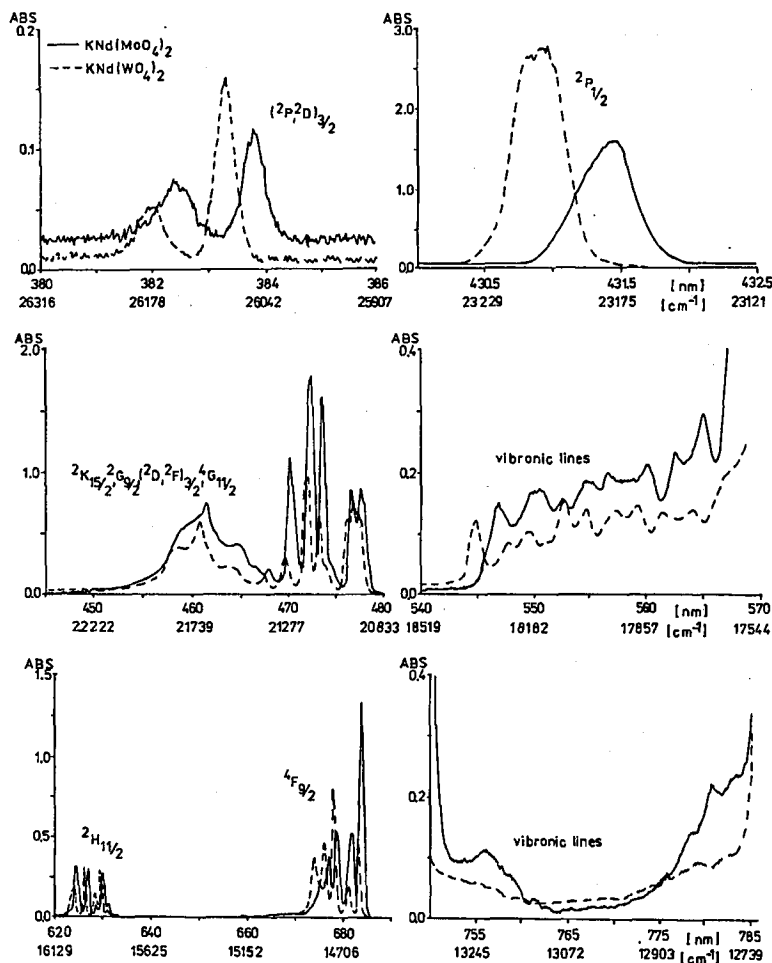


Fig. 2. Absorption spectra of neodymium tungstate and molybdate at 5 K.

To our knowledge, however, such high intensities as observed in molybdates have not been observed up to now in solids. This enhancement of intensities could be a result of different polarizability of tetrameric and separated MO_4^{2-} structures. It can lead to the change in intensities of hypersensitive transition of Nd^{3+} ion.

Moreover, external vibrational mode attributed to the translational and rotational motions of the unit cell differs significantly for two types of compounds. The relative intensities of internal vibration at $600\text{--}800\text{ cm}^{-1}$ to those at $\approx 400\text{ cm}^{-1}$ increase for molybdate. These effects must influence the electron-phonon coupling of the systems under investigation. An additional cooperative interaction appears between lanthanide ion pairs composed by two LnO_8 polyhedra in tungstate, giving very short Nd-Nd distance ($=4.21\text{ \AA}$) — which is much shorter than that

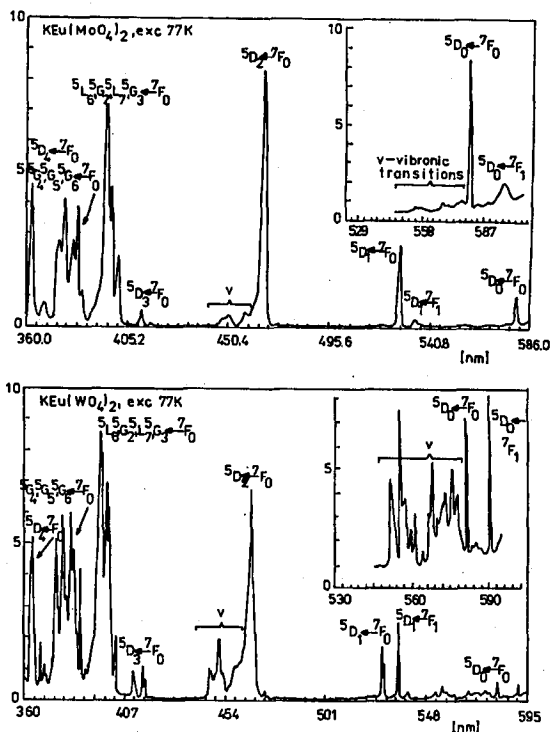


Fig. 3. Excitation spectra of europium single crystals at 77 K.

in dimeric $\text{Ln}_2\text{Ala}_2(\text{H}_2\text{O})_4$ carboxylate, where ion-pair interaction was stated. Ion-pair interaction could be produced by exchange interaction which varies according to $\exp[-2R/L]$, where L is the effective ion radius of the rare earth ion and operates only over short distances. Additional interaction can appear through the anion intermediary by superexchange interaction. These interactions can lead to an increase in intensities as well. Now we could not distinguish the intensities given by different mechanisms — it needs further investigation of the diluted systems. Similarly, at this moment Nd–Nd distance in the molybdate is not available, thus it is difficult to elucidate particular mechanisms and participations in overall intensity caused by them.

Coupling of two neodymium ions in dimer yields inhomogeneous broadening of optical lines. High resolution measurement performed at 5 K leads to broadening of the band corresponding to $^4I_{9/2} \rightarrow ^2P_{1/2}$ transition (half-width $\approx 26 \text{ cm}^{-1}$) in both the single crystals. Similar shapes of optical lines were observed in two types of neodymium dimers with DL-alanine and L-isoleucine, confirming thus the relation between dimeric structure and spectroscopy parameters close to the pseudodisordered effect.

Electron–phonon coupling is quite well observable at 5 K in high spectral region of electronic transitions, obeying the selection rule $\Delta J = 2, 0$ as well as

TABLE I
The experimental ($P_{\text{exp}} \times 10^8$) and calculated ($P_{\text{cal}} \times 10^8$) oscillator strength values of $f-f$ transitions and the τ_λ parameters.

Term	KNd(MoO ₄) ₂		KNd(WO ₄) ₂	
	P_{exp}	P_{cal}	P_{exp}	P_{cal}
⁴ I _{15/2}	36.74	25.42	—	—
⁴ F _{3/2}	402.49	335.16	244.30	316.73
⁴ F _{5/2} , ² H _{9/2}	890.55	936.52	753.34	829.53
⁴ F _{7/2} , ⁴ S _{3/2}	824.34	863.84	783.19	762.94
⁴ F _{9/2}	78.73	73.91	62.35	63.95
² H _{11/2}	19.43	19.99	16.71	20.09
⁴ G _{5/2} , ² G _{7/2}	7220.92	7239.54	3885.63	3895.74
² K _{13/2} , ⁴ G _{7/2} , ⁴ G _{9/2}	1375.88	1118.80	969.25	828.91
² K _{15/2} , ² G _{9/2} , (² D, ² F) _{3/2} , ⁴ G _{11/2}	300.70	175.72	198.55	157.10
² P _{1/2} , ² D _{5/2}	93.09	95.77	66.04	91.01
⁴ D _{3/2} , ⁴ D _{5/2} , ² I _{11/2} , ⁴ D _{1/2} , ² L _{15/2}	1789.67	1854.67	1730.68	1736.62
KNd(MoO ₄) ₂		KNd(WO ₄) ₂		
$\tau_2 \times 10^8 = 3.6137 \pm 0.0777$		$\tau_2 \times 10^8 = 1.6656 \pm 0.0496$		
$\tau_4 \times 10^8 = 1.0692 \pm 0.0703$		$\tau_4 \times 10^8 = 1.0186 \pm 0.0447$		
$\tau_6 \times 10^8 = 0.9003 \pm 0.1019$		$\tau_6 \times 10^8 = 0.7936 \pm 0.0649$		

in excitation spectra of europium single crystals. Two questions need reply: (a) why are differences in intensities of vibronic components observed in excitation and emission spectra and (b) what is the change of intensities of vibronic sidebands in lanthanide molybdates and tungstates. Table II compiles both the Stark components of electronic lines and energies of vibration modes composed of them. The vibronic lines were assigned on the basis of IR and Raman data [10]. Only those lines are listed which are repeated in the absorption and excitation spectra of neodymium and europium compounds.

According to Blasse's considerations, the differences in intensities of vibronic sidebands in excitation and emission spectra can be given both by the values of matrix elements of $\|U^{(2)}\|$ tensor operator for different electronic transition (⁵D_{0,2} and ⁷F_{0,2}) and by an appropriate energy denominators Δ included in relevant closure relation of Judd [16]. The change in intensities of vibronic components in neodymium molybdate and tungstate could be considered on the basis of theoretical model. Indeed, the change in polarizability of oxygen atoms involved in different clathrates and free MO₄²⁻ polyhedra can follow the intensity variation. An additional effect can be widening of the region of external vibration modes in IR spectra, providing probably better conditions for electron-phonon coupling with respect to the gap between the Stark components of electronic lines.

TABLE II
Stark components of electronic lines and energies of vibration modes composed of them for
KNd(WO₄)₂ and KNd(MoO₄)₂ crystals at 5 K.

KNd(WO ₄) ₂				KNd(MoO ₄) ₂			
Energy level ν [cm ⁻¹]	Stark comp. ν_0 [cm ⁻¹]	$\Delta\nu = \nu - \nu_0$	Assignm. to resp. normal modes	Energy level ν [cm ⁻¹]	Stark comp. ν_0 [cm ⁻¹]	$\Delta\nu = \nu - \nu_0$	Assignm. to resp. normal modes
${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$							
17877	17520	357	$\delta(\text{WO}_n)$	18164	17428	736	$\nu_{as}(\text{MoO}_4)$
17935	17520	415	$\delta(\text{WO}_n)$	18194	17428	766	$\nu_{as}(\text{MoO}_4)$
18193	17520	673	$\nu_{as}(\text{W} \langle \text{O} \rangle \text{W})$	18281	17428	853	$\nu_{as}(\text{MoO}_4)$
18255	17520	735	$\nu_s(\text{W} \langle \text{O} \rangle \text{W})$	17909	17183	726	$\nu_{as}(\text{MoO}_4)$
17877	17241	636	$\nu_{as}(\text{W} \langle \text{O} \rangle \text{W})$	17956	17183	773	$\nu_{as}(\text{MoO}_4)$
17963	17241	722	$\nu_{as}(\text{W} \langle \text{O} \rangle \text{W})$	18096	17183	913	$\nu_s(\text{MoO}_4)$
18025	17241	783	$\nu_s(\text{W} \langle \text{O} \rangle \text{W})$	17772	17027	745	$\nu_{as}(\text{MoO}_4)$
17617	16949	668	$\nu_{as}(\text{W} \langle \text{O} \rangle \text{W})$	17844	17027	817	$\nu_{as}(\text{MoO}_4)$
17877	16949	928	$\nu(\text{W}=\text{O})$	17956	17027	929	$\nu_s(\text{MoO}_4)$
${}^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$							
13035	12839	196	$T'(\text{Ln}^{3+})$	12844	12724	120	$T'(\text{Mo}^{6+})$
13237	12839	398	$\delta(\text{WO}_n)$	13133	12724	409	$\delta(\text{MoO}_4)$
13243	12839	404	$\delta(\text{WO}_n)$	12763	12381	382	$\delta(\text{MoO}_4)$
13080	12739	341	$\delta(\text{WO}_n)$	13133	12381	752	$\nu_{as}(\text{MoO}_4)$
13204	12739	465	$\nu_s(\text{WOW})$	13268	12381	887	$\nu_{as}(\text{MoO}_4)$
13204	12571	633	$\nu_{as}(\text{W} \langle \text{O} \rangle \text{W})$				
13237	12571	666	$\nu_{as}(\text{W} \langle \text{O} \rangle \text{W})$				
12788	12385	403	$\delta(\text{WO}_n)$				
12801	12385	416	$\delta(\text{WO}_n)$				
13204	12385	819	$\nu_s(\text{W} \langle \text{O} \rangle \text{W})$				
13243	12385	858	$\nu_s(\text{W} \langle \text{O} \rangle \text{W})$				

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