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COMPARATIVE STUDIES OF VIBRONIC TRANSITIONS IN ONE- AND TWO-PHOTON SPECTRA OF Gd^{3+} IN $Cs_2NaGdCl_6$

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Vibronic spectra of Gd^{3+} in $Cs_2NaGdCl_6$ were measured under one- and two-photon excitations. Following the vibrational analysis of the $Cs_2NaGdCl_6$ crystal an assignment of vibronic transitions was proposed. It was found that the vibronic transitions in one- and two-photon spectra are combined with the odd parity modes.

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1. Introduction

In the $Cs_2NaGdCl_6$ elpasolite crystal Gd^{3+} ions are situated in the center of symmetry. Therefore, the electric dipole $f-f$ transitions of active ions are forbidden in the investigated elpasolite crystal. As a result the vibronically induced electric-dipole lines accompanied by magnetic dipole transitions dominate the spectra. Thus it offers an opportunity for a precise examination of the mechanisms of vibronic transitions (for review see Ref. [1]).

Investigating two-photon induced vibronic spectra of transition metal ions in octahedral systems, McClure et al. [2] discovered that their structure is completely different in comparison with the respective vibronic transitions observed in one-photon spectra. While in the one-photon spectra they were associated with odd parity modes, in the two-photon spectra they were represented by even parity vibrations.

The vibronic transitions of Gd^{3+} ions in the $Cs_2NaGdCl_6$ crystal were observed in the one-photon excitation spectra by de Vries et al. [3]. It was found that magnetic dipole transitions were associated with odd parity modes. However, the intensity of the latter was lower than intensity of the zero-phonon transitions. Two-photon absorption spectra of Gd^{3+} in $Cs_2NaGdCl_6$ were reported by Bouazaoui et al. [4]. Theoretical models of the two-photon vibronic transitions were proposed by Sztucki and Stręk [5], and Sztucki [6].

In the present work we report an analysis of the vibronic transitions observed in two-photon excitation spectrum of Gd^{3+} in $Cs_2NaGdCl_6$. The vibronic lines

observed in one-photon emission spectrum are presented as well. Following the Raman and infra-red (IR) spectra of the $Cs_2NaGdCl_6$ crystal, an assignment of the observed lines is proposed. The nature of vibronic transitions accompanying one- and two-photon transitions of the Gd^{3+} ions in $Cs_2NaGdCl_6$ will be briefly discussed.

2. Experimental

The $Cs_2NaGdCl_6$ elpasolite single crystal was grown by the Bridgman–Stockbarger method. The cubic space group $Fm3m$ with the cell constant a = 1.07919 nm was confirmed by X-ray powder diffraction. The IR spectrum was recorded on a Brucker spectrometer with 2 cm^{-1} resolution. The Raman spectrum was obtained on a DFS 24 LOMO monochromator. The crystal was excited by an ILA 120 Carl-Zeiss Yena argon laser. A cooled GaAs detector was used. The luminescence spectrum was recorded on a Jobin-Yvon TIIR 1000 monochromator. As a detector an R955 photomultiplier was used. The sample was excited by an LPX 100 Lambda Physik excimer laser and by an IID-300B Lumonics dye laser.

3. Results

The received infra-red absorption and Raman spectra are shown in Fig. 1. Table I summarises the energies of the unit cell modes and their assignments. The modes with A_{1g}, E_g and T_{2g} symmetries are Raman active, the odd modes (T_{1u}) are only IR active. The T_{1g} and internal T_{2u} modes are inactive in Raman and IR

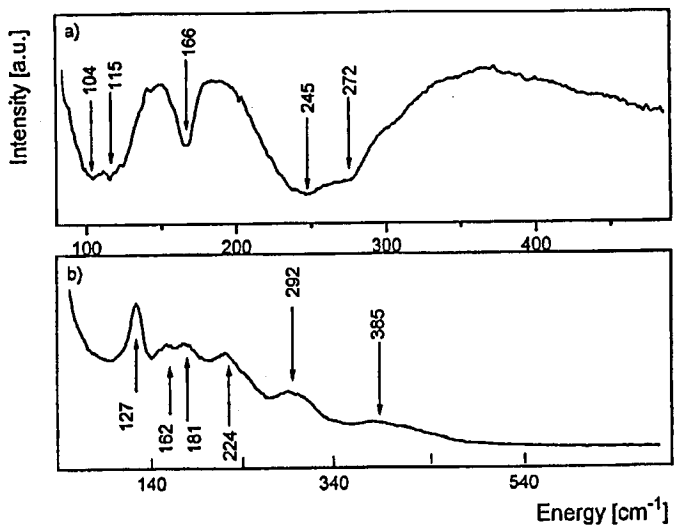

Fig. 1. The 5 K (a) IR spectrum and (b) Raman spectrum of the $Cs_2NaGdCl_6$ crystal.

TABLE I

Wave numbers, intensities and vibrational assignment for the elpasolite $Cs_2NaGdCl_6$ single crystal. (s — strong, vs — very strong, m — middle, b — broad, ν_s — symmetric stretching, ν_{as} — asymmetric stretching, δ_s — symmetric bending, δ_{as} — asymmetric bending).

IR	Raman	Assignment
	292, 300 m	$\nu_1(A_{1g})$ $\nu_s(GdCl_6)$ stretching
272 vs, b		$T'(T_{1u})$ Na^+ translation
245 vs, b		$\nu_3(T_{1u})$ $\nu_{as}(GdCl_6)$ stretching
	224 s	$\nu_2(Eg)$ $\nu(GdCl_6)$ stretching
	162, 181 s	$T'(T_{2g})$ Cs^+/Na^+ translation
166 m		$T'(T_{1u})$ Cs^+ translation
	127 vs	$\nu_5(T_{2g})$ $\delta_s(GdCl_6)$ bending
115 s		$T'(T_{1u})$ $(GdCl_6)$ translation
104 s		$\nu_4(T_{1u})$ $\delta_{as}(GdCl_6)$ bending

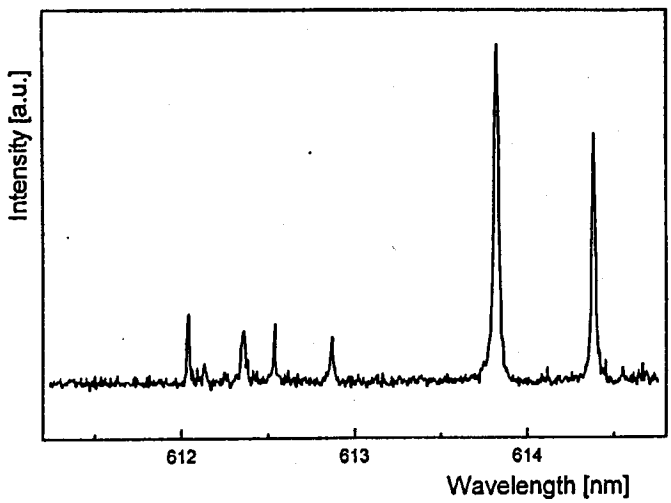

Fig. 2. Two-photon excitation spectrum of the $^6P_{7/2}$ term at 15 K.

spectroscopy. Among the ten vibrational modes described by Lentz [7] only the $\nu_3(T_{1u})$, $\nu_4(T_{1u})$ and $\nu_6(T_{2u})$ internal modes and the two lattice modes $T'(T_{1u})$ can promote electric dipole transitions. These modes are observed in the IR spectrum (see Fig. 1). The T_{2u} vibrational mode, forbidden in the first order approximation may appears in the emission spectrum at about 80 cm^{-1}.

Figure 2 presents two photon excitation spectrum of the $^6P_{7/2}$ term. On the left site of the zero-phonon lines the vibronic lines are present, their positions are shown in Table II. As far as we are aware the presented spectrum is the

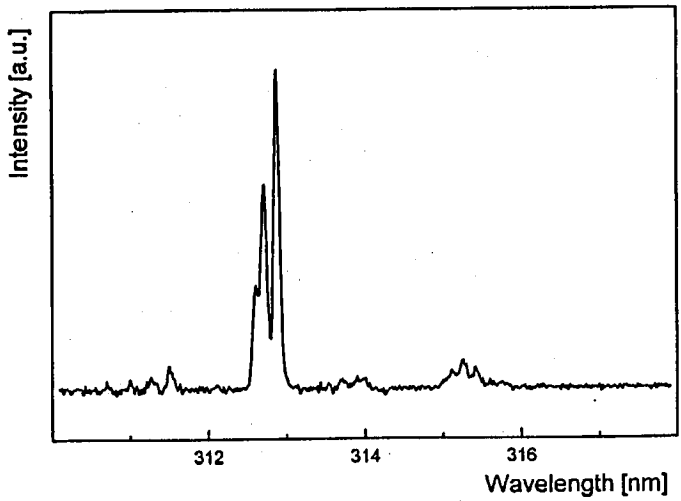

Fig. 3. The 15 K emission spectrum of the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition after one-photon excitation.

TABLE II

Energies of the lines in the two-photon excitation spectrum.

Energy	Assignment	Term
32544	Γ_7	
32574	Γ_8	
32625	$\Gamma_7 + \nu_6$	$^6P_{7/2}$
32643	$\Gamma_7 + \nu_4$	
32652	$\Gamma_8 + \nu_6$	
32670	$\Gamma_8 + \nu_4$	

second observation of vibronic lines in two-photon spectroscopy after the paper of Meijerink et al. [8]. The zero-phonon lines are associated with the $\nu_4(T_{1u})$, and $\nu_6(T_{2u})$ odd vibrational modes of the $GdCl_6^{3-}$ octahedron. The vibronic structure in a one-photon excitation spectrum is much more rich (see Fig. 2. in Ref. [3]).

The position of the Γ_7 component of the $^6P_{7/2}$ term matches well with the energy of the 308 nm excimer laser line. The excitation energy relaxes non-radiatively to the $^6P_{7/2}$ term and a $^6P_{7/2} \rightarrow {}^8S_{7/2}$ radiative transition is observed (see Fig. 3 where emission at 10 K is presented). In Fig. 3 there are three main peaks, i.e. at 31953 cm^{-1}, 31970 cm^{-1} and 31980 cm^{-1}, they are due to the transitions from the sub-levels of the $^6P_{7/2}$ term. The distances between Γ_7, Γ_8 and Γ_6 are the same as in the two-photon spectroscopy spectrum, i.e. 16 cm^{-1} and 10 cm^{-1}, respectively (see Table II and Table III). On the lower energy site there are two groups of three peaks at about 102 cm^{-1} and at 258 cm^{-1} from the center of gravity of

TABLE III

Energy levels and their assignment observed in the emission spectrum of the $Cs_2NaGdCl_6$ elpasolite single crystal at 10 K.

Line	Energy [cm^{-1}]	Assignment
1	31696	$\Gamma_7 \rightarrow {}^8S_{7/2} + \nu_3$
2	31710	$\Gamma_8 \rightarrow {}^8S_{7/2} + \nu_3$
3	31722	$\Gamma_6 \rightarrow {}^8S_{7/2} + \nu_3$
3	31852	$\Gamma_7 \rightarrow {}^8S_{7/2} + \nu_4$
4	31868	$\Gamma_8 \rightarrow {}^8S_{7/2} + \nu_4$
		$\Gamma_7 \rightarrow {}^8S_{7/2} + \nu_6$
5	31879	$\Gamma_6 \rightarrow {}^8S_{7/2} + \nu_4$
6	31953	$\Gamma_7 \rightarrow {}^8S_{7/2}$
7	31970	$\Gamma_8 \rightarrow {}^8S_{7/2}$
8	31980	$\Gamma_6 \rightarrow {}^8S_{7/2}$
9	32094	Gd_I
10	32116	Gd_I
11	32146	Gd_I
12	32177	Gd_I

Gd_I — Gd^{3+} ions in another crystallographic site (see text for explanation).

the ${}^6P_{7/2}$ term. One can note that in both groups of small peaks the distances between them are the same as the distances between Γ_J lines. Therefore these peaks are associated with the strongest vibrational modes $\nu_4(T_{1u})$, and $\nu_3(T_{1u})$ of the $GdCl_6^{3-}$ octahedron. The $\nu_6(T_{2u})$ vibrational mode has not been observed in the emission spectrum (we may tentatively assign the line at 31868 cm^{-1} to the $\nu_6(T_{2u})$ vibration associated with Γ_7 line). It was observed in Ref. [4], but in our opinion it should be reassigned because the line 3 in the emission spectrum at 31896 cm^{-1} is at 55 cm^{-1} from the Γ_7 not at 82 cm^{-1} (see Table IV in Ref. [4]).

At 140 cm^{-1} from the upper energy site of the ${}^6P_{7/2}$ term there is a group of four peaks. We assigned these lines to an emission of Gd^{3+} ions in another crystallographic site. Four components of the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition are observed, it points to a lower symmetry of the emitting ions.

4. Conclusions

In the present paper we have presented vibronic spectra of Gd^{3+} in the $Cs_2NaGdCl_6$ elpasolite crystal followed by one- and two-photon processes. We have found that the phonon symmetries of vibronic transitions are odd parity at either kind of spectroscopy. However, their structure is different. This result is in

opposite to the two-photon absorption spectra reported by McClure et al. [2] for octahedral crystals doped with transition metals, which have observed even parity modes. This difference is most probably due to a different mechanism of two-photon vibronic transitions occurring in Gd^{3+}ions [6]. The nature of two-photon vibronic transitions is under investigation.

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