Two-photon transitions of Gd^{3+} in cubic $Cs_2NaGdCl_6$

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Abstract. Two-photon absorption spectroscopy is used to investigate the $^8S_{7/2} \rightarrow {}^6P_J$, $^6I_{7/2}$ transitions of Gd^{3+} ions in the cubic elpasolite $Cs_2NaGdCl_6$. The Gd^{3+} ions occupy a centro-symmetric site (O_h); so the odd terms of the crystal field vanish and the pure electric dipole transitions should not be observed in one-photon experiments. As a consequence the electric dipole allowed two-photon transitions involving the $^6I_{7/2}$ and $^6P_{3/2}$ excited states are well observed in contrast with their weakness in the one-photon spectrum. Furthermore the magnetic dipole character of the transitions to the $^6P_{5/2}$ and $^6P_{7/2}$ levels is confirmed. The occurrence of the one-photon transition to $^6P_{3/2}$ is tentatively explained by the J mixing involving the $^6P_{7/2}$ excited state. A qualitative analysis of the relative intensities of the transitions to the ^6P_J and $^6I_{7/2}$ levels is presented.

1. Introduction

Recent observations of one-photon transitions within the $4f^7$ configuration of Gd^{3+} in $Cs_2NaGdCl_6$ have indicated that the intensities of zero-phonon lines are much weaker than most vibronic lines for the $^6I_{7/2}$ level and much stronger than the vibronic lines for the $^6P_{5/2}$ and $^6P_{7/2}$ levels (De Vries and Blasse 1988). In the cubic elpasolite $Cs_2NaGdCl_6$, the rare-earth Gd^{3+} ions occupy a centro-symmetric O_h site. Therefore, the pure electronic transitions between 4f states are strongly forbidden in the electric dipole approximation but they may have a magnetic dipole character. As a consequence of different selection rules, two-photon spectroscopy is a complementary technique for studying the electronic transitions. This is particularly true for the case of gadolinium where calculations of the transition intensities have been completed and agree nicely with experiments (Judd and Pooler 1982, Downer and Bivas 1983, Jacquier *et al* 1987, 1989).

De Vries and Blasse (1988) have reported one-photon excitation to the $^6P_{7/2}$, $^6P_{5/2}$ and $^6I_{7/2}$ excited states but they did not observe the $^6P_{3/2}$ level. Their work indicates that the weak phonon-assisted lines for the $^6I_{7/2}$ level agree with the electric dipole character of the transition to the ground state while the stronger zero-phonon lines assigned to the $^6P_{5/2}$ and $^6P_{7/2}$ levels are almost entirely of a magnetic dipole character.

In the present work§, one-photon absorption and excitation of the fluorescence at room temperature and low temperatures are reported. Then the two-photon absorption

§ The first observation of two-photon excitation in $Cs_2NaGdCl_6$ was previously reported by us in a NATO Advanced Research Workshop held at Cargese (Corsica 27 June–2 July 1988).

due to the transitions to the whole ^6P_J and $^6I_{7/2}$ manifolds is investigated by means of fluorescence measurements. The discussion is devoted to the relative intensities of the two-photon transitions and their related values in the one-photon spectra, mainly for the $^8S_{7/2} \rightarrow {}^6P_{3/2}$ transition.

2. Experimental methods

A crystal of $Cs_2NaGdCl_6$ was grown by the Bridgman technique in a sealed ampoule. A thin (less than a millimetre) plate of area a few square millimetres was cut and kept in a dry atmosphere. Indeed, a slight alteration of the surface was observed after a few minutes in air. Absorption measurements were performed with a Cary 2300 Varian spectrophotometer equipped with a continuous-flow He refrigerator providing a variable temperature down to 4 K. The one-photon and two-photon excitation spectra were recorded using a tunable dye laser, the frequency of which was doubled to reach the ultraviolet range of the Gd^{3+} absorption. In this way both one-photon and two-photon spectra could be recorded with the same optical arrangement with the addition of a doubling crystal and appropriate neutral filters for the fluorescence signal. Photon counting associated with a time-resolved technique with a fixed gate was used to ensure a quite good sensitivity of the detection (Malinowski *et al* 1990). Experiments were performed at various temperatures because of the possibility of a phase transition below
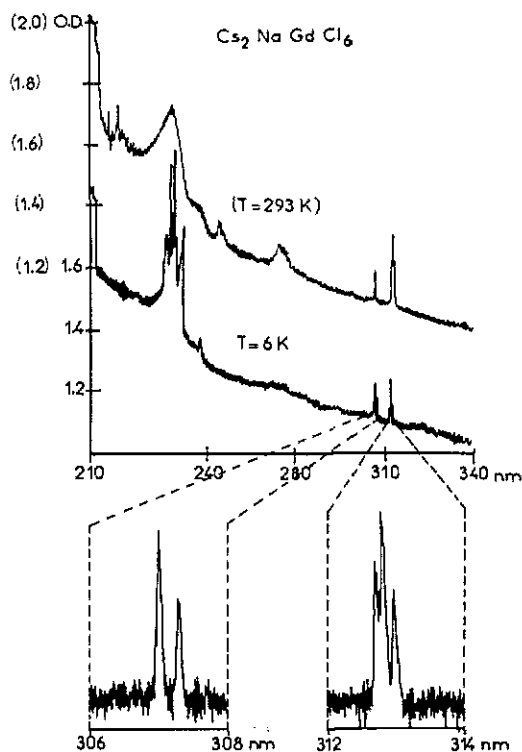

Figure 1. Absorption spectra at two temperatures and expansions of the ^6P_J wavelength region for the low temperature.

180 K as has been reported for the lighter members of the lanthanide series (Ce^{3+} to Tb^{3+} (Richardson *et al* 1985)). However, no evidence of such a phase transition was found from room temperature down to 4 K, in agreement with the earlier work of Schwartz *et al* (1976); therefore we mainly present the well resolved low-temperature data.

3. Results

Figure 1 presents the one-photon absorption measurements at room temperature and low temperatures. By comparison with other gadolinium materials it is easy to identify the transitions from the ground state $^8S_{7/2}$ to the various multiplets ^6P_J, ^6I_J, ^6D_J, ... with increasing energy. The lower part of figure 1 shows an enlargement of the ^6P_J states, namely $^6P_{7/2}$ and $^6P_{5/2}$ which are split into three and two components, respectively, according to the crystal-field decomposition of a J state in a site of O_h symmetry. It is noted that the $^6P_{3/2}$ state does not appear at both room temperature and low temperature; this is a direct consequence of the centro-symmetry of the site. On the other hand the transitions to the $^6P_{5/2}$ and $^6P_{7/2}$ levels are magnetic dipole allowed. Furthermore the temperature effect on the high-energy band intensity clearly indicates the role of phonons and consequently reveals the forced electric dipole nature of the corresponding vibronic transitions induced by the odd-parity vibration modes. In particular this is evident for the transition involving the $^6I_{7/2}$ state which almost disappears in the absorption spectrum recorded at 6 K. The assignment of the odd-parity vibrational modes of the $GdCl_6^{3-}$ octahedron was first reported by De Vries and Blasse (1988). Moreover, the comparison of the low-temperature absorption strength of the $^8S_{7/2} \rightarrow {}^6P_{7/2}$ and $^8S_{7/2} \rightarrow {}^6I_{7/2}$ zero-phonon transitions agrees at least qualitatively with earlier calculations of the magnetic dipole oscillator strengths (Carnall *et al* 1968).

As has been reported earlier (De Vries and Blasse 1988) this material presents an intense ultraviolet fluorescence which can be monitored for recording excitation spectra. Because of the sensitivity of the fluorescence technique it is possible to observe the $^6P_{3/2}$ level as shown in figure 2 where the one-photon and two-photon spectra are reproduced. We note that a weak line in the $^6P_{3/2}$ one-photon spectrum corresponds to the only intense line detected in the two-photon spectrum. Therefore this feature is attributed to the zero-phonon line of the $^8S_{7/2} \rightarrow {}^6P_{3/2}$ transition while the high-energy side bands are assigned to the vibronic satellites. As a proof, a room-temperature spectrum was run and exhibits the same feature symmetric towards the long wavelengths with respect to the electronic line. This is a consequence of the hot absorption arising from vibrational states of the ground level.

Figures 3 and 4 present the excitation spectra for the $^6P_{5/2}$ and $^6P_{7/2}$ levels. In both spectra, we observe the number of lines expected from the crystal-field decomposition. This behaviour confirms the absence of a phase transition at low temperatures. We note that all the lines exhibit an asymmetric shape towards short wavelengths which is not understood at the present stage of this study.

Figure 5 shows the zero-phonon lines of the $^8S_{7/2} \rightarrow {}^6I_{7/2}$ two-photon transition. The sequence of the three lines (due to the crystal-field splitting of $J = \frac{7}{2}$ in the O_h site symmetry) agrees with the one-photon data of De Vries and Blasse (1988).

4. Discussion

The comparison of the one-photon and two-photon spectra enables us to make some conclusive arguments concerning the nature of the electronic transitions and therefore
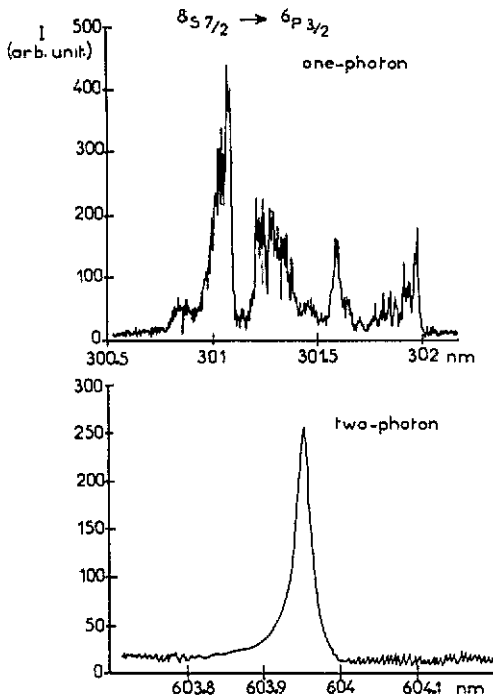
Figure 2. One-photon and two-photon excitation spectra of the fluorescence in the $^6P_{3/2}$ absorption range at 4 K. The spectra do not have the same horizontal scale because, apart from the zero-phonon line, no other structure is observed in the two-photon excitation spectrum.

of the wavefunction of the excited states with respect to the crystal site symmetry. The crystal-field decomposition of each J state involves doubly and quadruply degenerate crystal states. For each multiplet, it is easy to identify the quadruply degenerate component Γ_8 by looking at the intensity of each component in a group of lines. This is clearly observed in the one-photon absorption data in figure 1 where it provides the most intense line in the two enlargements dedicated to the $^6P_{5/2}$ and $^6P_{7/2}$ states. This is also true for the $^6I_{7/2}$ level (figure 5). In addition this is well confirmed in the excitation spectrum where a broadening of the corresponding line is measured.

The main question is raised by the observation of the $^6P_{3/2}$ state in the one-photon spectrum. Indeed the J selection rule implies that the absorption transition from the ground state $^8S_{7/2}$ is strictly forbidden in both electric and magnetic dipole approximations in the O_h site symmetry. However, this is only true when considering pure electronic states. The even components of the crystal-field potential can mix the $J = \frac{3}{2}$ state with $J = \frac{7}{2}$. Consequently this admixture will confer a magnetic dipole character on the transition $^8S_{7/2} \rightarrow {}^6P_{3/2}$. If this is the only mechanism which occurs, then the ratio of the intensities of the transitions to the $^6P_{3/2}$ and $^6P_{7/2}$ states is equal to the square of the admixture coefficient with the above state; this is approximately 5% ($(1/350)^{1/2}$; see table 2). In this analysis, we assume that the non-radiative relaxation processes towards the emitting $^6P_{7/2}$ (Γ_7) crystal state are completed and do not perturb the relative intensities of the excitation spectra. This value of 5% agrees with a previous result reported by Downer and Bivas (1983) for the two-photon intensity calculations of Gd^{3+} in LaF_3. They showed that only the rank-6 tensor operator of the crystal field can link the $^6P_{3/2}$ and $^6P_{7/2}$ states efficiently via the second-order perturbation theory involving the ^6I_J intermediate states. Indeed the rank-2 tensor operator of the crystal field may also link the $^6P_{3/2}$ and $^6P_{7/2}$ states directly in the D_{3h}-site symmetry while it does not
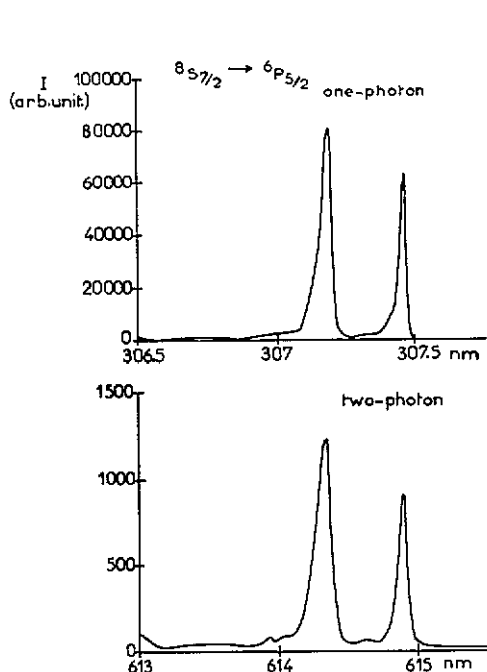
Figure 3. One-photon and two-photon excitation spectra of the fluorescence in the $^6P_{5/2}$ absorption range at 4 K. Note that the vibronic structures are almost non-existent in the one-photon spectrum.
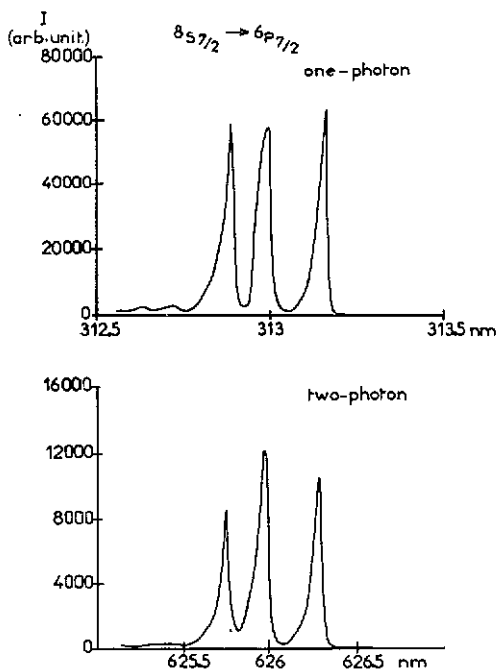
Figure 4. One-photon and two-photon excitation spectra of the fluorescence in the $^6P_{7/2}$ absorption range at 4 K.
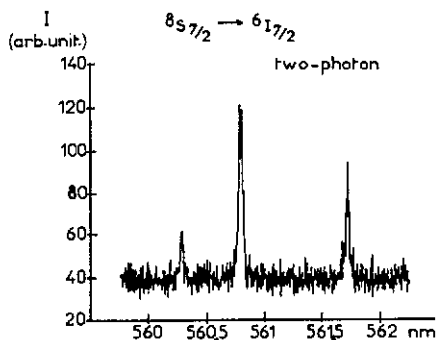

Figure 5. Two-photon excitation spectrum of the $^6P_{7/2}$ fluorescence at 4 K. Fluorescence arising from the $^6I_{7/2}$ has been observed but it is too weak to allow good analysis of the excitation spectrum.

appear in the crystal-field potential of the O_h-site symmetry of Gd^{3+} in the cubic elpasolite material. Finally it is interesting to note that the existence of a centro-symmetric crystal field prohibits other contributions to spin-forbidden Gd^{3+} transition intensities (Downer *et al* 1988) involving opposite parity excited configurations.

The relative intensities of the two-photon transitions presented in table 2 exhibit a different behaviour with two main features.

(i) The excitation lines assigned to the $^6P_{7/2}$ state are much more intense than those assigned to the $^6P_{5/2}$ state.

Table 1. Comparison of the positions of the zero-phonon lines of the $^8S_{7/2} \to {}^6I_{7/2}$ transition measured in one-photon and two-photon excitation spectra at low temperatures.

E (two-photon) (cm^{-1})	E (one-photon) from De Vries and Blasse (1988) (cm^{-1})	Assignment
35 695 (32)	35 713 (33)	Γ_6
35 663 (59)	35 680 (59)	Γ_8
35 604	35 621	Γ_7

Table 2. Relative intensities of the Γ_8 component of the $^8S_{7/2} \to {}^6P_J$ transitions with respect to the $^8S_{7/2} \to {}^6P_{3/2}$ transition at 4 K.

State	Energy	One-photon intensity	Two-photon intensity
$^6P_{3/2}$	33 115	1	1
$^6P_{5/2}$	32 554	350	18
$^6P_{7/2}$	31 950	350	110

(ii) The $^6P_{3/2}$ line is more intense in two-photon than in one-photon spectra with respect to the $^6P_{5/2}$ and $^6P_{7/2}$ lines.

An interesting feature concerns the observation of the zero-phonon lines in the two-photon excitation spectra of the $^8S_{7/2} \to {}^6I_{7/2}$ electronic transition. This illustrates quite well the use of two-photon spectroscopy since neither one-photon excitation nor absorption show the pure electronic transition, and that is the reason why we do not report it in figure 5.

Acknowledgments

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