High-resolution spectroscopy of Nd^{3+} in $YAlO_3$

1992 J. Phys.: Condens. Matter 4 L221

(http://iopscience.iop.org/0953-8984/4/12/005)

J. Phys.: Condens. Matter 4 (1992) L221–L224. Printed in the UK

LETTER TO THE EDITOR

High-resolution spectroscopy of Nd^{3+} in $YAlO_3$

A Lupei, V Lupei and S Georgescu
Institute of Atomic Physics, Bucharest, Romania

Received 6 February 1992

Abstract. High-resolution statical and dynamical spectrosocopy investigations of Nd^{3+} in a $YAlO_3$ laser crystal have been carried out at 77 K. New satellite lines have been detected around every normal transition. Up to four such satellites have been resolved at 77 K, with shifts depending on the transition. In the $^4F_{3/2}(1) \leftrightharpoons {}^4I_{9/2}(1)$ transition four clear satellites have been detected with lifetimes varying between $\simeq 10$ and $\simeq 105\,\mu s$. These satellites are most probably pair lines, with the ion–ion interaction of dipole–dipole type.

Doped with Nd^{3+}, yttrium aluminium perovskite ($YAlO_3$) is one of the most important laser crystals. Although the statistical spectroscopic properties of the 'isolated' Nd^{3+} ions in $YAlO_3$ are relatively well known (Weber and Varitimos 1971), less information on the luminescence quenching of the metastable $^4F_{3/2}$ level has been published. Voronko *et al* (1974) analysed the global luminescence decays for several Nd^{3+} concentrations in terms of direct donor–acceptor and migration energy transfer processes. The existence of a fast initial part in the decay was reported and connected with $YAlO_3$ structure data available at that time that assumed the existence of many (twelve) Y^{3+} sites in the first coordination sphere (at $\simeq 5.2$ Å), the interaction between Nd^{3+} ions being considered to be of dipole–dipole type. Since this study, performed at a time when many aspects of the energy transfer processes had not been elucidated, no other analysis of the Nd^{3+} luminescence quenching in $YAlO_3$ has been published (to our knowledge).

This letter presents some preliminary results of a high-resolution spectral and temporal spectroscopic investigation of Nd^{3+}:$YAlO_3$, revealing new features important for the understanding of the energy transfer processes in this system.

Samples of $YAlO_3$:Nd^{3+} grown by the Czochralski method with concentrations for 0.1 at.% to 1.5 at.% Nd^{3+} have been investigated. The measurements have been mainly performed at 77 K with spectral resolution of $\simeq 0.1$ Å. The transmission excitation and selectively excited luminescence spectra, as well as luminescence decay data, have been obtained using previously described set-ups (Lupei *et al* 1987, 1989).

For the weakly doped samples, the usual Nd^{3+} lines in $YAlO_3$ (Weber and Varitimos 1971) have been observed. Samples with concentrations larger than $\simeq 0.1$ at.% Nd^{3+} show around each line in absorption, excitation or selectively excited luminescence several satellites whose intensities grow strongly with the Nd^{3+} content. Figure 1 presents the transmission spectra for a sample with $\simeq 1.5$ at.% Nd^{3+} in the region of the $^4I_{9/2}(1) \rightarrow {}^4F_{3/2}(1)$ and $^4I_{9/2} \rightarrow {}^4G_{5/2}(1)$ transitions (the Stark sublevels are labelled 1, 2, ...). The excitation spectra, using for detection the $^4F_{3/2}$ fluorescence

0953-8984/92/120221+04$04.50

monitored with a low spectral resolution and a dye laser for excitation, show a similar structure (figure 2). In the $^4I_{9/2}(1) \rightarrow {}^4G_{5/2}(1)$ region one can observe at 77 K at least four resolved satellites shifted by a maximum of $\simeq 14$ cm^{-1} from the main line. The main line is distorted as a result of the strong absorption of the laser and reabsorption of emitted radiation.

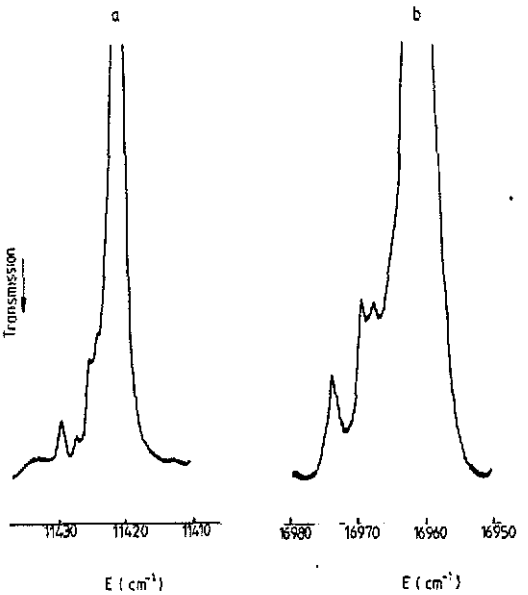

Figure 1. Transmission spectra of an $\simeq$ 1.5 at.% Nd^{3+}:$YAlO_3$ sample at 77 K (*a*) around the $^4I_{9/2}(1) \rightarrow {}^4F_{3/2}(1)$ transition and (*b*) around the $^4I_{9/2}(1) \rightarrow {}^4G_{5/2}(1)$ transition.

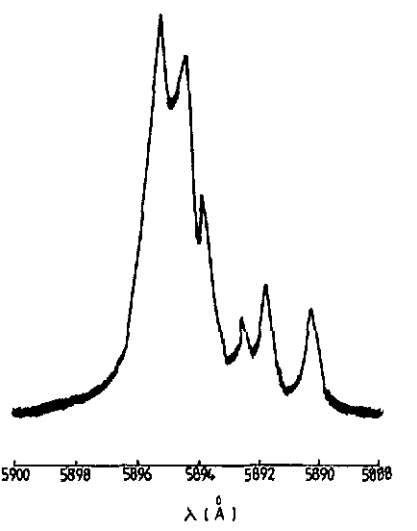

Figure 2. Excitation spectra of the $^4F_{3/2}$ luminescence for an $\simeq$ 1.5 at.% Nd^{3+}:$YAlO_3$ sample at 77 K when the $^4I_{9/2}(1) \rightarrow {}^4G_{5/2}(1)$ transition is scanned.

More information has been obtained using selectively excited and detected luminescence. In this way, different satellites in the pump region ($^4G_{5/2}$ level) have been connected with those in the luminescence region ($^4F_{3/2}$ level) and the decay times for every luminescent satellite could be estimated. Table 1 presents the shifts ($\Delta\nu$) of the satellites observed in the $^4I_{9/2}(1) \leftrightarrows {}^4F_{3/2}(1)$ transition, labelled P_1 to P_4, relative to the normal line N (situated at $\simeq$ 11 418 cm^{-1}) and their lifetimes τ_i (at 77 K). The lifetime for the normal line has been estimated from a sample with low concentration, since for large concentrations the decays are non-exponential. One can observe (table 1) large variations in lifetimes among the satellites.

Table 1. The shift ($\Delta\nu$), lifetimes (τ_i) and transfer rates (W_i) of the satellite lines in the $^4F_{3/2}(1) \leftrightarrows {}^4I_{9/2}(1)$ Nd^{3+} transition in $YAlO_3$ at 77 K.

	N	P_1	P_2	P_3	P_4
$\Delta\nu$ (cm^{-1})	0	$\simeq$3.5	$\simeq$4.5	$\simeq$6	$\simeq$8
τ (μs)	$\simeq$175	$\simeq$105	$\simeq$18	$\simeq$22	$\simeq$15
W_i (s^{-1})	0	$\simeq 3.8 \times 10^3$	$\simeq 4.9 \times 10^4$	$\simeq 4 \times 10^4$	6×10^4

The satellites, observed in every transition, are intrinsic to the Nd^{3+} system, and can most probably be associated with Nd^{3+}–Nd^{3+} pairs. There are several arguments in favour of this assignment: the strong dependence on Nd^{3+} content; the shorter lifetimes of the satellites as compared with isolated lines; $YAlO_3$ structure; comparison with other systems etc.

The structure of $YAlO_3$ crystals (Diehl and Brandt 1975) is complex and favourable to the formation of various classes of Nd^{3+}-ion pairs. Nd^{3+} ions substitute for Y^{3+} in $YAlO_3$ that has orthorhombic local symmetry. The possible Nd^{3+} pairs, characterized by two numbers (N, R_i), where N counts the Y^{3+} positions at a distance R_i from a given site taken as origin, are

$$(2; 3.64\ \text{Å}),\ (2; 3.73\ \text{Å}),\ (2; 3.79\ \text{Å}),\ (4; 4.97\ \text{Å}),\ (2; 5.18\ \text{Å}), \ldots . \qquad (1)$$

Since Nd^{3+} has a larger ionic radius (1.12 Å) than Y^{3+} (1.02 Å), each Nd^{3+} can induce at the site of its pair a small stress that leads to local crystal-field perturbations, responsible for most spectral shifts. The change of the decay times for the pairs from that corresponding to the isolated ions can be interpreted as resulting from a transfer of energy between the two companions by cross relaxation on intermediate $^4I_{13/2}$ and $^4I_{15/2}$ levels (Buisson and Liu 1984, Buisson *et al* 1984). The transfer rate W_i for a class of pairs can be defined as $W_i = \tau_i^{-1} - \tau_0^{-1}$, where τ_0 is the experimental decay time for the pair and τ_0 the lifetime of the 'isolated' ions. The transfer rates for pairs, estimated at 77 K, are given in table 1.

To associate the satellites with a class of pairs (1) one can use the transfer rates rather than the spectral shifts; i.e. the satellites P_4, P_2, P_3, P_1 correspond to the classes of pairs (1) ordered according to increasing distances. With this assignment the transfer rates show a linear dependence on $1/R_i^6$, which suggests that the interaction mechanism between the Nd^{3+} in $YAlO_3$ is essentially of dipole–dipole type. The transfer microparameter C_{DA} defined by $W_i = C_{DA} R_i^{-6}$ and using the transfer rates W_i at 77 K, is about $(1.2\text{–}1.4) \times 10^{-40}$ cm^6 s^{-1}.

This microparameter C_{DA} can be alternatively estimated from the non-exponential decay of the main line N in concentrated samples. For large times ($t > 100$–150 μs), the non-exponential part can be described by a Förster (1949) $e^{-\gamma t^{1/2}}$ law corresponding to a dipole–dipole interaction with more distant acceptors. From the experimental γ-values one can estimate the transfer microparameter C_{DA} ($\gamma = \frac{4}{3}\pi^{3/2}\eta_A C_{DA}^{1/2}$, with η_A the absolute Nd^{3+} content for a cross-relaxation quenching process). These estimation procedures give $C_{DA} \simeq 1.5 \times 10^{-40}$ cm^6 s^{-1}, in good agreement with values obtained by direct pair measurements.

Therefore, in the case of Nd^{3+}in $YAlO_3$, unlike several other Nd^{3+}-doped crystals (Nd^{3+}:$LiYF_4$ (Barthem *et al* 1986) or Nd^{3+}:YAG (Lupei *et al* 1987, 1989)) the ion–ion interaction responsible for energy transfer is most probably of dipole–dipole type, even for nearest-neighbour pairs. Structural differences between these crystals could explain the inefficiency of the superexchange interaction in the case of the Nd^{3+}:$YAlO_3$ system. More studies are necessary to elucidate this problem.

In conclusion, our experiments have for the first time provided evidence for the existence of a satellite structure of Nd^{3+} spectra in $YAlO_3$. These satellites are most probably pair lines, the measured quenching rates suggesting a dipole–dipole interaction between Nd^{3+} ions. The influence of this structure on the global luminescence decay shapes, as well as their influence on quantum efficiency measurements, will be discussed in other work.

References

Barthem R B, Buisson R, Vial J C and Harmand H 1986 *J. Lumin.* **34** 295
Buisson R and Liu J Q 1984 *J. Physique* **45** 1523
Buisson R, Liu J Q and Vial J C 1984 *J. Physique* **45** 1533
Diehl R and Brandt G 1975 *Mater. Res. Bull.* **10** 85
Förster Th 1949 *Z. Naturf.* **40** 321
Lupei A, Lupei V, Georgescu S, Ionescu C and Yen W M 1987 *J. Lumin.* **39** 35
Lupei V, Lupei A, Georgescu S and Yen W M 1989 *J. Appl. Phys.* **66** 3792
Voronko Yu K, Mamedov T G, Osiko V V, Timoshechkin M I and Shcherbakov I A 1974 *Sov. Phys.–JETP* **38** 565
Weber M J and Varitimos T E 1971 *J. Appl. Phys.* **42** 4996