

Excited-state relaxation dynamics of Cr^{3+} in $\text{YAl}_3(\text{BO}_3)_4$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 5229

(<http://iopscience.iop.org/0953-8984/14/20/318>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.104

The article was downloaded on 18/05/2010 at 06:42

Please note that [terms and conditions apply](#).

Excited-state relaxation dynamics of Cr³⁺ in YAl₃(BO₃)₄

G Dominiak-Dzik^{1,4}, W Ryba-Romanowski¹, M Grinberg², E Beregi³
and L Kovacs³

¹ Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 2 Okólna Street, 50-950 Wrocław, Poland

² Institute of Experimental Physics, University of Gdańsk, 57 Wita Stwosza Street, 80-952 Gdańsk, Poland

³ Crystal Physics Laboratory, Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Konkoly-Thege M. út 29-33, Budapest 1121, Hungary

E-mail: dzik@int.pan.wroc.pl

Received 29 January 2002

Published 9 May 2002

Online at stacks.iop.org/JPhysCM/14/5229

Abstract

The room temperature excitation spectrum of luminescence of Cr³⁺ in the YAl₃(BO₃)₄ single crystal have been used to estimate the crystal-field strength Dq and the Racah parameters B and C . The $Dq/B = 2.4$ value indicates that dopant ions occupy strong-crystal-field sites. Emission spectra of Cr³⁺ are consistent with a strong-crystal-field case in which the ²E excited state is the lowest. The influence of temperature on the R₁ line position has been examined and it has been found that the thermal line shift is consistent with predictions derived from consideration of ion–phonon interaction. The influence of temperature on emission lifetime in the 5–300 K temperature range has been analysed. In doing this, the energetic structure of Cr³⁺, consisting of the ground-state and excited electronic manifolds mixed by the spin–orbit interaction, has been constructed using the diabatic representation. An expression for the total probability of the depopulation of luminescent states was next derived and fitted to experimental data yielding the ²E–⁴T₂ separation energy $\Delta = 730 \text{ cm}^{-1}$ and the ⁴T₂ radiative lifetime $\tau_0 = 18.9 \mu\text{s}$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Following the success of alexandrite as a laser gain medium [1], there has been renewed interest in systems emitting broadband emission via the ⁴T₂ → ⁴A₂ transition of the Cr³⁺ ion. The

⁴ Author to whom any correspondence should be addressed.

crystals and glasses which emit broadband luminescence are of particular importance because of their suitability for use in the design of tunable solid-state lasers. Even in materials where the 4T_2 excited state is above the 2E level and therefore contains only a small fraction of excited ions, the spin-allowed ${}^4T_2 \rightarrow {}^4A_2$ transition occurs and tunable laser action can be obtained in the corresponding broad emission band. Then, the 2E excited state is more heavily populated and acts as a storage level for optical excitation.

Borates are materials that have potential for tunable laser applications. Härig *et al* [2] studied luminescence of stoichiometric and diluted $R(Cr_yX_{1-y})_3(BO_3)_4$ crystals with $R = Gd, Lu$; $X = Al, Ga$, and discussed the four-level laser system of the Cr^{3+} ion. Wang and co-workers reported some preliminary results on optical characterization of Cr^{3+} -doped $RX_3(BO_3)_4$, where $R^{3+} = Y^{3+}$ or Gd^{3+} and $X^{3+} = Al^{3+}$ or Sc^{3+} [3–5], and their usefulness as laser gain media [4]. With reference to the $YAl_3(BO_3)_4:Cr^{3+}$ system, the authors derived peak wavelengths and ligand-field parameters which are as follows: R_1 line at 682 nm, R_2 line at 684 nm, ${}^4A_2 \rightarrow {}^4T_2$ line at 595 nm, ${}^4A_2 \rightarrow {}^4T_1$ line at 425 nm, $Dq = 1680\text{ cm}^{-1}$, $B = 672\text{ cm}^{-1}$, and $C = 3225\text{ cm}^{-1}$ [4]. The value $Dq/B = 2.5$ indicates a strong crystal field for Cr^{3+} sites in the YAB host. On the basis of experimental data, the authors concluded that the 2E – 4T_2 separation energy is about 400 – 600 cm^{-1} [3].

In this paper an attempt is made to describe quantitatively the relaxation dynamics of the $YAl_3(BO_3)_4:Cr^{3+}$ system by means of the correlation of a theoretical model with experimental data collected during the study of the temperature dependence of luminescence spectra and lifetimes.

2. Experimental details

A single crystal of $YAl_3(BO_3)_4:Cr^{3+}$ was obtained by the top-seeded solution growth method. The growth technique is described elsewhere [3, 5]. The nominal concentration of Cr^{3+} ions was 0.01 at.%. The double borate $YAl_3(BO_3)_4$ has the trigonal crystal structure of the mineral huntite, $CaMg_3(CO_3)_4$, belonging to the space group $R\bar{3}2$ [6]. The cationic Cr^{3+} ion impurity enters the lattice by substituting at Al^{3+} sites where the symmetry is approximately octahedral.

The absorption of the Cr^{3+} ions was too low to be measured due to low concentration of active ions. (Goufu Wang *et al* presents the room temperature absorption in [3–5].) Excitation spectra were measured with the SPF 500 SLM AMINCO Spectrofluorometer. The measurements were carried out at 300 K, monitoring visible and infrared emission. Emission spectra have been recorded at several temperatures between 5 and 300 K. The sample was excited by an argon laser or by a Surelite optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser. The spectra were analysed with a Zeiss model GDM 1000 grating monochromator (set to a spectral bandwidth of 2 cm^{-1}) and detected by a cooled photomultiplier. An SRS 250 boxcar integrator averaged the resulting signal. A continuous-flow helium cryostat, Oxford model CF 1204, equipped with a temperature controller was used for the low-temperature measurements.

Lifetime measurements were performed with an optical parametric oscillator as an excitation source. The emitted light was detected by a photomultiplier connected to a Tektronix TDS 3052 oscilloscope. The temperature range of measurements was 5–300 K.

3. Results, calculations and discussion

3.1. Luminescence spectra

Luminescence spectra, recorded from the sample at several different temperatures, are presented in figure 1. The room temperature spectrum consists of two relatively narrow peaks

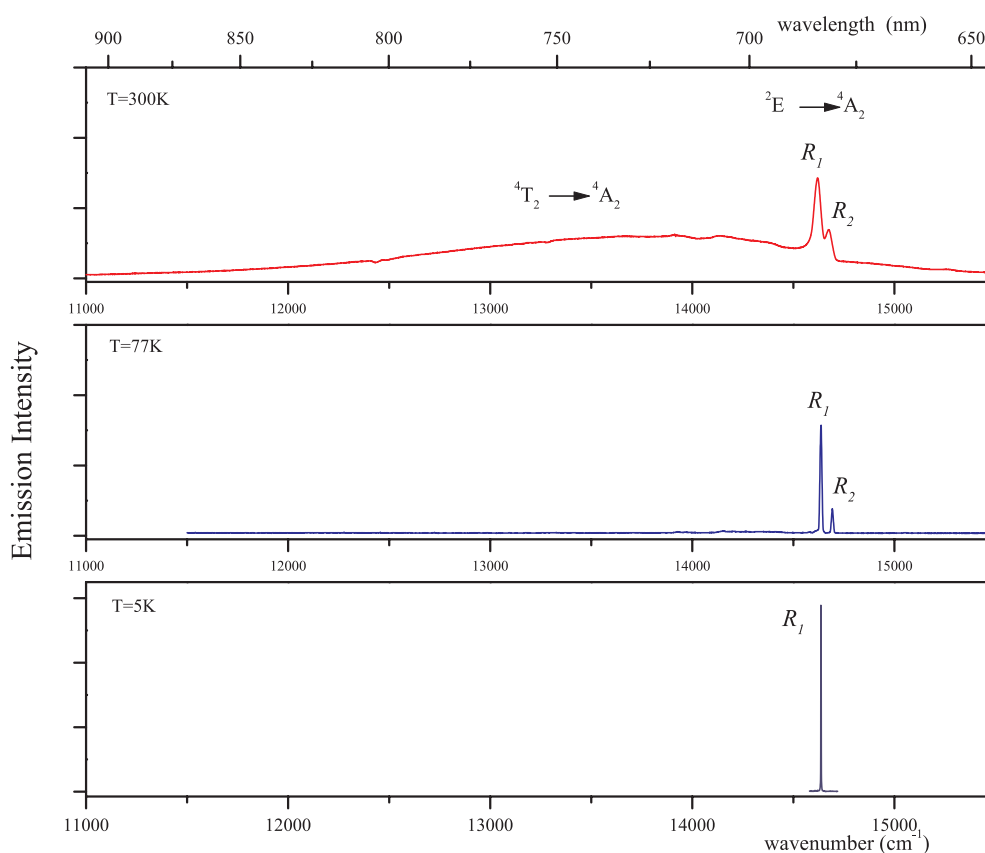


Figure 1. Luminescence spectra of Cr³⁺ in YAB measured at 5, 77, and 300 K.

at 14 621 and 14 676 cm⁻¹ superimposed on a structureless broadband emission extending from ~16 500 to 11 000 cm⁻¹ due to the spin-allowed ${}^4T_2 \rightarrow {}^4A_2$ transition. The two sharp lines (R lines) are attributed to the spin-forbidden transition from the split 2E excited state to the 4A_2 ground state. It should be mentioned that the R lines in the 300 K spectrum shown in figure 1 are broadened instrumentally because the larger slit width was applied in this case to allow proper recording of the weak wings of the broad band.

The existence of the luminescence from the 2E level implies that 4T_2 lies higher than 2E . So, excitation energy is stored via the population in the 2E state, which decays slowly to the ground state. In thermal equilibrium, the 4T_2 state attains a certain population and should decay rapidly to the ground state since this transition is spin allowed. Such behaviour is consistent with the emission from Cr³⁺ ions in high-field sites with octahedral coordination provided that the energy separation between the 4T_2 and 2E states is sufficiently small to ensure a measurable contribution of the 4T_2 decay. Thus, in thermal equilibrium the 2E as well as the 4T_2 states are occupied. The intensity of luminescence from these components will depend on their relative population. As the temperature is reduced, the broadband ${}^4T_2 \rightarrow {}^4A_2$ emission is found to decrease in intensity. At 77 K the luminescence spectrum contains two R lines solely and at 5 K it consists of one intense and sharp line (R₁ line) at 14 637 cm⁻¹. The spectral position of the R₁ line is temperature dependent. Points in figure 2 indicate the thermal shift of the R₁ line with respect to its position at 5 K. Thermal shifts of no-phonon lines in various systems

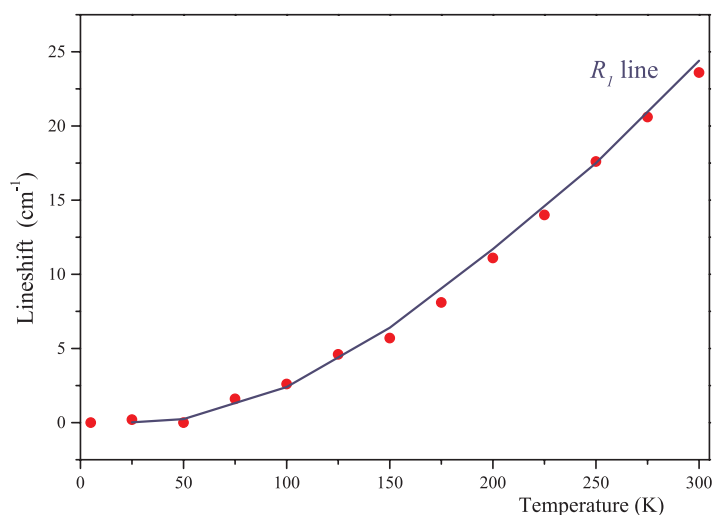


Figure 2. The shift of the R_1 line with respect to its position at 5 K for the YAB:Cr system. The solid curve was calculated from equation (1).

have been considered in numerous published works. It is generally recognized that the line shift due to thermal expansion of the host is negligible compared to that associated with the ion–phonon interaction. When the energy of the transition $|\Delta E| \gg \hbar\omega_D$, the thermal line shift ‘SE’ may be approximated by the relation [7]

$$\text{SE (cm}^{-1}\text{)} = \alpha \left(\frac{T}{T_D} \right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \quad (1)$$

where α is the coupling coefficient for the ion–phonon interaction and T_D is the Debye temperature of the crystal. The values of the integrals are tabulated in [7]. This equation was used to fit experimental data, treating α and T_D as adjustable parameters. The solid line in figure 2 presents the calculated dependence with $\alpha = 160 \text{ cm}^{-1}$ and $T_D = 400 \text{ K}$. It can be seen in figure 2 that the quality of the fit is reasonable. We did not observe the anomalous temperature dependence of the R-line positions or the splitting in the 15–77 K temperature range that were mentioned in [4].

3.2. Excitation spectrum

The room temperature excitation spectrum, shown in figure 3 (solid curve), consists of two bands centred at 16 615 (602 nm) and 23 390 cm^{-1} (428 nm). These bands have been attributed to spin-allowed transitions from the 4A_2 ground state to the 4T_2 and $^4T_{1a}$ excited states, respectively.

The energies of the 4T_2 and $^4T_{1a}$ states can be calculated from the excitation spectrum. In the absence of non-radiative internal conversion processes (we have assumed that we are dealing with this case), the excitation spectrum intensity is proportional to the absorption coefficient. Basic quantum mechanics results in an absorption lineshape proportional to the absorption coefficient divided by the photon energy. Thus, to obtain the lineshape we have divided the excitation spectrum by the photon energy. The Frank–Condon transition energies (indicated by arrows in the inset in figure 3) correspond to the respective maxima of the lineshape.

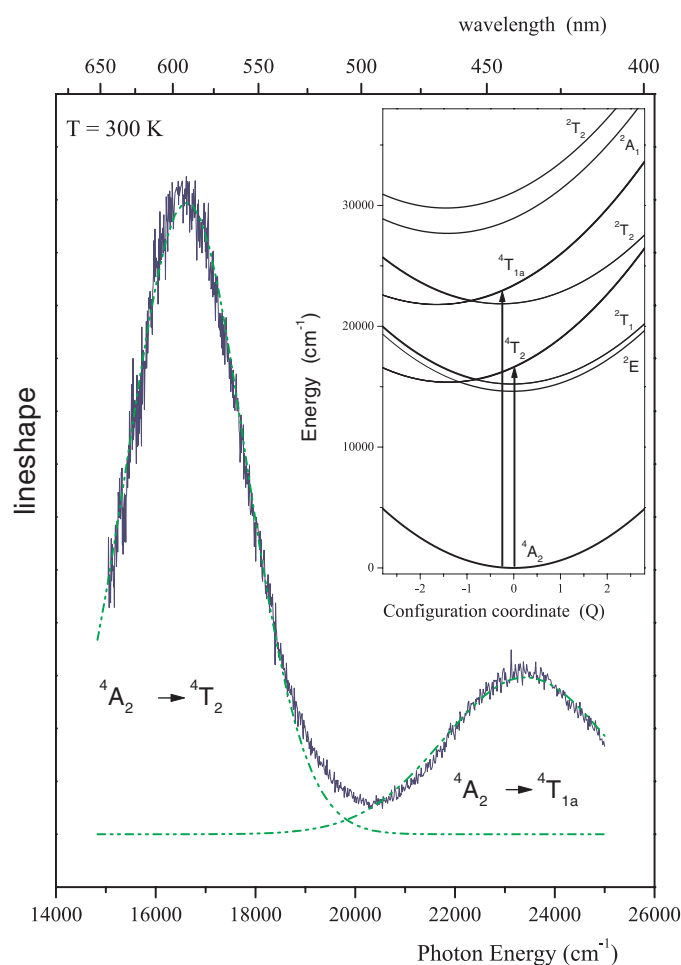


Figure 3. The excitation spectrum lineshape (solid curve) and computer fitting model for Cr³⁺ transitions based on Gaussian functions (chain curves). In the inset: the configuration coordinate diagram representing the energetic structure of the Cr³⁺ in YAl₃(BO₃)₄. Vertical arrows indicate absorption transitions.

We have estimated the maxima of the spectrum by fitting the lineshape to two Gaussians with the formula

$$I(E) = I_0 \frac{\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right]}{\sqrt{2\pi}\sigma}$$

where σ is the standard dispersion of the band representing the homogeneous as well as inhomogeneous broadening of the respective transition. The data obtained are $E_{4T_2} = 16\,620\text{ cm}^{-1}$, $\sigma_{4T_2} = 1160\text{ cm}^{-1}$ and $E_{4T_{1a}} = 23\,400\text{ cm}^{-1}$, $\sigma_{4T_{1a}} = 1280\text{ cm}^{-1}$ (see figure 3—dotted curves).

3.3. Crystal-field and Racah parameters

The crystal-field strength has been obtained as $10Dq = E_{4T_2} = 16\,620\text{ cm}^{-1}$. The energy of the ²E state has been calculated as the average energy of the R₁ and R₂ lines:

$E_{2E} = 14\,648\text{ cm}^{-1}$. When one puts our data into the relations [8]

$$B = Dq \frac{\frac{\Delta E^2}{(Dq)^2} - 10 \frac{\Delta E}{Dq}}{15 \left(\frac{\Delta E}{Dq} - 8 \right)} \quad (2)$$

and

$$C = \left(\frac{E(^2E)}{B} - 7.9 + \frac{1.8B}{Dq} \right) \frac{B}{3.05} \quad (3)$$

where ΔE is the energy of separation between the $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_{1a}$ transitions, one obtains $B = 684\text{ cm}^{-1}$ and $C = 3194\text{ cm}^{-1}$. The difference from other results [9] is mainly due to the fact that our $10Dq$ is about 200 cm^{-1} smaller than that obtained in the paper [9]. Having the crystal-field and Racah parameters, one can obtain the complete energetic structure of the system. One can represent this structure using a configuration coordinate diagram. In this approach, considering coupling to the fully symmetrical breathing mode, one approximates the electronic energies by parabolas:

$$\varepsilon_{\Gamma}(Q) = \varepsilon_{\Gamma}^0 + S_{\Gamma} \hbar \omega + \hbar \omega \frac{Q^2}{2} + \sqrt{2S_{\Gamma}} \hbar \omega Q \quad (4)$$

where S_{Γ} is the Huang–Rhys parameter of the Γ state. S_{Γ} is assumed to be zero for all states belonging to the ground electronic configuration t^3 (all components of the 4A_2 , 2E , and 2T_1 electronic manifolds), S_0 for the states belonging to the first excited electronic configuration t^2e , and n^2S_0 for the states from the $t^{3-n}e^n$ configurations. The quantity $S_0\hbar\omega$ is in fact the relaxation energy of the system in the 4T_2 state (the electron–lattice interaction relaxation energy). The details of the calculations are presented in the paper [10].

The resulting configuration coordinate diagrams are presented in figures 3 (inset) and 4. The difference between the energies of the 4T_2 and 2E states, Δ , is a crucial parameter since its magnitude determines the spectroscopic properties of Cr^{3+} . We relate Δ to other quantities as follows (see figure 4):

$$\Delta = 10Dq - S_0\hbar\omega - E_{2E}. \quad (5)$$

$10Dq$ and the energy of the 2E state can be directly obtained from the spectrum. To obtain Δ or $S_0\hbar\omega$, in the case of the high-field Cr^{3+} system, one can analyse the dependence of the R-line luminescence lifetime on temperature. The experimental result is a lifetime decreasing when temperature increases.

3.4. Luminescence lifetimes

The influence of temperature on the luminescence lifetime of $\text{Cr}^{3+}:\text{YAB}$ has been investigated in the 5–300 K temperature range and the results are indicated by points in figure 5. The observed temperature dependence of the emission lifetime is consistent with the recorded temperature dependence of the luminescence spectra presented in figure 1. At low temperature the luminescence originating exclusively from the 2E state has the experimentally measured lifetime $\tau_E = 2.11\text{ ms}$. At 5 K the 2E state is the only populated state. However, the increase of temperature brings about thermal population of the higher-lying 4T_2 state, so the decays become faster. The mixed $^2E, ^4T_2 \rightarrow ^4A_2$ luminescence has a much shorter decay time of $199\text{ }\mu\text{s}$ at 300 K.

To analyse the temperature reduction of the lifetime we have considered the energetic structure of the Cr^{3+} ion, consisting of the $\Gamma_8(^4A_2)$ ground and the $\Gamma_8(^4T_2)$, $\Gamma'_8(^4T_2)$, $\Gamma_7(^4T_2)$, $\Gamma_6(^4T_2)$, $\Gamma_8(^2E)$, $\Gamma_8(^2T_1)$, and $\Gamma_6(^2T_1)$ excited electronic manifolds mixed by the spin–orbit interaction. Since the $\Gamma_8(^4A_2)$ ground state is well separated energetically from the others, we

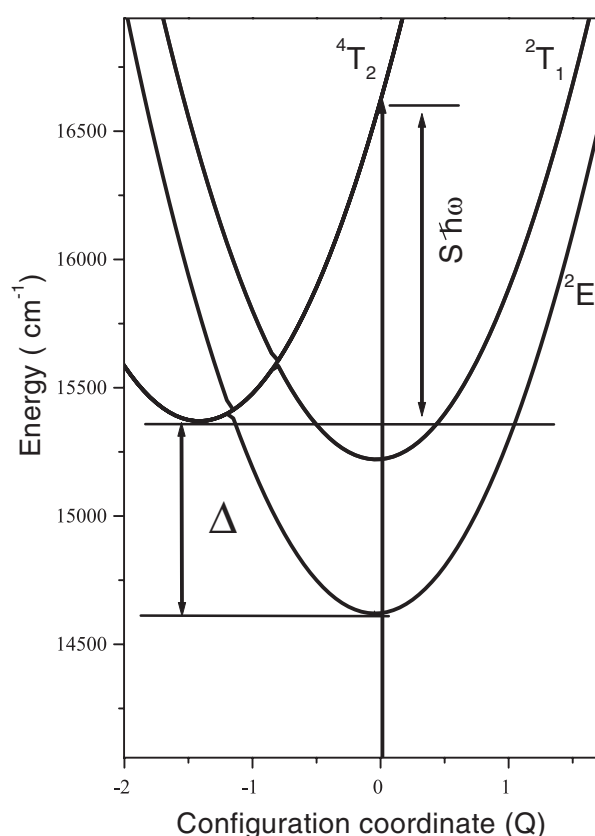


Figure 4. A configuration coordinate diagram representing first three excited electronic manifolds of the Cr³⁺ ions in YAB.

have omitted its coupling with the excited states. To describe the vibronic states of the system, we have used the diabatic representation [11, 12], where the electronic part of the wavefunction has been assumed to be independent of ionic positions. In this way the diabatic basis has been represented by the following Born–Oppenheimer functions:

$$\psi_{\Gamma}^n(q, Q, s) = \varphi_{\Gamma}(q, s) \chi_{\Gamma}^n(Q) \quad (6)$$

where $\varphi_{\Gamma}(q, s)$ and $\chi_{\Gamma}^n(Q)$ are the electronic and vibronic wavefunction, respectively, q and Q are the electronic and configuration coordinates, respectively, s represents the spin that is 1/2 or 3/2 for doublets and quartets, respectively. As the result of calculations, one obtains the structure of the vibronic states of energies E^k . The respective wavefunction is a mixture of doublets and quartets and is given by the following superposition:

$$\Phi^k(q, Q) = \sum_{jm} a_j^{km} \left(\frac{1}{2}\right) \varphi_j(q, \frac{1}{2}) \chi_j^m(Q) + \sum_{in} a_i^{kn} \left(\frac{3}{2}\right) \varphi_i(q, \frac{3}{2}) \chi_i^n(Q). \quad (7)$$

Here the first and the second sum represent the doublet and quartet contributions to the total wavefunctions, $a_i^{kn} \left(\frac{3}{2}\right)$, $a_j^{km} \left(\frac{1}{2}\right)$ are the respective coefficients obtained in the framework of the diagonalization procedure. Since only the transitions between the quartet states are allowed, one calculates the contribution related to the transition from the $\Phi^k(q, Q)$ to the l th vibronic

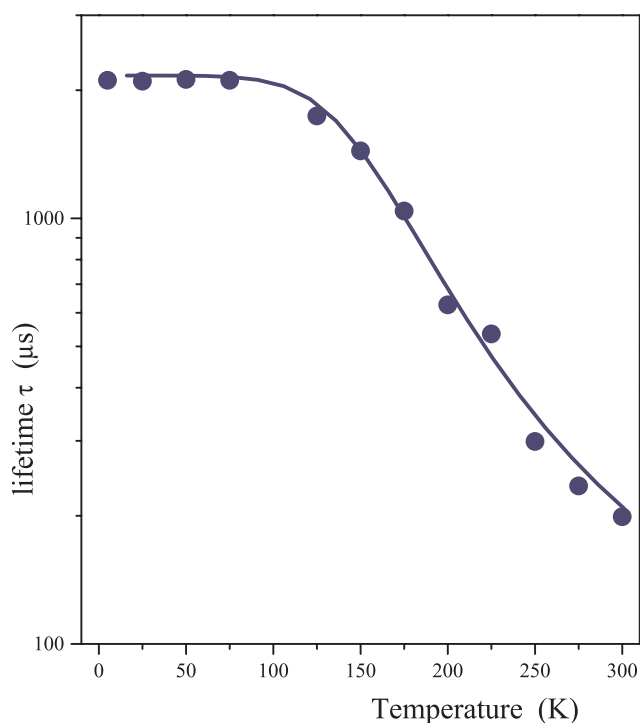


Figure 5. The influence of temperature on luminescence lifetime associated with the R_1 line. The points represent experimental values. The solid curve corresponds to fitting to the quantum model (see the text).

level of the ground electronic manifold 4A_2 as follows:

$$P_{kl} \propto \sum_i \sum_n \left| a_i^{kn} \left(\frac{3}{2} \right) \int \chi_i^{n*}(Q) \chi_{A_2}^l(Q) dQ \right|^2 n_i \quad (8)$$

where n_i is the degeneracy of the states, which is 4 for Γ_8 and Γ'_8 , and 2 for Γ_6 and Γ_7 . To calculate the total probability one has to summarize all transitions from the all occupied states of the excited electronic manifolds to all empty vibronic states of the ground electronic manifold. Because the vibronic wavefunctions in the ground electronic state are orthonormal, the total probability of depopulation (the inversion of the luminescence lifetime) is proportional to the following sum:

$$\begin{aligned} \tau_r^{-1}(T) &= \frac{1}{\tau_0} \sum_k \sum_l P_{kl}(E_{4T_2}, E_{2E}) \Theta[(E^k - E^0)/kT] \\ &= \frac{1}{\tau_0} \sum_k \sum_i \sum_n \left| a_i^{kn} \left(\frac{3}{2} \right) \right|^2 \Theta[(E^k - E^0)/kT] \end{aligned} \quad (9)$$

where Θ denotes the Boltzmann occupation function and τ_0 is the ${}^4T_2 \rightarrow {}^4A_2$ radiative lifetime. The details of the calculations are presented in paper [13]. In this approach we did not consider any special lifetime related to the ${}^2E \rightarrow {}^4A_2$ transition (theoretically this lifetime is infinity because the transition is spin forbidden). In fact, we never have the pure states and the doublet–quartet (${}^2E \rightarrow {}^4A_2$) transition, in the case of the high-field Cr^{3+} system, is allowed due to the spin–orbit coupling of the 2E and 4T_2 states. Because of this, in our model

the lifetime of the high-field Cr³⁺ centres depends on the ²E–⁴T₂ separation energy, Δ , and temperature (due to relation (9)). This dependence has been evidenced experimentally in the studies of chromium-doped gallium garnets [14].

Actually the temperature dependence of the lifetime is controlled also by the magnitudes of the spin–orbit coupling constant ξ , phonon energy $\hbar\omega$, and lattice relaxation energy $S_0\hbar\omega$. The best fitting to the experimental data obtained in the framework of our model is given by solid curve in figure 5. This fit has been obtained for $\xi = 140 \text{ cm}^{-1}$, $\hbar\omega = 300 \text{ cm}^{-1}$, $S_0\hbar\omega = 1250 \text{ cm}^{-1}$ (which gives $\Delta = 730 \text{ cm}^{-1}$) and $\tau_0 = 18.9 \mu\text{s}$. The magnitudes of parameters are reasonable. It should be mentioned however that a similar quality of fit can be obtained also for values of parameters different by 10–20% from those listed above. This particularly concerns the value of $\hbar\omega$. Also the theoretical curve does not change much when one simultaneously increases the magnitudes of ξ and τ_0 .

4. Conclusions

Chromium ions in YAl₃(BO₃)₄ are situated at the strong-crystal-field sites characterized by $Dq = 1662 \text{ cm}^{-1}$, $B = 684 \text{ cm}^{-1}$, $C = 3194 \text{ cm}^{-1}$, and the value $Dq/B = 2.42$. Luminescence measurements were made over a wide range of temperature and show that only the lowest ²E excited state is populated at low temperature, and at 5 K the chromium emission consists of one narrow R₁ line at $14\,636 \text{ cm}^{-1}$. It has been concluded that the ion–phonon interaction is responsible for the temperature dependence of the R₁-line spectral position. The observed temperature dependence of the emission lifetime has been analysed within a theoretical model, which is found to account well for the experimental data. Fitting of calculated results to those obtained in the experiment yielded a number of parameters which control the relaxation dynamics of the system under study, namely the spin–orbit coupling constant $\xi = 140 \text{ cm}^{-1}$, the phonon energy $\hbar\omega = 300 \text{ cm}^{-1}$, the lattice relaxation energy $S_0\hbar\omega = 1250 \text{ cm}^{-1}$, and the ⁴T₂ radiative lifetime $\tau_0 = 18.9 \mu\text{s}$.

References

- [1] Scheps R, Gately B M, Myers J F, Krasinski J S and Heller D F 1990 *Appl. Phys. Lett.* **56** 2288
- [2] Härig T, Struve B and Huber G 1981 *J. Lumin.* **24/25** 367
- [3] Wang G, Gallagher H G, Han T P J and Henderson B 1995 *J. Cryst. Growth* **153** 169
- [4] Wang G, Han T P J, Gallagher H G and Henderson B 1995 *Appl. Phys. Lett.* **67** 3906
- [5] Wang G, Gallagher H G, Han T P J and Henderson B 1996 *J. Cryst. Growth* **163** 272
- [6] Belokoneva E L, Azizov A V, Leonyuk N I, Simonov M A and Belov N V 1981 *Zh. Strukt. Khim.* **22** 196
- [7] Di Bartolo B 1968 *Optical Interactions in Solids* (New York: Wiley)
- [8] O'Donnell K P, Marschall A, Yamaga M, Henderson B and Cockayne B 1989 *J. Lumin.* **42** 365
- [9] Wang G, Gallagher H G, Han T P J and Henderson B 1995 *Radiat. Eff. Defects Solids* **136** 953
- [10] Koepke Cz, Wisniewski K, Grinberg M, Russell D L, Holliday K and Beall G H 1998 *J. Lumin.* **78** 135
- [11] Smith F T 1969 *Phys. Rev.* **179** 111
- [12] Grinberg M, Mandelis A and Fieldsted K 1993 *Phys. Rev. B* **48** 5935
- [13] Kaminska A, Suchocki A, Arizmendi L, Callejo D, Dieguez E, Jaque F and Grinberg M 2000 *Phys. Rev. B* **62** 10 820
- [14] Struve B and Huber G 1985 *Appl. Phys. B* **36** 195