Nuclear spin relaxation of Pr^{3+} in $YAlO_3$. A temperature-dependent optical–rf double-resonance study

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The decay rates of the nuclear spin polarization of Pr^{3+} in a $YAlO_3$ matrix were measured in the temperature range 3–9 K by time-resolved spectral hole burning and simultaneous radio-frequency irradiation In the low-temperature limit, diffusion of spin polarization to other regions of the inhomogeneously broadened optical resonance line dominates the relaxation At higher temperature, thermally activated multiple phonon processes become dominant

1. Introduction

Single crystals of rare earth compounds are used extensively for high-resolution coherent optical spectroscopy [1,2] and have been identified as interesting candidates for optical data storage [3] Information can be stored in these systems by burning a hole into the inhomogeneously broadened optical resonance line [4], thereby altering the nuclear spin polarization of those atoms whose optical resonance frequency falls into the range selected by the laser frequency The lifetime of the spin polarization and therefore the time for which data can be stored, depends on the relaxation rates that redistribute the populations between the different spin states This relaxation behaviour was analyzed in considerable detail in the system Pr^{3+} LaF_3 [5–8] Both groups found a temperature-independent behaviour at low temperatures, which appeared to be dominated by simultaneous mutual spin flips of Pr and F spins These processes can be energy conserving and therefore temperature independent At higher temperatures, thermally activated processes became more important From the observed activation energy, which matched the activation energy of 57 cm^{-1} of the first excited state, Shelby et al concluded that these processes were induced by multiple phonon processes [7]

Another important system is Pr^{3+} $YAlO_3$, which has been used extensively in high-resolution laser spectroscopy [9,10] and optical–radio-frequency double-resonance experiments [11] In this system, relaxation has been analyzed at 2 K by Bai and Kachru [12], who found that mutual spin flips were the dominant relaxation mechanism At higher temperatures, other processes that are not energy conserving should become important, but corresponding measurements have not been reported so far

Pure nuclear quadrupole resonance (NQR) or nuclear magnetic resonance (NMR) allows direct measurements of relaxation rates of nuclear spin polarization However, in these dilute systems, the sensitivity of conventional magnetic resonance experiments is too low to allow direct experimental observation On the other hand, optical hole-burning spectroscopy [4,13] allows a direct observation of the spin populations in these systems, as well as of their time dependence However, the evolution of the populations depends on the initial populations of all spin states and is in general multi-exponential Extracting the transition rates between the individual spin states from the observed decay of the individual populations allows a more general description of the system

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2. Experiment

The experiments were performed with a $5\times5\times1$ mm $YAlO_3$ (YAP) crystal, doped with 0 1% Pr The crystal was mounted on the cold finger of a He flow cryostat and the two laser beams propagated along the crystallographic *c* axis The laser frequency was resonant with the transition between the $^3D_4$ ground state and the $^1D_2$ excited state ($\lambda=610$ 6 nm) The inhomogeneous width of the optical absorption line was 5 GHz (fwhm) and the laser frequency was close to the line centre As shown in fig 1, the pump and probe laser beam were derived from the same ring dye laser, their frequencies were shifted independently with two acousto-optic modulators (AOM) In the experiments, we kept the pump laser frequency fixed at $\nu_{pump}=\nu_{laser}-160$ MHz while the probe laser frequency was swept between $\nu_{probe}=\nu_{laser}-(190\ \ 130)$ MHz by driving the corresponding AOM with a ramped radio frequency from a digital synthesizer A third rf synthesizer was set either to 7 05 MHz, resonant with the $|\pm1/2\rangle\leftrightarrow|\pm3/2\rangle$ transition, or to 14 1 MHz, selecting the $|\pm3/2\rangle\leftrightarrow|\pm5/2\rangle$ transition The rf signal was amplified to 1 W and applied to the crystal by a solenoid coil that was part of a tuned circuit The resulting rf field of 10 μT was oriented parallel to the *X* principal axis of the nuclear quadrupole tensor, along the crystal *c* axis

Fig 2 illustrates the timing of the experimental procedure The pump laser (uppermost trace in fig 2) was turned on for a fixed duration, usually 0 5 s,

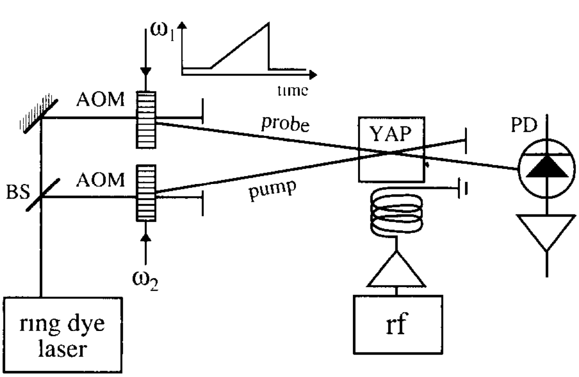

Fig 1 Summary of the experimental apparatus BS = beam splitter, AOM = acousto-optic modulator, rf = radio-frequency synthesizer, YAP = sample crystal, PD = photodiode

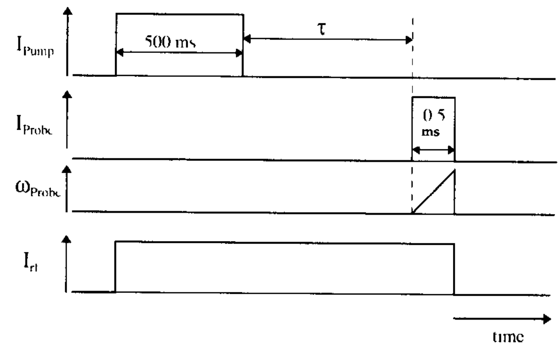

Fig 2 Timing of pump beam intensity (top trace), probe beam intensity (second trace), and probe beam frequency (third trace) The bottom trace represents the amplitude of the radio-frequency field, which is used in the double-resonance experiments

to burn a hole into the inhomogeneous optical absorption line The resulting state is characterized by a nonthermal distribution of the populations of the different nuclear spin states. After the end of the pump laser pulse, this spin polarization was allowed to decay for a time τ in the absence of laser irradiation After this delay, the hole spectrum was recorded by turning on the probe laser beam (second trace in fig 2) and scanning its frequency across the hole spectrum in a time short compared to the spin relaxation time (typically 0 5 ms)

Fig. 3 shows two spectra obtained with this procedure for different delays: the bottom trace corresponds to the spectrum immediately after the end of the pump pulse As usual, the large central hole appears when the pump and probe laser frequencies coincide, while the antiholes, indicating increased populations, mark those frequencies where the difference between pump and probe laser beam matches the energy level difference between two spin substates of the electronic ground state At these frequencies, the probe laser therefore measures the population change of one pair of ground state sublevels, the fractional numbers above the spectrum indicate the spin quantum number of these states The inset represents the relevant energy level scheme (not to scale) with the numbered levels representing hyperfine levels of the electronic ground states, while $|e\rangle$ represents the electronically excited state Its hyperfine splitting is not resolved under our experimental conditions but contributes to the observed width of the lines in the hole spectrum The remaining width is due to laser

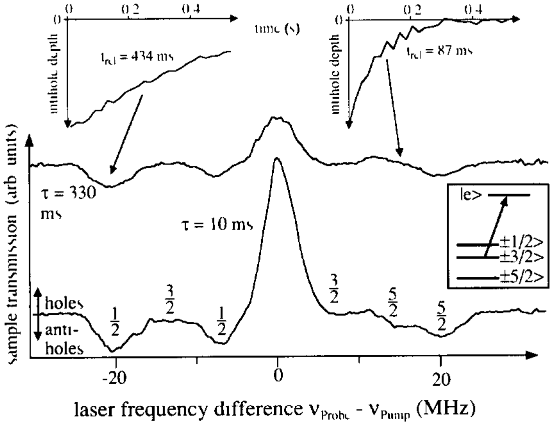

Fig 3 Experimentally observed hole-burning spectra for two different delays τ between the end of the pump laser pulse and the scan of the probe laser The numbers (1/2, 3/2, 5/2) indicate the nuclear spin sublevels whose populations create the indicated antiholes The inset indicates the relevant energy level scheme with the nuclear spin states in the electronic ground state $|e\rangle$ marks an electronically excited state whose hyperfine structure is not resolved The two curves at the top of the figure indicate the time-dependent depth of two antiholes

jitter; for the time scale of this experiment (0 5 s), our laser (Spectra Physics, model 380D) typically drifts by about 1 MHz

As the delay between pump and probe pulse is increased, the populations of the nuclear spin states approach their equilibrium values and the hole spectrum decays, as evidenced by the upper spectrum, which was recorded after a delay of 330 ms However, not all populations approach their equilibrium values at the same rate The two curves at the top of fig 3 show the behaviour of two sublevel populations whose lifetimes differ by a factor of 5 In addition, the decay of the sublevel populations is non-exponential and depends on the initial conditions This behaviour is consistent with the assumption that the relaxation rates for the three different transitions are unequal

A possible method for the analysis of such systems was demonstrated by Grechishkin and Shishkin [14] for pure nuclear quadrupole resonance (NQR) and used in hole-burning spectroscopy by Shelby et al [7] It uses strong rf irradiation to saturate one of the transitions, equilibrating the two populations Under these conditions, the system has only a single degree of freedom (the population of the level that is not influenced by the rf irradiation) and decays with a single rate constant.

We applied this method to our system, using rf irradiation at the two allowed magnetic dipole transitions (ω_{rf}=7 05, 14 1 MHz) As shown in fig 2, the rf field was applied simultaneously with the pump laser pulse, and left on until the spectrum was recorded. The effect of the rf irradiation can be seen directly in the hole-burning spectra of fig 4· in this experiment, the rf irradiation was tuned to the $|\pm 3/2\rangle \leftrightarrow |\pm 5/2\rangle$ transition As a result, two new holes appear at $\nu_{probe} - \nu_{pump} = \pm 14$ MHz, indicating that the populations of these two levels have been equilibrated. In addition, an analysis of the time dependence of the spectra shows that, within the experimental uncertainties, all lines decay now with the same rate constant We also tried to saturate the third transition between the $|\pm 1/2\rangle \leftrightarrow |\pm 5/2\rangle$ states. However, the magnetic dipole strength of this transition was too small to allow a reliable saturation without excessive heating or affecting the other transitions

3. Theory

For the following analysis, we assume that only the ground state sublevels are appreciably populated This condition is well satisfied under our experimental conditions (long pump pulse) and has been verified experimentally by integrating the hole spectrum The resulting integral vanishes within exper-

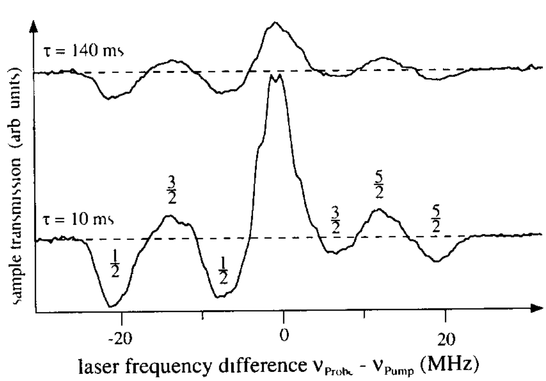

Fig 4 Hole-burning spectra with simultaneous rf irradiation (ω_{rf}= 14 1 MHz) for two different delays τ

imental accuracy for all delays between pump and probe laser pulse

In the absence of a magnetic field, the spin substates with opposite quantum number are degenerate We will treat the ground state spin system therefore as a three-level system We write the populations of the three pairs of spin states as $p_{1,3,5}$ and assume that the relaxation process can be described by a linear rate equation with time-independent coefficients c_{13}, c_{15}, c_{35},

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} p_1 \\ p_3 \\ p_5 \end{pmatrix} = \begin{pmatrix} -(c_{13}+c_{15}) & c_{13} & c_{15} \\ c_{13} & -(c_{13}+c_{35}) & c_{35} \\ c_{15} & c_{35} & -(c_{15}+c_{35}) \end{pmatrix} \times \begin{pmatrix} p_1 \\ p_3 \\ p_5 \end{pmatrix} \quad (1)$$

The eigenvalues and eigenvectors of this system are

$$\lambda_1 = 0\,, \quad \zeta_1 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

$$\lambda_{2,3} = -(c_{13}+c_{15}+c_{35}) \pm r\,,$$

$$\zeta_{2,3} = \begin{pmatrix} -c_{13}+c_{35}\pm r \\ c_{13}-(c_{15}\pm r) \\ c_{15}-c_{35} \end{pmatrix}, \quad (2)$$

with

$$r = \sqrt{c_{13}^2 + c_{15}^2 + c_{35}^2 - c_{13}c_{15} - c_{13}c_{35} - c_{15}c_{35}}$$

In the case of rf irradiation, one of the transition rates c_{13} or c_{35} is large compared to the others For $\omega_{\mathrm{rf}} = 7$ 06 MHz, we have $c_{13} \gg c_{15}, c_{35}$ and therefore $r \approx c_{13}$, $\lambda_2 \approx -\frac{3}{2}(c_{15}+c_{35})$, and $\lambda_3 \approx -2c_{13}$ In this case, the eigenvector ζ_3 decays rapidly, while ζ_1 is still time independent The evolution of the system is then determined only by a single eigenvalue and we expect an exponential decay of the hole spectrum From the experimental data, we can therefore determine $\lambda_2(\omega_{\mathrm{rf}} = 7\ \mathrm{MHz}) \approx -\frac{3}{2}(c_{15}+c_{35})$ and $\lambda_2(\omega_{\mathrm{rf}} = 14\ \mathrm{MHz}) \approx -\frac{3}{2}(c_{13}+c_{15})$

As we could not reliably saturate the third rf transition we had to use the data obtained without rf irradiation To avoid the many possible pitfalls of multi-exponential fitting, we decided to use only the initial decay of these lines For this purpose, we determined the populations of the different spin substates from the hole-burning spectrum and calculated the resulting decay rates as a function of the three rate constants c_{13}, c_{15}, and c_{35} In the experimental data, the amplitude of the holes at -14 and $+7$ MHz were too small to be used for the data analysis The remaining four antiholes, the hole, and the two experiments with rf irradiation provided a set of seven equations for the determination of the three rate constants We used a least-squares fitting procedure to extract these rate constants from the experimental data Comparison of the calculated decay rates with the experimental values allowed then an assessment of the reliability of these values and our theoretical model

Fig 5 summarizes the rate constants that we obtained with this procedure as a function of the sample temperature In all measurements, the rate c_{15} between the $\pm 1/2$ and $\pm 5/2$ substates was always the smallest, while the rate c_{35} was the largest. In that respect, our results differ from those observed in Pr^{3+} LaF_3, where the relaxation between the $\pm 1/2$ and $\pm 3/2$ substates was most efficient In close analogy to those results, the relaxation becomes temperature independent at low temperatures ($T < 4$ K in this case), indicating that mutual spin flips of neigh-

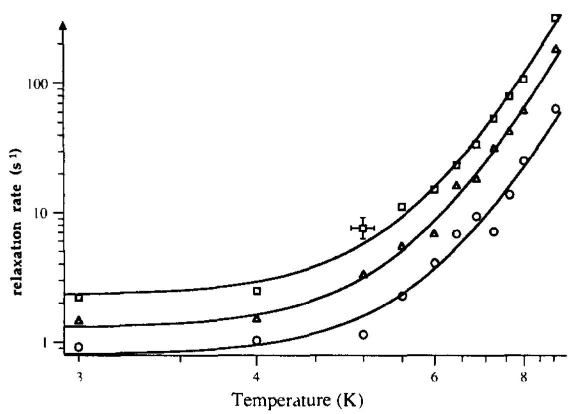

Fig 5 Decay rates as a function of temperature The symbols are measured data points, while the curves represent best fits with the function described in the text (□) $\pm 3/2 \leftrightarrow \pm 5/2$, (△) $\pm 1/2 \leftrightarrow \pm 3/2$, (○) $\pm 1/2 \leftrightarrow \pm 5/2$

bouring Pr nuclei dominate the relaxation in this region At higher temperatures, a thermally activated process dominates We obtained a good fit of the experimental data by using a function

$$c_{ij}(T) = A_{ij} + B_{ij}\, e^{-E/kT}\,, \tag{3}$$

using the same activation energy E for all three rates For the activation energy and the six independent constants A_{ij}, B_{ij}, we found

$$E = 36\ \text{cm}^{-1}\,,$$

$$A_{13} = 1\ 49\ \text{s}^{-1}\,,\quad B_{13} = 4\ 1\times10^{4}\ \text{s}^{-1}\,,$$

$$A_{15} = 0\ 93\ \text{s}^{-1}\,,\quad B_{15} = 1\ 5\times10^{4}\ \text{s}^{-1}\,,$$

$$A_{35} = 2\ 59\ \text{s}^{-1}\,,\quad B_{35} = 7\ 6\times10^{4}\ \text{s}^{-1} \tag{4}$$

The activation energy derived from our measurements is therefore somewhat smaller than the energy of the first excited state at 51 cm^{-1} We consider this as evidence that two-phonon processes of the type discussed in the LaF_3 case are important also in this system, but contributions from other processes are not negligible However, we cannot exclude the possibility that sample heating, either by the rf irradiation, or by the absorption from the laser may have caused some local heating in the sample, thereby distorting the temperature dependence.

4. Discussion

The relaxation of the Pr^{3+} nuclear spin polarization in $YAlO_3$ resembles closely the behaviour in LaF_3. In both cases, the relaxation rates approach a finite value at low temperatures In this temperature range, the relaxation is dominated by energy-conserving simultaneous spin flips of pairs of Pr ions For the same doping concentration, relaxation in $YAlO_3$ is roughly an order of magnitude faster than in LaF_3, in good agreement with the results of Bai and Kachru [12] At higher temperatures, thermally activated processes become dominant The activation energy appears to be somewhat lower than the excitation energy of the first crystal-field state, which would be expected if the relaxation is due to multiple phonon processes In addition, we found the largest relaxation rates for the $\pm 3/2$ to $\pm 5/2$ transition, in contrast to the LaF_3 case, where the relaxation of the $\pm 1/2 \leftrightarrow \pm 3/2$ transition decay is the fastest

Different experimental imperfections might be responsible for the difference between the observed and the expected activation energy. Thermal inhomogeneities would tend to blur the transition from the low-temperature regime to the thermally activated regime, resulting in a lower apparent activation energy. In our experiment, we tried to reduce such spurious effects due to inhomogeneous experimental conditions by using a pump laser beam that was wider than the probe laser beam An extension of the measurements to higher temperature could provide more clarity on the relaxation mechanisms involved In particular, the determination of the activation energy should become more precise. Experimentally, we could observe hole-burning spectra up to at least 15 K Measurements of the decay rates from delayed hole-burning spectra, as we used them here, however, could not be used in this temperature regime, since the relaxation times became shorter than the scan time required for recording a spectrum Other techniques which could be useful for measuring shorter time constants appeared to be more sensitive to laser drift and will require careful calibration.

The agreement between the observed decay of the hole-burning spectrum and the behaviour that we expect from the fitted decay rates was quite satisfactory overall Nevertheless, some discrepancy remained which appeared to be larger than the experimental uncertainties Possible explanations for these effects include the nonexponential relaxation behaviour due to spin diffusion observed by Bai and Kachru [12] and not included in our simple rate equation model, or correlations between the optical resonance frequencies of neighbouring atoms Another possibility is that the description of the system by only three energy levels is an oversimplification of the true dynamics The Pr nuclear spin ($I=5/2$) has a total of six energy levels, which are pair-wise degenerate in zero field. Our theoretical analysis is based on the assumption that their populations are also equal and decay at the same rates This assumption should be well satisfied as long as the different processes that contribute to the relaxation are independent and couple only to the magnetic dipole of the nuclear spins or to the quadrupole operator However, correlations between the different processes can break this symmetry and lead to differences between the rates for the "+" system consisting of the (+1/2, +3/2, +5/2) states and the corresponding "−" system While it is of course possible to check this hypothesis by applying a magnetic field that lifts the degeneracy of the two subsystems and allows the observation of individual populations, this will also affect the spin diffusion process, in particular the cross relaxation between the two subsystems

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