

Multiple transient spectral holes in the R₁-line of NaMgAl(oxalate)₃·9H₂O:Cr(III). Probing excited and ground state *g*-factors in an external magnetic field of 15 mT

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The *g*-factors of the ⁴A₂ ground state and the ²E excited state of chromium(III) doped into NaMgAl(oxalate)₃·9H₂O are accurately determined at 2.5 K by the observation of *multiple* transient spectral holes in the R₁-line (²E←⁴A₂ transition) in *minute* magnetic fields of ≈ 15 mT.

Optical transitions in condensed phases are inhomogeneously broadened by the variation of local fields.¹ Laser techniques such as spectral hole-burning can overcome this broadening and it is often possible to measure subtle details of the electronic structure of chromophores.^{1–4}

We have recently reported^{5,6} the temperature dependence of *transient* and *persistent* spectral hole-burning in a NaMgAl(oxalate)₃·9H₂O crystal doped with 5% of chromium(III). This compound is a rare example of a crystalline system which exhibits persistent *non-photochemical* hole-burning. The present work reports on the observation of multiple transient spectral holes in the R₁-line of chromium(III) doped NaMgAl(oxalate)₃·9H₂O in a minute external magnetic field of 15 mT. The sideholes facilitate an accurate determination of ground and excited state *g*-factors.

The crystal structure of NaMgAl(oxalate)₃·9H₂O originally reported by Frossard⁷ was reinvestigated by Mortensen⁸ and it was found that the space group is either *P*3̄c1 or *P*3c1 with six formula units per unit cell. The crystal structure was reinvestigated recently and it was concluded that the space group is indeed *P*3̄c1.⁹ However, in this latter work it was claimed on the basis of the space group that the crystal contains 10 water molecules of crystallisation. The results of elemental analysis^{6,10,11} are in best agreement with nine water molecules requiring some disorder in the *P*3̄c1 space group. There are six magnetically inequivalent sites composed of two sets of three, with each set being rotated by an angle of 17.7° around the crystal *c*-axis. EPR measurements established¹¹ that there is a rhombic contribution to the ligand field with parameters of the spin Hamiltonian of the ⁴A₂ ground state of *D* = −0.7786 cm^{−1} and *E* = 0.0306 cm^{−1}. It appears that the zero-field splitting tensor of all six molecular anions is aligned with the crystal *c*-axis. From magnetic susceptibility measurements it followed¹² that the ±3/2 spin component of the ⁴A₂ state is lowest.

NaMgAl(oxalate)₃·9H₂O and NaMgCr(oxalate)₃·9H₂O were prepared according to literature methods.^{7,10} Mixed crystals containing 1% of chromium(III) were grown by slow evaporation of aqueous solutions at room temperature.

Transient spectral holes were burnt by a temperature and current stabilised laser diode (Hitachi HL6738MG with Thorlabs LDC500 laser diode driver, Thorlabs TEC2000 temperature controller with a TCLDM9 thermoelectric laser diode mount). The laser current and hence the frequency was kept constant for 1 ms (hole-burning period) and subsequently modulated by a triangle ramp of ±0.5 mA amplitude in 0.5 ms (hole readout). The ±0.5 mA current variation provides a frequency scan of ±1.35 GHz. The transmitted laser light was passed through a monochromator set at a bandpass of ≈ 0.5 nm (Spex 1704 with 1200 grooves mm^{−1} holographic grating) and then detected by a cooled photomultiplier (RCA31034C). The signal was averaged on a digital storage oscilloscope after preamplification by a current–voltage converter (Products-For-

Research PSA). The sample was cooled by a closed-cycle refrigerator (Janis/Sumitomo SHI-4.5). The magnetic field was generated by a pair of water cooled Helmholtz coils built in the laboratory. The coils were arranged externally to the cold head of the cryocooler and had a radius of 125 mm with 250 turns of 1.08 mm copper wire, providing 15.3 mT at 8 A and ≈ 70 V.

Fig. 1 shows an 8% deep spectral hole burnt into the red edge of the R₁-line of NaMgAl(oxalate)₃·9H₂O:Cr(III) at 692.37 nm in zero field and at 2.5 K. When applying an external magnetic field along the crystal *c*-axis of *B*_{||*c*} = 15.3 mT, four sets of sidehole-pairs are observed. The inset in Fig. 1 illustrates the polarised absorption spectra of the R₁-line. The energy difference between the two polarisations is due to the ⁴A₂ ground state zero field splitting of 1.6 cm^{−1}. It appears that the R₁-transition originating from the ±3/2 spin component is strongly π polarised (*E*_{||*c*}) whereas the R₁-transition from the ±1/2 spin component shows a relatively strong σ component (*E*_{⊥*c*}). Note that the absorbance of the transition from the ±1/2 Kramers doublet is reduced at 2.5 K due to the thermalisation between the spin levels of the ⁴A₂ ground state. This can be described by a Boltzmann distribution. The observed polarisations in the R₁-line are in approximate agreement with trigonal

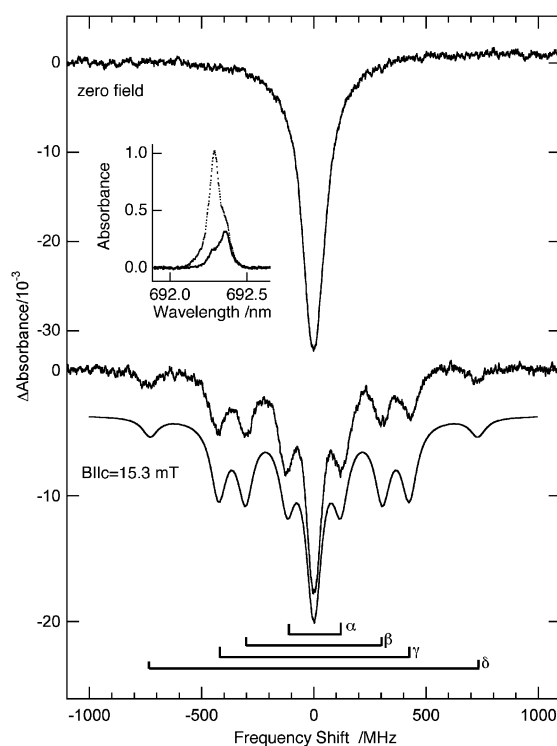


Fig. 1 Transient spectral holes in the red edge (692.37 nm) of the R₁-line in NaMgAl(oxalate)₃·9H₂O:Cr(III) in zero field and in *B*_{||*c*} = 15.3 mT at 2.5 K. The laser was polarised perpendicular to the *c*-axis, *E*_{⊥*c*}. The lowest trace shows a simulated spectrum applying predicted transition dipole moments in a trigonal approximation. The indicated splittings are discussed in the text. The inset shows the polarised absorption spectra of the R₁-line at 2.5 K: solid line = σ-, dotted line = π-polarisation.

transition dipole strengths,¹³ and would indicate that the lower 2E level is the $2A$. From the spectroscopy of the spin-allowed transitions^{8,10} trigonal field parameters $K = 290 \text{ cm}^{-1}$ and $K' = -1250 \text{ cm}^{-1}$ were deduced. The positive K value would be in accord with the above assignment. However, trigonal selection rules are violated in the R_2 line and $g \perp c \neq 0$ for both 2E levels indicating a very large perturbation by the rhombic field.

The laser light used in the hole-burning experiments illustrated in Fig. 1 was σ -polarised. Since the laser wavelength was at the red edge of the R_1 line we can restrict the analysis of the observed sidehole pattern to a four-level model involving the $\pm 1/2$ spin components in the ground state and effective $\pm 1/2$ spin components in the excited state. This is illustrated in Fig. 2. The Zeeman splitting is much less than the inhomogeneous broadening, and hence four sets of chromophores within the inhomogeneous broadened transition are in resonance with the laser. This leads to the observation of four pairs of sideholes spaced at energies corresponding to the ground state splitting, the excited state splitting and the sum and difference of the two splittings. In terms of the ground state and excited state g -factors, the four pairs of sideholes can be expected at $\pm g_z \mu_B B_z$ for i, m, b, f; $\pm g_z^{\text{ex}} \mu_B B_z$ for e, k, c, h; $\pm (g_z + g_z^{\text{ex}}) \mu_B B_z$ for l, a; and $\pm (g_z - g_z^{\text{ex}}) \mu_B B_z$ for g, d; where g_z and g_z^{ex} denote the g -factor in the z -direction of the ground state and the excited state, respectively, and μ_B is the Bohr magneton. The observed splittings γ , β , δ and α in Fig. 1 correspond to these pairs of sideholes. From the data shown in Fig. 1 it follows that $g_z = 1.98 \pm 0.02$ and $g_z^{\text{ex}} = 1.42 \pm 0.02$.

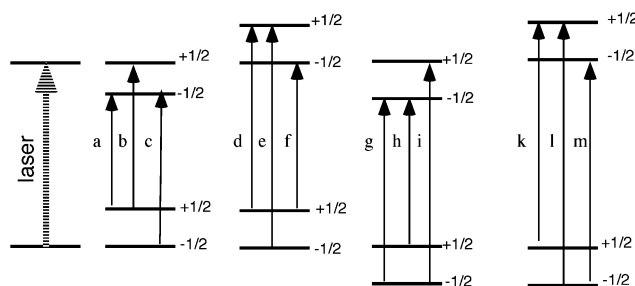


Fig. 2 Schematic energy diagram for the observed sideholes in the $(R_1({}^2E, M_s = \pm 1/2)) \leftarrow ({}^4A_2, M_s = \pm 1/2)$ transition in an external magnetic field, $B \parallel c$. The laser can be in resonance with four subsets of chromophores.

In the simulation of the 15.3 mT ($B \parallel c$) hole-burning spectrum shown in Fig. 1, transition dipole strengths calculated for the R_1 -line ($2A({}^2E) \leftarrow {}^4A_2$ transition) of a trigonal d^3 system were employed (Table 1). Relative to the resonant hole, depths of 0.1 and 0.4 are deduced for the $\pm (g_z + g_z^{\text{ex}}) \mu_B B_z$ and the $\pm g_z \mu_B B_z$, $\pm g_z^{\text{ex}} \mu_B B_z$, $\pm (g_z - g_z^{\text{ex}}) \mu_B B_z$ sideholes, respectively. In this calculation one must take into account that hole-burning is a sequel two-photon process. For example, the contribution to the depth of the sidehole at $-g_z \mu_B B_z$ by transition b in Fig. 2 is expected to be $\sigma/6 \times \sigma/3$. This has to be compared with the contribution to the resonant hole of $\sigma/6 \times \sigma/6$. The simulation in Fig. 1 shows that there are some significant variations in the calculated and experimental hole-depths. This is not surprising since the rhombic field seems to be a significant perturbation (see above) and the point symmetry of the molecular anion is C_2 . The low symmetry perturbation is most likely caused by the hydrogen-bonding of water molecules to the oxalate ligands. This hydrogen bonding may also be responsible for the non-photochemical persistent hole-burning observed in this system.

Table 1 Trigonal transition dipole moments for the $2\bar{A}({}^2E, M', M'_s) \leftarrow {}^4A_2(M_s)$ transition in terms of the parameter σ (adapted from ref. 13)

M_s	$M'_s = 1/2, M' = u+$	$M'_s = -1/2, M' = u-$
1/2	$\sigma+3$	$\sigma+6$
-1/2	$\sigma-6$	$\sigma-3$

The holewidth is significantly reduced in the external magnetic field: the zero field hole has a width of 125 MHz and the resonant hole in the 15.3 mT spectrum has a width of 85 MHz. The latter is dominated by the laser linewidth of ≈ 60 MHz. The laser lineshape is approximately given by a Gaussian. Due to the two-photon nature of the hole-burning experiment the laser line has to be convoluted with itself in order to determine the instrumental contribution ($\approx \sqrt{2} \times \text{width} = 85$ MHz). Thus it follows that the 85 MHz are basically given by the laser linewidth and we can safely assume that the actual holewidth is less than 5 MHz in 15.3 mT. We are currently investigating this question by the application of pseudo-external cavity diode lasers operating at substantially higher resolution. The observed narrowing of the holewidth in external magnetic fields supports a previous suggestion⁶ that the residual holewidth in zero field is due to indirect electron spin-spin, and ${}^{27}\text{Al}$ and ${}^1\text{H}$ superhyperfine interactions.^{2,14}

In the present work we used crystals with 1% chromium(III) concentration. The residual holewidth of ≈ 40 MHz (correcting for the laser linewidth) in zero field is substantially smaller than the ≈ 90 MHz width previously reported for the 5% crystal. This indicates that (indirect) chromium(III)–chromium(III) spin-spin interactions dominate the observed holewidth in the 5% crystal.

The present work shows that g -factors of both the ground and the excited state can be accurately determined by transient spectral hole-burning experiments in *minute* magnetic fields. In contrast to conventional optical Zeeman spectroscopy the present experiment allows the *direct* observation of the pure ground state and excited state Zeeman splittings.

The present work also illustrates the potential of diode laser spectroscopy. The spectral holes in Fig. 1 correspond to a relatively small change in optical density. Nevertheless, the data is of high quality due to the inherent stability of the laser diode used. The frequency of laser diodes can be rapidly scanned by the modulation of the injection current. This facilitates fast transient spectral hole-burning experiments that use only *one* diode laser to burn and read the spectral hole. In some early work¹⁵ sideholes in the R_1 -line of ruby in magnetic fields were measured by Stark-sweeping the electronic levels. In contrast to the present work, only the $\pm (g_z - g_z^{\text{ex}}) \mu_B B_z$ sideholes could be detected due to the limited scan range.

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