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Reference

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Electronic structure of $V^{3+}$ in NaMgAl(ox)$_3$·9H$_2$O probed by Fourier transform spectroscopy

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ABSTRACT

High-resolution Fourier transform absorption and luminescence spectroscopy reveal axial and rhombic zero-field splittings of the spin-forbidden electronic origins of $V^{3+}$ in NaMgAl(ox)$_3$·9H$_2$O (ox = oxalate) single crystals below 25 K. The temperature dependence of the integrated absorption of the split features display behavior consistent with a Boltzmann distribution within the zero-field split $3A_g$ ground state of $V^{3+}$. Weak luminescence is observed in the near-IR from the lowest energy spin-forbidden transition with a luminescence lifetime of less than 0.5 µs at 11 K and an estimated quantum efficiency of the order of $10^{-5}$.

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1. Introduction

The trisoxalatovanadium (III) anion, $[V(ox)_3]^{3-}$, has received attention in recent years because of its application as a component in multi-nuclear, mixed-valence molecular magnets [1]. In order to understand the complex magnetic properties of these multi-component systems, the electronic structure of the mononuclear (paramagnetic) components needs thorough investigation, which is lacking for the $[V(ox)_3]^{3-}$ anion. Pseudo-octahedral $V^{3+}$ has a $3T_1$ ground state that is difficult to study by classical electron resonance spectroscopy due to the large axial zero-field splitting (ZFS). Study of the ground-state electronic structures of integer-spin systems, like $V^{3+}$, has been reviewed recently [2].

Intra-configurational spin-forbidden d–d transitions, for $V^{3+}$ of the type $^3T_1(t_{2g})^2\rightarrow^1T_2(t_{2g})^2$, have negligible changes in geometry, and the resulting transition line widths can be of the order of 1 cm$^{-1}$, as for $V^{3+}$ in $\alpha$-Al$_2$O$_3$ [6,7]. A great deal of ground-state electronic structural information has been elucidated by studying these transitions using electronic absorption [7], luminescence [8], and Zeeman spectroscopies [6] for $V^{3+}$ in Al$_2$O$_3$, including the magnitude and sign of $D$ and $g$-values. The analogous transitions of $[V(ox)]^{3+}$ have received little attention [9].

This article describes the investigation of the electronic structure of $[V(ox)_3]^{3-}$ diluted in NaMgAl(ox)$_3$·9H$_2$O by high-resolution Fourier transform (FT) absorption and luminescence spectroscopies. FT spectroscopy combined with the narrow absorption line widths of the spin-forbidden d–d bands of $V^{3+}$ has allowed us to unambiguously resolve both axial and rhombic ZFSs within the $3A_g$ component of the ground state [10]. Very weak luminescence was also detected in the near-IR from the lowest energy electronic origin with an estimated quantum efficiency of the order of $10^{-5}$.

The crystal structure of NaMgAl(ox)$_3$·9H$_2$O has recently been reinvestigated and solved in the P3c1 space group [11]. The structure can be described as a 2D honeycomb lattice consisting of $[NaAl(ox)_3]$ with $[Mg(OH_2)_6]^{2+}$ sitting in the voids and the remaining 3 waters exhibiting disorder and lying in-between the $[NaAl(ox)_3][Mg(OH_2)_6]$ planes. The $Al^{3+}$ ions sit at a general position with C$_1$ symmetry. The molecular structure is shown down the c-axis in Fig. 1a. The trigonal field is coincident with the crystallographic c-axis, however, various anisotropic interactions between the water molecules and the oxalate ligands introduce a rhombic field to the $[Al(ox)_3]^{3-}$ unit [11]. The effect of these distortions on the splitting of the $^3T_1$ ground-state in the $V^{3+}$ ions in the diluted crystals is shown schematically in Fig. 1b. The intra-configurational spin-forbidden transitions that we are interested in are shown by solid, vertical lines.

2. Experimental section

The preparation of NaMgAl$_2$V$_x$(ox)$_{3-9Y}$(Y = H or D) was modified from the literature method for preparing the Fe$^{3+}$-doped crystal [12]. The vanadium source was VCl$_3$. Crystals were grown by slow evaporation from supersaturated aqueous (H$_2$O, D$_2$O or mixed H$_2$O:D$_2$O) solutions. The crystals produced were large, hexagonal and dichroic with dimensions of ~10 mm$^3$. 

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Absorption spectra were measured with a FT spectrometer utilizing light sources, polarizers, beam splitters and detectors to cover the spectral range from 6000 to 30,000 cm$^{-1}$ (Bruker IFS-66). Crystalline samples were mounted on copper apertures and placed in either an optical closed-cycle cryostat capable of reaching base temperatures of 10 K (Oxford Instruments, CCC1100 T) or 3.9 K (Sumitomo SHI-4-5).

Luminescence spectra were recorded using the FT spectrometer equipped with a liquid N$_2$-cooled InGaAs detector and with excitation from the 2nd harmonic of a Nd:YAG pulsed laser. Luminescence lifetimes were recorded using a Hamamatsu R316-02 PM tube equipped with a liquid N$_2$-cooled InGaAs detector and with excitation from a 405 nm (25 mW) laser diode. Luminescence was observed from the narrow band at 9635 cm$^{-1}$ with no observable Stokes shift. The room temperature absorption spectrum of the title compound just shows the broad spin-allowed $^3T_1 \rightarrow ^3T_2$ and $^3T_1 \rightarrow ^3D$ transitions centered at 16,900 and 24,050 cm$^{-1}$, respectively. The octahedral ligand-field strength and the Racah parameters are estimated from the transition energies of the spin-allowed and spin-forbidden transitions to be $D_q = 18,097$, $B = 556$, and $C = 2994$ (all in cm$^{-1}$). Upon cooling to 11 K, new absorption features appear in the near-IR and visible regions as shown in Fig. 2 for different values of $x$. These are assigned to transitions from the $^3D$ ground state component to one of the 3 possible components of the split $^1A_L$ ($^3T_2$) and $^1G$ ($^1E$) states expected in the near-IR and to the non-degenerate $^1A_L$ ($^3A_1$) state in the visible. At cryogenic temperatures, these absorption features narrow and three distinct bands become resolved as the concentration of $V^{3+}$ in the lattice was decreased from 15% to 1.3%. Concomitant with the narrowing of these bands their peak epsilon values dramatically increase. At 1.3% $V^{3+}$ concentration, they are comparable to those for the spin-allowed transitions. The average bandwidths (fwhm) at this concentration are 0.78(9) and 1.37(16) cm$^{-1}$ respectively, which approaches the spectral resolution limited by the FT spectrometer of 0.5 cm$^{-1}$. The slightly larger bandwidth of the $^1A_1$ transition is consistent with the slight difference in excited state geometry as expected from the small positive slope in the Tanabe-Sugano diagram for this state. The bands also display a large degree of polarization that is consistent with a previous report on this compound [13] and $[V(urea)_{3}(ClO_4)_3]$ [14].

Luminescence was observed from the narrow band at 9590 cm$^{-1}$ at low temperature with no observable Stokes shift. Fig. 3 shows the temperature dependence of this luminescence from a 2.9% $V^{3+}$ crystal grown from a 50:50 solution of H$_2$O:D$_2$O. The spectral resolution of the luminescence was 2 cm$^{-1}$ due to instrumental limitations, which explains the larger bandwidths of the origins in the luminescence spectra compared to absorption (dotted line). The splitting at 10.3 K is 9.3(3) cm$^{-1}$ in agreement with the lowest energy peak and the centroid of the two higher energy features from the absorption spectrum. Although the spectra are noisy, this splitting persists up to at least 65 K where the bands remain resolved and show slight changes in relative intensities with varying temperature. An even weaker temperature-dependent vibronic sideband (shown with a Gaussian profile) was also detected below the origin that is mirrored by the vibronic absorption feature at 9635 cm$^{-1}$. We were unable to observe emission to the $^1E$ state component of the ground-state multiplet, which has been reported in other $V^{3+}$ compounds [2,8].
The measured luminescence decay time for the 2.9% V$^{3+}$ partially deuterated crystal was of the order of 450 ns at 4.0 K. The decay was nearly temperature independent below 20 K with a steady decrease above 20 K (see inset Fig. 3). The lifetime increased to 790 ns at 4.0 K for a fully deuterated crystal with ~5% V$^{3+}$. The relative emission intensity exhibited similar temperature dependence to the decay time (inset Fig. 3). The total quantum yield of this feature is $f = 2.9 \times 10^{-5}$ below 20 K, which is similar to V$^{3+}$ in Al$_2$O$_3$ [8]. The low quantum yield here in analogy to V$^{3+}$ in Al$_2$O$_3$ was rationalized from efficient quenching of the low-energy emission by high-energy lattice phonon modes [8]. Similar high-energy phonons have been reported in the vibronic spectrum of NaMgCr(ox)$_3$·9H$_2$O [16]. Thus, we propose an efficient multi-phonon non-radiative pathway to be responsible for the low quantum yield here in analogy to V$^{3+}$ in Al$_2$O$_3$ [8].

As shown in Fig. 2, both electronic origins centered at 9590 and 20,465 cm$^{-1}$ have three resolved bands with similar energetic separations. The absorption profiles can be reproduced using three Gaussian bands as shown in the top panel of Fig. 4. As the separations. The absorption profiles can be reproduced using three Gaussian bands as shown in the top panel of Fig. 4.

The energy at which $f = 0$ for each Gaussian band was fitted to the $E$-values [18]. Using this assumption is only valid when $A_{t(ng)} \gg A_z$. A nice example is the class of [V(OH$_2$)$_6$]$^{3+}$-alums where the axial crystal field is ca. 3 times larger than that of [V(ox)$_3$]$^{3+}$, and the site symmetry is strictly trigonal ($C_{3v}$) [20]. However, we attribute the additional splitting to a large rhombic crystal field present in the title lattice. Structural and spectroscopic evidence supporting this claim has been given by Riesen and Rae, who argue that this is due to a complex H-bonding network involving the lattice waters and the oxalate ligands [11].

For the sake of comparison with the other trigonal V$^{3+}$ compounds, we analyzed our observed splittings with the $S = 1$ spin-Hamiltonian, $\hat{H}$, given by Eq. (3).

$$\Delta \epsilon_{1,0} = 3.1(1)$$

$$\Delta \epsilon_{2,0} = 11.4(3)$$

$$f_1/f_0 = 0.60(1)$$

$$f_2/f_0 = 0.83(2)$$

$\hat{H}_I = A_{t(ng)}[x^2 - y^2(L + 1)] + A_z[x^2 - y^2] + A_L \hat{S} \cdot \hat{J} + \hat{H}_{ft}$

(2)

where $A_{t(ng)}$ and $A_z$ are the trigonal and rhombic crystal fields, respectively, that operate on the orbital-angular momentum and $A_z \hat{S} \cdot \hat{J}$ is the spin-orbit coupling operator that mixes the spin and orbital-angular momentum. The mixing parameter, $A$, describes the configuration interaction of the $^3T_1$($F$) and $^3T_1$($P$) states, which we calculate to be 1.25 using the above values of 10 Dq and $B$ [17]. For our current analysis we have neglected the Jahn–Teller effect.

Piper and Carlin reported a trigonal crystal field of +690 cm$^{-1}$ for this compound [13]. The positive sign indicates an axial compression ($^3A_2$ below $^3E$) that has been confirmed crystallographically [11]. The $^3A_2$ and $^3E$ states mix and split by spin–orbit coupling to three singly ($|0 >$) and three doubly degenerate ($|1 >$) spinors. A related compound, K$_2$V(ox)$_3$·3H$_2$O, studied by magnetic susceptibility and absorption spectroscopy, yielded values of $A_{t(ng)} = 700$ cm$^{-1}$ and $A_z = 64$ cm$^{-1}$ [18]. Using the spin–orbit coupling value for K$_2$V(ox)$_3$·3H$_2$O, we calculated the splitting of the $^3T_1$ spinor levels shown as a function of $A_{t(ng)}$ in Fig. 5a. The ZFS of the $^3A_2$ state to first order will always be positive in a trigonally compressed octahedron (see inset Fig. 5a).

The spin–orbit coupling constant is ca. 50% of the free ion value. This is due to the Ham effect that is also present for V$^{3+}$ in Al$_2$O$_3$ [19].

Historically, the observed ZFS of pseudo-octahedral V$^{3+}$ compounds have been parameterized using $D$ and $E$, which originate from differences in spin-angular momentum.

$$\Delta \epsilon_{1,0} = 3.1(1)$$

$$\Delta \epsilon_{2,0} = 11.4(3)$$

$$f_1/f_0 = 0.60(1)$$

$$f_2/f_0 = 0.83(2)$$

$\hat{H}_I = D[2S_z^2 - S(S + 1)] + E(S_x^2 - S_y^2)$

(3)

Fig. 5b shows the same 11 K polarized FT absorption spectra shown in Fig. 2 of the 1.3% V$^{3+}$-doped NaMgAl(ox)$_3$·9H$_2$O crystal. Based on solely energetic considerations we immediately have a dilemma when assigning the $D$ and $E$ values. From a phenomenological standpoint, the energy of the rhombic term, $E$, cannot be larger than $\frac{1}{2}$ of the axial ZFS, $D$, and experimentally the largest
observed ratio to date for a trigonally distorted V$^{3+}$ complex was $|E|/D = 0.26$ determined by HF-EPR spectroscopy for V(acac)$_3$ [3]. If we analyze the ground-state electronic structure with a positive $D$, we immediately see that the magnitude of the $E$ is larger than possible $|E|/D = 0.58$. Therefore, we are forced to quantify the ZFS with a large and negative axial ZFS due to the large rhombic distortion (see Fig. 5c). This effectively changes the quantization axis of the spin-Hamiltonian relative to the molecular axis. This can be proven by calculating the Zeeman behavior along the Cartesian axes of the molecule. The physically more probable scenario for the ground-state electronic structure is obtained with $D = -9.79(6)$ cm$^{-1}$ and $|E| = 1.50(3)$ cm$^{-1}$. $D$ and $E$ values for this compound and other hexa-oxo trigonal V$^{3+}$ compounds are given in Table 1.

It is interesting that the only other hexa-oxo V$^{3+}$ compound with a large rhombic ZFS involves bidentate ligands, V(acac)$_3$ has a large splitting of the $3A_2$ ground state with $\Delta E_{20} = 5.57$ cm$^{-1}$ and $\Delta E_{20} = 9.37$ cm$^{-1}$ as determined by HF-EPR [3]. A recent 1D and 2D NMR study [21] corroborated an X-ray study of V(acac)$_3$, which found that the three acac ligands are inequivalent [22]. A similar result for the three oxalate ligands was recently confirmed by the X-ray study of NaMgAl(ox)$_3$·9H$_2$O [11]. We suspect that the rhombic field from tris-bidentate coordination to V$^{3+}$ is typically large, dependent on the particular crystal packing, and a general phenomenon.

5. Conclusions and outlook

The ZFSs of the ground state of V$^{3+}$–doped into NaMgAl(ox)$_3$·9H$_2$O have been observed directly by Fourier transform spectroscopy. The luminescence lifetime from this state was less than 1 ps, which resulted in an estimated quantum yield similar to V$^{3+}$ in $\text{Al}_2\text{O}_3$ of only $10^{-5}$. Analysis of the splittings required incorporation of a large rhombic field in addition to the axial field in order to describe the ground-state electronic structure. The rhombic ZFS effectively changed the sense of the quantization axis and resulted in parameterization of the axial ZFS with a large negative value. The physical origin of the rhombic field is caused by H-bonding of the H$_2$O molecules to the oxalate ligands [11]. These results further our understanding of the effect of low-symmetry distortions on the ground-state electronic structure of a magnetically relevant V$^{3+}$ compound.

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[10] The circumflex (‘’') indicates the state designation is lower than cubic point symmetry. The spectral assignments agree well in the $D_1$ point group.