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Electronic structure of V^{3+} in $NaMgAl(ox)_3 \cdot 9H_2O$ 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 $NaMgAl(ox)_3 \cdot 9H_2O$ (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 $^3\hat{A}_2$ 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 $^3T_{1g}$ 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 received renewed attention in part due to the evolution of high field, high-frequency electron paramagnetic resonance (HFEPR) and inelastic neutron scattering spectroscopies [2–5].

Intra-configurational spin-forbidden d–d transitions, for V^{3+} of the type $^3\Gamma(t_{2g})^2 \rightarrow {}^1\Gamma(t_{2g})^2$, 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 α-Al_2O_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_2O_3, including the magnitude and sign of D and g-values. The analogous transitions of $[V(ox)_3]^{3-}$ have received little attention [9].

This article describes the investigation of the electronic structure of $[V(ox)_3]^{3-}$ diluted in $NaMgAl(ox)_3 \cdot 9H_2O$ 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 $^3\hat{A}_2$ 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 $NaMgAl(ox)_3 \cdot 9H_2O$ has recently been reinvestigated and solved in the P3c1 space group [11]. The structure can be described as a 2D honeycomb lattice consisting of $[NaAl(ox)_3]^{2-}$ 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 $NaMgAl_{1-x}V_x(ox)_3 \cdot 9Y_2O$ (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_2O, D_2O or mixed H_2O:D_2O) solutions. The crystals produced were large, hexagonal and dichroic with dimensions of ~10 mm^3.

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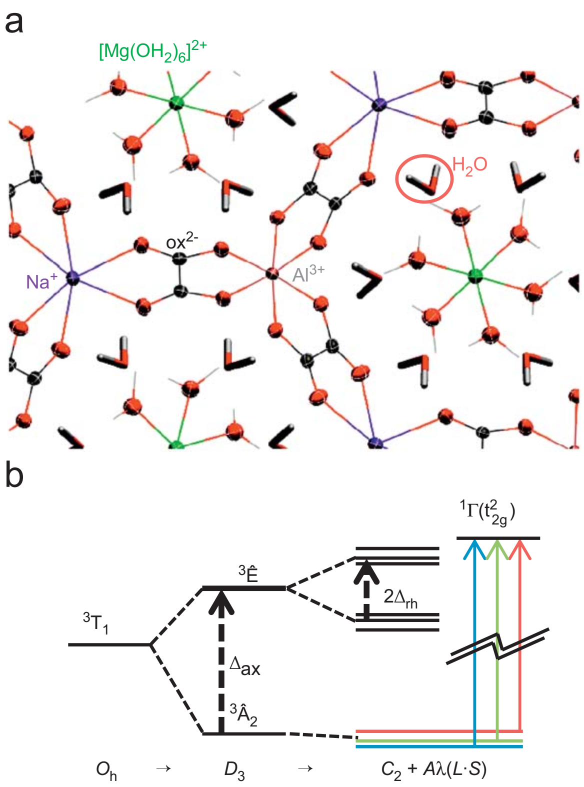

Fig. 1. (a) Representative view down the *c*-axis of $NaMgAl(ox)_3 \cdot 9H_2O$. Crystal structure solved by Riesen and Dae [11]. (b) Schematic splitting diagram of the $^3T_1$ ground-state of $[V(ox)_3]^{3-}$. Solid vertical lines depict the $\Gamma(^3\hat{A}_2)\rightarrow{}^1\Gamma$ transitions.

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 a 405 nm (25 mW) laser diode. Luminescence lifetimes were recorded using a Hamamatsu R316-02 PM tube mounted on a Spex 1404 monochromator and a digital scope and excitation with the 2nd harmonic of a Nd:YAG pulsed laser (Quantel Brilliant B).

3. Results and discussion

The room temperature absorption spectrum of the title compound just shows the broad spin-allowed $^3T_1\rightarrow{}^3T_2$ and $^3T_1$ d–d 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 $10\,Dq = 18{,}097$, $B = 556$, 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 $^3\hat{A}_2(^3T_1)$ ground state component to one of the 3 possible components of the split $\hat{E}$, $\hat{A}_1(^1T_2)$ and $\hat{E}(^1E)$ states expected in the near-IR and to the non-degenerate $\hat{A}_1(^1A_1)$ 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} for the bands centered at 9590 and 20,465 cm^{-1}, respectively, which approaches the spectral resolution limited by the FT spectrometer of 0.5 cm^{-1}. The slightly larger bandwidth of the $\hat{A}_1(^1A_1)$ 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 $[V(urea)_6](ClO_4)_3$ [14].

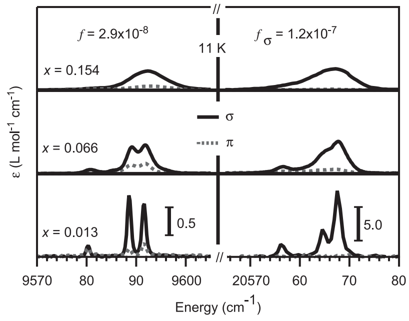

Fig. 2. 11 K polarized FT absorption spectroscopy of the (a) $\Gamma(^3\hat{A}_2)\rightarrow\Gamma(^1E,^1T_2)$ transitions and (b) $\Gamma(^3\hat{A}_2)\rightarrow\hat{A}_1(^1A_1)$ transition of $NaMg[Al_{1-x}V_x(ox)_3] \cdot 9H_2O$ single crystals as a function of V concentration ($x = 0.013$, 0.066, 0.154). Different scale bars are shown for the different transitions. The molecular axis is parallel to the *c*-axis and the standard polarization nomenclature is used.

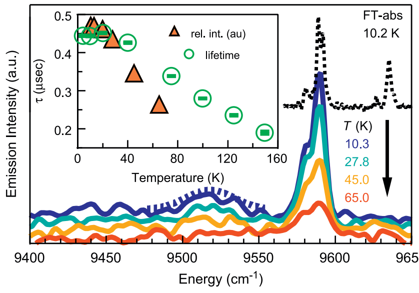

Fig. 3. Variable-temperature FT emission spectra of the $\Gamma(^3\hat{A}_2)\leftarrow\Gamma(^1E,^1T_2)$ spin-forbidden transition of $NaMgAl_{1-x}V_x(ox)_3 \cdot 9Y_2O$ ($x = 0.029$, $Y = H_{0.5}D_{0.5}$). The 10.2 K "σ"-polarized absorption spectra of this crystal collected at 0.5 cm^{-1} resolution is also shown (dotted line). Inset: relative integrated emission intensity (△) and luminescence lifetime (○) of the electronic origin as a function of temperature.

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_2O:D_2O. 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} is 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 $^3\hat{E}$ state component of the ground-state multiplet, which has been reported in other V^{3+} compounds [2,8].

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