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Structure–spectra relationships. Cr(III) phosphorescence as a probe for structural phase transitions in alums

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Contents

Abstract

The structural variety of the alums is reviewed. Structure–spectra relationships are exemplified by the ^2E_g–^4A_g phosphorescence of chromium alums and chromium-doped aluminium alums. The importance of exchange coupling between chromium ions in neat and diluted crystals is demonstrated by the concentration dependence of the phosphorescence properties. Structural phase transitions were observed in alums containing the monovalent cations Na^+, NH_4^+, K^+ and Tl^+, but not Rb^+ and Cs^+. The phosphorescence of the ammonium alum is presented in more detail. © 1997 Elsevier Science S.A.

Keywords: Cr(III) phosphorescence; Alums; Structural phase transitions

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1. Introduction

Alums form a large class of compounds in which cations of the charge +1 and +3 (M(I) and M(III) respectively) are fixed in a framework of water molecules and XO_4^{2-} ions: $M_IM_{III}(XO_4)\cdot 12H_2O$. M(I) can be Na^+, K^+, Rb^+, Cs^+, Tl^+,

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NH_4^+, NH_3OH^+ (Hy), $CH_3NH_3^+$ (Me) or $N_2H_5^+$. Guanidinium (Gu) [1] and dimethylammonium [2] form hexahydrates. M(III) can be Al^{3+}, Ga^{3+} [3–7], In^{3+}, Ti^{3+} [8,9], V^{3+} [10,11], Mn^{3+} [12], Fe^{3+} [13], Co^{3+} [14,15], Ru^{3+} [16,17], Rh^{3+} [18,19], Ir^{3+} [18,19] or Cr^{3+}. A Cs^+Sc^{3+} alum has been reported, which decomposes above 0°C [20]. XO_4^{2-} can be SO_4^{2-}, SeO_4^{2-} or BeF_4^{2-} [21–28]. In the following the short notation $M_IM_{II}XD(H)h(d)$ will be used, where D or H stands for dodecahydrate and hexahydrate and h or d for the protonated or deuterated forms, respectively. The alums occur in three structural modifications α, β or γ [29,30]. The common type is the α-form. CsAlSDh and CsCrSDh are examples of the β-form. NaAlSDh is the only known γ-alum [30,29,31]. NaCrSDh is an α-alum [32] as well as almost all selenates [30,33,34]. MeCrSDH has been assigned to the β-type [30], whereas an X-ray structure determination showed it to belong to the α-class [35]. The corresponding aluminium alum was shown to be dimorphic [36]. All alums crystallize in the cubic space group *Pa*3. The M(I) and M(III) form a face-centred lattice of the NaCl type [30]. Six water molecules surround the trivalent cation forming an almost regular octahedron. The remaining six water molecules are arranged around the monovalent cation in a disordered octahedral geometry. The XO_4^{2-} ions are located on the threefold axis, sometimes with disorder. In the β-alums the $M_{III}O_6$ octahedron is oriented within 1° of the crystal axis with the water molecule coordinated in a trigonal-planar arrangement. The plane of the water molecules is twisted with respect to the MO_6 octahedron by 19–22° [17,37–39]. In the α-alums the plane of the coordinated water molecules is aligned with the MO_6 axis but tilted away from the MO bond axis [37,38].

2. Phosphorescence of chromium alums and chromium-doped alums

Cr(III) (d^3 configuration) shows phosphorescence from its ^2E_g state with well-resolved fine structure. Unlike infrared and Raman spectroscopy where all molecules of the crystal contribute to the spectra, the phosphorescence originates exclusively from the chromium. Thus one gets information on the close neighbourhood of the emitting ion. The photophysics of the isolated complex ions [40] and of Cr(III) in oxide and halide lattices [41] has been extensively studied. The weak interactions that occur in crystalline complex salts are far less understood. Band splitting is usually explained by multiple site effects. However, hydrogen bonds and chromium–chromium interactions should not be neglected.

The $^4A_{2g}$–^2E_g transition of the $Cr(H_2O)_6$ moiety is found between 14 000 and 15 000 cm^{-1} depending on the environment of the hexaaquoion, both in absorption [42–47] and in emission [48–52]. The phosphorescence spectra of chromium alums consist of prominent zero-phonon lines at the short wavelength side of the band system. Structural changes manifest themselves in wavelength shifts, and changes in the band pattern, intensities and phosphorescence decay times.

A systematic study of the low-temperature phosphorescence spectra of a series of chromium alums [53] showed some structure–spectra relationships that are characteristic for chromium alums. The spectra of the β-alums are approximately

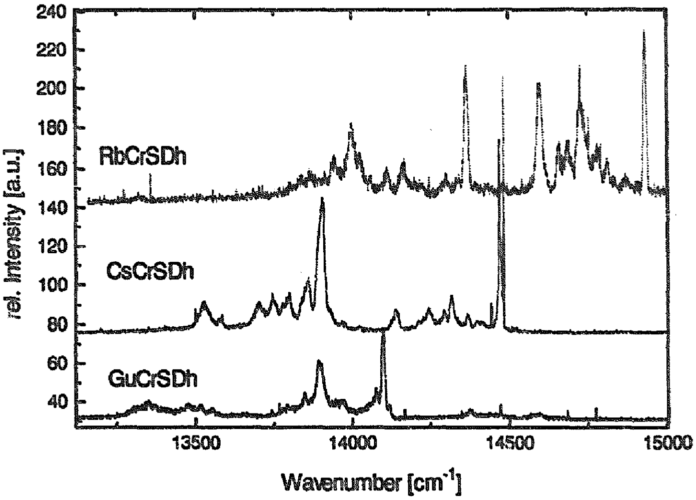

Fig. 1. Phosphorescence spectra of chromium alums RbCrSDh (α-alum), CsCrSDh (β-alum) and GuCrSDh (hexahydrate) at 25 K. Spectra are normalized to the zero-phonon emission lines; excitation wavelength 435 nm.

500 cm^{-1} redshifted with respect to those of the α-alums. Even more redshifted are the spectra of the hexahydrates (Fig. 1). In the group of α-alums two classes are distinguishable: one has only one intense zero-phonon band, while the other has spectra in which the zero-phonon bands are split into as many as five components. The bands are almost independent of M(I) ($\Delta\nu \leq 10$ cm^{-1}). In the following they will be numbered ν_1 to ν_5 in order of decreasing energy. The chromium alums with light monovalent cations have their bands split (Fig. 2). The splitting pattern is temperature dependent.

3. Concentration dependence of emission spectra

As far as the detection of phase transitions is concerned, chromium alums may be studied either in neat crystals or diluted in isomorphic colourless and diamagnetic crystals like aluminium or gallium alums. In very dilute crystals (≤1 mol% Cr) Cr–Cr interactions may be neglected. Structure sensitivity will be caused either by site effects or by coupling to the lattice. In neat crystals the Cr–Cr exchange interactions provide additional means for recognizing structure changes. It is surprising that exchange coupling between adjacent $Cr(H_2O)_6$ ions has generally been neglected, although many authors studied the phosphorescence of chromium-doped alums at low and high concentrations [52.54,55].

Optical transitions on exchange-coupled pairs were first recognized by Schawlow et al. [56]. In the case of a heavily doped ruby, the luminescence spectrum shows additional sharp lines as well as the well-known *R*-lines. The same effect is observed on the heavily chromium-doped alums. The exchange interaction can be described

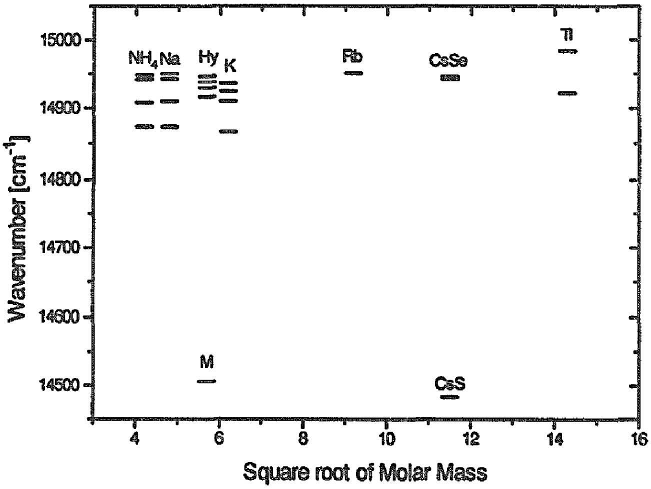

Fig. 2. Band positions of zero-phonon emission lines of various chromium alums.

by the hamiltonian [57]:

$$H_{ex} = -\sum_{i,j} J_{ai}(S_{Ai} \cdot S_{Bj})$$

The eigenvalues are obtained as

$$E(S) = -J[S(S+1) - S_a(S_a+1) - S_b(S_b+1)]$$

The energy splitting thus corresponds to a Landé pattern. The ground state of each chromium ion is the orbital singlet $^4A_{2g}$ and orbital effects are small. Its spin is 3/2 and the coupled pair can thus have the total spin $S=3,2,1,0$. The excited state ^2E_g has the spin 1/2. The total spin of the coupled pair $^2E^4A$, in which one ion is in the ground state and the other in the excited state, is $S^*=2,1$. The corresponding pattern for chromium pairs is shown in Fig. 3.

If the selection rules are taken into consideration and higher cluster transitions excluded, then there are at least three transitions caused by exchanged coupled chromium ions at low temperature [41,58]. If the temperature is high enough, so that the $S^*=2$ level is occupied, six lines are expected. In high dopant alums a multitude of emission lines are expected.

The systems studied best are the potassium, methylammonium and ammonium alums and their deuterated analogues. The ammonium alum will be discussed in more detail. Fig. 4 shows how the emission spectrum of chromium-doped NH_4AlSDh depends on the chromium concentration. The zero-phonon lines are blue shifted in the diluted samples and the promoting modes of symmetry species t_{1u} and t_{2u} become prominent. The crystals containing low chromium concentration (0.1 and 1 mol%) show only the emission lines of the isolated chromium ions. Neat NH_4CrSDh, on the other hand, shows only transition of exchange coupled Cr ions

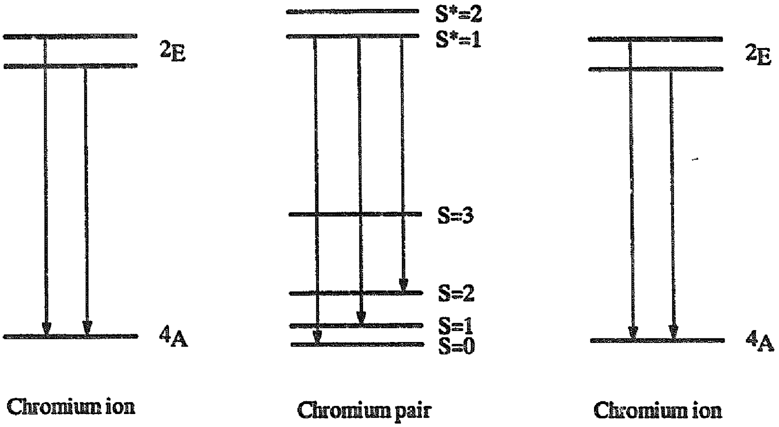

Fig. 3. Energy levels of exchange coupled chromium pairs (schematic).

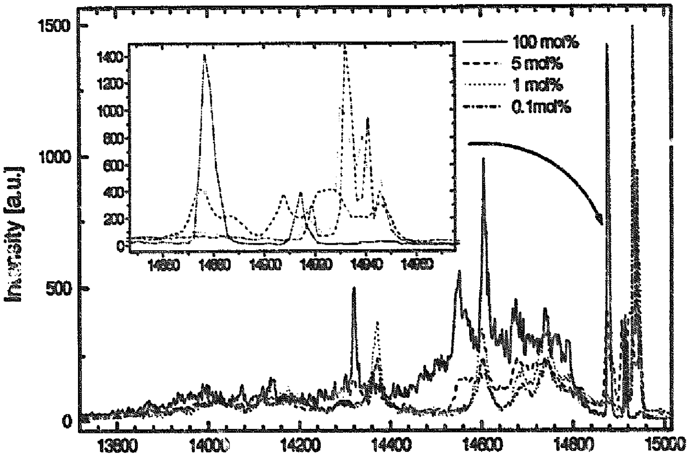

Fig. 4. Phosphorescence spectra of $NH_4(Al,Cr)SDh$ containing different amounts of chromium at 24 K; laser excitation at 532 nm.

that superimpose the vibronic side bands. The lines of the isolated ions are absent. The spectrum of the alum with 5 mol% Cr has emission lines of isolated ions as well as of chromium pairs. This spectrum is not very well resolved, because the emission lines of the isolated ions are broadened and overlap with the emission lines of the chromium pairs.

The weakly doped alums have the zero-phonon transition split into at least four lines (see insert of Fig. 5) ν_1 to ν_4 with $\Delta\nu$ 10–20 cm^{-1}. In a strictly octahedral environment the ^2E_g state is not split [58,59]. Four emission lines can only be explained by the assumption of different lattice sites. This agrees with Brach et al.

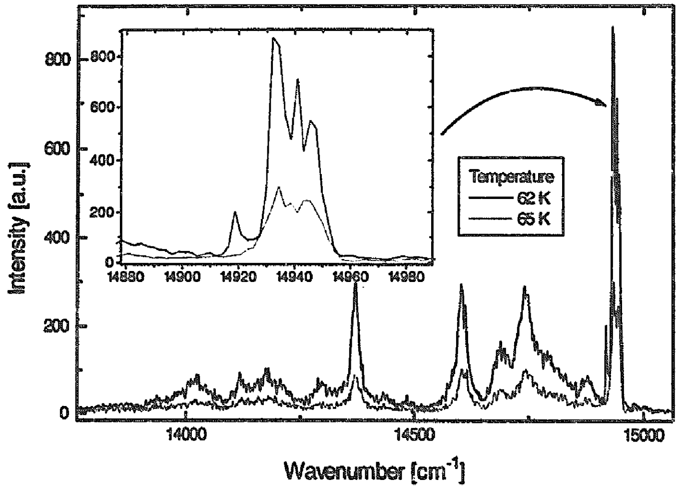

Fig. 5. Spectral change on passing through the phase transition for NH_4AlSDh doped with 1 mol% Cr(III).

[52] who assume triclinic symmetry of the low-temperature phase. They observed birefringence at low temperatures on chromium-doped alums.

On the other hand, the sulphate disorder [60] introduces a trigonal crystal field and symmetrically inequivalent chromium sites, which differ in the degree of hydrogen bonding. Best and Forsyth [37] have shown that the geometry of the hydrogen bonds affects the energy of the t_{2g} orbitals.

4. Phase transition in chromium-doped $NH_4Al(SO_4)_2 \cdot 12H_2O$

Phase transitions become apparent in sudden changes of the spectral pattern and anomalies in the temperature dependencies of the phosphorescence intensities and decay times. Because of the concentration dependence of the luminescence spectra of NH_4AlSDh it is possible to separate transitions of the isolated chromium ion and chromium pair transitions. It is possible to observe the phase transition at the single ion and at the ion pairs so that we can get more accurate information about the origin of the phase transition. In addition, it is possible to investigate the influence of the chromium interaction on the phase transition.

Fig. 5 shows the effect on passing through the phase transition from 62 to 65 K. ν_4 almost disappears and the other lines become comparable in intensity, indicating similar population of the different lattice sites. The intensities relative to the zero-phonon bands and the positions of the vibronic side bands are not affected by the phase transition.

In ammonium alums the phase transition can be quenched by rapid cooling. Fig. 6 shows the effect on neat NH_4CrSDd. In this case the low-temperature and the high-

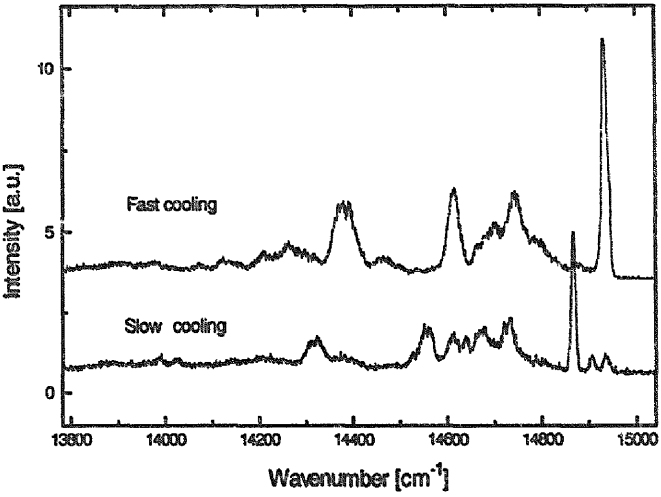

Fig. 6. Phosphorescence of NH_4CrSDd at 25 K. The spectrum obtained by fast cooling represents the high-temperature phase in a metastable state.

temperature phases can be studied at the same temperature. The high-temperature phase exhibits only one exchange-coupled zero-phonon line as in the spectra of the alums with heavy M(I), where no phase transitions were observed. The spectrum of the low-temperature phase shows three zero-phonon lines with $\Delta\nu$ 30–40 cm^{-1} and the vibronic side bands are more complex. The phosphorescence decay time of NH_4CrSDh (Fig. 7) shows a sharp drop at the transition temperature from about 3.5 to 0.5 μs.

A systematic study of the phosphorescence of a series of chromium alums was undertaken by Hühn [53]. Table 1 presents the transition temperatures obtained from phosphorescence intensities and decay times [61,53]. The hydrogen isotope effect and the mass dependence show that these phase transitions are caused by a dynamic effect.

The structures of the low-temperature phases are not very well known. The observation that the crystals become opaque on cooling [42,62] implies that domains are formed and points to a structural phase transition. Brach at al. [52] postulated the absence of any symmetry (triclinic) in the low-temperature phase of K(Al,Cr)SDh from measurements of birefringence. Bielecki et al. [63] came to the same conclusion on the basis of ESR measurements. The existence of a ferroelectric low-temperature phase of neat KCrSDh was ruled out, because the dielectric constant exhibited no anomalous temperature dependence [52]. The methylammonium alums, on the other hand, become ferroelectric on cooling (T_c 160–170 K). The effect is explained by freezing of the rotation of the methylammonium cations along the [111] axis [64–69]. The low-temperature phase of CH_3NH_3AlSDh was found to be orthorhombic (space group $Pca2_1$) [70]. That of NH_4(Al,Cr)SDh was assumed to be trigonally distorted on the basis of ESR measurements [71]. A change of sign of the trigonal distortion in NH_4(Al,Cr)SDh and K(Al,Cr)SDh was inferred from the

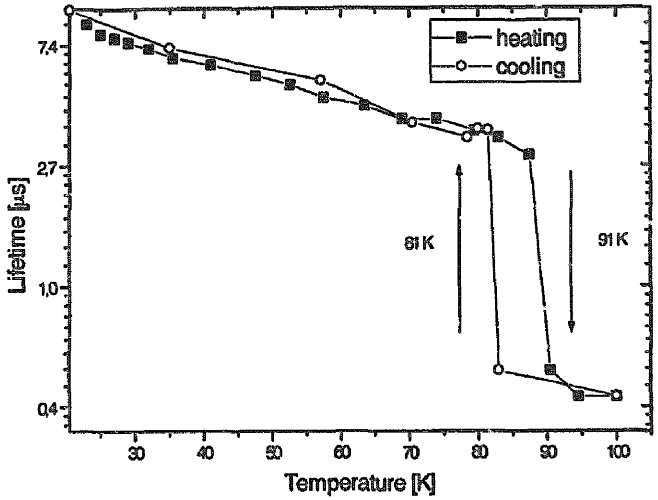

Fig. 7. Temperature dependence of the phosphorescence decay times of NH_4CrSDh measured at 14 942 cm^{-1} showing hysteresis.

Table 1
Phase transitions in chromium alums M(I)CrSDw (w = h, d) from phosphorescence data [53]

M(I)	w	T_c/K
NH_4	h	85 ± 10^a
ND_4	d	50 ± 10^a
Na	h	71 ± 2
K	h	60 ± 1
K	d	55 ± 2
Rb	h	$-^b$
Cs	h	$-^b$
Tl	h	27 ± 2

[a] Hysteresis, average between cooling and heating.
[b] No phase transition observed, $T > 25$ K.

temperature dependence of the zero field splitting [72]. The luminescence evidence also points to an appreciable reduction in symmetry, probably by a displacement of the $Cr(H_2O)_6$ ions from their lattice sites in the high-temperature phase.

5. Conclusions

Phosphorescence is an additional tool for detecting phase transitions. It is supplementary to other methods. The concentration dependence of the luminescence spectra is considered to be caused by chromium–chromium interaction. It provides an additional structure sensitivity method for detecting phase transitions.

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