

## Polarized Crystal Spectra of Transition-metal Hydrates

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IN an attempt to measure intensity mechanisms and the strength of non-cubic fields, Holmes and McClure<sup>1</sup> measured the spectra of several transition-metal hydrates. Although they were successful

in determining that the mechanism by which the spectral bands obtained intensity was vibronic they were not able to measure accurately the axial fields caused by water as ligand. In this note, we

<sup>1</sup> O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, 1957, **26**, 1686.

report results obtained on a system more favourable for the latter purpose.

We have obtained the absorption spectra of trivalent vanadium and chromium in the colourless diluent crystal  $[\text{C}(\text{NH}_2)_3]\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (GASH). Some attention has been paid previously to the fine-line spectra of  $\text{Cr}^{3+}$  in this compound.<sup>2</sup> This hexagonal crystal<sup>3</sup> belongs to the space group  $P31m$ , with three molecules per unit cell; the site symmetry at two of the trivalent metal ions is  $C_3$ , and  $C_3$ , for the third. The field is predominantly

blue side, clearly illustrating that the vibronic mechanism determines the spectral intensities; the oscillator strengths of these bands are of the order of  $10^{-5}$ . The sign and magnitude of the trigonal field parameter  $v$  may be estimated from the splitting of the  ${}^3T_1$  state of  $\text{V}^{3+}$  as  $v = +2440$   $\text{cm}^{-1}$ ; this is of the same sign, as was found earlier for this ion in corundum and the oxalate,<sup>5</sup> but of much larger magnitude. As was observed in corundum, the splitting of the  ${}^3T_2$  state is comparatively small, being only  $340$   $\text{cm}^{-1}$  in our work.

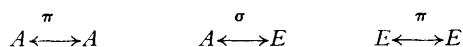
*Spectra of  $M^{3+}$  in  $[\text{C}(\text{NH}_2)_3]\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at  $25^\circ$*

Ion and ground state	Band maxima, ( $\text{cm}^{-1}$ )	Molar extinction Coeff. <sup>a</sup>	$\Gamma(C_3)$	$\Gamma(O_h)$	
$\text{V}^{3+}$	18520 $\pi$	3.6	${}^3A$	} ${}^3T_{2g}$	
$3d^2({}^3A)^b$	18690 $\sigma$	4.4	${}^3E$		
	26180 $\pi$	7.8	${}^3A$	} ${}^3T_{1g}$	
	27400 $\sigma$	5.6	${}^3E$		
	$\text{Cr}^{3+}$	17390 $\pi$	5.5	${}^4A$	} ${}^4T_{2g}$
$3d^3({}^4A)$	17860 $\sigma$	4.6	${}^4E$		
	24510 $\sigma$	8.6	${}^4E$	} ${}^4T_{1g}$	
	25000 $\pi$	8.2	${}^4A$		

<sup>a</sup> Accurate to 10%.

<sup>b</sup> B. N. Figgis, J. Lewis, and F. Mabbs, *J. Chem. Soc.*, 1960, 2480.

cubic, as in the alums, but there is in this crystal a trigonal field parallel to the optical axis large enough to be observed by optical spectra. We find, as did McClure in his studies on corundum as diluent,<sup>4</sup> that it is preferable to use selection rules pertaining to the actual symmetry of the complex; in the present work, this means  $C_3$ , for which the selection rules are



Here  $\sigma$  ( $\perp$ ) or  $\pi$  ( $\parallel$ ) refer to the polarization of the electric vector of the light with respect to the trigonal axis.

The absorption maxima of the spin-allowed transitions are presented in the Table. The coincidence of the axial spectra (incident light parallel to the  $C_3$  axis) and the  $\sigma$ -spectra confirm the expectation that the electric dipole excites the transitions. The red side of the broad bands decreases markedly in width as the temperature is lowered to  $80^\circ \text{K}$ , while there is little change in the

The parameter  $v$  has the value  $+980$   $\text{cm}^{-1}$  as obtained from the splitting of  ${}^4T_1$  for hydrated chromium in  $[\text{C}(\text{NH}_2)_3]\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . This is of the same order of magnitude as that observed in the oxalate, but somewhat smaller than noted in corundum. The splitting pattern of the  ${}^4T_2$  state implies that  $v$  changes sign for this excited state, which is an unreasonable situation. Further experiments at low temperatures may resolve this difficulty. McClure<sup>4</sup> has commented on some of the difficulties involved in determining the axial field parameter from polarized spectra.

It is interesting to note that the sign of  $v$  changes for the oxalate on going from  $\text{V}^{3+}$  to  $\text{Cr}^{3+}$ , but the sign does not change in the hydrate, nor in the more rigid corundum lattice. Another feature of some interest, observed also for the trisoxalate of chromium,<sup>5</sup> is that the spectra are more intense in solution than in the crystal. In the case of  $\text{Cr}^{3+}$ : GASH, the solution spectra are more intense by a factor of two.

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<sup>3</sup> R. M. Macfarlane and W. A. Runciman, *Phil. Mag.*, 1962, 7, 1081.

<sup>4</sup> S. Geller, *Bell System Tech. J.*, 1962, 41, 425; S. Geller and D. P. Booth, *Z. Krist.*, 1958, 111, 117.

<sup>5</sup> D. S. McClure, *J. Chem. Phys.*, 1962, 36, 2757.

<sup>6</sup> T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 1961, 35, 1809. The parameters  $K$  and  $v$  are related as  $K = -v/3$ .