Structural manifestations of the Jahn-Teller effect in the β-alums[1]

G.J. McIntyre and J.A. Cowan (ILL)
P.L.W. Tregenna-Piggott
and H.-P. Andres (University of Bern)
S.P. Best (University of Melbourne)
C.C. Wilson (ISIS, Oxford)

The temperature dependence of the single-crystal neutron-diffraction structures, determined principally on D9 and LADI, of the alums $CsM^{III}(SO_4)_2 \cdot 12D_2O$, where M^{III} = Ti, V, Mn and Ga, are reported [1]. Structural differences are highlighted by the titanium and manganese alums, which undergo cubic ($Pa\bar{3}$) to (twinned) orthorhombic (Pbca) phase transitions at ~ 13 K and ~ 156 K respectively. The structural instability exhibited by these salts is interpreted as arising from co-operative Jahn-Teller interactions, and these measurements characterise the structural changes that result from the coupling between the electronic and vibrational states. Although the symmetry changes associated with the phase transformations are analogous for the Ti and Mn alums, the low-temperature geometries of the tervalent hexa-aqua cations are markedly different. Whereas the MnO_6 framework is subject to a pronounced tetragonal elongation, changes in the Ti-O bond lengths are very modest; but significant changes in the O-Ti-O bond angles and in the disposition of the co-ordinated water molecules are identified.

It is shown by elementary calculations within the Angular Overlap Model that the large difference in the transition temperatures, and in the low-temperature stereochemistries of the $[Ti(OD_2)_6]^{3+}$ and $[Mn(OD_2)_6]^{3+}$ cations, are related to the sensitivity of the energies of the t_{2g} (O_h) and e_g (O_h) orbitals to the various asymmetric vibrations (stretching, bending and libration) of the hexa-aqua complex.

Single-crystal neutron-diffraction data are reported for the Ti, V, Mn and Ga caesium sulphate alums, which form part of a series of isomorphous salts, of formula $CsM^{III}(SO_4)_2 \cdot 12D_2O$ (CsMSD). A large number of tervalent cations can be accommodated in this crystal system and all known salts crystallise in the cubic space group $Pa\bar{3}$, with the $[M(OH_2)_6]^{3+}$ cation on a site of S_6 symmetry. The majority of these salts exhibit no structural instability in the temperature range 5 – 298 K. In figure 1, plots of the intensities 4 0 0 and 3 3 $\bar{3}$ reflections of CsTiSD are displayed as a
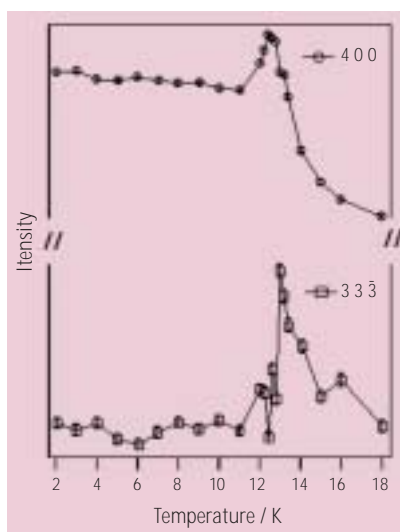

Figure 1: Plot of the 4 0 0 and 3 3 $\bar{3}$ reflections of CsTiSD as a function of temperature.

function of temperature. Both reflections show a discontinuous increase in intensity at 12.2 K, with a cusp-like feature for the strongest reflections, indicative of a first-order transition with release of extinction. Similar behaviour was observed for the manganese alum. The variable-temperature neutron-diffraction measurements identify cubic-to-orthorhombic phase transitions for the titanium and manganese alums, with transition temperatures of ~12 and ~156 K respectively. Extensive data sets were acquired at 2 and 5 K for CsTiSD and CsMnSD and matched against a model that allowed for three domains, related by the cubic three-fold axis:

$$|F_o| = \sqrt{[p_1 F_c^2(hkl) + p_2 F_c^2(klh) + p_3 F_c^2(lhk)]},$$

with $p_1 + p_2 + p_3 = 1$. The domain populations refined to 0.502(7) : 0.342(9) : 0.156(6) for CsTiSD and 0.878(3) : 0.094(2) : 0.028(2) for CsMnSD.

The anomalous structural behaviour may be related to the nature of the ligand field, imposed by hydrogen-bonding constraints, which results in orbitally non-degenerate ground terms for the vanadium and gallium alums but degenerate ground terms for the titanium and manganese alums. According to the Jahn-Teller theorem, complexes with orbital degeneracy are unstable with respect to asymmetric displacements that lift the degeneracy, and the phase transitions may be attributed to co-operative Jahn-Teller phenomena. The Jahn-Teller effect is commonly associated with a displacement along
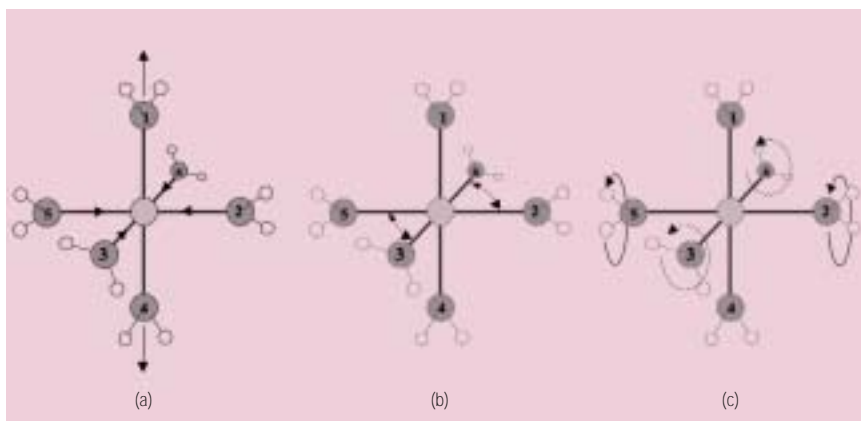
Figure 2: Examples of symmetrised distortions of a hexa-aqua complex: (a) the Q_θ component of the $\nu_2(MO_6)$, e_g (T_h) stretching vibration; (b) The Q_ξ component of the $\nu_5(MO_6)$, t_g (T_h) bending vibration; (c) the Q_ξ component of the $\tau[M(OH_2)_6]$, t_g (T_h) twisting libration.

the $\nu_2(MO_6)$ skeletal coordinate depicted in figure 2(a).

For the CsMnSD alum, the low-temperature structure is indeed characterised by a large displacement of the $[Mn(OD_2)_6]^{3+}$ along the coordinate depicted in figure 2(a). For the $[Ti(OD_2)_6]^{3+}$ cation, however, changes in the Ti-O bond lengths are very modest; but significant changes in the O-Ti-O bond angles and in the disposition of the coordinated water molecules are identified. The contrasting structural behaviour can be related to the occupancy of the one-electron orbitals. The $[Mn(OD_2)_6]^{3+}$ has the electron configuration $t_{2g}^3e_g^1$. The energies of the e_g orbitals are very sensitive to changes in the Mn-O bond lengths, giving rise to a strong Jahn-Teller effect and a high transition temperature. The $[Ti(OD_2)_6]^{3+}$ has the electron configuration t_{2g}^1; the t_{2g} orbitals are σ-nonbonding but weakly π-antibonding; the energies are more sensitive to displacements along the bending vibration and twisting

libration, depicted in Figs. 2(b) and 2(c). The data were found to be of sufficient quality to enable us to quantify the displacements along each of the internal co-ordinates depicted in figure 2. Calculations using Density-Functional Theory (DFT) and the Angular-Overlap Model (AOM) were then undertaken to calculate the variation of the energy of the hexa-aqua cations in the

multi-dimensional coordinate space. An example calculation is presented in Fig. 3 below. The theoretical curves relate to the energy of the $[Ti(OD_2)_6]^{3+}$ cation as a function of the angular parameter ϕ_{v2}, holding the radial parameter, ρ_{v2}, constant. There is a good correspondence between the experimental value of ϕ_{v2} and the calculated minima. Equally good agreement between theory and experiment was obtained when examining the distortions along other internal displacement coordinates. It is inferred that the $[Ti(OD_2)_6]^{3+}$ and $[Mn(OD_2)_6]^{3+}$ cations are at the minima of multi-dimensional Jahn-Teller potential-energy surfaces. Given the constraints imposed by hydrogen bonding, it seems a remarkable feat of nature that the structural changes that accompany the phase transitions, can locate the aqua ions at the minima, and facilitate the transmission of long-range order.
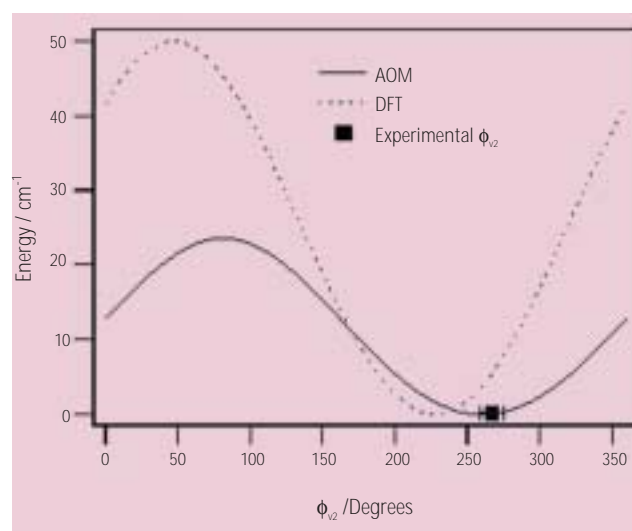

Figure 3: AOM and DFT calculations of the energy of the ground state of the $[Ti(OD_2)_6]^{3+}$ cation as a function of ϕ_{v2}.

References: **[1]** P.L.W. Tregenna-Piggott, H-P. Andres, G. J. McIntyre, J.A. Cowan, S.P. Best and C.C. Wilson, Aqua Ions 2. Structural manifestations of the Jahn-Teller Effect in the β-Alums. Inorg. Chem., 42, 1350 (2003)