SYNTHESIS, STRUCTURE AND MAGNETISM OF MANGANESE AMIDINATE CLUSTERS

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Since the discovery of Mn_{12}-acetate in the early 80s and the subsequent determination of its single molecule magnet (SMM) characteristics, interest in the area of large metal clusters, particularly Mn cluster chemistry, has continued to grow. To date, several SMMs have been identified including Fe_8, V_4, Mn_4 and Mn_{12} clusters but it has been found that Mn clusters often possess large values of ground state spin - an important requirement for SMM behaviour. Our group is interested in the synthesis of new Mn clusters and the investigation of their structural and magnetic properties. The focus currently is on the incorporation of bridging ligands other than O-donor ligands such as benzamidinate (bza-), which is an N-donor, isoelectronic analogue of benzoate. A $[Mn_4O(bza)_6]$ tetramer was formed by the reaction of a MnII salt with deprotonated ligand under an inert atmosphere. The core consists of four MnII atoms arranged tetrahedrally around an oxygen atom. Each metal atom has a pseudo-tetrahedral arrangement of nitrogen atoms around it with each of the six bza- groups forming a bridge between two metal centres. A $[Mn_3O(bza)_6(pyr)_3]$ trimer was formed from a comproportionation reaction between a MnII salt and MnO_4^- in the presence of bza. The cluster is mixed valent (2MnIII, MnII) and possess an oxo-centred Mn_3O unit with 6 bza-groups providing peripheral ligation and three pyridine groups in terminal positions. The magnetic properties are similar to those of the benzoate analogue. Work is in progress on larger clusters of benzamidinate and with other bridging ligands.

Keywords: MANGANESE CLUSTERS BENZAMIDINATE SINGLE MOLECULE MAGNETS

THERMAL VIBRATION ANALYSIS OF TWO ORGANIC PHOSPHATES. COMPARISON WITH FAR-IR SPECTRA

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The thermal vibration of two organic phosphates, L-histidine phosphate phosphoric acid (LHP) $(C_6H_{10}N_3O_2)^+$ $(H_2PO_4)^-$ (H_3PO_4) and L-arginine phosphate monohydrated (LAP) $(C_6H_{15}N_4O_2)^+$ $(H_2PO_4)^-$ (H_2O) was analysed from six atomic displacement parameters (ADP) sets obtained from X-ray and neutron diffraction data at two temperatures. Special care was put in obtaining high quality ADPs. In the case of X-ray data a pseudoatom model of the electron density was used in order to obtain a good deconvolution between static electron density and thermal vibration. In the thermal vibration analysis, the molecules were considered as rigid bodies vibrating independently. An additional internal vibration was supposed present in the organic cations. Using this approach, molecular normal mode frequencies were obtained from each ADP set. The coherence of the molecular modes calculated from each ADP set is discussed, showing than the molecular modes are very sensitive to the quality of the ADPs. The molecular mode frequencies are compared with the crystal normal mode frequencies observed in far-IR spectra for both crystals. This comparison can be helpful in the interpretation of the far-IR spectra, even when there is no direct equivalence between molecular and crystal normal modes.

Keywords: TLS NORMAL MODES ELECTRON DENSITY

NON-ANALYTICITY OF DIFFUSE-SCATTERING INTENSITY FOR SMALL WAVE VECTORS IN RECIPROCAL SPACE OF SOLID SOLUTIONS

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Non-analyticity of interatomic interactions (II) in crystals is one of the fundamental problems concerning II, which do not decrease with distance. The discrete crystal structure of a short-range-ordered solid solution with anisotropy of its elastic properties can be adequately studied by the radiation diffuse scattering (DS) [1], if one take into account the non-analyticity of DS intensity, I(k), for small wave vectors, k, in reciprocal space. Non-analyticity of I(k) at k = 0 (i.e. dependence of limiting intensity I(k) on n = k/|k| when k is tending to zero vector, 0, along the direction n) can take place only in a case when Fourier components of mixing energies can be presented as w(k) = A(k) + N(k). Here A(k) is analytical function, i.e. isotropic for all directions of small k, and (when k —> 0 lim A(k) = A(0) independently on n; N(k) is non-analytical function of k, i.e. its limiting magnitude lim N(k) = f(n) is not equal to N(0) (when k —> 0 along n) [2–4]. This I(k)-curve discontinuity at k = 0 appears when a short-range ordering or clustering in a solid solution is governed by anisotropic long-range II [1]. Such dipole–dipole-like II between solute atoms may have a strain-induced origin in elastically-anisotropic crystals [1,4,5]. Comparison of equilibrium values of I(k) at different reciprocal-space points is performed by using data obtained by measurements of the elastic DS of neutrons along lines (001)—>(002), (001)—>(011), and (111)—>(002) in short-range-ordered Ni–Fe single crystals [6].

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ANHARMONIC REFINEMENT OF γ-TYPE BIMEVOXES

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BIMEVOXes materials are well known for their high oxide ion conduction. They derive from the parent compound $Bi_4V_2O_{11}$ and are obtained by partial substitution for vanadium with another metal in order to stabilize, at room temperature, the high temperature γ-$Bi_4V_2O_{11}$ polymorph which is highly conductive.

The structure of this prototype is built upon well-ordered Aurivillius-type Bi_2O_2 layers in between oxygen deficient perovskite-type V-O sheets. Because of the high oxygen disorder in these materials due to the high mobility of these anions, a classical structure resolution of such compounds compels to use numerous split-sites to take into account the large atomic displacement generated by the diffusion of oxide anions in the γ-$Bi_4V_2O_{11}$ form or by the statistical disorder of the V-substituted site and its associated oxygen surrounding in BIMEVOXes.

A much more elegant description of these structures was performed using anharmonic atomic displacement refinement up to the fifth order. This concept was applied to the high temperature γ-$Bi_4V_2O_{11}$ form and to a BICOVOX composition, from powder neutron diffraction data collected at 943 K and single crystal data collected at room temperature respectively.

Keywords: ANHARMONIC DISPLACEMENT PARAMETERS NEUTRON DIFFRACTION BIMEVOX