MS14-O3

Ice-like disorder and phase transitions in cadmium cyanide

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Materials with strongly correlated disorder can be challenging to characterize crystallographically and are thus often poorly understood despite increasing evidence of the link between local deviations from the average structure and advanced material function. $Cd(CN)_2$ has attracted considerable interest for its very strong isotropic negative thermal expansion (NTE). On average, it adopts the interpenetrated diamondoid structure of cubic ice-VII, a topology is able to host a variety of unexpected phenomena, from the two-in-two-out ice rules proton that govern proton disorder in water ice, to magnetic monopoles and loop states in spin-ices.[1]

The correlated disorder in $Cd(CN)_2$ has its signature in the highly structured diffuse scattering, which (unusually) increases in intensity down to a phase transition at 150 K. There exist two types of disorder in $Cd(CN)_2$. [113]Cd NMR has shown that the Cd environment favours the two-in-two-out configuration of cyanides which mimics the proton disorder in ice.[2] This static disorder of the CN groups is intrinsically related to an off-centering of the Cd of up to ~1 Å along the <100> directions.[3]

Our interest is in understanding the possible role played by disorder in the NTE of this material. Key indications for the existence of such a link come from comparing the behaviour of $Zn(CN)_2$ and $Cd(CN)_2$: the former is substantially less disordered, and also shows much weaker NTE. Moreover, previous DFT studies of ordered $Cd(CN)_2$ variants fail to predict accurately its elastic properties, and entirely miss the instability responsible for its 150 K phase transition.

Using a combination of X-ray and neutron powder, single-crystal and total scattering diffraction data, alongside DFT calculations and [113]Cd NMR; I will explore the ice-rules disorder in $Cd(CN)_2$ and its implications for the microscopic mechanism of NTE. In addition I will present the low temperature structure of $Cd(CN)_2$ and characterise the phase transition in terms of the soft mode responsible for the NTE. Finally, we show that $Cd(CN)_2$ can be considered a dipolar equivalent of a defective spin-ice state capable of hosting monopolar excitations.

References:

[1] S.T. Bramwell et al., (2009) Nature 461, 7266
[2] S-I Nishikiori et al., (1990) Can J Chem 68, 2770
[3] V. E. Fairbank et al., (2012) Phys Rev B, 86, 104113

MS14-O4

Al/Si ordering in mullite

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The average crystal structure of mullite ($Al_{4+2x}Si_{2-2x}O_{10-x}$) is not easy to interpret in terms of the distribution of vacancies and Al/Si on the tetrahedral sites. Satellite reflections and diffuse scattering must be investigated to understand the ordering phenomena in the structure. From the reflection conditions of satellite reflections and the corresponding superspace group, the ideal distribution pattern of vacancies and tetrahedra can be directly derived. However, little is known about the distribution of Si within these tetrahedra, especially with respect to surrounding vacancies. Different NMR and neutron diffraction studies could not give a clear answer [1]. We apply density function theory (DFT) to investigate the Al/Si ordering in mullite. As DFT is not feasible with large structures, incommensurately modulated structures are not suitable and commensurate cases or approximations must be used. For this study, commensurate cases with up to 346 atoms in the composition range $0.2 \le x \le 0.5$ were generated from a superspace model with full vacancy ordering [2]. For each composition, symmetry compliant permutations of Al/Si distributions were analyzed with force-field methods (GULP package [3]). The energetically most stable permutation of each composition was then determined with DFT calculations (VASP) and integrated into the initial superspace model for comparison. The Al/Si ordering for $x > 1/3$ is defined by one unified superspace model (see Figure below) with Si present in triclusters. A second unified model without Si in triclusters for $x < 1/3$ requires the rotation of certain $AlSiO_7$ diclusters with respect to the first model. Si_2O_7 diclusters are always sandwiched between two vacancies for the analyzed solid solution range. Structure model refinements in (3+1)d superspace based on synchrotron single crystal X-ray diffraction measurements of mullite with $x \approx 0.4$ cannot distinguish between Al and Si, but the Al/Si ordering can be estimated from the modulated volumes of the tetrahedra. The refined models, which is not fully ordered as only 1st order harmonic functions are used to describe the modulations, agree qualitatively with the predictions from the DFT calculations, i.e. larger volumes are observed where Al is predicted, and smaller volumes where Si is predicted. The unified superspace models derived from DFT are considered to represent the ideal, most ordered state of mullite, from which the not fully ordered real structure can be derived.

Figure 1: DFT relaxed models of mullite with x = 0.429 (upper left) and x = 0.5 (bottom left), and the common superspace model.
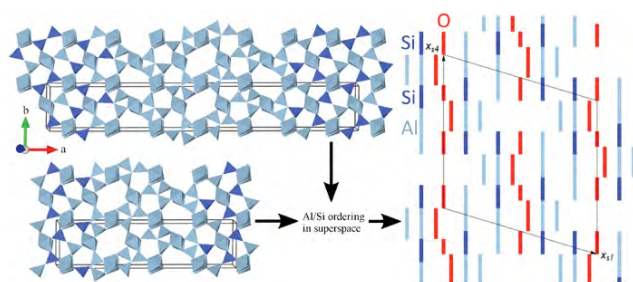
References:

[1] Schneider et al. (2015), J. Am. Ceram. Soc., 98, 2948

[2] P.B. Klar et al. (2017), Acta Cryst., B73, 377

[3] J.D. Gale (2006), Z. Krist., 220, 552

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Nanocluster model and its application for crystal structure prediction of complex intermetallics

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One of the important thing to know about intermetallics is what they consist of and how building units connection is related to their structure and properties. An automatic procedure of representation of crystal structures as assembling of primary nanoclusters was developed and implemented into the ToposPro program package [1]. This approach is especially efficient to elucidate complex intermetallic structures. Thus, a collection of Topological Types of Nanoclusters (TTN) was created, which can be used for generating topological models of new intermetallics [2]. Further, the robustness of the obtained models can then be proved by quantum-mechanical calculations. In this work theoretical and experimental studies were successfully combined. Using the Nanoclustering procedure we found a group of intermetallics containing icosahedra and icosahedron-based two-shell Mackay clusters as primary building units. Among these the family of compounds belonging to $Sc_{57}Rh_{13}$ structure type (SG *Pm-3*) [3] seems to be incomplete since isostructural compounds are reported only for Sc-T systems where T = Rh, Ir, Ru, Pt. It is worth to note that one more structural type with stoichiometry 54:17 similarly composed from icosahedra and Mackay clusters arranged in the bcc mode (SG *Immm*) exists. Both cited structures can be considered as derivatives from an "ideal" cubic phase with 60:13 stoichiometry [3]. According to our DFT modeling and taking into account thermodynamics aspects, an intermediate phase of orthorhombic symmetry containing Mackay clusters of Pd@Sc12@Sc30Pd12 composition should exist. The Sc-Pd system was studied long ago, but only an approximate composition $\sim Sc_4Pd$ with no structural data was reported for the Sc-richest phase. Single crystals suitable for X-Ray investigation were mechanically extracted from the arc-melted alloys after the appropriate thermal treatment. Some disorder affects this orthorhombic structure of $\sim Sc_{56}Pd_{15}$ composition, but Mackay clusters do not suffer from it. It is worth noting that new structure is quite unusual: the TTN collection includes merely 60 intermetallic compounds containing Mackay clusters as building units. The obtained results motivate us to continue a deeper exploration of related binary/ternary systems.

References:

[1]. Blatov, V.A (2012), Struct Chem 23, 955–963.

[2]. Akhmetshina, T. G., Blatov V.A., Proserpio D.M., Shevchenko, A.P (2018) Acc Chem Res 51, 1, 21-30.

[3]. Cenzual, K., Chabot, B., Parthé, E. (1985) Acta Crystallogr Sect C 41, 313–319.

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