

heat measurements. Spin glasses provide an important class of frustrated magnets. Typically based on disordered systems, they have found relevance in diverse areas of research, such as neural networks, the origin of life, and algorithm theory. Despite the theoretically prediction that these materials have a non-zero residual entropy, there have been no clear experimental studies of the entropy of a spin glass. This presentation describes an experimental study of the magnetic properties and zero point entropy of a series of $S=1/2$ spin glasses. Diamagnetic dilution in the spinel systems CuAl_2O_4 and CuGa_2O_4 forms isomorphic solid solutions $\text{Zn}_x\text{Cu}_{(1-x)}\text{Ga}_2\text{O}_4$ and $\text{Zn}_x\text{Cu}_{(1-x)}\text{Al}_2\text{O}_4$ that provides an opportunity to investigate the effect that non-magnetic substitution has on the spin glass properties of CuGa_2O_4 and on the entropy of the related spin glass states. Low temperature specific heat measurements were carried out on both CuGa_2O_4 and CuAl_2O_4 in order to determine the magnetic entropies, and compare them with the value theoretically predicted for $S = 1/2$ spin glasses. Both spinels were found to possess a non-zero magnetic entropy at 0K, with values that are significantly greater than the predicted value. These studies also indicate that the ground state degeneracy of these frustrated magnets can be controlled by chemical substitution.

Keywords: magnetic frustration, specific heat, magnetic ordering

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Polaronic behavior of Mn_4O_4 heterocubane clusters in LiMn_2O_4 spinel

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Crystals of LiMn_2O_4 undergo a structural phase transition near the room temperature. The high temperature (HT) form adopts a normal spinel-type structure (cubic, $Fd\bar{3}m$) with the octahedral sites populated statistically with heterovalent Mn^{III} and Mn^{IV} in the equal ratio. The low temperature (LT) form adopts a $3 \times 3 \times 1$ superstructure (orthorhombic, $Fddd$) with respect to the HT form, containing Mn^{III} , Mn^{IV} , and the intervalent Mn atoms. The synchrotron X-ray single-crystal electron-density analysis, carried out at the beamline 14A, Photon Factory, Tsukuba, revealed a large anisotropy of the atomic displacement parameters for part of O atoms, suggesting a possible occurrence of the bond-length fluctuation along the pseudo-tetragonal Jahn-Teller distortion parallel to the a-axis in the heterocubane Mn_4O_4 cluster. The cluster presumably shares three electrons among four e-parentage orbitals of Mn and behaves as a core of Zener-type polaron. The heterocubane Mn_4O_4 clusters are isolated from each other and embedded in an orbitally-ordered way in the charge-ordered matrix containing Mn^{III} and Mn^{IV} . The transition between the LT and HT forms of LiMn_2O_4 can thus be regarded as an order-disorder transition of the Zener-type heterocubane polarons.

Keywords: zener polaron, synchrotron X-ray diffraction, phase transition

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Magnetic structure of the quasi-one-dimensional, frustrated, spin-1 antiferromagnet CaV_2O_4

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We present the magnetic structure determination of the quasi-one-dimensional, frustrated, spin-1 chain material CaV_2O_4 by means of neutron diffraction. This material crystallizes in the post-spinel-type CaFe_2O_4 -type structure at room temperature (orthorhombic Pnam) and contains zig-zag chains of edge-sharing VO_6 octahedra along the crystallographic c direction. Nearest and next nearest neighbour V^{3+} -ions (spin-1) are almost equally spaced leading to competing antiferromagnetic exchange interactions and resulting in considerable geometrical frustration. The non-magnetic Ca^{2+} -ions act as spacers between the chains minimizing the interchain exchange coupling and making this system a low-dimensional quantum magnet. Upon cooling the material undergoes two phase transitions. A structural transition from orthorhombic to monoclinic occurs at $T_c=140\text{K}$. This distortion partially lifts the frustration of the system thus assisting the onset of long-range antiferromagnetic order below $T_N=71\text{K}$. By performing neutron diffraction experiments on CaV_2O_4 in the magnetically ordered phase, we found that it consists of two collinear antiferromagnetically coupled sub-chains, which are canted with respect to each other. The canting is a result of the distorted octahedral environment of the V^{3+} -ions, which lifts the orbital degeneracy of the Vanadium $3d^2$ electrons. Furthermore, the ordered magnetic moment of the V^{3+} -ions turned out to be is strongly suppressed, possibly due to strong quantum fluctuations caused by geometrical frustration and low-dimensional interactions. The analysis was challenging because the small monoclinic splitting resulted in twinned peaks whose intensity could only be separated by measuring a single crystal on a four-circle diffractometer.

Keywords: neutron diffraction, magnetic frustration, magnetic neutron scattering

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Federated repositories of X-ray diffraction images

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There is a pressing need for the archival and curation of raw X-ray diffraction data. However, the relatively large size of these datasets has presented challenges for storage in a single worldwide repository. This problem can be avoided by using a federated approach, where each institution or university utilizes its institutional repository. Institutional repositories are relatively stable and adequately funded, ensuring persistence. Here we describe a simple repository solution utilizing Fedora open source database software, and data annotation and deposition tools that can be deployed at any site cheaply and easily. Datasets and associated metadata from federated repositories are given a unique and persistent handle, providing a simple mechanism for search and retrieval via web interfaces. We call this initiative 'The Australian Repositories for Diffraction Images (TARDIS)' and have created a website (<http://www.tardis.edu.au>) where the deposition tools can be downloaded freely. The site will also function as a central portal allowing searching and browsing across all registered Australian repositories. In addition to ensuring that valuable data is not lost, the provision of raw data has several uses for the crystallographic community. Most importantly, structure determination can only be truly repeated or verified when the raw data is available. In addition, the availability of raw data is extremely useful for the development of improved methods of image analysis and data processing.

Keywords: raw data, databases, validation

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Virus particle explorer: An X-ray and electron microscopy database for icosahedral virus structures

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Three-dimensional crystal structures of 96 different virus capsids, from 27 families and 42 different genera of viruses, have been solved to near-atomic resolution and deposited in the Protein Data Bank. The enormous amount of information contained in these structures is difficult to access, even for scientists trained in structural biology. Virus Particle Explorer (VIPER) is a web-based (<http://viperdbscripps.edu/>) catalogue of structural information that describes the icosahedral virus particles. In addition to high-resolution crystal structures, VIPER now includes virus structures obtained by cryo-electron microscopy (EM) techniques. The VIPER database is a powerful resource for virologists, microbiologists, crystallographers and EM researchers. This presentation will describe the novel features of VIPER, using several examples to show the power of this resource for research and educational purposes.

Keywords: virus structure,, protein-protein interactions, virus assembly

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Metal and small molecule agent environment in macromolecules

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Over 90% of X-ray protein structures deposited in the Protein Data Bank contain ordered small molecules, such as enzyme substrates, cofactors or ions. These ligands can be divided into two groups: molecules that are relevant to protein function, and non-physiological agents introduced during sample preparation (purification, crystallization or cryocooling). Our analysis shows that the structural and chemical quality of small molecule models in protein structures does not correlate with structure resolution. In particular, the analysis of metal-protein interaction distances, coordination numbers, B-factors (displacement parameters), and occupancies of metal binding sites in protein structures determined by X-ray crystallography and deposited in the PDB shows many unusual values and unexpected correlations. Our analysis of cation B-factors versus average B-factors of atoms in the cation environment reveals substantial numbers of structures contain either an incorrect metal ion assignment or an unusual coordination pattern. While validation of polypeptide models is a routine part of protein structure refinement, small molecule models within a protein structure are usually not validated and require new approach to validation process.

Keywords: macromolecular crystallography, macromolecular complex, structural genomics

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On atomic displacement parameters and coordinates in protein structures

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Macromolecular models refined against X-ray diffraction data are typically described by a set of atomic coordinates and atomic displacement parameters (ADPs). During the refinement process, coordinates and ADPs are usually considered independent of each other. However, as can be demonstrated here, up to 50% of the total ADP variation in macromolecular structures may be successfully predicted solely based on the atomic coordinates and just three additional parameters per structure. This finding may have serious implications in macromolecular structure refinement, particularly at low resolution, as well as in structure validation.

Keywords: macromolecular structure refinement, atomic displacement parameter, structure validation