

## Poster Sessions

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#### The Effect of High-Pressure on Molecular Magnetism

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Polynuclear clusters of paramagnetic metal ions have attracted intense study since the discovery that such molecules can display the phenomenon of single-molecule magnetism [1]. The energy barrier to the relaxation of the magnetisation implies a large ground state spin multiplicity ( $S$ ) and a significant zero-field splitting ( $D$ ) of that ground state. The strength of coupling and the magnitude of the zero-field splitting are governed by the molecular geometry. Here we show that the application of hydrostatic pressure can significantly change the intra-molecular bond lengths and angles – and in some cases the connectivity – in a host of molecular or molecule-based complexes and in-so-doing greatly modify the observed magnetic parameters [2-7].

Two 'Mn<sub>6</sub>' SMMs, hydroxo-bridged Cu dimers and Cu-based chains can all be structurally and magnetically distorted by pressure. We describe the combined high pressure crystallographic and high pressure magnetism and high pressure EPR experiments performed on these materials.

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#### Structural and related electronic transitions in GaFeO<sub>3</sub> under high pressure

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Structural studies of GaFeO<sub>3</sub> (SG  $Pc2_1n$ ), an antiferromagnetic ( $T_N=200$  K) *Mott* insulator to 70 GPa, complemented by <sup>57</sup>Fe Mössbauer spectroscopy and resistance measurements at compression and decompression reveal a fascinating sequence of structures. Starting

at ~ 25 GPa a new structure, an orthorhombic perovskite ( $Pbnm$ ), is sluggishly formed followed by a  $V(P)$  drop of -5.4%. The complete formation of the perovskite occurs at 42 GPa. In the 0 – 35 GPa range  $T_N$  reaches 300 K and  $R(P)$  decreases by one-order of magnitude, later on, in the 50 - 57 GPa range, the electrical transport activation energy drops from 0.28 to 0.11 eV. At 50 GPa an isostructural transition is detected, characterized by a discontinuous drop of  $V(P)$  by ~3%. Mössbauer spectra reveal a non-magnetic component coexisting with the magnetic one at ~ 60 GPa. Its abundance increases and above 77 GPa no sign of a magnetic hyperfine interaction is detected down to 5 K. Concurrently, one observes a continuous yet precipitous decrease in  $R(P)$  taking place in the 58-68 GPa range, leading to an onset of the metallic state at  $P > 68$  GPa. These electronic/magnetic features of the high pressure (HP) perovskite are consistent with a *Mott* transition (*MT*).

With pressure decrease, below 52 GPa, the *insulating* perovskite is recovered, and at 23 GPa a 1<sup>st</sup>-order structural transition takes place to the LiNbO<sub>3</sub>-type structure with  $R3c$  SG. This structure remains stable down to ambient pressure and with recompression it is stable up to 50 GPa, afterwards it transforms back to the *HP* perovskite structure. It is noteworthy that this transition occurs at the same pressure, regardless of the preceding structures:  $Pbnm$  or  $R3c$ . The results are compared with hematite (Fe<sub>2</sub>O<sub>3</sub>, SG  $R\bar{3}c$ ) [1, 2] and other ferric oxides. The mechanisms of the transitions are discussed.

[1] J. Staun Olsen, C.S.G. Cousins, L. Gerward, H. Jhans, B. Sheldon, *Phys. Scr.* **1991**, *43*, 32-330. M.P. Pasternak, G. Kh Rozenberg, G. Yu. Machavariani, O. Naaman, R.D. Taylor, R. Jeanloz, *Phys. Rev. Lett.* **1999**, *82*, 4663-4666; G. Kh. Rozenberg, L.S. Dubrovinskii, M.P. Pasternak, O. Naaman, T. Le Bihan, R. Ahuja, *Phys. Rev. B.* **2002**, *65*, 064112-1-8.

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#### Structure and properties predictions for high-pressure crystal structures: BI<sub>3</sub>, Mg, and Si

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The recent rich diversity of diffraction studies on crystalline materials at high pressures has provided an opportunity for structural search methods based on first-principles methods to be employed for possible full characterization of structures. In this study, we report on our recent studies using several structure search methods including quasi-random searches, and the metadynamics technique as applied to systems where diffraction data provides a challenge to full characterization of structures. We will focus on several materials where excellent diffraction data has presented additional questions for a full knowledge of several high-pressure crystalline structures. We will use examples including our recent work on BI<sub>3</sub>, Mg and Si.

A combination of structure search methods has, for example, been employed to predict the crystalline structure of BI<sub>3</sub> that is agreement with the recently published diffraction data [1]. The use of a combination of methods is demonstrated to reveal the crystalline structure consisting of BI<sub>3</sub> dimers as fundamental components that is most consistent with the diffraction data and reported properties such as phase transition pressures and metallization of this material.

Our investigation of the phase diagram of Mg addresses the question on phase transitions in this material. First-principles metadynamics and density functional methods were employed to investigate the temperature dependence of structural transitions in Mg. The phase identified as a double hexagonal close-packed phase and its location in the phase diagram of Mg at high pressure and temperature is

characterized with these methods.

Our recent study of crystalline materials under uniaxial stress will be illustrated by results on Si at high pressures. This study has revealed that there may be other interesting crystalline structures of Si to be found at high pressures in addition to those already well characterized.

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**Keywords:** prediction, pressure, first-principles

## MS40.P07

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### The influence of the Jahn-Teller effect at Fe<sup>2+</sup> on the structure of chromite at high pressure

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The crystal structure of chromite FeCr<sub>2</sub>O<sub>4</sub> was investigated under high pressure with single-crystal x-ray diffraction techniques. A total of 7 datasets were collected up to 13.7 GPa at ambient temperature. The cubic unit-cell parameter decreases continuously from 8.3832 (5) Å to 8.2398 (11) Å up to 11.8 GPa. Fitting the P-V data to a Birch-Murnaghan equation of state (EoS) gives  $K_0 = 209$  (13) GPa,  $K' = 4.0$  (fixed), and  $V_0 = 588$  (1) Å<sup>3</sup>. The FeO<sub>4</sub> tetrahedra and CrO<sub>6</sub> octahedra are compressed isotropically with pressure, the Fe-O and Cr-O bond distances decreasing from 1.996 (6) to 1.949 (7) Å and from 1.997 (3) to 1.969 (7) Å respectively. From the structural refinements, the tetrahedral site occupied by the Fe<sup>2+</sup> is more compressible (187%) than the octahedral site occupied by the Cr<sup>3+</sup>. A discontinuous volume change is observed between 11.8 GPa and 12.6 GPa, consistent with a structural phase transition from cubic (space group  $Fd\bar{3}m$ ) to tetragonal (space group  $I4_1/amd$ ). At the phase transition boundary, the two Cr-O bonds parallel to the *c*-axis shorten from 1.969 (7) Å to 1.922 (17) Å and the other four Cr-O bonds parallel to the *ab* plane expand from 1.969 (7) Å to 1.987 (9) Å. The angular distortion in the octahedron decreases continuously up to 13.7 GPa, whereas the values of angular distortion in tetrahedron rise dramatically after the phase transition. This anisotropic deformation of the octahedra leads to a tetrahedral compression ( $a > c$ ) along the *c*-axis. The Jahn-Teller effect at Fe<sup>2+</sup> becomes observable at the phase transition pressure and gives rise to the tetrahedral angular distortion, which in turn results in the phase transition in FeCr<sub>2</sub>O<sub>4</sub>. With increasing pressure, the tetrahedral bond angles, referenced to the *c*-axis direction, decrease from 109.5° to 106.6 (7)°, resulting in a stretched tetrahedral geometry along the *c*-axis. A qualitative molecular orbital picture shows that, for the d<sup>6</sup> electronic configuration of Fe<sup>2+</sup>, the metal-ligand antibonding orbitals of t<sub>2</sub> symmetry in the undistorted structure split into orbitals of e + b<sub>2</sub> symmetry as a result of the Jahn-Teller effect at Fe<sup>2+</sup>. These two orbital sets behave differently in response to the shortening of the Fe-O bond in the tetrahedron with increasing pressure, and dictate the preferred distortion mode for the tetrahedral unit.

**Keywords:** chromite, Jahn-Teller effect, high pressure

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### Anharmonic atomic vibration of Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> relaxor under high pressure

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Lead-based relaxor ferroelectrics with complex perovskite structures exhibit a strong frequency-dispersive dielectric permittivity with the broad temperature dependence, superior piezoelectric properties [1,2]. Relaxors have huge electro-mechanical coupling and they are applied for ultrasonic transducer. X-ray and neutron experiments of lead relaxors show diffuse scattering around the Bragg peaks along <110> directions. We aim to clarify the microstructure origin of diffuse scattering features in the relaxor and paraelectric phases of Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (PMN) which has a cubic perovskite structure with  $Pm\bar{3}m$ . All atoms are located at the special positions and no variable positional parameters.

X-ray single-crystal diffraction studies of PMN were performed by four-circle diffractometer using synchrotron radiation ( $\lambda = 20.0137$  keV) at PF KEK with a diamond anvil cell at pressures up to 12 GPa. Average intensity data of reflections in the half-reciprocal space observed by omega scanning mode were used for structure refinement because of a large diffuse streak. The thermal vibration of atoms of PMN was investigated as a function of pressure at room temperature including anharmonic temperature factor in the least-squares refinement.

We study the influence of anharmonicity on the diffraction intensities. We adopt a multimodal distribution in the probability density function based on Gram-Charlier series expansion. The coefficients of anharmonic temperature factor T(H) is adopted up to fourth order as variable parameters. These tensors are constrained by the site symmetry. R-factor of the least-squares refinements at each pressure is extremely improved by applying the anharmonic tensor up to fourth order  $D_{ijkl}$  in comparison with the harmonic model second rank  $B_{ij}$ . Difference Fourier maps of the projection on to (100) at atoms of Pb and Nb(Mg) indicate the deformation of the electron density. Time and space average of dynamical phenomena or microdomain disorder is observed. Diffuse streaks found along <110> direction in the reciprocal lattice on (100) can be interpreted by the deformation mainly around Pb atom found in the difference Fourier maps. These deformations disappear at 7.2 GPa and PMN becomes paraelectric crystal with the centric symmetry.

The present result is consistent with the first-principles MD simulations [3], which showed that a random field in the chemically disordered regions induces such ordered and disordered regions in polarization.

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**Keywords:** relaxor PMN, high-pressure diffraction, anharmonicity