

Phys. **1999**, *12*, 107-114. [3] D. Errandonea, J. Pellicer-Porres, F.J. Manjón, A. Segura, Ch. Ferrer-Roca, R.S. Kumar, O. Tschauner, J. López-Solano, P. Rodríguez-Hernández, S. Radescu, A. Mujica, A. Muñoz, G. Aquilanti, *Physical Review B* **2006**, *73*, 224103-1-224103-15. [4] R. Lacombe-Perales, D. Martínez-García, D. Errandonea, Y. Le Godec, J. Philippe, G. Le Marchand, J. C. Chervin, A. Polian, A. Muñoz, J. López-Solano, *Physical Review B* **2010**, *81*, 144117-1-144117-10.

Keywords: high_pressure, X-ray_diffraction, phase_transition

MS40.P04

Acta Cryst. (2011) **A67**, C500

The Effect of High-Pressure on Molecular Magnetism

Alessandro Prescimone,^a Simon Parsons,^a Euan K. Brechin,^a Stephen Hill,^b Stan Tozer,^b ^a*EaStCHEM School of Chemistry, Joseph Black Building, The King's Buildings, Edinburgh, EH9 3JJ, (UK)*. ^b*National High Magnetic Field Laboratory 1800 E. Paul Dirac Drive, Tallahassee, FL 32310, (United States)*. E-mail: a.prescimone@ed.ac.uk

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 'Mn₆' 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.

[1] R. Sessoli *et al.*, *J. Am. Chem. Soc.* **1993**, *115*, 1804. [2] A. Prescimone *et al.*, *Angew. Chemi. Int. Ed.* **2008**, *47*, 2828. [3] *Dalton Trans* **2009**, 4858 [4] A. Prescimone *et al.*, *Dalton Trans* **2009**, 7390. [5] *Dalton Trans* **2007**, 5282. [6] A. Prescimone *et al.*, *Dalton Trans* **2010**, 113. – [7] *Z. Naturforsch. B.* **2010**, *65b*, 221.

Keywords: high-pressure, crystallography, magnetism

MS40.P05

Acta Cryst. (2011) **A67**, C500

Structural and related electronic transitions in GaFeO₃ under high pressure

G. Kh. Rozenberg,^a R. Arielly,^a W. M. Xu,^a E. Greenberg,^a M. P. Pasternak,^a G. Garbarino,^b S. Clark,^c ^a*School of Physics and Astronomy, Tel Aviv University, 69978, Tel Aviv, (Israel)*. ^b*European Synchrotron Radiation Facility (ESRF), 6 rue Jules Horowitz, BP 220, F-38043 Grenoble Cedex, (France)*. ^c*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, (USA)*. E-mail: emtsm@post.tau.ac.il

Structural studies of GaFeO₃ (SG $Pc2_1n$), an antiferromagnetic ($T_N=200$ K) *Mott* insulator to 70 GPa, complemented by ⁵⁷Fe 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 1st-order structural transition takes place to the LiNbO₃-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 (Fe₂O₃, 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.

Keywords: high-pressure, phase transitions, mott transition

MS40.P06

Acta Cryst. (2011) **A67**, C500-C501

Structure and properties predictions for high-pressure crystal structures: BI₃, Mg, and Si

Dennis D. Klug, Yansun Yao, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6 :E-mail: Dennis.Klug@nrc.ca

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 BI₃, Mg and Si.

A combination of structure search methods has, for example, been employed to predict the crystalline structure of BI₃ 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 BI₃ 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