

MS05.24.4*Acta Cryst.* (2005). A61, C14**Volume Collapse at the Jahn-Teller Transition in LaMnO₃**

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We have investigated the Jahn-Teller (JT) transition accompanied by the orbital order-disorder transition in LaMnO₃ by high temperature X-ray powder diffraction with synchrotron radiation and also neutron powder diffraction. The unit cell volume of LaMnO₃ decreases with increasing temperature in a narrow temperature range below $T_{JT} = 750$ K, and then undergoes a volume collapse at T_{JT} . We interpret this effect as due to the more efficient packing of the MnO₆ octahedra in the orbitally disordered or orbital liquid state. The orbital melting phenomenon can be qualitatively compared with the melting of ice. By constructing a model Hamiltonian involving the pseudospin of Mn³⁺ e_g states, the staggered JT distortion and the volume strain coordinate, we show that the anharmonic coupling between these primary and the secondary order parameters leads to the first-order J-T phase transition associated with a comparatively large reduction of the unit cell volume. We explain the temperature dependence of the JT distortions and volume strain and discuss the volume change as a function of the anharmonic coupling constant. A continuous change to a second-order transition as a function of the model parameters is obtained. This behaviour has been observed experimentally by us on doping LaMnO₃ with Ba.

Keywords: neutron diffraction, X-ray diffraction, Jahn-Teller phase transition

MS05.24.5*Acta Cryst.* (2005). A61, C14**Nucleation and Growth Mechanisms in Solid-Solid Phase Transitions**

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We present a recent powerful strategy[1-4] to elucidate the mechanistic details of reconstructive phase transitions at the experimental temperature and pressure. We implement molecular dynamics simulations, starting from putative intermediates worked out with a topological approach[2,5], and obtain a first dynamic trajectory. A path sampling scheme [6] is applied on top of this, which allows driving the system towards the most probable transition route.

With this scaffolding we are able to discriminate between many mechanisms suggested for the B1-B2 transition in ionic compounds. For NaCl we find the Hyde&O'Keeffe mechanism to be favored. Furthermore, the process starts at a single ionic site, followed by layer displacement and setup of an interface of B33 structure between regions of B1 and B2 structure. With many variations on the form and on the propagation of the interface, the mechanism dominates in the compound class of alkali halogenides.

The approach opens new simulation scenarios at a level of detail that was not accessible up to now. Furthermore, it allows discriminating between many possible mechanisms in favor of the most probable, real mechanism.

[1] Zahn D., Leoni S., *Phys. Rev. Lett.*, 2004, **92**, 250201. [2] Leoni S., Zahn D., Krist Z., *Phys. Rev. Lett.*, 2004, **219**, 339. [3] Zahn D., Leoni S., Krist Z., *Phys. Rev. Lett.*, 2004, **219**, 345. [4] Zahn D., Hochrein O., Leoni S., *Phys. Rev. Lett.*, submitted. [5] Leoni S., Nesper R., *Acta Cryst.*, 2000, **A56**, 383. [6] Bolhuis P., Dellago C., Chandler D., *Faraday Discuss.*, 1998, **110**, 421.

Keywords: first order, nucleation, intermediates

MS06 CRYSTALLOGRAPHY AND FORENSIC SCIENCE

Chairpersons: David Rendle, Izumi Nakai

MS06.24.1*Acta Cryst.* (2005). A61, C14**Application of X-ray Diffraction in the Forensic Science Laboratory of Stuttgart Germany**

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The great importance of X-ray diffraction in the forensic science analysis is based on the fact that X-ray diffraction examinations are non-destructive, and therefore leave the original specimen intact and available for further analytical study, if necessary. These are often the only methods that allow a further differentiation of materials under laboratory conditions. The examples I will present include comparative and reconstructive investigations, as well as the identification of unknown samples. In our laboratory we analyze all kinds of polycrystalline substances or specimens with crystalline components, because in a criminal case any type of specimen may turn out to be of forensic interest. These materials are e.g. paints (from automobiles, buildings, tools), building materials, minerals, ceramics, metals, alloys, explosives, gemstones, soils, extender and impurities of drugs and abrasives. The applied preparation techniques, the selected diffraction method, and the used strategies of measurement depend on the forensic nature of the criminal case, as well as on the type, quantity and consistency of the suspected specimen, and the involved trace carrier. Accordingly, specimens are either examined undisturbed on the trace carrier, or removed, separated under microscopic control, and prepared using specially selected techniques. The sample holders are chosen based on their suitability in the use of micro X-ray fluorescence analysis in addition to X-ray diffraction. The samples are analyzed with a GADDS microdiffractometer based on Debye-Scherrer geometry with devices for fixed, scanning, oscillating or rotating samples.

Keywords: forensic science, preparation technique, strategy of measurement

MS06.24.2*Acta Cryst.* (2005). A61, C14**Soil Mineralogy and Other Properties in Forensic Investigations**

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Recently there has been an increased usage of soil materials in forensic science. Forensic soil science requires appropriate methods for sampling, separation and analysis. We have developed the following systematic examination sequence. Firstly, soil morphological features are visually examined and then with a stereo binocular microscope. Secondly, infrared spectroscopy and magnetic susceptibility analyses are made on whole samples. These are then sieved and the smallest size fractions used for X-ray diffraction analyses. Further analyses using a petrographic microscope, SEM, TEM, ICP-MS or XRF may be necessary.

The following six criminalistic and environmental forensic case studies demonstrate how soil properties have been used to discriminate between and match soils for critical evidence in: (i) solving a double murder case by identifying the similarities between mineral assemblages (kaolinite crystallinity and presence of mica, talc and rutile) in soils on a shovel and also from a quarry. The soils had a common provenance and revealed the location of two buried bodies, (ii) identifying the locality of stolen ferns from a conservation park, (iii) identifying the provenance of soil removed from a site containing aboriginal artifacts, (iv) a sexual assault case in which a comparison between soil minerals on jeans, shoes and a vehicle, with samples from a road side, (v) identifying the provenance of an industrial dust settling on parked vehicles. The mineralogy of these dusts identified them as coming from a cement works. (vi) identifying the possible overseas provenance of soil on boots belonging to a suspected terrorist.

Keywords: provenance, clays, XRD

MS06.24.3*Acta Cryst.* (2005). A61, C14-C15**Applications of XRD in Forensic Casework**

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Within the NFI powder XRD is mainly used for:

1. Characterization of powders of unknown composition

In The Netherlands the number of anonymous threatening letters sent to politicians and other VIP's has increased since 9/11 and the murder of Pim Fortuyn. To aggravate the threatening effect some senders enclose cartridges or powders in the letters. The risk of such enclosed powders is assessed by means of a standard procedure. If the risk is considered negligible or absent, the powder is characterized by means of FTIR, XRF and XRD. This generally leads to a quick and clear characterization of the powder. Mostly these powders are composed of household articles, such as flour, sugar or washing powder. In some cases more particular compounds, e.g. medicines, are present, which can be important information for the criminal investigation process.

2. Comparison of materials found at a scene of crime

In a particular case threatening letters were produced on pink sheets of paper. In the house of the suspect a bundle of similar pink paper was found. A comparative investigation of pink papers from different origin was carried focussing on the characterization of fillers and the cellulose crystallinity. The result was that the questioned paper and the paper found at the suspect's house could not be distinguished from each other and that all other papers contained different fillers.

3. Characterization of pyrotechnical mixtures

In The Netherlands, strict regulations are effective with respect to the composition of consumer fireworks. The maximum allowable mass of the explosive charge depends on the chemical composition of the charge. By means of XRD the components of pyrotechnical mixtures can be identified easily and quickly.

Keywords: forensic mineralogy, paper, powder X-ray diffraction

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X-ray Chemical Analysis for Forensic Applications using Synchrotron Radiation

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A synchrotron radiation (SR) light source is one of the important technologies in the forensic science. Especially, it was expected that the use of high-energy X-rays from SPring-8 as an excitation source for X-ray fluorescence (XRF) analysis would be suitable for distinguishing the difference in the origin of the trace amount of samples. We first developed high-energy XRF utilizing 116 keV SR to conduct a scientific investigation to aid in the solving of an arsenic murder that occurred in Wakayama City on July 25, 1998 [1]. We have successfully detected the ppm levels of Sn, Sb, and Bi included in arsenic acid as the impurities. As a result, it was found that the trace heavy element compositions are distinct from each other, reflecting the different places of production. This technique has already come into routine use by the Forensic Science Laboratory of the Hyogo Prefecture Police Headquarters to solve several important criminal cases occurring all over Japan [2]. They have been beginning an analysis for various forensic samples such as gunshot residue particles, tiny glass pieces, paint chips, fluorescent powders.

In this talk, some experimental results of chemical analyses applied to the actual criminal investigations will be presented.

[1] Nakai I., *X-ray spectrometry: Recent Technological Advances*, 2004, 355.

[2] Ninomiya, T., *X-ray spectrometry: Recent Technological Advances*, 2004, 553.

Keywords: synchrotron radiation applications, forensic microanalysis, X-ray fluorescence analysis

MS07 CRYSTAL CHEMISTRY OF INORGANIC AND MINERAL COMPOUNDS

Chairpersons: Wulf Depmeier, Herta Effenberger

MS07.24.1

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The Zintl-Klemm Concept Applied to Cations in Oxides. An Alternative Interpretation of the Structures of Silicates

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The structures of ternary and quaternary silicates are reinterpreted on the basis of the Zintl-Klemm concept and the Pearson's generalised octet rule. The three-dimensional skeletons formed by the Si atoms can be interpreted as if the Si atoms were behaving as Zintl polyanions, adopting the structure of either main-group elements or Zintl polyanions showing the same connectivity. An example of this behaviour is the mineral pabstite BaSn[Si₃O₉]. In this compound, the Ba and Sn atoms donate 6 e⁻ per formula unit to the three Si atoms, converting them into Ψ-S atoms, i.e. 2-connected atoms. Thus, the Si (Ψ-S) atoms adopt the structure of the triangular S₃ molecules. The O atoms are then located close to both, the hypotheticalal 2-electron bonds and the lone pairs, giving rise to a tetrahedral coordination. In some silicates, the Si atoms clearly show an amphoteric character so that some Si atoms act as donors (bases) adopting an octahedral coordination, whereas others behave as acceptors (acid), adopting a tetrahedral coordination. Although the octahedral coordination seems to be favoured by the application of pressure, the results reported here indicate that the coordination sphere of silicon is not a function of the assumed ionic radius of the Si⁴⁺ cations but it depends on the nature of the other cations accompanying them in the structure.

Keywords: silicate structures, Zintl-Klemm concept, cation arrays

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Uranyl Selenates: From Finite Clusters to Nanotubules

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Structural chemistry of uranyl selenates with over than 50 compounds first characterized by the authors is described on the basis of graph theory adapted to the description of heteropolyhedral structures [1]. Structural motifs in uranyl selenates are based upon corner-sharing UO₇ pentagonal bipyramids and SeO₄ tetrahedra. Structural diversity of these motifs range from finite clusters and chains to complex sheets and nanotubules [2, 3]. It is shown that most of the 0-D, 1-D and 2-D graphs corresponding to the uranyl selenate motifs can be considered as derivatives of highly regular {3.6.3.6} graph consisting of 3-connected white and 6-connected black vertices. Structural and geometrical isomerism induced by tetrahedra orientation and selective hydration of UO₇ polyhedra will be described. The model of nanotubule formation in uranyl selenate systems based upon the rolling of 2-D sheets is discussed. Self-assembly of organic amines governing by competitive hydrophobic/hydrophilic interactions and structure of organic/inorganic interfaces in uranyl selenates will be discussed.

[1] Krivovichev S.V., *Crystallogr. Rev.*, 2004, **10**, 185. [2] Krivovichev S.V., Kahlenberg V., Kaindl R., Mersdorf E., Tananaev I.G., Myasoedov B.F., *Angew. Chem. Int. Ed.*, 2005, **44**, 1134. [3] Krivovichev S.V., Kahlenberg V., Tananaev I.G., Kaindl R., Mersdorf E., Myasoedov B.F., *J. Amer. Chem. Soc.*, 2005, **127**, 1072.

Keywords: uranium compounds, structural motifs, nanochemistry

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Molecule-Mineral Inner-Surface Interactions in Nanoporous Silicates

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We have carried out single-crystal and powder Raman studies of zeolites, SiO₂-clathrates and other silicate structure types with small nanopores (beryl, cordierite) to investigate the nature of inner-surface molecule-crystal interactions and the role of hydrogen bonding.