

**MS05.24.4***Acta Cryst.* (2005). A61, C14**Volume Collapse at the Jahn-Teller Transition in LaMnO<sub>3</sub>**

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We have investigated the Jahn-Teller (JT) transition accompanied by the orbital order-disorder transition in LaMnO<sub>3</sub> by high temperature X-ray powder diffraction with synchrotron radiation and also neutron powder diffraction. The unit cell volume of LaMnO<sub>3</sub> 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 MnO<sub>6</sub> 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 Mn<sup>3+</sup> e<sub>g</sub> 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 LaMnO<sub>3</sub> 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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