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Isostructural phase transitions and crossovers under non-ambient conditions. Vladimir Dmitriev, Dmitry Chernyshov. *Swiss-Norwegian Beamlines at ESRF, Grenoble, France.*

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It is convenient to consider a change in the structure of crystalline material as a reason for remarkable modifications in its physical properties: a structural phase transition often results in the anomalous behaviour of macroscopic parameters in condensed matter. However, is it always true that a detected change in properties, discontinuous or smooth, manifests itself as a change in the crystal structure? Isostructural transformations exemplify a violation of such a rule. They connect phases with identical structures but with different properties; a volume collapse, giant magneto-elastic coupling, or negative thermal expansion may serve as examples of corresponding macroscopic responses.

Isostructural phase transformations have two possible regimes: the transition can be discontinuous (first-order) or transformation can be smooth (crossover regime). One finds a limited number of examples of discontinuous isostructural phase transitions. At the same time, many examples of anomalous but continuous variation of material parameters within the stability range of the same phase have been reported. Normally structural information collected for non-ambient conditions are limited and therefore an isostructural transformation occurring in the crossover regime may be easily mixed with a second order phase transition. In our talk, we show typical anomaly types for isostructural phase transformations. Generic model-free phase diagrams, with their specific features as critical lines and points, will be presented and analyzed. Phase transformations observed in rare-earth metals and their compounds provide an experimental illustration of different transformation regimes.

Keywords: phase transition, isostructural, crossover

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Elastic and non-elastic response of shape memory alloys to stress fields. W. W. Schmahl^a, S.

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Pseudoplastic or pseudoelastic shape memory is based on recoverable ferroelastic twin domain accommodation in stress fields. The twins are associated to a martensitic phase transition. Pseudoelasticity (superelasticity) occurs when the high-symmetry phase (paraelastic “austenite”) is thermodynamically stable in the stress-free state, and the phase transition to the distorted phase (ferroelastic “martensite”) is induced by the application of stress. Those ferroelastic twin variants which are suitably oriented in the stress field become stable and the spontaneous strain of the

martensitic transition leads to a large shape change during the process. When stress is released, the system falls back to the (stable) austenite state and the original shape is “pseudoelastically” recovered. Pseudoplastic shape memory occurs when ferroelastic “martensite” is thermodynamically stable, and the effect is due to ferroelastic domain switching in the stress field. In this case a release of stress does not recover the original domain configuration. The original shape (and domain configuration) is then restored via a thermal transition to the paraelastic austenite and stress-free cooling to martensite.

Microdiffraction experiments using 100keV x-rays at beamline BW5@HASYLAB reveal the formation of stress-induced martensite in the stress field concentrated at the tips of cracks progressing through austenitic NiTi [1] and in localized shear transformation bands in uniaxially stressed NiTi [2]. Careful examination of neutron diffraction 2.54 Å neutron diffraction data on SPODI@FRM-II show that the macroscopic strain of the material is dominated by twin re-accommodation, while the observable crystallographic distortions on unit-cell level reflect residual stresses arising in the twin-microstructure (rather than elastic distortions).

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Elastic properties of YCrO₃ perovskite up to 60 GPa.

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Perovskite compounds are largely applied in several technological fields due to their peculiar electric, magnetic, piezoelectric and optical properties. YCrO₃, a GdFeO₃-type perovskite, has become an attracting material due to its multifunctional biferroic behavior [1], and to its recent use as interconnection for the SOFC's [2]. A recent work revealed that the YAlO₃-YCrO₃ system exhibits the lowest relaxation coefficient, if compared with other structures hosting Cr³⁺ in octahedral coordination [3]. In the last decade, many studies have been devoted to assess the high pressure behavior of orthorhombic perovskites. However, data on YCrO₃ under high-pressure conditions are lacking. For these reasons, we investigated the high pressure evolution of the YCrO₃ perovskite (s.g. *Pbnm*) using synchrotron powder diffraction, up to 60 GPa. The P-V data, fitted with a third-order Birch-Murnaghan equation of state gave a $V_0 = 218.23(4) \text{ \AA}^3$, and to a volumetric bulk modulus $K_{T0} = 208.4(5) \text{ GPa}$, with a $K'_0 = 3.7(1)$, with a volume reduction of ~17.5% in the studied pressure range. The elastic moduli of the individual crystallographic axes showed that the *b*-axis is appreciably less compressible than both *a*- and *c*-axis ($K_{a0} = 195(5) \text{ GPa}$, $K_{b0} = 223(7) \text{ GPa}$, and $K_{c0} = 200(6) \text{ GPa}$, respectively),

implying that YCrO_3 became more distorted with increasing pressure. The polyhedral bulk moduli for YO_{12} and CrO_6 polyhedra led to: $V_{0,\text{poly}}, K_{p0}$: 46.09(2) \AA^3 , 254(2) GPa for YO_{12} , and 10.40(1) \AA^3 , 251(5) GPa for CrO_6 . The volume compressibilities of the YO_{12} and CrO_6 sites are therefore equivalent. That results are different to those previously reported for the orthorhombic YAIO_3 perovskite in which the b -axis is significantly more compressible than both c and a [4]. Considering the elastic moduli of both YCrO_3 and YAIO_3 , the two structures under pressure show a different anisotropic behavior along [101] (both YCrO_3 and YAIO_3 structures). Furthermore, for the YAIO_3 perovskite the compressibility of the A site is ~15% less than that of the AlO_6 octahedron [4]. Such contrasting trends can be explained by the stronger confinement of Y ions in YAIO_3 due to the smaller size of octahedral network in the orthoaluminate compared to the orthochromate. As known from previous work [3], the decrease of mean octahedral bond distance, $\langle\text{B-O}\rangle$, from YCrO_3 to YAIO_3 is accompanied by shortening of the average $\langle\text{A-O}\rangle$ distance and decreasing of interpolyhedral tilting. The associated strong confinement of Y cation in YAIO_3 does not occur in YCrO_3 . Here the A site is easier to compress and does not hamper the enhance of octahedral tilting and rotation expected at high pressure conditions.

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Pressure-induced Phase Transformations in Lead-based Relaxor Ferroelectrics. B. J. Maier^a, R. J. Angel^b, B. Mihailova^a, W. G. Marshall^c, C. Paulmann^a, J. M. Engel^d, M. Gospodinov^e, U. Bismayer^a.

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The structural peculiarities of relaxor ferroelectrics, exhibiting very high dielectric and elastoelectric response, remain a challenging problem. Pressure is a strong driving force that can trigger incipient atomic clusters existing at ambient conditions to develop into long-range ordered domains detectable by conventional diffraction methods. Thus, the analysis of pressure-induced transformation processes can help to elucidate the structural complexity of relaxors. Our high-pressure X-ray diffraction data on lead scandium tantalate (PST) and lead scandium niobate (PSN) as well as doped variants reveal a thermodynamically second-order phase transition for all compounds [1,2]. An increase in the intensities of $h,k,l = \text{all odd reflections}$ is observed while the intensity of h,h,h peaks, $h = 2n+1$, does not change with pressure. This indicates a glide-plane pseudo-symmetry of the

structural distortion along the $\langle 111 \rangle$ cubic directions and unambiguously reveals anti-phase octahedral tilting as the cause for the increased reflection intensities.

Rietveld refinements to neutron powder diffraction data on PST and PSN reveal anti-phase octahedral tilts already below the critical pressure that continuously evolve with pressure [3]. The high-pressure phase has either or symmetry, depending on whether the presence of 1:1 cation ordering is neglected or taken into account.

The influence of Ba^{2+} , Bi^{3+} , and La^{3+} substitution for Pb^{2+} on the phase transition will be discussed. Ba^{2+} smears out the phase transition and enhances the local ferroic distortion, while Bi^{3+} lowers the critical pressure and enhances the structural distortions associated with the phase transition. La^{3+} substitution for Pb^{2+} yields a smaller tolerance factor, thus octahedral tilting occurs already at room pressure, although the average structure remains metrically cubic.

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Correlations between microstructures evolution and elastic properties of LEK 94. Giovanni Mazzolai^a,

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It is well known that high-cycle fatigue (HCF) is the main source of failures in the components made from single crystal Ni-base superalloys of today's aircraft and spacecraft propulsion systems. Under fatigue loading cyclic stress produces alternating slip reversals on the critical slip systems which eventually results in fatigue crack initiation along "critical" octahedral $\langle 111 \rangle$ planes. It is important to determine the stresses and strains along these planes and corresponding slip systems in order to use them to calculate several multiaxial critical plane parameters to determine the amount of fatigue damage and also the "critical planes" along which HCF failures would initiate [1]. The intensity of the stress levels and the stress states are related to the geometry of the component, to the orientation of the crystal lattice with respect to the component geometry, and to the micromechanics of the deformation and slip mechanisms observed in corresponding single crystal materials and to the temperature histories during cyclic operation and most important to the elastic constants and thermal expansion coefficients of the material.

In the course of our project we investigate the elastic anisotropy of the quasi single crystal Ni-base superalloy LEK94 between room temperature and 1200°C with the aid of resonant ultrasound spectroscopy. This method yields sets of elastic constants of high internal consistency because all independent constants are determined on one single sample in one run.

The influence of microstructure evolution on fatigue crack initiation has been shown to play a dominant role, especially on cracks which are of a size comparable to the scale of characteristic microstructural features. Microstructures