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MICROSTRUCTURAL DEVELOPMENT RELATED TO PHONON ANOMALIES LEADING TO DISPLACIVE TRANSFORMATIONS IN METALLIC PHASES. By L.E. Tanner, A.J. Schwartz*, D. Schryvers[1] and S.M. Shapiro[2], Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA, U.S.A. [1] Electron Microscopy for Materials Research, University of Antwerp (RUCA), Antwerp, Belgium, [2] Physics Department, Brookhaven National Laboratory, Upton, NY, U.S.A.

The phonons of crystalline phases (pure metal and alloyed) that undergo first-order displacive transformations on cooling exhibit anomalously low energies along those branch(es) related to the atomic displacements of the ensuing structural changes. Present at elevated temperature equilibrium, these effects become more pronounced as $T \rightarrow T_c$ (or M_s), the bulk transformation temperature, though the "softening" is never complete at T_c . The coupling between the soft phonons and local parent lattice distortions (defects) sets the stage for heterogeneous nucleation. [Phys. Rev. B **44**, 9301 (1991); Ultramicroscopy, **37**, 241 (1990)]. HRTEM and neutron scattering observations of Ni-Al, Ti-Ni-Fe, Ti-Pd-Fe, Ti-Pd-Cr, Ti-Mo and Zr-Nb transformations illustrate the foregoing and will be discussed in terms of nonclassical heterogeneous nucleation theory.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

MS-21.03.07

DOMAIN WALLS IN CRYSTALS WITH INCOMMENSURATE PHASES. By Y. Ishibashi, Synthetic Crystal Research Laboratory, School of Engineering, Nagoya University, Nagoya 464-01, Japan.

The domain wall is a transient region where two domains with different values of the order parameter meet. Fundamental features of domain walls, like the spatial variation of the order parameters in the wall, the wall energies and the activation energies, are discussed on the basis of the Landau-type thermodynamic potentials applicable to crystals, which have the incommensurate phases. The domain walls to be considered will be those between two commensurate domains, two incommensurate domains, and a commensurate domain and an incommensurate domain. It will be clarified how the factors stabilizing the incommensurate phase should affect characteristics of the domain walls. In particular, the contribution from the Lifshitz invariant to the wall structure and so on will be discussed.

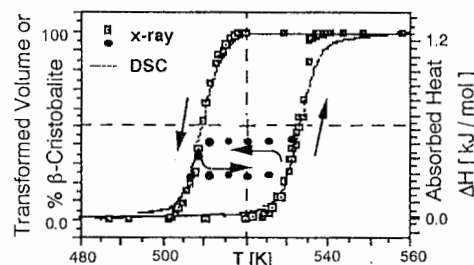
MS-21.03.08 PHASE TRANSITIONS IN QUASICRYSTALS By F. Dénoyer*, P. Launois and M. Lambert, Laboratoire de Physique des Solides, Associé au C.N.R.S., Batiment 510, Université Paris-Sud, 91405 Orsay Cédex, France.

The Al-Cu-Fe equilibrium diagram has been the subject of many experimental investigations. It has been shown that a phase transformation between a high temperature icosahedral quasicrystalline phase and a low temperature rhombohedral microcrystalline phase occurs in the vicinity of the composition 63.5-24-12.5. The material also exhibits an "intermediate" modulated quasicrystalline state.

In this short lecture, we will perform a review of the experimental and theoretical works related to these phase transformations.

MS-21.03.09

ATHERMAL TRANSFORMATION KINETICS AND THERMAL HYSTERESIS AT WEAKLY FIRST ORDER PHASE TRANSITIONS. By W.W. Schmahl, Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt, Germany. Although thermal hysteresis is a common feature of first order phase transitions, there is only rudimentary knowledge about its origin and characteristics. The non-quenchable α/β -cristobalite phase transition near 520 K is associated with a 'thermal' hysteresis of ± 15 K and α/β -phase coexistence in the hysteresis loop. Measurements by x-ray diffraction (0.03 K/min) or DSC (5K/min) give practically the same result (see figure). The transformation proceeds instantly as a function of temperature; thermal activation is not a relevant factor. These 'athermal' features are similar to martensitic transformations in metals and alloys and to field-reversal hysteresis in ferroics. The bulk Landau-free energy isotherms suggest that local strain-fields control nucleation and initiate both phase coexistence and 'thermal' hysteresis.



MS-21.03.10 A 2 θ -RESOLVED HADOX STUDY OF BaTiO₃ LINZ CRYSTALS. By H. Onitsuka, M. Hatakeyama, Y. Soejima and A. Okazaki*, Department of Physics, Kyushu University, Fukuoka 812, Japan.

X-ray diffraction intensities in a reciprocal-lattice plane can be measured with high resolution in two dimensions by improved high-angle double-crystal X-ray diffractometry (HADOX). In addition to the original experimental arrangement in HADOX, two slits have been introduced: one for limiting the area of the specimen crystal to be examined, and the other for defining the resolution of 2θ . Thus we can correlate the original ω scanning of the specimen with the 2θ scanning of the detector, and determine two-dimensional intensity distribution. This technique, named the 2θ -resolved HADOX, enables us to determine separately and precisely changes in lattice constants and changes in crystal orientation. This is required in the structural study of first-order transitions. The method has been applied to the cubic-to-tetragonal phase transition in BaTiO₃ Linz crystals grown by the method of top-seeded solution growth; the results are compared with those of previous experiments on butterfly crystals of BaTiO₃. It is found that the two types of crystals behave in quantitatively different manners around the transition: the transition temperature, the temperature range of two-phase coexistence etc. are different. In

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both types of crystals, on the other hand, the lattice constant of the cubic phase shows a different temperature dependence when the tetragonal phase coexists, and the orientation of crystal grains shows anomalous behaviour. The results are discussed in terms of the effect of stresses, and in connection with dielectric properties.

MS-21.03.11 ORDER PARAMETER COUPLING AT THE O/D PHASE TRANSITION IN NiTiO₃. By H. Boysen* and F. Frey, Institut f. Kristallographie, Universität München, Germany and M. Lerch, FB Materialwissenschaften, TH-Darmstadt, Germany.

At ambient temperature NiTiO₃ has the ordered ilmenite structure (space group $R\bar{3}$) which may be described as a nearly hexagonal close packing of oxygens, the cations occupying 2/3 of the octahedral voids in an ordered sequence along the threefold axis. At $T_c \approx 1560$ K a second order phase transition leads to a disordered corundum structure ($R\bar{3}c$) with a random occupation of the same cation sites. Besides the order parameter η describing the cation exchange, there are further critical (displacive) degrees of freedom $\Phi_{1,3}$ which belong to the same irreducible representation Γ_2^+ (A_{2g}). The temperature dependence of the order parameters was investigated by Rietveld analysis of neutron powder diffraction data measured between 300 K and 1650 K. η shows a critical behaviour starting at $T_1 \approx T_c - 200$ K. Only one of the other displacive parameters (Φ_2) matches this behaviour, while the other two follow their own different temperature dependence starting far below T_1 . The excess strain $\Delta c/c$ couples quadratically to η , while $\Delta a/a$ follows Φ_3 . The temperature factors strongly increase as $T \rightarrow T_c$. The reasons for these unexpected deviations from common phase transition theories (e.g. Landau) could be found from refinements with anharmonic temperature factors. In the average structure the probability densities of the cations show deformations which may be attributed to the fact that different cation species occupy different positions in their individual unit cells. Furthermore, close to (below) T_c some additional density is found in normally empty octahedra. Therefore, these (probably dynamic) delocalizations of the atoms have to be included in more accurate phase transition theories.

This work was supported by funds of the BMFT (03SC3LMU).

PS-21.03.12 LASER-INDUCED PHASE TRANSITIONS IN LAYERED SEMICONDUCTOR PbI₂. By S.K. Chaudhary, University College, M.D. University Rohtak - 124001 (INDIA).

The phenomenon of polytypism has attracted the attention of both physicists and mineralogists for many years. Recently, it has also attracted the attention of solid-state physicists by virtue of the fact that various polytypic modifications of the same substance have been found to possess different semiconducting, dielectric and photovoltaic properties.

The phase transitions in PbI₂ crystals have been studied by various researchers. When heated, the 2H structure transforms to 12R. High-purity single-crystals of PbI₂ were grown by the zone-refinement method. Their structure was shown to be of the 12R type by X-ray diffraction techniques. A pulsed ruby laser was then used to irradiate the crystal at room temperature. It is observed that its structure changes to 2H, the most stable polytype, after the laser irradiation. The results have been explained by thermodynamical and structural considerations.

PS-21.03.13 STRUCTURAL PROPERTIES OF GUEST MOLECULES IN UREA INCLUSION COMPOUNDS AT LOW TEMPERATURE

By Ian J. Shannon* and Kenneth D.M. Harris, Department of Chemistry, University of St. Andrews, St. Andrews, Scotland, U.K.

Urea inclusion compounds are examples of crystalline "host-guest" systems, comprising an extensively hydrogen bonded urea "host" substructure which contains essentially infinite, uni-directional tunnels. This host substructure is stable only when each tunnel contains a dense packing of "guest" molecules; such suitable guest molecules include straight-chain alkanes and certain derivatives such as α, ω -dihalogenoalkanes (K.D.M. Harris, S.P. Smart and M.D. Hollingsworth, *J. Chem. Soc., Faraday Trans.*, 1991, 87, 3423-3429) and diacyl peroxides (K.D.M. Harris and M.D. Hollingsworth, *Proc. Roy. Soc. Lond. A*, 1990, 431, 245-269). At ambient temperature, the urea inclusion compounds of each of these families of guest species have been shown to exhibit different characteristic modes of inter-tunnel packing of guest molecules. For example, for the diacyl peroxide/urea inclusion compounds predominantly three-dimensional ordering of the guest is observed, with $\Delta_g = 4.6$ Å irrespective of the length of the guest molecule (Δ_g is the offset, along the tunnel axis, between positions of guests in adjacent tunnels).

In the present study, urea inclusion compounds containing n-alkane, α, ω -dihalogenoalkane, diacyl peroxide and carboxylic acid anhydride guest molecules have been analysed, using single crystal X-ray diffraction, at temperatures between 90 K and 296 K. Transitions have been found to occur in the guest substructure for several of the guests considered.

The structural changes associated with these transitions will be discussed in detail.

PS-21.03.14 REVERSIBLE SOLID-STATE PHASE TRANSITION OF A "THERMOSALIENT CRYSTAL". By S. Zamir* and J. Bernstein, Department of Chemistry, Ben-Gurion University of the Negev, POB 653, Beer-Sheva 84105, Israel, and Daniel J. Greenwood, Boehringer Ingelheim Pharmaceuticals Inc., Ridgefield, CT 06877, U.S.A.

"Thermosalient behaviour" was first noted by Gigg *et al.* (1987). *J. Chem. Soc. Perkin Trans. 1*, 2411, and described also as "hopping crystals" or "jumping crystals". These terms characterize vigorous mechanical movements of a crystal on heating or cooling through a phase transition. The phenomenon was previously studied in two systems: *myo*-inositol derivatives (Gigg *et al.*, 1987) and perhydropyrene (Ding *et al.* (1991). *Acta Cryst.* B47, 739). We present here a third compound, oxitropium bromide, with similar behaviour.

The reversible phase transition to be discussed involves highly anisotropic parameter changes corresponding to about 4% volume expansion upon heating. The lower and upper temperature crystal forms, both orthorhombic, have been characterized by their different IR spectra, DSC and powder diffraction patterns.

Upon heating, the transition is endothermic, and occurs around 56.5-57.5°C, with enthalpy of transition of about 2 kJ/mole. Upon cooling, the transition occurs around 34-36°C, due to hysteresis. Various aspects of the transition and crystal chemistry will be presented.

Crystal Data: Oxitropium Bromide, C₁₉H₂₆NO₄Br. Orthorhombic, SG P2₁2₁2₁, Z=4 for both forms.

	Low Temp. Form	High Temp. Form
<i>a</i> (Å)	7.388(2)	7.479
<i>b</i> (Å)	10.118(3)	11.254
<i>c</i> (Å)	24.705(4)	22.890
<i>V</i> (Å ³)	1846.7	1926.6