21-Crystallography at Non-Ambient Temperatures and/or Pressures; Phase Transitions

The true symmetry of the anions A or template molecules M is of lower grade than cubic symmetry, predominatly in the various SOD-compounds under scope. With increasing temperatures the guest/host symmetry misfit is diminished by dynamics of the guest atoms. They approach spherical character by hopping between equivalent positions with hopping frequences up to 10^{15} Hz close to T_{dec}, the temperature of peritectical decomposition of the host structure. T_{dec} is the temperature critical to the guest/host interaction. In the given SOD-compounds the values of T_{dec} vary between 900 and 1500K for the same type of host composition $[T_{6-n}T'_nO_{12}]$. Thus a given host structure of lattice energy U_h might serve to test the real v.d.WAALS and COULOMB forces given by the atoms of the guest complexes encapsulated in the 4^66^8-SOD-cage. There is some evidence for a *dot gas* character of the guest complexes close to T_{dec}, from the high chemical potential provided by the dynamics of the atoms intra-cage rotation, the translational movement being forbidden by the periodic $^3_\infty$matrix of cages. Upon cooling structural phase transitions occur through cooperation of the guest atoms with the host structure on a certain level of hopping frequencies, thus lowering the symmetry of the host structure[2]. Phase transitions present critical phenomena in the individual type of interactions between the chemical species of the guest- and of the host structure as revealed in the peak shapes by DSC-microcalorimetry. Some SOD-phases show no structural phase transitions, surprisingly, but irregularities in the trace of regular DSC-experiments run with a 5K/min cooling rate. The shift in the c_p-curves, the value of 0.20 J/gK is observed in the hydrosodalite type $[Na_3\square(OD_2)_4]_2[Si_3Al_3O_{12}]_2$ at T_g = 150K, resemble the glass transition of polymers and inorganic glasses. Contrary to the findings in *orientational glasses* we like to introduce the term *dot glass* to this group of new materials, which differ by the periodic $^3_\infty$matrix of cages as in zeolite like materials.

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PS-21.03.21 **MECHANISMS OF PHASE TRANSITIONS IN HEXAGONAL MODEL WITH 1q AND 3q INCOMMENSURATE PHASES**

Krzysztof Parlinski† & Gervais Chapuis*

Institut de cristallographie, Université de Lausanne, BSP, 1015 Lausanne, Switzerland
†(on leave from the Institute of Nuclear Physics, Cracow, Poland)

A hexagonal two-dimensional model of particles with displacive degree of freedom and interacting via potential energy with harmonic and anharmonic third and fourth order terms has been studied by the molecular-dynamics technique. The phase diagram of the model exhibits normal, k=0 commensurate, one-dimensional (1q) and three-dimensional (3q) incommensurate phases. The 3q phase can be visualised as a sequence of columns, oriented along the hexagonal axis. The columns form a hexagonal discommensuration lattice. At higher temperature, the 3q incommensurate phase is more stable than the 1q phase.
The simulation shows that: (i) The 1q → k=0 phase transition is driven by the antistripples, which are topological defects of the stripe discommensuration lattice. (ii) In the 3q → k=0 phase transition, the columns are suppressed. The first eliminations occur at random, the following ones rather close to already annihilated columns. (iii) The 1q → 3q phase transition which preserves the modulation wavelength, is driven by anisotropic antistripples nucleated equidistantly on the discommensuration planes of the 1q phase. The appearing 3q phase may contain deperiodization (dislocation) loops at the sites of a hexagonal discommensuration lattice. (iv) In the 3q → 1q phase transition with constant modulation wavelength, the columns of phase 3q merge into each other to form a stripe of discommensuration plane. (v) The mechanism of the 3q → 3q' phase transition associated with a change of the modulation wavelength, exhibits three types of deperiodization loops.

PS-21.03.22 STRUCTURAL TRANSITIONS AND MAGNETIC PROPERTIES IN $LaFe_{13-x}Al_x$ SYSTEM. By W.H. Tang*, J.K.Liang, X.H.Yan, G.H.Rao, and S.S.Xie. Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China.

The excellent magnetic properties of the $LaCo_{13}$ intermetallic compound raised the interest of many researchers. For exploring new rare-earth 3d transition-metal permanent magnet, it is important to investigate intermetallic compounds related to the $NaZn_{13}$ type structure. As is well known, those materials which have cubic structure are impossible to be used as permanent magnets because of their high symmetry. From the point of view of crystal structure, we attempt to lower the symmetry of cubic $NaZn_{13}$ by proper heat treatment or elemental substitution, in order to improve magnetic anisotropy.
After annealing at 773K for about two months, structural transitions from cubic to orthorhombic have been observed for $LaFe_{13-x}Al_x$, (x=6,7). The results of X-ray diffraction and magnetic measurements show that under the given heat treatment procedure, only those cubic $NaZn_{13}$ phase samples with mictomagnetic character change their structures. Selected-area electron diffraction patterns confirm that, after annealing at 773K, $LaFe_{13-x}Al_x$ have a body centered orthorhombic structure with a structural modulation along the a-axis. For $LaFe_6Al_7$, the modulated period is 0.068a* (a= 8.21Å). The structural transitions result in the change of magnetic properties from mictomagnetism to ferromagnetism.

PS-21.03.23 INVESTIGATION OF THE FERROELECTRIC TRANSITION IN POTASSIUM IODATE. By J.G. Zhang, Institute of Crystal Materials, Shandong University, Jinan, China

Potassium iodate crystals are ferroelectric and belong to the triclinic system with space group P1. They possess thermoelectric properties in the range from -195°C to +300°C. Irreversible spontaneous polarization along the pseudo three-fold axis is observed. Four phases exist in this temperature range: the first one exists above 212°C, the second one between 72 and 212°C, the third one between -15 and 72°C, and the last one below -15°C.

Monodomain and multidomain crystals with good optical characteristics were selected. Observations were performed on 2-mm thick (001) ground and polished plates. An investigation of the ferroelectric transition was carried out using an OPTON polarizing microscope, a Leitz heating stage, a long-focus objective lens and a thermocouple temperature measurement device with automatic compensation.

In the hexagonal structure of KIO_3, potassium ions are at the vertices, oxygens at face centers and iodine ions at body centers. The crystals are paraelectric in phase I. In phase II, iodine ions move along the body diagonal, and spontaneous polarization takes place with formation of 120° domains. In phase III, iodine atoms move perpendicular to the oxygen ions in on {100} planes, and crystals become triclinic. Below 212°C, potassium iodide crystals are mostly 120 and 60° multi-domain crystals.

PS-21.03.24 CHANGE OF LATTICE PARAMETERS AS EVIDENCE OF AUSTENITE THERMAL INSTABILITY IN MANGANESE STEELS. By V.E. Danilchenko, A.V. Nedolya* and V.M. Nadutov, Metal Physics Institute and Department of Physics, Zaporozhye State University, Ukraine.

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The γ-solid solutions in some steels are unstable during ageing. This instability is connected with partial excretion of the carbon from solid solution and, as a result, austenite lattice parameters are seen to decrease in some temperature ranges. Formation of the new phases, physical and mechanical properties are due to change in carbon content in austenite thermal instability range.

Fe-12,0wt%Mn-1,1wt%C and Fe-11,1wt%Mn-1,1wt%N alloys with many crystal structures have been selected for investigation. The austenite thermal instability range is determined during step heating by X-ray powder diffraction. In the carbon-containing alloy, the thermal instability occurs in the temperature range 300-600°C and at 400-800°C for the nitrogen-containing one. This difference is connected with differences in the mobility of carbon and nitrogen. In the thermal instability range, the precipitation of carbide and nitride is found by qualitative analysis. The quantity of carbon (nitrogen) at maximum temperature instability is evaluated. The results of investigations show that only some part of the carbon or nitrogen in the alloy formed the carbide or nitride. Probably, the remainder of carbon (nitrogen) precipitates as atoms in the structure defects. After heating, defects induce a high pressure which forces carbon and nitrogen in octa- and tetrapores of the bcc lattice of austenite. Increase of lattice parameters in γ-solid solution confirms this assumption at temperature conditions where the solubility of carbide or nitride is hardly possible.

Thus the greater stability of the nitrogen-containing γ-solid solution over the carbon-containing γ-solid solution is related to the different mobilities of carbon and nitrogen. Part of carbon or nitrogen precipitated forms carbide or nitride, and the remainder is concentrated in defects in atomic state.

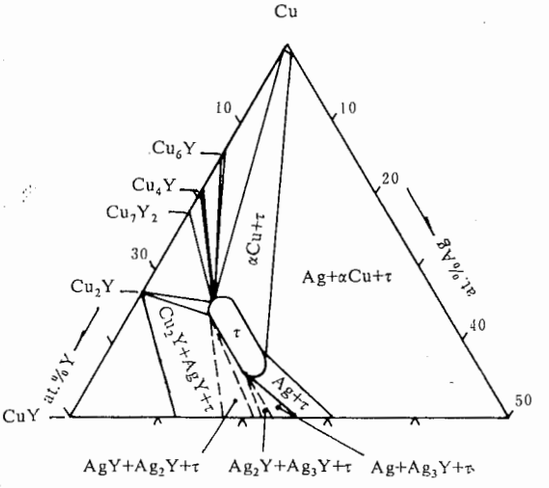
PS-21.03.25 STUDY ON THE SELF-PHASE-TRANSITION CHARACTERESTIC OF ULTRAFINE PARTICLES. By LIU Cunye *, DENG Zhaojiang, REN Hongxiang and Li Jian, Department of Physics Southwest China Teachers University, Chongqing, Sichuan CHina , 630715

The study of the atomic structure has been extended to ultrafine pritcle (UFP) containing hundreds and millions of atoms, the macroscopic concepts of surface energy and chemical potential is applied to investigate the surface structure of UFP, the growth process of UFP is described by using the equation of macroscopic theory to be revised.

By experiment and theoretical research, we find that UFP possesses one kind of the characturestic of the s elf-phase-transition(SPT), namaly, UFP has a trend of the spontaneous phase transition, it is name 'SPT effect' in this paper. The SPT process of UFP does not need that rigorous surroundings condition, which is necessary for the phase transition process of macroscopic matter (such as sur roundings temperature, pressure, surroundings atomsphere, etc.). The SPT process of UFP depend on own microstrecture, praticle size, morphology, etc. The time-dependence of the SPT process submits to a power-law. We have done a preliminary research for the SPT mechanism of metal and metal oxide UFP.

PS-21.03.26 THE ISOTHERMAL SECTION OF THE PHASE DIAGRAM OF Ag-Cu-Y TERNARY SYSTEM AT 500℃. By D.X.Li, L.M.Zeng * and Y.H.Zhuang, Department of Physics, Guangxi University, Nanning 530004, China.

The isothermal section of the phase diagram of Ag-Cu-Y ternary system (Cu ≥ 50at.%) at 500℃ has been investigated by X-ray diffraction. The section consists of seven single-phase regions: α-Cu, Cu_6Y, Cu_4Y, Cu_7Y_2, Cu_2Y, CuY and $Ag_3Cu_{12}Y_5$(τPhase); sixteen two-phase regions: Ag+αCu, αCu+τ, Cu_6Y+τ, Cu_4Y+τ, Cu_7Y_2+τ, Cu_2Y+τ, Cu_2Y+AgY, AgY+τ, Ag_2Y+τ, Ag_3Y+τ, Ag+τ, αCu+Cu_6Y, Cu_6Y+Cu_4Y, Cu_4Y+Cu_7Y_2, Cu_7Y_2+Cu_2Y and Cu_2Y+CuY and ten three-phase regions: Ag+αCu+τ, αCu+Cu_6Y+τ, Cu_6Y+Cu_4Y+τ, Cu_4Y+ Cu_7Y_2+τ, Cu_7Y_2+Cu_2Y+τ, Cu_2Y+CuY+AgY, Cu_2Y+AgY+τ, AgY+Ag_2Y+τ, Ag_2Y+Ag_3Y+τ and Ag+Ag_3Y+τ. A new ternary compound (τ phase) has been found. The compound, which is $Ag_3Cu_{12}Y_5$, has a limited solid solubility. The composition range is 23-27at.%Y, 9-19at.%Ag. τphase has a cubic structure of β-Mn (A13) type with a = 7.127(4) Å at 25℃. The maximum solid solubility of silver and yttrium in α-Cu at 500℃ is 0.8at.% and 1.5at.% respectively.



PS-21.03.27 THE CHANGE OF THE PHASE COMPOSITION OF THE NATURAL URANIUM OXIDE BY HEATING. L.V.Zvezdinskaya[1]*, V.N. Shtanov[2], A.V.Timofeyev[1]. [1]Institute of the geology of the ore deposits, petrography, mineralogy and geochemistry, Russian Academy of Sciences, Moscow, Russia; [2]Moscow State University, Moscow, Russia.

The changes of the morphology and phase composition of the pitchblende by the heating from 25° to 900°C were analysed by the thermomicroscopy and X-ray diffraction (the heating rate 10° C/min). For the investigation the cubic pitchblende (a_o = 5,452 ± 0,018 A) from one of the uranium deposits (North Kazakhstan) was picked out. The surface of the mineral heated to 300°C does not change; the parameter a_o being practically constant. In the range of 390 - 700°C the pitchblende is oxidized; this process is accompanied by the fissure formation. It proceeds most intensivly at 465 - 510°C and probably is connected with the partial polymorph conversion of the former formed rhombic U_3O_8 into the hexagonal modification. From 765°C the sample surface is warped, the fracture size being increased. At 800°C the pitchblende spherolites are decrepitated into the smaller ones. In the range of 885 - 905°C the mineral surface slowly raises over the metall container bottom