

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

The  $\gamma$ -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  $\gamma$ -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  $\gamma$ -solid solution over the carbon-containing  $\gamma$ -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 CHARACTERISTIC 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 particle (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.

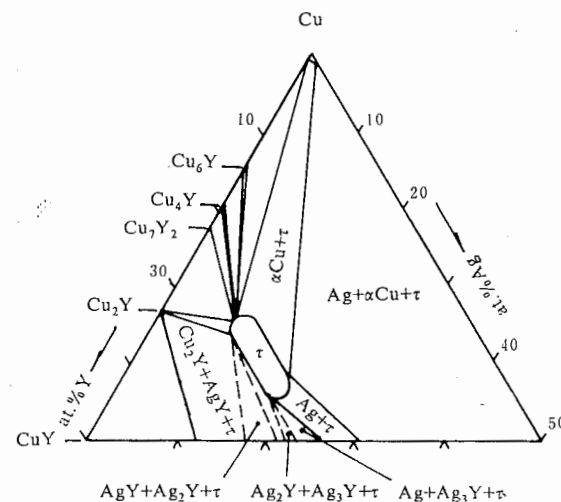
By experiment and theoretical research, we find that UFP possesses one kind of the characteristic of the self-phase-transition (SPT), namely, UFP has a trend of the spontaneous phase transition, it is name 'SPT effect' in this paper. The SPT process of UFP does not need that rigorous surroundings condition, which is necessary for the phase transition process of macroscopic matter (such as surroundings temperature, pressure, surroundings atmosphere, etc.). The SPT process of UFP depend on own microstructure, particle 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°C. 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 ( $\text{Cu} \geq 50\text{at.}\%$ ) at 500°C has been investigated by X-ray

diffraction. The section consists of seven single-phase regions:  $\alpha$ -Cu,  $\text{Cu}_6\text{Y}$ ,  $\text{Cu}_4\text{Y}$ ,  $\text{Cu}_7\text{Y}_2$ ,  $\text{Cu}_2\text{Y}$ ,  $\text{CuY}$  and  $\text{Ag}_3\text{Cu}_{12}\text{Y}_3$  ( $\tau$ Phase); sixteen two-phase regions:  $\text{Ag}+\alpha\text{Cu}$ ,  $\alpha\text{Cu}+\tau$ ,  $\text{Cu}_6\text{Y}+\tau$ ,  $\text{Cu}_4\text{Y}+\tau$ ,  $\text{Cu}_7\text{Y}_2+\tau$ ,  $\text{Cu}_2\text{Y}+\tau$ ,  $\text{Cu}_2\text{Y}+\text{AgY}$ ,  $\text{AgY}+\tau$ ,  $\text{Ag}_2\text{Y}+\tau$ ,  $\text{Ag}_3\text{Y}+\tau$ ,  $\text{Ag}+\tau$ ,  $\alpha\text{Cu}+\text{Cu}_6\text{Y}$ ,  $\text{Cu}_6\text{Y}+\text{Cu}_4\text{Y}$ ,  $\text{Cu}_4\text{Y}+\text{Cu}_7\text{Y}_2$ ,  $\text{Cu}_7\text{Y}_2+\text{Cu}_2\text{Y}$  and  $\text{Cu}_2\text{Y}+\text{CuY}$  and ten three-phase regions:  $\text{Ag}+\alpha\text{Cu}+\tau$ ,  $\alpha\text{Cu}+\text{Cu}_6\text{Y}+\tau$ ,  $\text{Cu}_6\text{Y}+\text{Cu}_4\text{Y}+\tau$ ,  $\text{Cu}_4\text{Y}+\text{Cu}_7\text{Y}_2+\tau$ ,  $\text{Cu}_7\text{Y}_2+\text{Cu}_2\text{Y}+\tau$ ,  $\text{Cu}_2\text{Y}+\text{CuY}+\text{AgY}$ ,  $\text{Cu}_2\text{Y}+\text{AgY}+\tau$ ,  $\text{AgY}+\text{Ag}_2\text{Y}+\tau$ ,  $\text{Ag}_2\text{Y}+\text{Ag}_3\text{Y}+\tau$  and  $\text{Ag}+\text{Ag}_3\text{Y}+\tau$ . A new ternary compound ( $\tau$  phase) has been found. The compound, which is  $\text{Ag}_3\text{Cu}_{12}\text{Y}_3$ , has a limited solid solubility. The composition range is 23-27at.% Y, 9-19at.% Ag.  $\tau$  phase has a cubic structure of  $\beta$ -Mn (A13) type with  $a = 7.127(4)$  Å at 25°C. The maximum solid solubility of silver and yttrium in  $\alpha$ -Cu at 500°C 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<sup>1</sup>\*, V.N. Shtanov<sup>2</sup>, A.V. Timofeyev<sup>1</sup>. <sup>1</sup>Institute of the geology of the ore deposits, petrography, mineralogy and geochemistry, Russian Academy of Sciences, Moscow, Russia; <sup>2</sup>Moscow State University, Moscow, Russia.

The changes of the morphology and phase composition of the pitchblende by the heating from 25°C to 900°C were analysed by the thermomicroscopy and X-ray diffraction (the heating rate 10°C/min). For the investigation the cubic pitchblende ( $a_0 = 5.452 \pm 0.018$  Å) 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  $a_0$  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 intensively at 465 - 510°C and probably is connected with the partial polymorph conversion of the former formed rhombic  $\text{U}_3\text{O}_8$  into the hexagonal modification. From 765°C the sample surface is warped, the fracture size being increased. At 800°C the pitchblende spherulites are decrepitated into the smaller ones. In the range of 885 - 905°C the mineral surface slowly raises over the metall container bottom

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

441

and then sharply falls down owing to the escape of the gases contained in the pitchblende. The sample phase composition after the heating to 900°C represents the mixture of the following uranium oxides:  $UO_2$  ( $a = 5.438 \pm 0.028 \text{ \AA}$ ), orthorhombic  $U_2O_5$  and  $U_3O_8$ , hexagonal  $U_3O_8$  and  $UO_3$ .

PS-21.03.28 PHASE TRANSITIONS IN  $Li_xV_2O_5$ . By H. Katzke and W. Depmeier, Inst. f. Mineralogie, Universität Kiel, D-W 2300 Kiel, Germany.

The quasi two-dimensional layer compound  $V_2O_5$  is one of the most extensively investigated compounds for the development of solid state batteries working at ambient temperature.

The electrochemical intercalation of  $Li^+$ -ions into the van der Waals-gaps of  $V_2O_5$  has been studied *in situ* under ambient conditions in aqueous  $Li^+$ -solutions. The results differ in several aspects from those of chemical or thermal intercalation. A series of electron transfer rate controlled isomorphous phase transitions could be detected, and a new orthorhombic vanadium bronze  $\zeta$ - $Li_xV_2O_5$  identified.

A theoretical model is based on repulsive O...O-interactions and helps to explain the observed shortening of the a-axes. A unified reaction-pathway diagram for electrochemical, chemical and thermal intercalation is presented, as well as a group-subgroup diagram connecting the various phases.

PS-21.03.29 Low-temperature structural study and phase transitions in superionic conductor tetramethylammonium trichlorogermanate(II),  $N(CH_3)_4GeCl_3$ . K. Fütterer<sup>1</sup>, W. Depmeier<sup>2</sup>, <sup>1</sup>Institut für Mineralogie und Kristallographie, TU Berlin, D-W-1000 Berlin 12, Germany; <sup>2</sup>Mineralogisch-Petrographisches Institut, Univ. Kiel, D-W-2300 Kiel 1, Germany

Tetramethylammonium trichlorogermanate(II),  $N(CH_3)_4GeCl_3$ , (TGC) is orthorhombic at ambient conditions, with space group  $Pna2_1$  and lattice parameters  $13.07 \times 8.89 \times 9.12 \text{ \AA}^3$ . The room-temperature crystal structure of TGC ( $\gamma$ -phase) has been determined (Depmeier, Möller, Klaska, Acta Cryst. 1980, B36, 803). DSC measurements revealed three phase transitions at 424K, 204K and 176K, respectively (Möller, PhD-thesis, Univ. Konstanz 1980). At 424K the compound undergoes a phase transition to a cubic, ionic conducting ( $\alpha$ -)phase,  $a = 6.552 \text{ \AA}$ , with a change of the electrical conductivity at  $T_c$  of 6 orders of magnitude.

This contribution reports structural studies on the two low-temperature phase transitions at 204K ( $\gamma$ - to  $\delta$ -phase) and 176K ( $\delta$ - to  $\epsilon$ -phase). Guinier powder and single crystal x-ray experiments were carried out, which clearly confirm the occurrence of two phase transitions, matching the transition temperatures observed by DSC within 5K.

Precession photographs of ( $h; k; 0,1,2$ ) and ( $0,1,2; k; l$ ) reciprocal lattice planes (indices refer to the orthorhombic room temperature lattice) were recorded at 183K and 158K. The exposures strongly suggest the occurrence of an incommensurately modulated phase (IC phase) between 200K and 170K, with  $q=0.145 \cdot b^*$ . Satellite reflections up to fourth order are observed, some of them being even more intense than the corresponding main reflections. No satellite reflections are observed in the  $hk0$ -plane, which points to a transverse modulation wave with the polarization vector perpendicular to the  $a,b$ -plane. A temperature dependent study of the  $\gamma$ - and the  $\delta$ -phase on a four-circle diffractometer is under work.

Possible structural models of the  $\delta$ - and  $\epsilon$ -phase will be discussed as well as the temperature dependent behaviour of the modulation wave vector and the modulation amplitude.

PS-21.03.30 LOW TEMPERATURE PHASE TRANSITION IN AN ALUMINATE SODALITE. By X. Hu, Hahn-Meitner-Institute Berlin and W. Depmeier<sup>\*</sup>, University Kiel, Germany.

Subject of this work is the aluminate sodalite  $Sr_8[Al_{12}O_{24}](SO_4)_2$ , abbreviated to SAS. It shows at least one phase transition at a temperature far below room temperature ( $T_c = 135K$ ), actually the first low temperature phase transition observed in the family of aluminate sodalites so far. Electron diffraction studies revealed an incommensurately modulated phase below the phase transition temperature (Hu 1992). There is also evidence for a lock-in phase transition at about 40K.

Aluminate sodalites possess a typical framework structure with non-framework guest species. Both the framework itself and the guest species are charged. Thus, there are strong Coulomb interactions between guests and host and between the two different guests. In the case of SAS the dominant interactions are described as follows:

- (i) repulsive interaction between framework oxygens and oxygens of the cage anion  $SO_4^{2-}$ ,
  - (ii) attractive interaction between cage cations and framework oxygens, and
  - (iii) attractive interaction between the cage cations and cage anions.
- Other interactions are possible, but less dominant.

We will present results characterizing the low temperature phase transition and speculate about the factors leading to this transition in SAS.

### References:

Hu, X. (1992). PhD Thesis. TU Berlin.

PS-21.03.31 STUDY OF PHASE TRANSITIONS IN  $LiNbO_3$  CRYSTAL BY MEANS ELASTIC SCATTERING OF LIGHT. By S.V. Ivanova and I.I. Naumova. Lebedev Physical Institute, Russian Academy of Sciences, Leninsky pr. 53, Moscow 117924, Russia.

Lithium niobate ( $LiNbO_3$ ) crystal at the room