

05.1-4 HIGH RESOLUTION TEM STUDY OF 2H-TaSe₂ AT LOW TEMPERATURES. By T. Onozuka,* N. Otsuka and H. Sato, School of Materials Engineering, Purdue University, W. Lafayette, IN 47907, U.S.A.

The hexagonal incommensurate phase of 2H-TaSe₂ has been investigated by means of high resolution transmission electron microscopy with the resolution of 3 Å between 85K and 120K. The temperature dependence of the orientation, the intensity and the width of stripe patterns (with the width of around 300 Å at 97K) which appear in the incommensurate phase has been investigated along with the lattice fringes of around 9 Å. These results can be summarized as follows: The stripe patterns are proven to be interference fringes due to the primary and secondary diffraction beams from the incommensurate phase. The incommensurate phase is hexagonal at higher temperatures but at least one of Q (modulation) vectors shift slightly as the temperature is lowered and the structure deviates from the hexagonal symmetry. The distortion is observed magnified as the rotation of the interference fringes. The fringes do not have any relation to the discommensuration as confirmed by the observation of the lattice fringes. The double honeycomb model for the incommensurate hexagonal phase can be denied definitely.

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05.1-5 THE INFLUENCE OF HIGH PRESSURE ON THE JAHN-TELLER EFFECT OF Cu²⁺ IN Cs₂PbCu(NO₂)₆. By H. Sowa, H. Ahsbals, E. Hellner, Institute for Mineralogy, and D. Reinen, Institute for Chemistry, University of Marburg, Lahnberge, 3550 Marburg, FRG

At 298K and 1bar Cs₂PbCu(NO₂)₆ crystallizes with an elpasolite-related structure. Caused by the Jahn-Teller effect in the ²E_g ground state of Cu²⁺ (e⊗E vibronic coupling) the lattice symmetry is reduced to orthorhombic (Fmmn: a=11.04(1)Å, b=11.01(1)Å, c=10.74(1)Å). The Cu(NO₂)₆ octahedra are tetragonally elongated; the cooperative order is antiferrodistortive, though there are planar dynamics in the (001) plane (Mullen et al., Solid State Comm. (1975) 17, 1249).

IR-spectroscopic and structural (X-ray and neutron diffraction) measurements at high pressure indicate that the temperature for the transition to the cubic high-temperature α-phase shifts to lower temperatures with increasing pressure. Also the extent of the local Jahn-Teller distortion decreases. At about 20kbar, Cs₂PbCu(NO₂)₆ becomes cubic (Fm3: a=10.72(1)Å). As may be deduced from the temperature ellipsoids of the N atoms, the Jahn-Teller distortion is now three-dimensional dynamic as in the α-modification (S. Klein and D. Reinen, J. Solid State Chem. (1978) 25, 295).

Presumably the potential barrier 2|β| in the lower potential surface of the "mexican hat" decreases with increasing pressure. At 20kbar and 298K the thermal energy kT (≈200cm⁻¹) reaches the warping energy 2|β| which determines the transition from the static to the dynamic Jahn-Teller effect.

We will also report on high-pressure results on K₂SrCu(NO₂)₆ with a ferrodistortive order of elongated Cu(NO₂)₆ octahedra.

05.1-6 SUPER-LATTICE MELTING IN Ag_{0.35}TiS₂.

By J.L. de Boer, K.D. Bronsema and G.A. Wiegers, Laboratory of Inorganic Chemistry, Materials Sciences Center, University of Groningen, The Netherlands.

In the system Ag-TiS₂ there are two structurally related phases, being a first- and a second-stage intercalate of silver in the layered compound TiS₂. In both phases silver atoms are on part (≈1/3) of the sites of triangular lattice planes; which are 12.2 Å apart in the second-stage phase and 6.43 Å apart in the first-stage phase. Both phases show fast-ionic conduction of silver.

Single crystals of first-stage Ag_{0.35}TiS₂ were grown by vapour transport. The three-dimensional melting of the silver sublattice, as reported recently¹⁾ to be of second-order nature, was studied by single crystal X-ray diffraction. A superstructure a/3 × a/3 × 2c, space group P31c is present at 110 K; the order-disorder transition to the substructure with a = 3.428 Å, c = 6.398 Å, space group P3m1, was studied by measuring the super reflections on a CAD-4 diffractometer as a function of temperature²⁾. In this way the temperature dependence of the occupancy of the silver sites in P31c; 2a, 2c and 2d, could be determined, T_c = 301 K.

1) R.M. Suter, M.W. Shafer, P.M. Horn and P. Dymon, Phys. Rev. B 26 (1982) 1495.

2) J.L. de Boer and A.J.M. Duisenberg. This conference.

05.1-7 POLYTYPISM AND PHASE TRANSITION OF Sb₅O₇I. 1. THE INTERLAYER INTERACTIONS. By I. R. Jahn and W. Altenburger, Institut für Kristallographie der Universität Tübingen, and V. Krämer, Kristallographisches Institut der Universität Freiburg, Germany.

In the layer structure antimony (III)-oxide-iodide (SOI) the phenomena of polytypism and structural phase transition combine in a unique manner. The polytypism of SOI shows special features. Neighbouring Sb₂[Sb₃O₇]-layers of pseudo trigonal symmetry are rotated by 180° against each other and coupled by the intermediate iodine ions. Since the Sb of the Sb₃O₇-prism can occupy two equivalent positions, neighbouring layers may be identical or enantiomorphic to another; therefore two basic structural units exist: the centrosymmetric type 2MC (modified Ramsdell notation) and the acentric 2MA (V. Krämer, Acta Cryst. (1975), B31, 234; (1978) B34, 2695). Eight higher polytypes, combinations of both, are identified till now, and among these there are three types with eight layers as the maximum stacking period.

The ferroelastic room temperature phase of all polytypic modifications is characterized by an antiferro-shifting of the iodine ions perpendicular to the stacking axis. However, the large spread of their transition temperatures (438 K ≤ T_c ≤ 481 K) clearly points to a well-defined influence of the stacking sequence. We analysed the structural data of 2MC, 2MA and 4MA (A. Bussmann, Thesis, Freiburg (1978)) and found three basic Sb-I-displacement patterns, realised in their pure form in 2MC, 2MA, and in the centrosymmetric 4-layered type 4TC, respectively. The other polytypes of SOI can be interpreted as isolated points in a ternary diagram with the three basic types as the pure end members (Fig. 1).

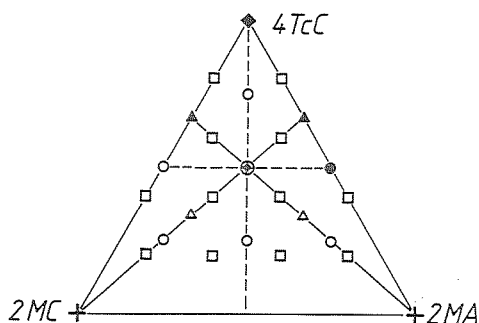


Fig. 1. The n -layered polytypes of $Sb_{507}I$ in the ternary diagram. Symbols for $n = 2$:+, 4 :◇, 6 :△, 8 :○, 10 :□. Crosses and filled symbols denote identified types.

To check the validity of this model, the transition temperatures of 2MC, 2MA, 4TcC were taken as a measure of the three different interlayer interactions. Then the T_C of the other types can be calculated. A very good agreement with the experimental transition temperatures is obtained.

In the case of the higher polytypes where T_C is not unambiguously related to a single stacking sequence, additional information can be gained by measurement of the optical extinction angle α ($0^\circ \leq \alpha \leq 13^\circ$). The value of α depends directly on the ratio n_f/n , where $n_f \leq n/2$ is the number of enantiomorphic layers in the n -layered polytype.

Using both the interlayer interactions and the extinction angle, a systematic treatment of all possible polytypes up to $n = 10$ will be given, from which we are able to predict T_C and α for a large number of new polytypes which have not been identified so far.

05.1-8 SHAPE CHANGE ASSOCIATED WITH PHASE SEPARATIONS ON AGING IN IN-PB AND IN-TL-PB ALLOY SYSTEMS. By Y. Koyama and O. Nittono, Faculty of Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan.

Some features of phase separations and shape changes during aging in In-(35-50)at%Pb and In-35at%Tl-13.5at%Pb alloys have been studied using X-ray diffractometry as well as electron microscopy. The In-Pb alloys undergo a phase separation from the fcc phase to a mixed (fcc+fct:c/a<1) phase on aging. With regard to the substructure, the {110} tweed structure develops in the early stage and finally the {110} twin forms inside the fct precipitates. The most interesting feature is that the precipitation of the fct phase proceeds by a bainitic mechanism, accompanying an appreciable surface relief. The surface relief indicates that the structural change in the separation is related to a cooperative atomic motion. On the other hand, the In-Tl-Pb alloys undergo first a phase separation from the fcc parent phase to a mixed (fct:c/a<1+fct:c/a>1) phase and subsequently from the mixed phase to the equilibrium (fcc+fct:c/a>1) phase. The former proved a spinodal decomposition by the appearance of the <100> modulated structure and a continuous change between the modulated and {100} banded structures during aging. The latter is characterized by the nucleation and growth of the fcc phase and also by the annihilation of the fct(c/a<1) phase. Moreover, all alloys, which were deformed in the fcc parent phase, showed an appreciable shape change when kept within a temperature range of the two-phase region and then heated to the fcc parent phase. The macroscopic shape change can be explained as a reversible shape memory effect in these separations on the analogy with that in a martensitic transformation. In the present study, the origin of the shape change is discussed in detail on the basis of the changes in substructures observed in both alloy systems.

05.1-9 HYDROGEN AND DEUTERIUM ORDERING IN β_1 - V_2H , β - V_2D AND β_2 - Ta_2D . By M. Hirabayashi,¹⁾ T. Kajitani,¹⁾ H. Kaneko,¹⁾ N. Niimura,²⁾ Y. Noda³⁾ and S. Sato⁴⁾, 1) The Research Institute for Iron, Steel and Other Metals, 2) Laboratory of Nuclear Science, 3) Faculty of Engineering, Tohoku University, Sendai, 4) The Institute for Solid State Physics, University of Tokyo, Tokyo, Japan

Transition metal hydrides (deuterides) V_2H , Ta_2H and Ta_2D undergo the order-disorder change of H (D) sublattice successively from β_1 through β_2 to α upon heating. X-ray and neutron diffraction studies were done to reveal the isotopic effect between V_2H and V_2D , and the successive disordering process in Ta_2D . As for β_1 - V_2H and β - V_2D , the crystal structures are found to be not isomorphic; symmetry and space group are respectively tetragonal, I41/amd and monoclinic, C2/m. The H (D) arrangement can be distinguished in the four-body correlation. The D arrangement in β_2 - Ta_2D , which is an intermediate phase at the temperature range of 40-60°C, was studied by neutron diffraction.* A proposed model is characterized with a statistical distribution of D atoms in tetrahedral sites of the sublattice with $\sqrt{2}a \times \sqrt{2}a \times a/2$ (a is the lattice parameter of bcc Ta). The results explain well the successive phase changes β_2 - β_1 - α of Ta_2H as well as Ta_2D .

* The work is progressing in cooperation with Drs. A. Schurtz and P. Leung at IPNS in Argonne Nat. Lab., Ill.

05.1-10 POTENTIAL ENERGY STUDY OF THE DISORDERED STRUCTURE OF INDOLE. By S. K. Talapatra, S. C. Biswas, S. B. Sarkar and Chitra Samanta, Department of Physics, Jadavpur University, Calcutta 700032, India

The pairwise nonbonded interaction potentials of the Buckingham 6-exp type were applied to the study of molecular reorientations in indole (C_8H_7N) crystals.

The variation of the intermolecular energy U (Kcal/mol) with rotation angle of the molecule about its best plane normal passing through the centre of gravity gave an interesting result. The indole molecule has no two-fold axis of symmetry about its plane normal, but two identical potential wells appeared in the energy curve and they were separated by an angle of 180°. This confirms the x-ray finding (Roychowdhury & Basak, Acta Cryst., B31, 1559, 1975) that indole has a disordered structure with molecules capable of assuming two alternative orientations.

Similar potential wells were also obtained from the energy study of 1:1 complex of indole with *s*-trinitrobenzene, in which the indole molecules are capable of assuming two alternative orientations (Hanson, Acta Cryst., 17, 559, 1964). The computations were made using the energy functions of Giglio (Nature, 222, 339, 1969) with our computer program (Talapatra et al., Ind. J. Phys. 55A, 281, 1981) with a summation radius of 15Å.