

**05.1-11** THE INFLUENCE OF MARTENSITE REHEATING RATE ON THE SHAPE MEMORY EFFECT. By Z. Bojarski, H. Morawiec, P. Matyja. Institute of Physics and Chemistry of Metals, Silesia University, Katowice, Poland

The kinetics of martensite to parent phase transformation has been studied as a function of the rate of heating using the high temperature X-ray diffraction method. The heating rate was in the range 0.5 - 200°C/min. For phase analysis it was necessary to plot the diffraction pattern in the angular region  $2\theta = 50 - 58^\circ$ . The following sequence of phase transformations during martensite reheating was found:  $\beta'_1 \rightarrow \beta_1 \rightarrow \alpha \rightarrow \gamma_2 \rightarrow \beta$ . This sequence is independent of the rate of heating. The temperatures of respective phase transitions were shifted to higher values with increase in heating rate. The temperature at which the peak of the ordered  $\beta_1$  phase appears, simultaneously indicates the start of shape recovery. Isothermal studies have shown, at higher temperatures, the transition from  $\beta'_1$  martensite to ordered  $\beta_1$  phase takes place more rapidly. Considering the dependence of the kinetics of the phase transformation on reheating rate of martensite, it can be concluded that the increase of heating rate results in the increase of the transformation rate.

As regards the shape recovery phenomenon, with rise of the velocity of transition from martensite to the ordered parent phase an increased percentage recovery has been observed.

Crystals supercooled to 22°C transformed completely with a click after an incubation period of minutes to 50 hours. Shape change was measured as change in inter-edge angles and seen as surface tilts. Traces of laths were taken as habit plane traces. Each crystal of I produced several orientations (variants) of II. The orientation relation was irrational, close to  $[001]_{II} \parallel [111]_{II}, (100)_{II} \parallel (101)_{II}$ . Martensite computations predicted distinguishably different habit planes and shape changes for different lattice-invariant shears (Fraser and Kennedy, Acta Cryst., (1974) A30, 13). Observed and computed shape, habit plane ( $5^\circ$  from  $\{210\}_I$ ) and O.R. were in agreement for LIS  $(100)[001]_I = (110)[100]_{II}$ . This could be due to transformation twinning displacements. Lattice deformations  $\eta_1 = \eta_2 = 1.192, \eta_3 = 0.596$  (// the common  $[111]$ ) (Kennedy, J.Sol.State Chem., (1980) 34, 31). This large structure-change is martensitic at lower temperature and the accommodation requirements are relaxed at higher temperatures. It is comparable with the NaCl  $\rightarrow$  calcite-like transformation in  $RbNO_3$ , where the lattice correspondence is the same and the twinned martensite substructure is not stable (Kennedy Kriven and Fraser, Proc. ICOMAT 1979, p. 208).

**05.1-12** MARTENSITIC AND ALTERNATIVE MECHANISMS OF CHANGE OF FIRST COORDINATION IN MnS AND  $NH_4Br$ . By S.W. Kennedy, W.L. Fraser and E. Summerville. Physical and Inorganic Chemistry Dept., University of Adelaide, Adelaide, S.A. 5001, Australia.

The transformation  $\gamma \rightarrow \alpha$  MnS, from wurtzite (CN4 in hcp) to NaCl type (6 in cpp),  $\Delta V = -20\%$  at 200°C, and NaCl to CsCl type in  $NH_4Br$  (I  $\rightarrow$  II),  $\Delta V = -16\%$ , equilibrium at 137°C, were examined by X-ray diffraction, light microscopy, and SEM, on single crystals 30-150 $\mu$ m wide.

MnS showed two different mechanisms, whilst in  $NH_4Br$  the mechanism changed in detail with temperature, being martensitic in supercooled crystals. Many crystals of MnS transformed suddenly with a click and production of regular shape changes. Three orientation relations, of which there were two in each crystal, differed by  $0^\circ, 5^\circ$  and  $15^\circ$  around  $[0001]_\gamma$  from  $[001]_\alpha // [0001]_\gamma, (010)_\alpha \parallel (1\bar{2}10)_\gamma$ . This mechanism is based on a lattice correspondence for which the deformations are large:  $\eta_1 = 0.76, \eta_2 = 1.32, \eta_3 = 1.23$ , but which is non-diffusive (Kennedy, J.Mater.Sci., (1974) 9, 2053). In other crystals which transformed more slowly, the orientation relation corresponded to basal plane shear. This mechanism requires diffusive hopping of some only of the cations, accompanied by uniform contraction of basal planes by 7.5%. This transformation can be compared with zinc-blende  $\rightarrow$  NaCl also in MnS, where there is a choice of a shuffle-dominated mechanism (cations diffuse one step, cube contracts) or a non-diffusive lattice deformation; and both occur (Kennedy, Harris and Summerville, J.Sol.State Chem., (1980) 31, 355).

$NH_4Br$  I crystals were platelets on  $\{100\}_I$ . At 130°C fine platelets of II had traces  $5^\circ$  from  $\langle 100 \rangle_I$  but growth was from edges at  $0.25\mu m hr^{-1}$ . At 100°C the product showed fine substructure but no clear shape change.

**05.1-13** PHASE TRANSITIONS IN n-DECYLAMMONIUMCHLORIDE. By K.J. Schenk and G. Chapuis, Institut de Cristallographie, BSP Dorigny, CH-1015 Lausanne (Switzerland). DSC and X-ray studies of  $C_{10}H_{21}NH_3Cl$  reveal the existence of three phases: a monoclinic phase up to 28°C (MRT), an orthorhombic phase between 28°C and 44°C (OIT) and another orthorhombic phase above 44°C. All the transitions have first order character. DSC measurements indicate the OIT-OHT transition to take place in two steps; these could however not be observed on powder diagrams. Repeated heating and cooling between 20°C and 60°C proved the phases and transition temperatures to be reproducible. A monoclinic metastable phase (MMRT) is obtained by crystallization at room temperature. Two first order transitions take it to OIT and OHT at 39°C and 42°C, respectively. The former is characterized by a striking thermal hysteresis and the latter by a huge transition enthalpy, 5.5 kcal/Mol.

The metastable phase disappears definitively as soon as the MMRT-OIT transition occurs (300 cal/Mol). The space group of the MMRT phase is  $P2_1$  and the cell contains two molecules. Cell parameters are:  $a=5.6996(4), b=7.1638(5), c=15.490(1) \text{ \AA}$  and  $\beta=91.297(5)^\circ$ . The structure is composed of interpenetrating layers of n-decylammonium ions alternating with layers of chlorine and nitrogen. The ammonium groups are linked to three chlorine atoms by hydrogen bonds. The hydrogen bonding scheme belongs thus to the  $L_3^3(6)$  type. The chains are packed according to the  $O_b$  pattern.

The MRT-OIT transition involves a doubling of the b- and c-axis. The c-axis decreases continuously during the OIT-OHT transition. This behavior is in stunning opposition to all other layer compounds which exhibit an abrupt increase of their c-axis during the corresponding transitions.

Single crystal studies of the unknown phases as well as a comparison with NMR data will be presented.