The Landau theory of symmetry in phase transitions has been applied to the consideration of ordering in cubic solids. The results provide a unified interpretation of some order-disorder processes in cation deficient rock-salt type solids, including Zr$_{1-x}$S and Sc$_{1-x}$S, which is based upon vacancy ordering in alternate 1,1,1 planes. In addition, an ordering based upon the equivalence of every sixth 420 plane will be shown to be a common feature of Lu$_2$S$_3$ and Sc$_2$S$_3$ as well as defect-ordering T1$_{1-x}$O$_{1-x}$. A combination of the two ordering types provides an interpretation of the recently reported electron diffraction patterns for low-temperature (below 600 K) ordered Sc$_{1-x}$S. The incommensurate nature of the vacancy ordering in this solid will be discussed.

The following compounds: Ni(NH$_3$)$_6$(C10$_4$)$_2$, Ni(NH$_3$)$_6$(BF$_4$)$_2$, Cd(NH$_3$)$_6$(C10$_4$)$_2$ and Cd(NH$_3$)$_6$(BF$_4$)$_2$ were investigated by X-ray powder diffraction in temperature range from 100K to 300K. In each case at low temperatures phase transition was observed. The transition temperatures $T_c$ were different for each studied compound. The crystallographic system, lattice type and unit cell parameters of the low-temperature phases were determined by numerical indexing of low-temperature powder patterns. Next, the most probable space groups were proposed what allowed to construct the hypothetical models of the obtained unit cells. The analysis of these models enabled to put forward the hypothesis on the reasons of the observed structural changes. This hypothesis let also to connect the transition temperatures with the rightly estimated parameters, i.e. - distances between external electronic shells of the neighbouring ions.

It was found that a superionic conductor $\alpha$-Ag$_2$S having $\alpha$-AgI-type structure with anion disorder and being stable above 226°C could be retained at low temperature by quenching. The crystal is fairly stable below room temperature but the transition from a disordered $\alpha$-phase to an ordered $\beta$-phase occurs above room temperature. Such a recovery process is time-dependent and its rate varies with sample temperature. A nucleation and a growth of the ordered phase in this non-equilibrium disordered phase was studied by measuring the integrated intensity and the width of a superlattice reflection with X-ray and neutron diffraction. A time-dependent variation of 111 Bragg reflection was measured at 100, 150, 180 and 220°C. It was found that the intensity variation with time took place with two steps. After a sufficient time of recovery the intensity curve can be fitted with a function of the square root of time. Before going into this step the curve deviates from the $\sqrt{t}$ dependence and in this first step a line broadening of the reflection can be observed. The line width (FWHM) is related to a mean coherent length for the area with ordered structure created in the disordered phase. A relation between the intensity and the width was found to be independent of the rate of recovery process. A mechanism of the nucleation and the growth of the ordered phase in the non-equilibrium disordered phase will be discussed. Neutron quasielastic scattering spectra were also measured at various temperatures for the equilibrium $\beta$ and $\alpha$-phase as well as the non-equilibrium $\alpha$-phase in order to study a dynamic property of Ag$_2$S with superionic nature. The results will also be discussed.

Here, we report on the behaviour of the integrated intensities and the full width at half maximum (FWHM) of the ~ 80 cm$^{-1}$ Raman bands (hard modes) in these compounds above and below $T_c$ which is interpreted in terms of interaction of the hard modes with central peak, flip mode and soft mode. The integrated intensity curves in the "intermediate phase" reveal a "precursor order parameter" type of dependence. From the FWHM vs. Temperature curves in the intermediate phase, the flip mode frequency is estimated to be $3 \times 10^{10}$ Hz.

The excess specific heat was measured up to $T_c$ * 60° K and interpreted in term of a three states Potts Model for Pb$_3$$(PO_4)$$_2$. In the As - P mixed crystals a second phase transition is found above the ferroelastic transition (R3m - C2/c) which confirms the appearance of an intermediate phase with local monoclinic symmetry in a trigonal matrix.

05.1-39 THE STRUCTURAL ASPECTS OF THE PHASE TRANSITION IN SOME HEXAMINE COMPOUNDS.

By E. Dynowska, Institute of Physics, Polish Academy of Sciences, Warszawa, Poland.

05.1-40 X-RAY AND NEUTRON DIFFRACTION AND SCATTERING STUDY ON THE NON-EQUILIBRIUM STATE OF $\alpha$-Ag$_2$S.


The Landau theory of symmetry in phase transitions has been applied to the consideration of ordering in cubic solids. The results provide a unified interpretation of some order-disorder processes in cation deficient rock-salt type solids, including Zr$_{1-x}$S and Sc$_{1-x}$S, which is based upon vacancy ordering in alternate 1,1,1 planes. In addition, an ordering based upon the equivalence of every sixth 420 plane will be shown to be a common feature of Lu$_2$S$_3$ and Sc$_2$S$_3$ as well as defect-ordering T1$_{1-x}$O$_{1-x}$. A combination of the two ordering types provides an interpretation of the recently reported electron diffraction patterns for low-temperature (below 600 K) ordered Sc$_{1-x}$S. The incommensurate nature of the vacancy ordering in this solid will be discussed.

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05. PHYSICAL PROPERTIES AND STRUCTURE