05.1–24 PHASE TRANSITIONS IN $KCdF_3$. By

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$KCdF_3$ has the cubic perovskite structure at high temperatures and undergoes two phase transitions at 463K and 478K. X-ray scattering experiments (Hidaka, Hosogi, Ono and Horai, Solid State Commun. 23, 503-506, 1977) indicated that both transitions occur because modes involving rotations of nearly regular octahedra condense out. They argued that, on cooling, the changes in symmetry are cubic → tetragonal → orthorhombic with the wavevector of the condensing mode being $\frac{1}{2}(\underline{a}^* + \underline{b}^*)$ at 478K and $\frac{1}{2}(\underline{a}^* + \underline{b}^* + \underline{c}^*)$ at 463K. However our scattering experiments on both powdered samples and single crystals of $KCdF_3$ show that the symmetry of the phase between 463K and 478K is orthorhombic rather than tetragonal.

It is shown that at 478K one of the triply degenerate octahedral rotational modes at $\frac{1}{2}(\underline{a}^*+\underline{b}^*+\underline{c}^*)$ as well as the singlet at $\frac{1}{2}(\underline{a}^* + \underline{b}^*)$ condense out simultaneously: at 463K a further component at $\frac{1}{2}(\underline{a}^* + \underline{b}^* + \underline{c}^*)$ condenses. A phenomenological theory based on Landau's theory of phase transitions is constructed which describes the sequence of transitions and allows one to calculate the temperature dependence of the order parameters.

05.1–25 PHASE TRANSITION IN $K_2Cd_2(SO_4)_3$: INVESTIGATION OF THE NONLINEAR DEPENDENCE OF SPONTANEOUS STRAIN AND MORPHIC BIREFRINGENCE ON ORDER PARAMETER AS DETERMINED FROM EXCESS ENTROPY MEASUREMENTS. By V. Devarajan and E. Salje, Institut für Kristallographie und Petrographie, Universität Hannover, Welfengarten 1, 3000 Hannover 1, Federal Republic of Germany.

Crystals of the langbeinite - structure $(M_2^+)(M_2^{++})(SO_4)_3$ represent the archtype ferroelastic without ferroelastic domain formation. Their phase transition mechanism is not yet fully understood although good structural data at different temperatures are available for some of them. Therefore, accurate differential scanning calorimetric and optical birefringence studies were carried out on single crystals of $K_2Cd_2(SO_4)_3$. From the measured excess entropy (ΔS) variation with temperature, information about the temperature evolution of the order parameter was elucidated. It was found that the first order character of the phase transition is due to a negative 4th order term in a Landau free energy expression and not due to the symmetry allowed 3rd order term which was found experimentally to be small. The spontaneous strains and morphic birefringences show different temperature dependences. A least square fit to a polynomial expression in order parameter revealed that the spontaneous strains have a strong quadratic and cubic dependence on order parameter and a negligible linear dependence. The optical birefringences were calculated theoretically from structural data and atomic polarisabilities. It was found that when variations in the spontaneous strains alone were taken into consideration the observed birefringence values could not be reproduced. Much better results were obtained when variations in sublattice coordinations were also taken into account. It is concluded that $K_2Cd_2(SO_4)_3$ is an improper ferroelastic because the macroscopic strain does not play the role of an order parameter although this would have been possible from symmetry arguments.

05.1–26 LOW TEMPERATURE PHASE TRANSITIONS IN $Cr_xMn_{1-x}As$. U. Sondermann* and K. Bärner+,

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The ternary phases $Cr_xMn_{1-x}As$ show at low temperatures $T < 320K$ a complex magnetic behaviour marked distingtly for $0.2 < x < 0.6$. Diffraction data suggest two antiferromagnetic modes Ha and Hc, a double helimagnetic arrangement with propagation vector along a and c of the orthorhombic MnP-type structure. Quite recently a reaxamination /1/ was done by neutron and x-ray diffraction in order to obtain the equilibrium diagram. For $x > 0.38$ nothing but a second order transition at about 230K from the paramagnetic to the Hc-state was observed. These results disagree with the diagram /2/ laid down by physical properties refering to further phase transitions or different magnetic ordering.
In order to solve this inconsistency we have done low temperature x-ray experiments on powder samples for which the magnetic susceptibility, Hall resistance, thermoelectric power and specific heat were known. The results clearly show a transition from a one phase area to a two (or more) phase one. Observing the Bragg peak intensities for various temperatures we were able to watch the increase and decrease of the different phases. At 77K the amount of the new phase decreases with increasing x. The transition temperature T_t becomes smaller for greater x, e.g. T_t=176K± 6K for x=0.4.

The experiments and their results will be represented and discussed with regard to the physical properties. The existence of a ferromagnetic phase is indicated.

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/2/ Wöhl, R., Berg, H. and Bärner, K., Phys. Stat. Sol. A 47 (1980) 179