05.1–49 PHENOMENOLOGICAL THEORY OF THE MAGNETOSTRUCTURAL TRANSITIONS IN MANGANESE ARSENIDE.

By M.Clin and P.Tolédano,Groupe de Physique Théorique, Faculté des Sciences,80000 Amiens,France.

At atmospheric pressure MnAs undergoes a succession of two phase transitions:a second-order phase transition at T_1=394K from the paramagnetic $P6_3/mmc1'$ phase to another paramagnetic phase of orthorhombic $Pnma1'$ symmetry, followed by a strongly first-order transition at T_2=313K to a ferromagnetic phase of $P6_3/mm'c'$ symmetry.A number of theoretical models have attempted to explain this sequence of phases,assuming an exchange magnetostrictive mechanism (C.P.Bean and D.S.Rodbell,Phys.Rev.126,104 (1962)) and a coupling between one component primary and secondary order-parameters (I.M.Vitebskii,V.I.Kamenev, and D.A.Yablonskii,Sov. phys.Solid state 23,121 (1981)). We present a phenomenological model based on the Landau theory of phase transitions,in which a three-dimensional order-parameter,transforming as the single irreducible representation τ_4 at the M Brillouin zone point ($\vec{k}=\frac{1}{2}\sigma\sigma$) of the hexagonal high-temperature space-group,explains the whole series of phases in MnAs.Thus the 394K transition is a purely structural (ferroelastic) transition with a doubling of the hexagonal cell,whereas the 313K transition is simultaneously magnetic and structural with a fourfold increase of the high-temperature cell. For this later transition,the magnetic and elastic properties are accounted via coupling terms which are linear in magnetization and strain,and respectively cubic and quadratic in the order-parameter components. The various macroscopic features of MnAs are discussed in connexion with the three-components order-parameter expansion,which includes sixth-degree invariants.Besides the antiferromagnetic helicoidal phase arising in MnAs at high-pressure is discussed.

05.1–50 A NEUTRON-DIFFRACTION STUDY OF THE FERROELECTRIC PHASE OF KH_2PO_4 AND KD_2PO_4.

By R.J. Nelmes, Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, U.K., and W.F. Kuhs, Institut Laue-Langevin, Avenue des Martyrs, 38042 Grenoble Cedex, France.

KH_2PO_4 (hereafter KDP) and its deuterated isomorph DKDP have a transition from a tetragonal paraelectric phase to an orthorhombic ferroelectric phase on cooling through T_c = 123 K in KDP and 230 K in fully deuterated DKDP. Extensive studies of the tetragonal phase, by us and our colleagues, have shown the temperature dependence of atomic thermal parameters above T_c to be inconsistent with the generally accepted pattern of atomic displacements in the ferroelectric soft mode. This conclusion has led directly to some substantial revision of ideas about the nature of the KDP transition. For example, new investigations of the soft mode through diffuse X-ray and neutron scattering show that it is necessary to include an acoustic component in the mode, a possibility not previously entertained: this mixed optic-acoustic soft mode both gives a significantly better fit to the diffuse intensities and also has atomic displacements in much closer accord with the structural results. To test this and other related new ideas, and to provide a better basis for further analysis of the diffuse scattering, it became necessary to obtain accurate structural parameters near T_c in the ferroelectric phase. We decided to work at T_c – 10 K, where KDP and DKDP are both known to be fully ordered. With an electric field applied to obtain monodomain single-crystal samples, we collected full three-dimensional neutron-diffraction data out to $\sin\theta/\lambda \sim 1.2 Å^{-1}$ from both KDP and DKDP. Data analysis reveals markedly anharmonic thermal motion for the proton (deuteron) and also the oxygen atoms in the ordered O—H(D)····O bonds. These and other significant details of the structure below T_c will be presented.

05.1–51 POSITIONAL AND ORIENTATIONAL ORDERING IN $R_{(1-x)}Ga_{2(1+x)}$ SOLID SOLUTION (R=RARE EARTH).

By L. Zevin and J. Pelleg, Ben-Gurion University of the Negev, Beer-Sheva, Israel and G. Kimmel and D. Dayan, Nuclear Research Center, Negev, Israel.

Previous studies in the light rare-earth-gallium systems have shown (Kimmel, Dayan, Grill, Pelleg, J. Less Com. Met. (1980) 75,133) that a wide range of solid solubility of Ga exists in the hexagonal RGa_2 compound up to about 80% of Ga. This solid solution is formed by an uncommon substitution of the R atoms by Ga-pairs(Pelleg, Zevin, J. Less Com. Met. (1981) 77,197). This fact is expressed in the formulae $R_{(1-x)}Ga_{2(1+x)}$. When the concentration of Ga in the solid solution (referred to as ε) is relatively moderate it is hexagonal and the space group remains P6/mmm with R in (a):000; 2Ga in (d): 1/3, 2/3, 1/2 and the Ga pairs oriented randomly in the directions $<10\bar{1}0>$ or $<11\bar{2}0>$. At concentrations close to 80% at Ga (x ≃ 1/3, and the composition close to RGa_4) we observed:

a) A strong orientational ordering of the pairs in the [1010] direction, which induce transition to an orthorhombic phase, where [010] of the orthorombic phase parallel to the [1010] of the hexagonal lattice, and the parameter of the orthorhombic cell is slightly greater than a $\sqrt{3}$.

b) A positional ordering of the centers of the gravity of the Ga pairs in the position 1/2, 1/2, 0 of the orthorombic lattice. 2/3 of these positions are occupied by the oriented Ga-pairs in a random manner. The space group of the ordered structure is Pmmm and the mode of ordering is well confirmed by comparison of calculated and observed intensities of the numerous superlattice lines. Heat effects were observed in all the light R system with Ga investigated, when the Ga concentration reaches saturation in the ε-phase, and thus complete ordering of the pairs occurred. The disorder transformation observed seems to be of the first order.

Pair-wise substitution of the R-atoms in RGa_2 helped to establish the common crystallographic features for crystalline phases in the Ga-rich side of the R-Ga systems. According to the fraction x of the R atoms substituted, these phases are: $RGa_{2(x=0)}$; ε - the solid solution $R_{1-x}Ga_{2(1+x)}$ (0 < x < 1/3) , ordered phase of RGa_4 type (x ≃ 1/3); RGa_6 (x = 1/2) and pure $Ga_{(x=1)}$. The common structural units for all these phases are hexagons f formed by Ga atoms. They are equilateral in RGa_2, corrugated in RGa_6 and planar, but distorted in pure Ga. Gradual replacement of R atoms by Ga-pairs and ordering of the pairs makes the structure of the saturated solution, i.e. RGa_4, very similar to the structure of RGa_6. The latter may be obtained by the replacement of the remaining 1/3 R atoms in the f: 1/2, 1/2, 0 of Pmmm by the Ga-pairs. The replacement of the remaining R-atoms in RGa_6 by the Ga-pair leads to the formation of a second net of hexagons, characterizing pure Ga.