05. PHYSICAL PROPERTIES AND STRUCTURE

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

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At atmospheric pressure MnAs undergoes a succession of two phase transitions: a second-order phase transition at $T_\text{C} = 394K$ from the paramagnetic $P_\text{6}$/mmm phase to another paramagnetic phase of orthorhombic $P\text{mmm}$ symmetry, followed by a strongly first-order transition at $T_\text{C} = 313K$ to a ferromagnetic phase of $P\text{6}$/ cubic symmetry. A number of theoretical models have attempted to explain this sequence of phases, assuming an exchange magnetostrictive mechanism (C.P. Bean and D.B. Rodbell, Phys. Rev. 126, 1041 (1962)) and a coupling between one component primary and secondary order-parameters. We present a phenomenological model based on the Landau theory of phase transitions, in which a three-dimensional order-parameter in the single irreducible representation $\Gamma_8$ 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.

For this later transition, the magnetic and elastic properties are accounted via coupling terms which are linear in magnetisation and strain, and respectively cubic and quadratic in the order-parameter components. For this later transition, the magnetic and elastic properties are accounted via coupling terms which are linear in magnetisation and strain, and respectively cubic and quadratic in the order-parameter components. The various macroscopic features of MnAs are discussed in connection with the three-components order-parameter expansion which includes sixth-degree invariants. Besides the antiferromagnetic halloidal 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 $KDP$.

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$KH_2Po_4$ (hereafter KDP) and its deuterated isomorph KDDP have a transition from a tetragonal paraseclectic phase to an orthorhombic ferroelectric phase on cooling through $T_\text{C} = 123K$ in KDP and 230K in fully deuterated KDDP. Extensive phase, by us and our colleagues, have shown the temperature dependence of atomic thermal parameters above $T_\text{C}$ to be inconsistent with the generally accepted model 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 $T_\text{C}$ in the ferroelectric phase. We decided to work at $T_\text{C} = 10K$, where KDP and KDDP 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 $\sin(\theta) = 1.2\AA^{-1}$ from both KDP and KDDP. Data analysis reveals markedly anharmonic thermal motion for the proton (deuteron) and also the oxygen atoms in the ordered 0-$\text{H(D)}\cdots\cdots\cdots$ bonds. These and other significant details of the structure below $T_\text{C}$ will be presented.

05.1-51 POSITIONAL AND ORIENTATIONAL ORDERING IN $R(1-x)Ga_2(1+x)$ SOLID SOLUTION ($R=$ RARE EARTH).

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Previous studies in the light rare-earth-gallium systems have shown (Kimmel, Dayan, Grill, Pelleg, J. Less. Com. Mat. (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 a uncommon substitution of the R atoms by Ga-pairs (Pelleg, Devin, J. Less. Com. Mat. (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 $R$) is relatively moderate and the phase group remains $P6_3/mmm$ with $R$ in $a<0.2$; $2a$ in $(d)$; $1/2$, $1/2$, $1/2$ and the Ga pairs oriented randomly in the directions $\langle 100 \rangle$ or $\langle 010 \rangle$. At concentrations close to 80% at $Ga (x = 1/2)$ and the composition close to RGa$_2$ we observed:

a) A strong orientational ordering of the pairs in the (1010) direction, which induce transition to an orthorhombic phase, were (1010) of the orthorhombic phase parallel to the [100] 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 orthorhombic lattice. 2/3 of these positions are occupied by the orientated Ga-pairs in a random manner. The space group of the ordered structure is $Pmmn$ and the node 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 $R$-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 R Ga$_2$ 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: R Ga$_2$($y=0$) $- \cdot$ the solid solution $R_{1-x}Ga_{2(1+x)}$ ($0 < x < 1/3$), ordered phase of R Ga$_2$ type ($x = 1/3$); R Ga$_2$ ($x = 1/2$) and pure Ga($y=1$). The common structural units for all these phases are hexagons formed by Ga atoms. They are equivalent in R Ga$_2$, occupied in Ga$_2$, 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. R Ga$_2$, very similar to the structure of R Ga$_2$. The latter may be obtained by the replacement of the remaining 1/3 R atoms in the $f$: 1/2, 1/2, 0 of $Pmmn$ by the Ga-pairs. The replacement of the remaining R-atoms in R Ga$_2$ by the Ga-pairs leads to the formation of a second net of hexagons, characterizing pure Ga.