

**05.1-20** HEXAGONAL PEROVSKITES OF THE  $\text{LnMnO}_3$  TYPE. By W. Sikora\* and V.N. Syromiatnikov, Joint Institute of Nuclear Research, Dubna, USSR and Institute of Metal Physics, Sverdlovsk, USSR.

On the basis of the Ln group-theoretical analysis of the structural and magnetic data of the  $\text{LnMnO}_3$  perovskites (Ln = Er, Ho, Lu, Sc, Tm, Y), it is shown, that in these compounds there should exist a phase which has the symmetry of  $D_{6h}^4$ . Earlier experimental investigations indicated the  $C_{6v}^3$  crystal symmetry in the vicinity of the magnetic phase transition, but the symmetry consideration of the magnetic structure based on the paramagnetic group  $C_{6v}^3$  does not agree with the idea of the one irreducible representation. Starting with the phase symmetry  $D_{6h}^4$  one can get all the experimentally observed magnetic structures (similarly as with  $C_{6v}^3$  group). Besides, it is shown that the structural phase transition  $D_{6h}^4 \rightarrow C_{6v}^3$ , with displacements of Mn atoms, must precede the magnetic one. The components of the magnetic moments in the basal plane are strictly connected with these displacements. This gives a new physical explanation of the possibility of the existence of two irreducible representations in magnetic structures. The above-mentioned phase  $D_{6h}^4$  in high temperature was observed in  $\text{YMnO}_3$ .

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**05.1-21** ON THE ORIENTATIONAL RELAXATION OF COMPLEX IONS AND THE HIGH TEMPERATURE FERROELECTRIC PHASES OF POLY AND MONO CRYSTALLINE  $\text{KNO}_3$ . By R. Kamel and Y.A. Badr, Faculty of Science, Cairo University, Cairo, Egypt.

It is well known that, under atmospheric pressure, there exist only two stable phases of potassium nitrate II & I, with a first order phase transition at 133°C. A third phase III can be obtained in a metastable state by slow cooling of phase I after annealing the sample above 185°C for a prolonged period. Thereafter, this metastable phase appears at about 125°C and disappears at about 114°C. Substituting the tetrahedral  $\text{NH}_4^+$  ions in place of  $\text{K}^+$  ions in the lattice forming the mixed crystal  $\text{K}_{1-x}(\text{NH}_4)_x\text{NO}_3$  stabilizes the ferroelectric phase III for values of x greater than about 0.2 and extends its existence over a wider temperature range.

The ferroelectric phase of  $\text{KNO}_3$  has recently raised considerable interest because of its simple crystal structure which renders the understanding of its ferroelectric nature less difficult. This inorganic compound provides also a good tool for the understanding of the mechanism of reversal of permanent dipoles under the application of an A.C. electric field.

It is presently aimed to give a more thorough study on changes occurring in these samples at such high temperatures above 185°C, in relation to the appearance of the ferroelectricity in these crystals, and the role of the  $\text{NO}_3^-$  ions in these phenomena which is here thought to be essential.

Differences in the ferroelectric behaviour of poly and single crystals of  $\text{KNO}_3$ , as detected by DTA & TMA, and dielectric constant and dielectric loss were detected. Infrared absorption spectroscopy and polarized light microscopy confirmed a proposed assumption about the

role of orientational motion of the complex ions on the detected phase transition above 185°C, and the ferroelectricity associated with it.

Pyro-current and dielectric loss were found to be more pronounced in the case of polycrystals than for single crystals.

The temperature dependence of the D.C. resistivity, dielectric constant, and dielectric loss showed thermal hysteresis of about 15°C between heating and cooling in the high temperature region.

We consider that two mechanisms contribute to the ferroelectric behaviour of  $\text{KNO}_3$  crystals above 185°C, namely, the reorientational disorder of the  $\text{NO}_3^-$  ions associated with dipoles, and the migration of the excess vacancy concentration existing in thermodynamic equilibrium at high temperatures.

**05.1-22** TETRAGONAL TO CUBIC PHASE TRANSITION STUDIES ON SILVER CHLORATE. By S.V. Suryanarayana and Vilas Deshpande, Department of Physics, Osmania University, Hyderabad-500007 India.

Silver chlorate crystallizes at room temperature in the tetragonal system and belongs to the space group  $I4/m$ . Some recent studies done with dilatometric, NQR and DSC techniques have shown that it undergoes a high temperature first order phase transition at about 412 K. The high-temperature phase has been reported to be cubic with a lattice constant equal to 9.42 Å at 435 K. However the Bravais lattice of this cubic phase or the type of the structure have not been investigated. Further, there is no systematic study reported on the thermal expansion behaviour of either the low-temperature or the high-temperature phases. In the present paper the results of the X-ray powder diffractometer work done by the authors at different temperatures below and above the transition point are being reported. It has now been established that the high-temperature phase has a primitive cubic lattice with a lattice parameter of  $6.800 \pm 0.001$  Å at 413 K. There is also evidence to suggest that the structure of this phase is the same as that of sodium chlorate. The possible mechanism of phase transition will be discussed. The temperature dependence of the coefficients of thermal expansion of the crystal below and above the transition temperature will be discussed.