ESRF	**Experiment title:** Thermodiffraction of the low-temperature to intermediate temperature phase and stucture determination of the low-temperature structure of $KNiCl_3$ and $RbMnBr_3$.	**Experiment number:** HE 02
Beamline: D16	**Date of experiment:** from: 20/01/97 to: 24/01/97	**Date of report:** 4-97
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Report:

$KNiCl_3$ crystalises with the hexagonal perovskite structure* and undergoes a series of structural phase transitions at 444K and 285-275K. At the first phase transition the crystal structure changes from a hexagonal unit cell of size a x a x c to an enlarged hexagonal unit cell of size $a\sqrt{3}$ x $a\sqrt{3}$ x c. This transition is driven by the need for a reduction of the space around the K - ion. The crystal structure at 3OOK. as determined by neutron powder diffraction, as well as by single crystal X-ray scattering, shows a disorder in the structure directed along the c-axis. This disorder has been clearly demonstrated by means of electron microscopy[2].

Machida *et* al.3 reported a first order structural phase transition over a temperature range of about 1OK at 285K. A large hysteresis has been observed for this transition. Petrenko et *al.*[4] reported that the low temperature structure is orthorombic but that in large crystals at T c 270K the room temperature (γ) phase is also still present. Such behaviour indicates a reorganisation of the crystal structure. While this experiment was awaiting execution, such a 'row like' structure in space group Pbcm or $Pca2_1$ was proposed[5].

We performed a powder thermodiffraction study on $KNiCl_3$. The crystal structure of the γ phase (300K) was determined for a data set taken at 290K in order to test the sample quality and the line shape of the reflections. It proved possible to refine the crystal structure to a reasonable degree of accuracy; (Pig. I). We found that the line shape ot the (001)-type reflections are much broader than the remaining reflections. This indicates the disorder of the structure along the c-axis in the γ phase. The refined structure is in agreement with the average structure which can be obtained from neutron and single crystal X-ray data. It is obvious that one of the most important facets of refining powder diffraction data from D16 is the determination of the lineshape parameters and that an appropiate code for anisotropically broadened reflections is a necessity.

A thermodiffraction experiment at a selected 20 was performed at various temperatures between 290K and 255K and in the reverse direction in order to study the hysteresis behaviour of the phase transition and in order to make a correlation with the dielectric measurements of Matchida[3]. We observed a detailed picture of the phase change, this was primarily due to the high resolution of the D16 diffractometer. A coexistence of the γ phase and the δ phase over at least 10K is present in the phase change temperature range; Fig.2. It was also observed on warming the sample up, that the phase transition to the γ phase starts to form at a temperature 10K higher. There are also indications that both γ and δ phase am present above and below the phase transition in each phase

Logistic problems during the experiment prevented us from obtaining data sets at intermediate temperatures during the phase transition in order to refine the changes in structure and the partial volume change of the γ to δ phases during the transition.

At present the structure of the δ phase is being modeled on a data set obtained at 220K. It is already obvious from the synchrotron data that the structure of the δ phase is not described by the space groups suggested b y Petrenko[5].

References

(1) D.Visser et al. Aca Cryst B36(1980) 28.
(2) D. Visser and A. Prodan. Phys. Stat. Sol. (a) 58 (1980) 481.
(3) K. Matchida et al. Solid State Comm. 91(1994) 17.
(4) O.A. Petrenko et al. J. Appl. Phys. (79) 6614
(5) O.A. Petrenko et al. J. Phys.: Condens. Matter (8) 10899.

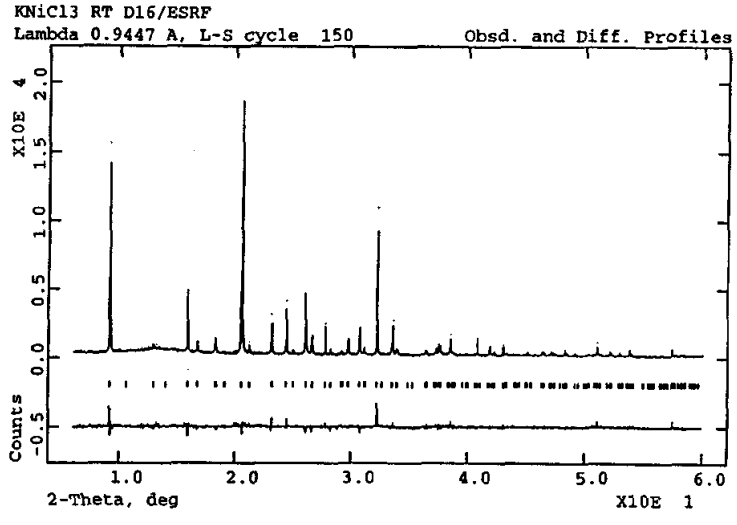

Fig.1 Diffraction Pattern of KNiCl3 at 290K fitted with the GSAS code.

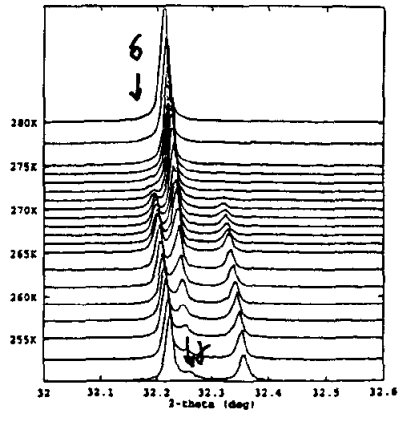

Fig.2 Thermodiffraction pattern of a selected 28 range. Showing the coexistence of they and δ phase and their precussors of both phases above and below the transitionThe temperatures of the transitions are slightly lower than the literature values. This due to the use of a cryostream cooler.