FINAL REPORT - Dr. A. W. Hewat, Harwell Fellow 1970-73

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1. Introduction

The whole of the work during the period of the fellowship was done within the Materials Physics Division, under the general supervision of Dr. B. T. M. Willis, and was concerned with neutron diffraction investigations of ferroelectric and related materials. These materials have attracted increasing attention in recent years, firstly because they have provided basic new information on the interatomic forces which determine the structure of crystals and their dielectric properties, and secondly because of their application to electromechanical and electronic devices. Our work has been on basic physical research, but close contacts have been made with organisations such as the Admiralty Research Laboratory at Holton Heath, Dorset and the Mullard laboratories, Redhill, Surrey. The work has also led to the introduction at Harwell of a new technique for neutron diffraction, "Profile Analysis", which has attracted considerable interest from SRC (University) and other users.

2. Brief description of Published Work

At a certain 'Curie' temperature, some crystals undergo a structural transition to a polar phase, and in a ferroelectric the polarity of this phase can be switched by an external electric field, just as in a ferromagnet an applied magnetic field will switch the direction of polarization of the magnetic domains. In 1960, Cochran showed how the dielectric properties of a ferroelectric depend on an instability developing in the crystal dynamics: for certain modes of vibration (soft modes) the interatomic forces are so evenly balanced that, when the temperature is lowered the balance is upset, and one or more of these soft modes 'condense' to give a change in the crystal structure. The presence of these soft ferroelectric modes means that the dielectric properties of the material become anomalous for temperatures near the transition temperature, and it is in part these unnusual dielectric properties which make the materials of interest for commercial applications. We have worked then on the lattice dynamics and structural transitions of such materials in an attempt to understand the physical reasons for their unique properties. This kind of knowledge should help with the development of new materials having the most desirable combinations of properties. For example, $K(Ta,Nb)O_3$ (KTN) and $Pb(Zr,Ti)O_3$ (PZT), two of the materials on which we have worked, are simple examples of compounds whose properties are sensitive to the relative proportions of (Ta,Nb) or (Zr,Ti). Unless the physical reasons for this are understood, the development of such compounds is a matter of trial and error.

The first results of our collaboration with Edinburgh University were reported at the 2nd European Meeting on Ferroelectricity in 1971, and published in Journal de Physique[1]. We showed that in KTN, the ferroelectric structure corresponds with the condensation of a particular soft mode. Further work on this structure was later published in Ferroelectrics[b]. We also showed that features in the X-ray diffraction pattern of this material were caused not by

atomic disorder as had been thought, but by the very anisotropic properties of the acoustic phonon dispersion surface i.e. by atomic vibrations. Further work on this aspect was reported at the 10th Annual Solid State Physics Conference[7]. Our fin l results on the lattice dynamics of this material will appear in J. of Physics C (Solid State)[14].

This experimental work on atomic vibrations was complemented by theoretical work on the problem of calculating atomic vibrational amplitudes. A new way of performing these calculations was described in J. of Physics C (Solid State)[4], and further applications of the method were published for ferrpelectric barium titanate[2] and the super-conductor niobium-tin[3]. In another paper we showed how the measurement of atomic vibrational amplitudes could be used to detect soft modes of vibration in ferroelectric perovskites[5].

Returning to the structural aspects of the ferroelectric transition, we measured the atomic displacements which occur when potassium niobate becomes ferroelectric, and related these to the soft vibrational modes and the dielectric properties of this material[9]. This work required the development of a new furnace for single crystal neutron-diffraction experiments, and the construction of this furnace was described in J. Applied Crystallography[8].

At this time we realized that a more powerful method would have to be developed for the neutron diffraction study of structural transitions in ferroelectric crystals. The Profile Refinement technique for neutron powder diffraction patterns was shown to be such a method, and a computer program developed for use at Harwell[10]. Some of the first results obtained with this technique were reported at the Institute of Physics Conference on "Electron Density and Related Topics"[11]. Results for the three ferroelectric transitions in potassium niobate were published in J.Physics C (Solid State)[12]. In a paper in Nature[13] we showed that the technique was also capable of revealing the role of hydrogen bonding in crystal structures such as ammonium dihydrogen phosphate (ADP). This material has an anti-ferroelectric transition which is practically impossible to study using conventional X-ray or neutron diffraction.

A full report on the structural transition in this material will be published in Acta Crystallographica[18].

The Profile Refinement technique has generated considerable new interest in the use of powder diffraction at Harwell. Scientists from several universities have started to use the technique or have proposals for experiments at Harwell on problems such as defect studies (Oxford), crystal structures transitions (Cambridge), ferroelectrics (Edinburgh), piezoelectrics (Admiralty Research) structure of minerals (Bradford), alloys (Sheffield), organic crystals (Surrey, Glasgow) and molecular crystals (London).

Our own work on Profile Analysis has been concentrated on structural transitions in ferroelectrics and antiferroelectrics, and this aspect was recently reported at the 3rd International Meeting on Ferroelectricity [15]. In particular the latest work on barium titanate [16] and sodium niobate [17] will be published shortly. A review paper on the Profile Refinement technique is in preparation with Dr. B. T. M. Willis[19].

I would like to thank Dr. Willis for his collaboration and generous advice in all of this work, Dr. G. G. E. Low and Dr. V. S. Crocker for making me welcome in the Materials Physics Division and the Fellowship Board for granting me a fellowship under which all of the above work was performed.

A. W. HEWAT
October 1973

Publications of A. W. Hewat 1972/73

1. "KTN, Structural and Dynamical Studies"
with G. Zaccai and K. D. Rouse
2nd Europ. Meet. Ferroelect., Dijon (1971)
published in J. de Physique 33 (No. 4 suppl.) C2 (1972).

2. "Vibrational Amplitudes in Ferroelectric Tetragonal Barium Titanate"
J. Phys. Soc. Japan 32, 1156 (1972).

3. "Mössbauer Recoil Free Fraction and Debye-Waller Factors for Nb_3Sn"
Phys. Letters 39A, 249 (1972).

4. "Vibrational Amplitudes and Debye-Waller Factors from Elastic Constants and Raman Frequencies"
J. Physics C 5, 1309 (1972).

5. "Low Frequency Zone Boundary Modes in Perovskite Ferroelectrics Indicated by Anistropic Debye-Waller Factors"
Phys. Stat. Solidi (b) 53, K33 (1972).

6. "Soft Modes and the Structure of Ferroelectric Tetragonal Potassium Tantalate Niobate"
with K. D. Rouse and G. Zaccai
Ferroelectrics 4, 153 (1972).

7. "Sharp Low Frequency Valleys in the Acoustic Dispersion Surfaces of Ferroelectric $K(Ta,Nb)O_3$", with G. Zaccai
10th Annual Solid State Physics Conf., Manchester, 3-5 Jan. 1973 (unpublished).

8. "Three Dimensional Vacuum Furnace for Neutron Diffraction from Ferroelectric Crystals"
J. Appl. Cryst., 6, No. 1, 42 (1973).

9. "Soft Modes and the Structure, Spontaneous Polarization and Curie Constants of Perovskite Ferroelectrics: Tetragonal Potassium Niobate"
J. Physics C, 6, pp 1074-1084 (1973).

10. "The Rietveld Computer Program for the Profile Analysis of Neutron Diffraction Powder Patterns, Modified for Anisotropic Thermal Vibration"
UKAEA Research Group Report No. R7350, January 1973.

11. "The Neutron Powder Pattern Profile Refinement Technique for the Precise Determination of Crystal Structures"
Inst. Physics Conf., "Electron Density and Related Topics" Cardiff 16-18 April 1973.

12. "Cubic-Tetragonal-Orthorhombic-Rhombohedral Ferroelectric Transitions in Perovskite Potassium Niobate: Neutron Powder Profile Refinement of the Structures".
J. Physics C, 6, 2559 (1973).

13. "Location of Hydrogen Atoms in ADP by Neutron Powder Profile Refinement"
Nature, in press (1973).

14. "Soft Modes and the Structure of Ferroelectric Tetragonal KTN
II The Lattice Dynamics of the Cubic Phase"
with G. Zaccai
J. Phys. C., in press (1973)

15. "Neutron Powder Profile Refinement of Ferroelectric and Antiferroelectric Crystal Structures: Sodium Niobate at 22°C".
3rd Int. Meet. Ferroelect., Edinburgh 10-14 Sept 1973
to be published in "Ferroelectrics".

16. "Structure of Rhombohedral Ferroelectric Barium Titanate"
Ferroelectrics, in press (1973)

17. "Antiferroelectric Structure of Sodium Niobate I The T1 and T2 Phases"
Phil. Mag., in preparation (1973).

18. "Hydrogen bonding and the Paraelectric and Antiferroelectric Structures of Ammonium Dihydrogen Phosphate".
Acta Cryst., in preparation (1973).

19. "The Neutron Powder Profile Refinement Technique and Crystal Structure Transitions - a Review"
with B.T.M. Willis
J. Appl. Cryst., in preparation (1973).