Neutron Scattering Studies of Ferroelectric Crystals with Incommensurate Phases

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General survey is given of the recent results obtained by the authors on the incommensurate ferroelectrics by means of the neutron scattering method. They are classified according to the symmetry requirement, crystal structures and other properties observed. Relation between the symmetry requirement and the magnitude of the incommensurate parameter is pointed out and its relevance to the origin of the lattice instability is considered.

§1. Introduction

In the present paper we give a brief survey of the neutron scattering studies carried out for the past few years by authors. The list of the crystals under investigation is given in Table I. In these studies we have concentrated on the measurements of the temperature dependence of the primary and higher order lattice modulations in the incommensurate phases and particularly in the vicinity of the incommensurate to commensurate phase transitions. In a few crystals the dynamical aspects of the transitions have been investigated by the neutron inelastic scattering method.

The general survey of the incommensurate ferroelectrics is carried out by trying in §2 to classify the crystals according to their behavior. Then in §3 the smallness of the deviation of the incommensurate wave vectors from the commensurate ones is discussed in relation to the symmetry and the origin of the incommensurability.

§2. Classification

In order to group the incommensurate crystals according to their behavior we need some criteria for classification. First let us pay attention to the wave vectors which describe commensurate structures to which incommensurate phases are closely related. An incommensurate

Table I. Incommensurate crystals under investigation

$(ND_4)_2BeF_4$,[1,2] Rb_2ZnBr_4,[3] Rb_2ZnCl_4,[4] K_2ZnCl_4,[4] $\{N(CH_3)_4\}_2ZnCl_4$,[5] $\{N(CD_3)_4\}_2ZnCl_4$,[6] $\{N(CH_3)_4\}_2CuCl_4$,[7] $SC(NH_2)_2$,[8] $SC(ND_2)_2$,[8] Deuterated ammonium Rochelle salt,[9] $RbD_3(SeO_3)_2$.[10]

structure is generally described by a wave vector

$$q_1 = q_c + \delta \qquad (1)$$

q_c gives the wave vector characterizing the commensurate structure and δ indicates the deviation of the incommensurate structure from it. Satellite reflections appear when the scattering vector Q equals $G + nq_1$, where G is a reciprocal lattice vector and n is a integer.

The first clue of the classification is to ask whether q_c is zero or finite. This clue seems really to work. For example incommensurate ferroelectrics are classified by q_c into proper or improper ferroelectrics. The polarization itself is modulated in the incommensurate phases when $q_c = 0$ and the spontaneous polarization appears properly at the incommensurate to commensurate phase transition. When $q_c \neq 0$ the primary lattice distortion modulated with the wave vector q_1 induces the polarization wave as the secondary lattice distortion which transforms eventually into the spontaneous polarization in the commensurate phase. In this case the ferroelectricity is improper. Although all the observation falls nicely in this classification this criterion is not adequate one from the basic point of view. More appropriate criterion is to ask whether the Lifshitz condition is satisfied at q_c or not. As was given a proper interpretation by Levanyuk and Sannikov[11] the Lifshitz condition is a criterion as to whether an incommensurate structure is required from the symmetry of a crystal. If the Lifshitz invariant exists at q_c for the irreducible representation characterizing a second order phase transition, an incommensurate structure is a natural consequence of the symmetry. On the other hand

when the Lifshitz invariant does not exist, a commensurate structure is a requisite of the symmetry. If this is the case only some special situation built in the free energy of the crystal gives rise to an incommensurate structure.

According to this criterion the incommensurate structures are divided broadly into two main categories: those which accord with the Lifshitz condition and those which do not. Let us call them the incommensurate structures of the *Lifshitz type* and those of *non-Lifshitz type* respectively. Of the crystals listed in the Table I only thiourea belongs to the non-Lifshitz type and all others fall in the Lifshitz type. Another example of the non-Lifshitz type crystal is $NaNO_2$.

The Lifshitz criterion leads us to predict existence of an incommensurate phase. The incommensurate phase of $RbD_3(SeO_3)_2$ has been found[10] in this way. The deviation δ being very small, it would have been difficult to notice the incommensurability without this criterion. If an incommensurate phase is non-existent though the criterion predicts it, we take it that a potential incommensurate phase is overridden by the commensurate phase because of the overwhelming commensurability energy.[13] Ammonium Rochelle salt[9] is one of the example of this type, though an incommensurate lattice modulation of another kind coexists within the commensurate phase.

In the next step we classify the crystals with respect to the structures. In this regard the β-K_2SO_4 and related structures are rich in the incommensurate crystals. Grouping all the crystals into β-K_2SO_4 and others, we further classify the former crystals with respect to the commensurate wave vector q_c to which the incommensurate structures are related. Most of the incommensurate structures with the β-K_2SO_4 structure are related to $q_c = 1/3$, while $(ND_4)_2BeF_4$ is related to $q_c = 1/2$ and $\{N(CH_3)_4\}_2ZnCl_4$ to $q_c = 2/5$.

Fractions which constitute the values q_c decide the order of the commensurability energy with respect to the primary order parameter. For example, in K_2SeO_4 it is given by[13] $Q^3(q_c)P_z$ which is sixth order with respect to the primary order parameter $Q(q_c)$, with P_z being the induced spontaneous polarization. For $q_c = 1/2$ it is of fourth order while in case $q_c = 2/5$ it is of tenth order. This energy determines

the degree the crystals tend to approach commensurate structures and accordingly the temperature ranges of the incommensurate phases and the magnitudes of the spontaneous polarization which appears abruptly at the Curie temperature. The lower the order of the commensurability energy, the narrower the temperature range of the incommensurate phase and the larger the spontaneous polarization.

Additional clue of the classification comes from the nature of lattice distortions in the commensurate phase. The macroscopic lattice distortion taking place in the commensurate phase, whether they are proper or improper in the sense mentioned earlier, can either be polarization or non-polar lattice strain. In the latter case the crystal can be ferroelastic in the commensurate phase. In case of incommensurate crystals belonging to the β-K_2SO_4 structure the secondary lattice distortion induced by the coupling to the primary Σ_2 lattice distortion is of the Σ_4 nature which ends up as either polarization P_z or shear strain S_{xz}.[13] The former has been always realized but the latter case was recently found[7] in $\{N(CH_3)_4\}_2CuCl_4$, which has been confirmed to be ferroelastic.[14]

The distinct dynamical nature of the lattice instability related to the incommensurate phase transitions is also a clue to the classification of the incommensurate systems. In K_2SeO_4[13] and (Rb_2ZnBr_4) well defined soft phonon has been observed above the transition temperature by the inelastic scattering of neutrons. On the contrary the fluctuation of the relaxational type has been observed in $(ND_4)_2BeF_4$ in which the relevant phonon mode shows only a slight sign of softening.[2] As was well known the fluctuation in $NaNO_2$ is relaxational. Thiourea falls in the intermediate category in which the damping of the relevant phonon mode is conspicuous.

§3. **Magnitude of δ and Origin of Incommensurability**

In §2 we have pointed out the importance of distinction between the symmentry-allowed and symmetry-forbidden incommensurate structures, namely those of Lifshitz type and non-Lifshitz type. The formal distinction with respect to symmetry reveals its real implication in the magnitude of the parameter, δ, which indicates the deviation of the incommensurate structures from the related commensurate

structures. The range of the parameter δ is summarized in Fig. 1 separately for each group of crystals belonging to the Lifshitz type and those of non-Lifshitz type. In the figure the arrows indicate the change of δ within the incommensurate phases. It is clear that the magnitude of δ of one group makes a striking contrast to the other. The contrast is also clearly visible in the crystals other than the incommensurate ferroelectrics. A few examples are indicated in the figure.

This observation on the magnitude of the parameter δ in relation to the symmetry suggests that there should be a clear distinction as to the origin of the incommensurability between the Lifshitz and non-Lifshitz types. In the Lifshitz type incommensurate systems the incommensurability can not be attributed to an *accidental* cancellation of the short-range force by the Coulomb force for a mode with an incommensurate wave vector, because if it is the case there is no reason for the incommensurate lattice-instability to take place within a very restricted range of the wave vector in the very vicinity of the commensurate wave vector. The alternative interpretation is that the lattice instability is primarily commensurate and this lattice instability is disturbed by an insignificant concomitance of atomic forces of different origin. One may say that in the case of Lifshitz type the crystal can not settle the period of lattice distortion wave to an exact commensur-

able value even if the lattice instability takes place primarily with a commensurate wave vector. On the contrary in the case of lattice instability of non-Lifshitz type only a significant cause can bring about an incommensurate lattice instability around the commensurate points of non-Lifshitz type. Or one may say that the crystal has a strong tendency to settle the period of instability to the commensurate value in the non-Lifshitz type. This speculation is supported by a beautiful example of the existence of a forbidden band of the incommensurate wave vectors in the vicinity of the commensurate wave vector in the modulated structure of AuCu type alloys,[15] in which a compositional order-disorder type transition takes place at the zone boundary of the non-Lifshitz type. The primarily commensurate lattice instability in the cases of the Lifshitz type should have a certain origin in the geometry of the crystal which is not evident in the interpretation of the lattice instability in K_2SeO_4 by the rigid ion model.[16]

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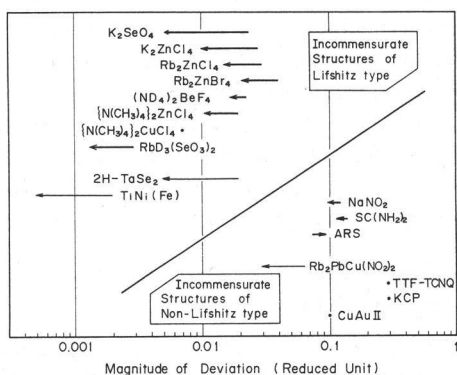16) M. S. Haque and J. R. Hardy: Phys. Rev. **B21** (1980) 245.

Fig. 1. Magnitude of deviation parameter δ. Arrows indicate change of the parameter in the incommensurate phase. Solid points give the magnitudes if they are invariable.