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$Ba_2NaNb_5O_{15}$에서의 Incommensurate상의 초공간 대칭성

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Superspace Symmetry of the Incommensurate Phase in Barium Sodium Niobate

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요 약

Incommensurate 구조에 기인한 회절점들의 체계적인 소멸칙 (extinction rule)의 분석을 통하여 $Ba_2NaNb_5O_{15}$ (BSN)에 나타나는 incommensurate상의 대칭성이 4차원 초공간군(superspace group) $C^{cmm2}_{1\,s\,\bar{1}}$ 에 속함을 알 수 있었다. Lock-in superstructure의 공간군은 Ima2(C^{22}_{2v})임을 밝혀 내었으며, 그리고 BSN에서의 incommensurate상의 원인을 간략하게 논술하였다. 특히 HREM이미지를 통하여 discommensuration이 존재함을 확인하였다. 덧붙여, BSN의 구조상 전이에 대하여 군론적 해석을 제시하였다.

Abstract

It is shown that the symmetry of the incommensurate phase in $Ba_2NaNb_5O_{15}$(BSN) belongs to the four dimensional superspace group $C^{Cmm2}_{1\,s\,\bar{1}}$ from an analysis of the systematic extinction of the extra reflections due to the incommensurate structure. The resulting superstructure is characterized by the space group Ima2(C^{22}_{2v}) and the origin of the incommensurability in BSN is briefly discussed. Especially, HREM image have shown the presence of discommensurations. In addition, a group-theoretical consideration of structural phase transitions in BSN is suggested.

INTRODUCTION

The structure of an ordinary crystal has a three-dimensional space-group symmetry. For incommensurate crystals, however, the translation symmetry is destroyed in at least one direction, but are not disordered (amorphous) substances.[1] The order becomes apparent if one considers the Fourier expansion of the matter distribution in space : one sees that the Fourier wave vectors are still expressible as integral linear combination of basic ones, but now (3 + d) of them are needed.[2] The symmetry of an incommensurate crystal can be described by the space group in a higher-dimensional space…superspace ; this space group is called a superspace group.[1, 2] The physical incommensurate crystal is a three dimensional section of a generalized crystal structure in superspace called the supercrystal.

Normally one can select a subset of three basic vectors in such a way that they span a reciprocal lattice and describe a so-called basic (or average) structure which does have lattice periodicity and which describes a kind of average crystal structure. The remaining basic vectors are needed in order to describe the deviation of the incommensurate crystal with respect to the basic structure. In the modulated crystals, the Fourier wave vectors are integral linear combination of $\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$ and $\vec{q}$, where the first three vectors span the reciprocal lattice of the undistorted basic structure and $\vec{q}$ is the wave vector of the modulation.

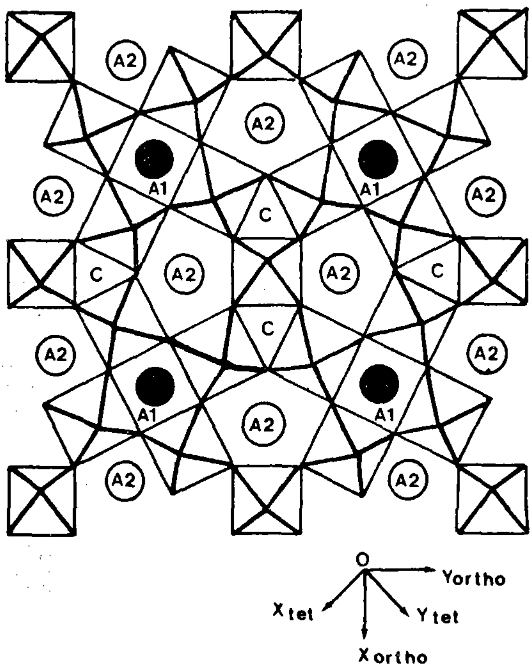

Fig. 1. The average structure of BSN projected on the basal plane. The Al sites are filled with Na, the A2 sites are filled with Ba and the C sites are empty. The relation between the tetragonal axes and orthorhombic is shown : $a_0 = a_t + b_t$ and $b_0 = -a_t + b_t$

$Ba_2NaNb_5O_{15}$ with the tetragonal tungsten bronze (TTB) structure has successive structural phase transition (see Table 1). Neutron scattering performed by Schneck et al.[3] has shown that the modulation wave vector $\vec{q}$ is :

$$\vec{q} = (1+\delta)(\vec{a}_t^* + \vec{b}_t^*)/4 + \vec{c}^*/2 = (1+\delta)\vec{a}_o^*/2 + \vec{c}^*/2 \quad (1.1)$$

as confirmed by our electron diffraction patterns [4], where $\vec{a}_t^*$, $\vec{b}_t^*$ and $\vec{c}^*$ being the reciprocal lattice vectors of the tetragonal "normal" phase stable above T_I and $\vec{a}_{os}^*$ being that of the orthorhombic "average" lattice (see Fig.1). One of the principal objectives of the present paper is to formulate the superspace symmetry of the incommensurate phase of BSN by observing the systematic absences which occur in its diffraction patterns.

EXPERIMENTAL PROCEDURE

$Ba_2NaNb_5O_{15}$ materials were prepared by conventional solid-state reaction process. Specimens suitable for electron microscopy were prepared in a two-step process. In the first step, the crushed crystalline fragments were glued to electron microscope copper rings. Subsequently, the specimens were thinned further by ion beam milling.

All observations were performed on a JEOL JEM 2000EX electron microscope equipped with a top entry goniometer stage at an operating voltage of 200 kV. For the present investigation specimens have been first annealed near 280℃ during 16−24 hours and then quenched in water.

Table 1. Summary of successive structural phase transitions in BSN.

Phase	V	IV	III	II	I
Temp.(℃)		−160	T_C=270	T_I=300	580
	Tetragonal (?)	Commensurate Orthorhombic	Incommensurate Ferroelastic	Tetragonal Ferroelectric	Tetragonal Paraelectric
Lattice Parameter	(?)	$2a_0 \times 2b_0 \times 2c$	(basic lattice) $a_0 \times b_0 \times c$	$a_t \times b_t \times c$	$a_t \times b_t \times c$
Space Group	(?)	Ima2(C_{2v}^{22})		P4bm(C_{4v}^{2})	P4/bmm(D_{4h}^{5})

ANALYSIS OF THE ELECTRON DIFFRACTION PATTERNS

1) Four Dimensional Description

As shown by de Wolff[6], a one-dimensionally modulated structure is conveniently described by using four dimensional space. Then all reflections in the modulated structure can be assigned by using four Miller indices h, k, l, m as

$$\vec{K}=h\vec{a}^{*}+k\vec{b}^{*}+l\vec{c}^{*}+m\vec{q},\ h,\ k,\ l,\ m \text{ integers} \quad (3.1)$$

where $\vec{a}^{*}$, $\vec{b}^{*}$, $\vec{c}^{*}$ are the basic vectors for the basic structure (in the present case, Cmm2) and $\vec{q}$ is the wave vector of the modulation wave which is given by $\alpha\vec{a}^{*}+\beta\vec{b}^{*}+\gamma\vec{c}^{*}$ with α, β, γ, not all fixed rational numbers.

In BSN, the modulation wave vector $\vec{q}$ is (see Fig.2(b)) :

$$\vec{q}=(1+\delta)\vec{a}_{o}^{*}/2\times\vec{c}^{*}/2$$
$$=\vec{q}_{i}+\vec{q}_{r} \quad (3.2)$$

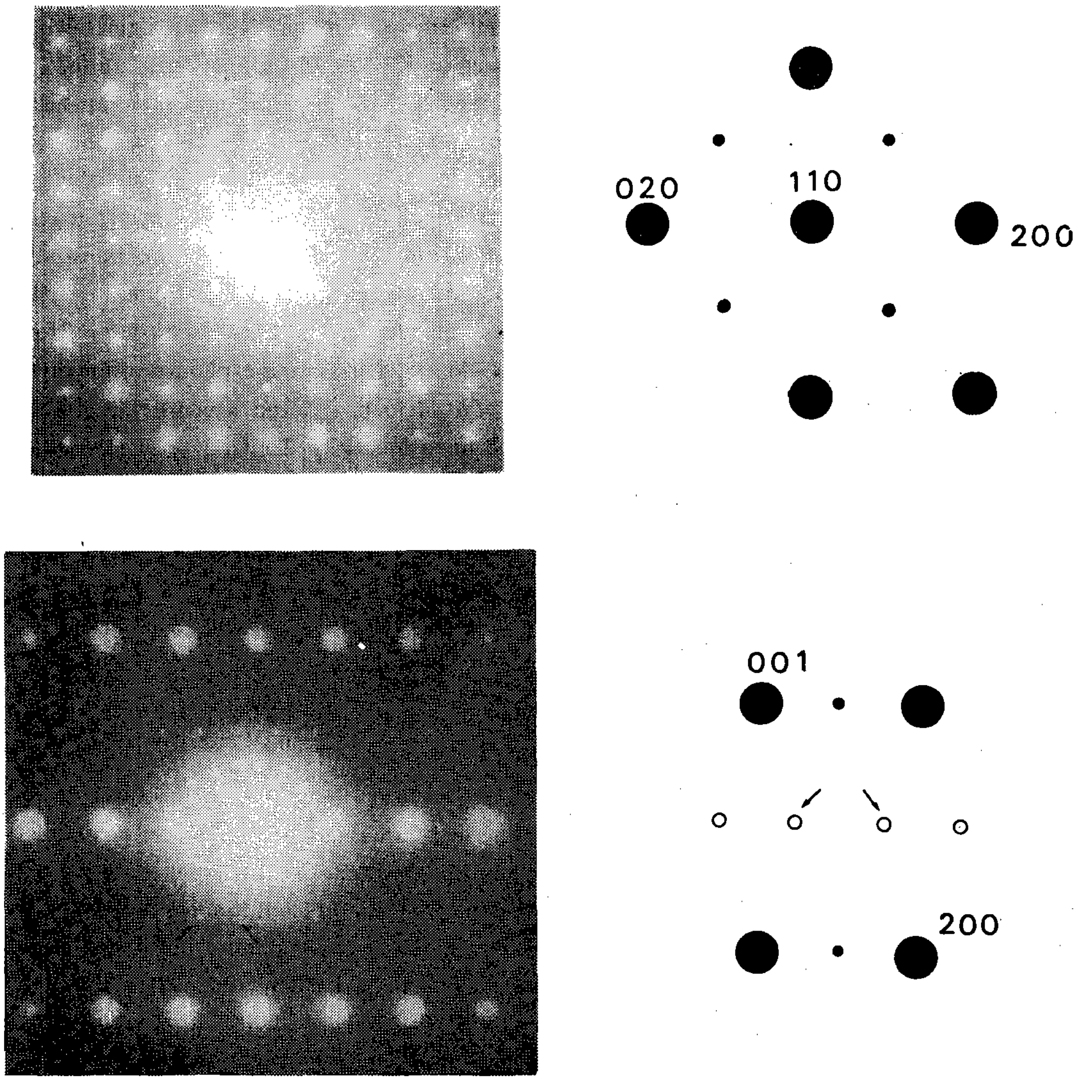

Fig. 2. Electron diffraction pattern of incommensurate phase along the [001] zone axis (a), along the [010] zone axis (b). Incommensurate reflections are indicated by arrows. Notice the superstructure spots.

where the coordinate of $\vec{q}_i=(1+\delta)\vec{a}_o^*/2$ is irrational, i.e. representing a incommensurate modulation and that of $\vec{q}_r=\vec{c}^*/2$ is rational 1/2, i.e. representing c−doubling.

If $\vec{q}_r\neq0$, satellites in one row or plane are not assigned by eq.(3.1) to the same reflection.[7] To avoid this, it is convenient to choose another basis $\vec{a}_s^*$, $\vec{b}_s^*$, $\vec{c}_s^*=\vec{q}_r$ in such a way that

$$\vec{K}=H\vec{a}_s^*+K\vec{b}_s^*+L\vec{c}_s^*+m\vec{q}_i,\ H,\ K,\ L,\ m \text{ integers} \quad (3.3)$$

which means that the components of $\vec{q}_r$ with respect to this basis are integers. Eqs.(3.1), (3.2) and (3.3) show that the diffraction spots in the incommensurate phase of BSN can be described as

$$\begin{aligned}\vec{K}&=h\vec{a}_o^*+k\vec{b}_o^*+l\vec{c}_o^*+m\vec{q}\\&=h\vec{a}_o^*+k\vec{b}_o^*+(2l+m)\vec{c}^*/2+m\vec{q}_i\\&=H\vec{a}_o^*+K\vec{b}_o^*+L\vec{c}^*/2+m\vec{q}_i \quad (3.4)\end{aligned}$$

$$\text{with } H=h,\ K=k \text{ and } L=2l+m \quad (3.5)$$

The incommensurate reflections are indexed using new four indices H, K, L, m and the systematic reflection conditions are derived to determine the superspace symmetry.

2) Reflection Conditions and Superspace Symmetry

Fig.2 shows diffraction patterns in the incommensurate phase of BSN. The electron beam is parallel to the [001] axis of the average structure in (a) and to the [010] axis in (b). The average structure is determined by the fundamental spots, which lead to the space group Cmm2(C_{2v}^{11}).[8]

The incommensurate reflections as indicated by arrows in Fig.2(b) are indexed by means of eq.(3.4) and eq.(3.5). The reciprocal lattice, which is formed by analyzing the diffraction spots, shows that the reflection conditions are (see Fig.3) :

$$L+m=2n,\ H+K=2n' \quad (3.6)$$

where $m=0, \pm1$ and n, n' are integers. The reflection condition of H+K even means that the superspace symmetry involves C−centering. From eq.(3.2) and eq.(3.6), we know that the superspace symmetry of the incommensurate BSN belongs to the four dimensional Bravais class $C_{1\bar{1}1}^{Cmmm}$ = Cmmm(α, 0, 1/2) defined by de Wolff et al.[7]

We further examine the extinction rules for BSN to derive the superspace group and its symmetry operations. The following extinction rules are seen in our data(see Fig.3) : H+L+m odd for (H, 0, L, m) and K odd for (0, K, L, m). As above shown, the basic phase of BSN has the three−dimensional space group Cmm2 which consists of (E : 0, 0, 0), (σ_y : 0, 0, 0), (σ_x : 0, 0, 0) and (C_{2z} : 0, 0, 0) [in fact, there also exist four operators by C−centering]. Since the wave vector $\vec{q}_i$ is parallel to the a_o axis and the unit cell is orthorhombic, the former two operators transform $\vec{q}_i$ into $\vec{q}_i$ while the latter two transform $\vec{q}_i$ into $-\vec{q}_i$. As is easily derived from corresponding symmetry operators in superspace,[9] H+L+m odd for (H, 0, L, m) is explained by the presence of (σ_y: 0, 0, 0, 1/2), and K odd for (O, K, L, m) is obtained from (σ_x:1/2, 1/2, 0, 0), i. e. C-centering.

The superspace group generated by these consists of (E : 0, 0, 0, 0), (σ_x : 0, 0, 0, 0), (σ_y : 0, 0, 0, 1/2), (C_{2z} : 0, 0, 0, 1/2) and C−centering. It is concluded that the superspace group of incommensurate BSN is identified as C_{1s1}^{Cmm2}=Cmm2(α, 0, 1/2)(0, s, 0).

3) Superstructure and the Orign of Incommensurability

Schneck et al[3]. reported that the space group of the lock−in commensurate Origin superstructure is Bbm2 with $2a_o\times b_o\times2c$ unit cell; while our present investigation leads to a different result. The observed reflection conditions for superstructure is (see Fig.3) : h+k+l even for (hkl) ; k+l even for (0kl) ; h, l even for (h0l) ; h+k even for (hk0) ; h even for (h00) ; k even for (0k0) ; l even for (00l), which lead to the polar group Ima2 (C_{2v}^{22}) with $2a_o\times2b_o\times2c$ unit cell[8]. This result is consistent with the group−theoretical consideration taking into account pure supergroup−subgroup relations as given in section 4.

The structural model of the incommensurate phase predicts sinusoidally modulated lattice structures in the vicinity of T_I and a domain structure in the temperature range close to T_C[10]. The walls of the domain structure, which are termed discommensurations (see Fig.4), may be interpreted in terms of solitons. The sinusoidally modulated structure as well as the domain structure are compatible with the presence of sharp incommensurate reflection in the diffraction pattern. As was shown by Fujiwara[11], sharp incommensurate reflections result from commensurate domains which are separated by antiphase boundaries if the domain width varies statistically. While higher−order satellites are often detected in domain structure, we cannot, however, detect no higher−order satellites in BSN. This is puzzling result, since the temperature dependence of (which is large in BSN), and the nonsinusoidal shape of the modulation are usually given from a common origin, in the framework of the current phenomenological theories[12].

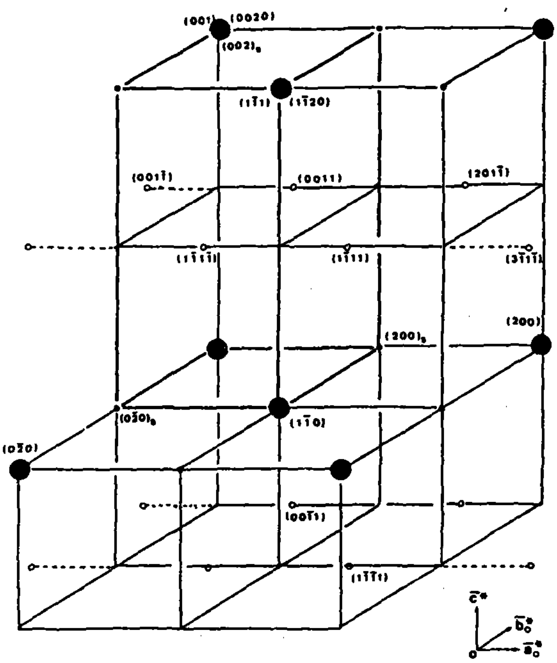

Fig. 3. Reciprocal lattice of the incommensurate phase of BSN. The incommensurate reflections are indexed using H. K. L. m. The reflections are indexed in the average or thorhombic cell (intense lines) and the superstructure unit cell. Especially the incommensurate reflections are indexed using H. K. L. m. ● main. • superlattice and ∘ incommensurate reflections.

GROUP−THEORETICAL CONSIDERATION OF THE PHASE TRANSITIONS IN BSN

We focused our interest on a theoretical concept of the phase sequence taking into account pure supergroup−subgroup relations and correlated symmetry reduction. It is evident that the phase transition P4bm−Ima2 occurs via transient incommensurate phase. It appears plausible that the incommensurate and the ferroelastic phase transions take place as two coupled phenomena and should be seen as two steps of a cascade of phase transitions involving symmetry reduction to the respective maxima space group[13].

We hence treat the system as a sequence of phase transitions each involving symmetry reductions to the maximum subgroup[8]. An allowed maximal nonisomorphic subgroup of P4bm is Cmm 2. During this transformation the crystal system is changed and so the spontaneous strain occurs, forming ferroelastic phase. In a second step the commensurate phase with the space group Ima2 is adopted as a maximal nonisomorphic subgroup of Cmm2 due to c−doubling. The total phase sequence is hence P4bm−Cmm2−Ima2.

CONCLUSIONS

The superspace group approach was applied to barium sodium niobate in the incommensurate phase so as to idendify its superspace symmetry. Our obtained conclusions are summarized as follows :

(1) The idendified superspace group of the in-

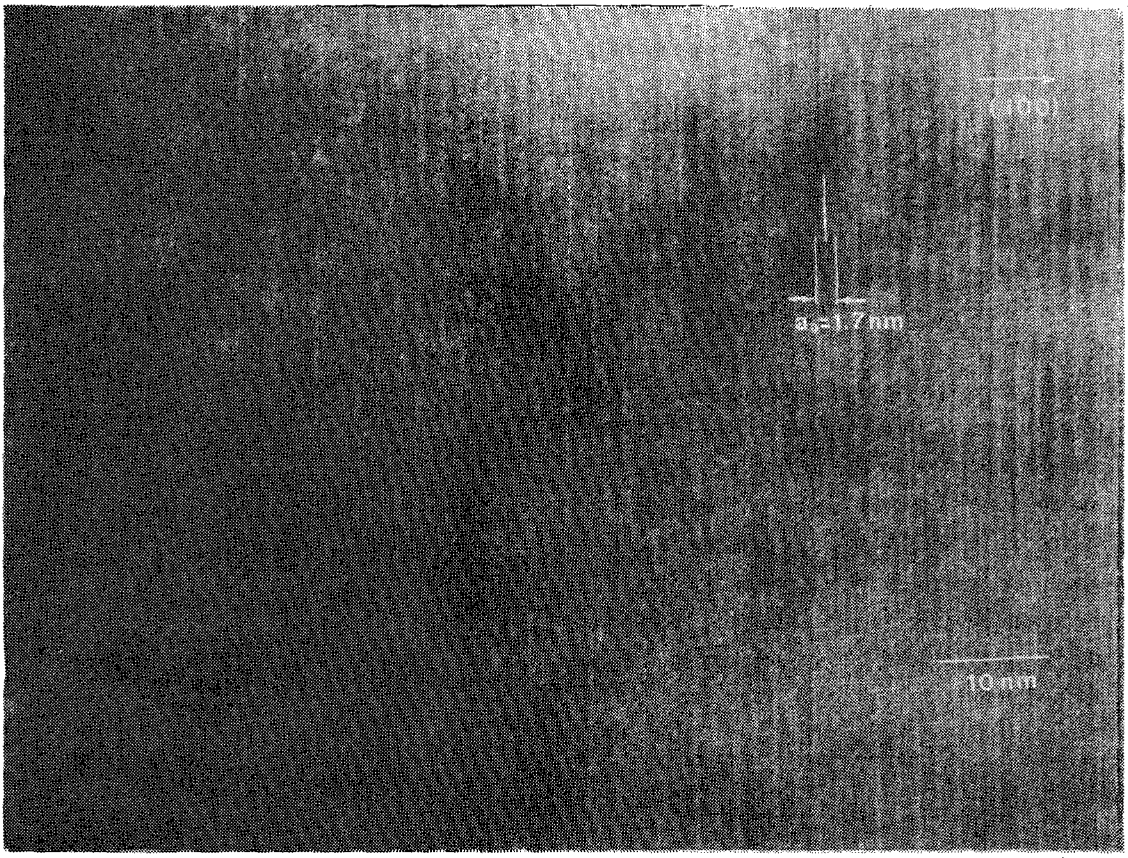

Fig. 4. HREM image of incommensurate BSN along the [010] zone axis. Notice that discommensurations (dark wavy lines) and $a_0/2$ translation can be seen.

commensurate BSN is $C^{Cmm2}_{1\,s\,1}$, and the superspace symmetry operators are (E : 0, 0, 0, 0), (σ_x : 0, 0, 0, 0), (σ_y : 0, 0, 0, 1/2), (C_{2z} : 0, 0, 0, 1/2) together with C−centering.

(2) It is verified that the space group of the lock−in superstructure is Ima2 (C^{22}_{2v}).

(3) It is suggested that the structural phase sequence in BSN is B4bm−Cmm2−Ima2 considering pure supergroup−subgroup relations.

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