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Optical and x-ray studies on incommensurate phase transitions of ferroelectric ammonium fluoroberyllate $(NH_4)_2BeF_4$

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The optical activity of the incommensurate phase of $(NH_4)_2BeF_4$ was measured for the first time by using a high-accuracy universal polarimeter. The optical activity manifests unexpected behavior with respect to the temperature: It increases at first with decreasing temperature, but vanishes at the lock-in transition to the commensurate phase. The intensity of the x-ray-diffraction spectrum responsible for the incommensurate lattice also indicates analogous behavior. A structural mechanism was put forward to explain this optical and x-ray evidence. Both the incommensurate and commensurate phases are assumed to be the result of the development of different order parameters on a common basic superlattice. We then acquired the consistent interpretations of these new phenomena in terms of the proposed model. It should be noted that according to our model the lock-in transition corresponds to the crystallization of the basic superlattice from the dispersed domains.

I. INTRODUCTION

Most of the crystals belonging to the A_2BX_4-type family exhibit two successive phase transitions: between the high-temperature paraelectric (P) and the incommensurate (I) phases at T_i, and between the I and the ferroelectric commensurate (C) phases at T_c. The condensation of the soft mode at T_i in such a crystal results in the modulation of the original lattice to a special superlattice whose periodicity is an irrational multiple of the period of the underlying P lattice. Therefore the translation invariance is lost in the direction of this incommensurate modulation, and, as a result, the crystal as a whole becomes a unit cell. Most information of structural changes occurring in the I phases of these crystals comes from magnetic resonance techniques.[1–6] Important elucidations revealed by these techniques include changes of the crystal texture in the high- and low-temperature regions within the same I phase. In the former region the frozen-out incommensurate modulation wave is pinned, and can be described by a "plane wave," while in the latter region the nearly commensurate parts, called "domains," come into existence and are separated by static soliton lattices called "discommensurations" or "domain walls," where the phase of the modulation wave changes more rapidly than in a plane wave. The density of the soliton lattices decreases as the temperature approaches T_c, and becomes zero at T_c. However, in order to investigate these physically important phenomena in more detail, it is necessary to detect directly the structural changes by some physical method using spatial dispersion phenomena. The typical methods in this sense are, of course, x-ray and neutron diffraction. Nevertheless, it seems to us that the evidence obtained by x-ray and neutron diffraction concerning changes of the texture is subtle. Although it is a natural expectation that in the low-temperature region of the I phase there should exist diffraction spectra due to the nearly commensurate parts, no definite verification has been reported yet. Moncton *et al.*[7] and Iizumi *et al.*[8,9] have tackled this problem by using neutrons, but the results commonly indicated that such spectra did not exist and that incommensurate spectra became commensurate at T_c. Thus the important result of magnetic resonance experiments was apparently not verified by diffraction work.

Another physical quantity associated with spatial dispersion is optical activity. A gyration tensor represents the antisymmetrical part of the optical susceptibility tensor. Therefore it should be a quantity directly proportional to the antisymmetrical part of the dynamical matrix of the scattering atoms, and also to their relative separations in an optically active crystal. In this sense, the optical activity can reveal microscopic properties of the crystal. As we were recently successful in constructing a new apparatus, the high-accuracy universal polarimeter (HAUP), with which we can measure optical activity of any crystal,[10] we have applied it to the study of incommensurate structures of A_2BX_4-type crystals, hoping that useful knowledge of incommensurate phase transitions, which could not be obtained otherwise, would become available. This paper reports the structural change in the I phase of $(NH_4)_2BeF_4$ revealed by HAUP and x-ray-diffraction techniques.

$(NH_4)_2BeF_4$ undergoes two successive phase transitions at $T_i = -90.0\,^\circ\mathrm{C}$ and $T_c = -96.0\,^\circ\mathrm{C}$.[11] The crystal symmetry of the P phase is orthorhombic D_{2h}^{16}–$Pcmn$,[12] the ferroelectric C phase is also orthorhombic, but C_{2v}^{9}–$Pn2_1a$,[13] and the intermediate I phase is undetermined, with the incommensurate modulation along the a axis. The polar axis in the C phase is parallel to the b axis, and the lattice parameter of the a axis is doubled there. Temperature changes of the lattice strains were previously measured,[14] and some features characteristic of the incommensurate state have been clarified. It is especially noteworthy that the sign of the Grüneisen constant changes, becoming negative within the incommensurate temperature region.

II. OPTICAL ACTIVITY AND BIREFRINGENCE

Simultaneous measurements of optical activity and birefringence of $(NH_4)_2BeF_4$ were made by using the HAUP. It is obvious from symmetry that the P phase is optically inactive, but the C phase, which belongs to a nonenantiomorphic class, is allowed to possess a single gyration-tensor component, g_{13}. A (101) plate specimen, 4.0×2.7 mm^2 in area and 0.220 mm thick, was subjected to the HAUP, where the temperature of the specimen was changed from -80 to -110°C with an accuracy of ±0.01°C. A He-Ne laser with a wavelength of $\lambda=6.328$ Å was used as the light source. The results are shown in Fig. 1, the temperature dependence of g_{13} in panel (a), and that of Δn in (b). The P phase was found to be optically inactive. The g_{13} tensor in the I phase manifests a remarkable temperature-dependent change: It increases rapidly starting from T_i with decreasing temperature, but gradually levels off around a temperature denoted by $T_m=-94.8$°C, then begins to decrease, forming a broad maximum at T_m, and finally vanishes at T_c. In the C phase g_{13} comes into existence again, and quickly increases with decreasing temperature. On the other hand, the birefringence Δn along the same direction increases linearly with decreasing temperature in the P phase, and changes its temperature derivative starting from T_i. However, it does not reveal a discernible change at T_c. The above data would be the first evidence of optical activity displayed by a ferroelectric crystal with an incommensurate phase.

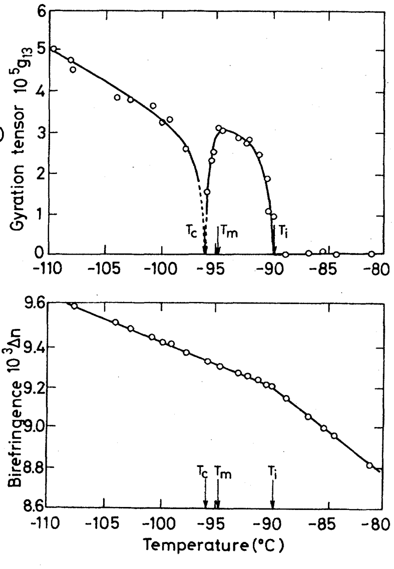

FIG. 1. Temperature changes of the gyration tensor g_{13} and the birefringence Δn of $(NH_4)_2BeF_4$. (a) indicates that of g_{13} and (b) that of Δn.

III. X-RAY STUDY ON PHASE TRANSITIONS

In order to acquire complementary information about optical properties, we made precise intensity measurements of x-ray reflections $(\frac{1}{2}(1+\delta),0,2)$ and $(\overline{\frac{1}{2}}(1+\delta),0,2)$, which are responsible for the incommensurate structure. We minimized the divergence of the incident x-ray beams in order to increase the resolution of the measurements of x-ray spectra. A narrow incident slit 0.4 mm wide, set in front of the specimen, was separated as far apart as 1.112 mm from a crystal monochromator holding a (111) plate silicon crystal. In this system we obtained the Cu $K\alpha_1$ x-ray beams with a divergence of 1.2′ and a wavelength accuracy of $\Delta\lambda/\lambda=1.43\times10^{-3}$. The receiving slit in front of the scintillation-counter tube was widened to the extent that it accepted the entire reflected beam of each spectrum. The intensities of the reflections were measured by the step-scanning mode of the rotation angle of the specimen, which was changed by 0.15′ increments around each maximum reflection position. In Fig. 2 a comparison is made between the measurements of Iizumi *et al.*[9] and our measurements on the same spectrum $(\frac{1}{2}(1+\delta),0,2)$, the half-width of the reflection in the former experiment being approximately $2\times10^{-2}a^*$, while $1.2\times10^{-3}a^*$ in the latter.

A. Measurements of the incommensurate deviation δ

The temperature dependence of the incommensurate deviation δ was measured by using a specimen which was rod shaped along the b axis and bounded by narrow crystal surfaces, a (100) plane of 0.30 mm and a (001) plane of 0.20 mm of the widths. The spectra used were a pair of $(\frac{1}{2}(1+\delta),0,2)$ and $(\overline{\frac{1}{2}}(1+\delta),2,0)$ reflections, and another pair of (202) and ($\bar{2}$02) reflections. The exact positions of the reflections were read from the intensity maxima of the reflection curves. The method of deriving δ is the same as that by Kudo.[15] The change of δ with respect to the reduced temperature $(T-T_c)/(T_i-T_c)$ is shown in Fig. 3, where the results by Kudo[15] and Iizumi *et al.*[9] are also indicated for comparison. It is found that our result agrees well with that of Kudo.

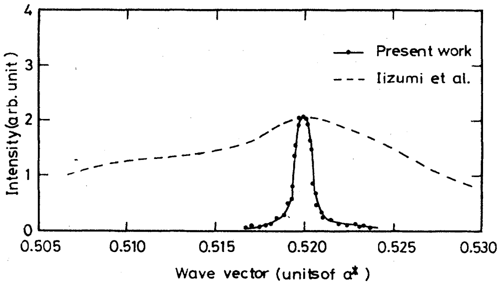

FIG. 2. Comparison of reflection profiles of $(\frac{1}{2}(1+\delta),0,2)$ between $(NH_4)_2BeF_4$ and $(ND_4)_2BeF_4$ obtained by us and Iizumi *et al.* (Ref. 9), respectively.

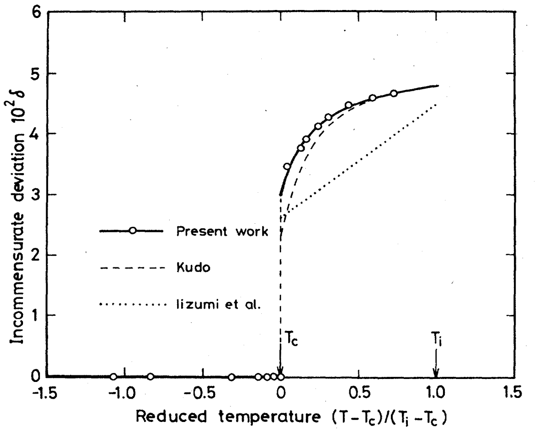

FIG. 3. Changes of the incommensurate deviation δ with respect to the reduced temperature $(T-T_c)/(T_i-T_c)$. Solid line indicates the present results, the dashed those of Kudo (Ref. 15), and the dotted those of Iizumi *et al.* (Ref. 9).

B. Changes of reflection intensities

Reflection curves of $(\frac{1}{2}(1+\delta),0,2)$ and $(\frac{1}{2}02)$ spectra at various temperatures are depicted with respect to the wave-vector coordinate (in units of a^*) in Fig. 4. The $(\frac{1}{2}(1+\delta),0,2)$ spectrum appears at −90 °C, and its intensities increase with decreasing temperature. However, the intensities have a maximum around −94 °C, begin to decrease afterwards, and finally vanish in the vicinity of T_c. Below T_c, the $(\frac{1}{2}02)$ spectrum, whose positions are sufficiently separated from those of the previous $(\frac{1}{2}(1+\delta),0,2)$ spectrum, appears suddenly and its intensities increase quickly. It is very important to note that this spectrum comes into existence only below T_c and there are no indications of the coexistence with the incommensurate spectrum in the I state. Temperature changes of integrated reflections and of the half-widths of the incommensurate reflection are shown in Figs. 5(a) and 5(b), respectively. Integrated reflections of $(\frac{1}{2}(1+\delta),0,2)$, which take place below T_i, vanish at T_c. The half-width of the reflection conspicuously increases in the vicinity of T_c. These facts contradict the cases for $(NH_4)_2BeF_4$,[9] K_2SeO_4,[8] and 2H-$TaSe_2$.[7] It is interesting that temperature dependences of integrated reflections of the incommensurate spectrum and of the optical activity of the I state of $(NH_4)_2BeF_4$ are essentially similar.

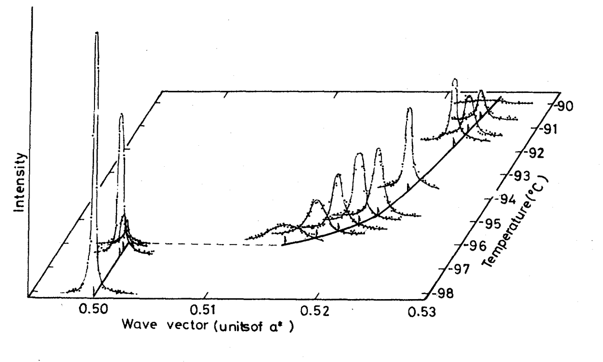

FIG. 4. Reflection curves of $(\frac{1}{2}(1+\delta),0,2)$ and $(\frac{1}{2}02)$ spectra of $(NH_4)_2BeF_4$ expressed by temperature and wave-vector (in units of a^*) coordinates.

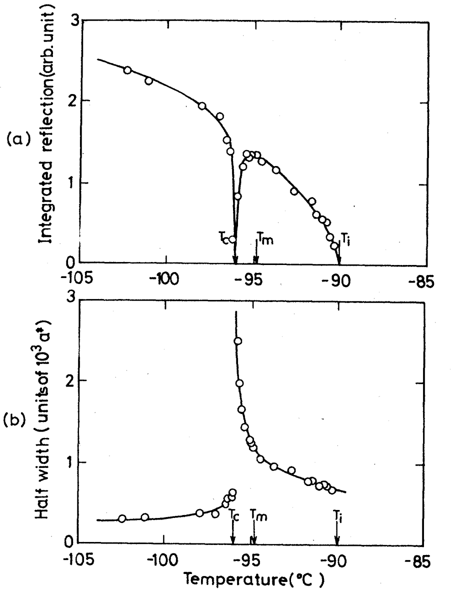

FIG. 5. Temperature changes of integrated reflections and half-widths of $(\frac{1}{2}(1+\delta),0,2)$ and $(\frac{1}{2}02)$ spectra of $(NH_4)_2BeF_4$. (a) indicates that of integrated reflections and (b) that of half-widths.

IV. INTERPRETATIONS OF THE OPTICAL AND X-RAY RESULTS

In the present experiments we found new phenomena taking place in $(NH_4)_2BeF_4$ that have not yet been reported. Here we try to explain them on the basis of a model that corresponds to a renewed interpretation of the fundamental ideas of the incommensurate structure put forward by McMillan[16] and proved by magnetic resonance techniques by Blinc *et al.*[4–6]

Our basic idea is that the underlying structures of the I and C phases of $(NH_4)_2BeF_4$ are the same superlattice structure, whose modulation wave vector $\mathbf{q}_0=\mathbf{a}^*/p$ (p represents an integer) is commensurate with the P lattice. The basic superlattice (BSL) has a period of p times that of the P phase. Then the difference between the I and C phases (ferroelectric) emerges from the difference of the order parameters developed in the common BSL.

It is of natural consequence that the BSL whose structural period is an integral multiple of that of the P phase is still centrosymmetrical and, consequently, optically inactive. However, the P-I transition can actually occur, according to an irreducible representation with another wave vector $\mathbf{q}$ on the a^* axis, since the Lifshitz invariance can exist by symmetry. However, because the length of the vector $\mathbf{q}$ is nearly equal to $\mathbf{q}_0$, the resulting I phase can be regarded as corresponding to $\mathbf{q}_0$, but being space-modulated by the incommensurate deviation of δ.

In this case the order parameter should be complex. Let it be defined as $\Phi_0 e^{i\varphi}$. Then both the amplitude Φ_0 and phase φ depend on the position along the *a* axis of the crystal, and thus both order parameters are inhomogeneous in the crystal. According to the recent theoretical analysis by Blinc *et al.*[5], the space variation of Φ_0 increases with decreasing temperature, but becomes appreciable only in the soliton phase region. Therefore it would not be unrealistic to neglect the space variation of Φ_0 in the present discussions, where we are not concerned with the detailed structure of the soliton phase regions. Accordingly, we will consider only the space variation of φ in the following.

On the other hand, the *C* phase is ferroelectric, so the polarization *P* exists as another order parameter. We assume that the ferroelectricity of the *C* phase occurs in the underlying BSL via some improper ferroelectric mechanism.

Let us consider at first the change of optical properties at the successive phase transitions in terms of the above-mentioned model. Although the BSL is optically inactive, the *I* phase can be optically active since the amplitude mode modulates the lattice period of the BSL irrationally, and accordingly removes the translational periodicity from the *I* phase. Therefore g_{13} in the *I* phase would be proportional to the magnitude of Φ_0, which increases with decreasing temperature. On the other hand, in the *C* phase, g_{13}, which is induced by P_s through the electrogyration effect, will also increase in the same fashion. It is a characteristic feature of our model that the optical activities of both phases are induced by different order parameters on a common structure. We will try to explain conspicuous temperature-dependent changes of g_{13} and x-ray-diffraction intensities of the incommensurate spectrum with this model.

A. Structural change in the *I* phase

When the original lattice of the *P* phase transforms into the BSL at T_i, there is no preference for selecting a particular unit cell as the origin of a new BSL on a purely thermodynamical basis. However, the condition that the whole crystal should remain as a single crystal after the transition imposes the role of the unique origin of the new BSL upon a certain unit cell with some local affinity. In this way the entire specimen is deformed by the unique mode from the origin. In reality, however, an incommensurate mode is further developed on this unique BSL. This is the "plane-wave lattice" in the *I* phase.

Let us consider a one-dimensional incommensurate modulation lattice along the *a* axis. The periodic lattice distortion of the BSL is represented as

$$\psi_0(\mathbf{r})=\Phi_0 e^{i\mathbf{q}_0\cdot\mathbf{r}} , \tag{1}$$

where Φ_0 is the amplitude of the BSL. Here $\mathbf{q}_0$ and $\mathbf{r}$ are represented as

$$\mathbf{q}_0=(2\pi/p)\mathbf{a}^*, \quad \mathbf{r}=x\mathbf{a} , \tag{2}$$

where *x* is a fractional coordinate in the unit of *a*. Now $\psi_0(\mathbf{r})$ can be expressed, by using *x*, as

$$\psi_0(x)=\Phi_0 e^{i(2\pi/p)x} . \tag{3}$$

On the other hand, the plane wave of the incommensurate modulation is expressed as

$$\psi(\mathbf{r})=\Phi(\mathbf{r})e^{i\mathbf{q}_0\cdot\mathbf{r}} . \tag{4}$$

Then, $\Phi(\mathbf{r})$, the modulation function, reads as

$$\Phi(\mathbf{r})=\Phi_0 e^{-i(\mathbf{q}_0-\mathbf{q})\cdot\mathbf{r}}=\Phi_0 e^{-i\delta\mathbf{q}_0\cdot\mathbf{r}} , \tag{5}$$

or, in the same way as in (3),

$$\Phi(x)=\Phi_0 e^{-i(2\pi/p)\delta x}=\Phi_0 e^{-i\varphi(x)} . \tag{6}$$

This function is the complex order parameter which modulates the BSL in the *I* phase, Φ_0 and $\varphi=(2\pi/p)\delta x$ being, of course, the amplitude and phase modes of the two-dimensional order parameters.

It is well argued by the Landau theory of the incommensurate and the lock-in phase transitions that the anisotropy energy, responsible for the lock-in transition in the thermodynamical potential, becomes more operative as the temperature is lowered from the vicinity of T_i,[17] until the spatial variation of the phase mode $\varphi(x)$ stops at the prescribed values of *x*. It means that the nearly commensurate regions take place at these values of *x*. It should be emphasized that these regions just correspond to the BSL.

Attention must be directed to the fact that a BSL expressed by (3) runs from a specific origin of the *P* lattice as discussed above. However, the thermodynamically stable BSL's are not exclusively limited to it, but can be expressed by the equivalent lattices; the equivalent BSL's start from *p* consecutive unit cells contained within one wavelength of the BSL, as schematically shown in Fig. 6 by taking $p=3$. The equivalent BSL's are enumerated as follows:

$$\begin{aligned}
&\psi_0^0(x)=\Phi_0 e^{i(2\pi/p)x} ,\\
&\psi_0^1(x)=\Phi_0 e^{i(2\pi/p)(x-1)}=\psi_0^0(x)e^{-i(2\pi/p)} ,\\
&\psi_0^j(x)=\Phi_0 e^{i(2\pi/p)(x-j)}=\psi_0^0(x)e^{-i(2\pi/p)j} ,\\
&\psi_0^p(x)=\psi_0^0(x) ,
\end{aligned} \tag{7}$$

where $\psi_0^j(x)$, for instance, is a BSL whose origin is displaced from that of the first BSL, $\psi_0^0(x)$, by *j* unit cells, and so differs in its phase by $e^{-i(2\pi/p)j}$ from that of the first BSL.

We will consider the key problems of x-ray and optical evidence by using this concept of the BSL.

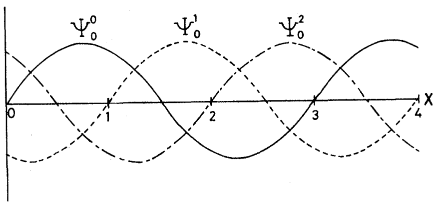

FIG. 6. Schematic illustration of equivalent BSL's in the case of $p=3$.

B. X-ray diffractions from the I and C phases

In order to discuss the x-ray-diffraction intensities in the I and C phases, let us denote structure factors of the spectra responsible for the BSL, the incommensurate lattice modulated by a plane wave, and phase solitons (discommensuration) by F_B, F_P, and F_D, respectively. The volume of the specimen used was so small that the integrated reflections can be safely regarded as being proportional to the square of the structure factors and to the irradiated volume. As the BSL is the basic lattice of the I and C phases, F_B can be viewed as being independent of the temperature in the present discussions. On the other hand, $|F_P|$ should depend on the magnitude of Φ_0. By using the well-known relation[5]

$$\Phi_0=\alpha(T_i-T)^{1/2} , \tag{8}$$

$|F_P|$ can be written as

$$|F_P|=\beta\Phi_0=\alpha\beta(T_i-T)^{1/2} , \tag{9}$$

where α and β are constants. Then the integrated reflection I_P in the high-temperature region of the I phase is expressed as

$$I_P=B\,|F_P|^2 v=B\alpha^2\beta^2(T_i-T)v , \tag{10}$$

where v is the total volume of the specimen, and B is a constant depending on the glancing angle of the spectrum. As seen in Fig. 6(a) this relation approximately holds in the high-temperature regions of the I phase. However, this relation begins to break down as the temperature approaches T_m. The reason is that with decreasing temperature the x-ray diffractions split into two parts, one from the discommensurations and the other from the newly emerging BSL's. The predominant effect, in a word, is the segregation of the total volume into two parts. Here it is convenient to introduce the soliton density n_s according to Blinc *et al.*[4]

$$n_s=d/x_0 , \tag{11}$$

where d is the soliton width and x_0 the intersoliton distance along the a direction. Then total volumes of the BSL's and the discommensurations, v_B and v_D, respectively, are expressed as

$$v_D=n_s v$$

and (12)

$$v_B=(1-n_s)v .$$

Then the integrated reflection I_D of the incommensurate spectra issued from the discommensurations can be expressed as

$$I_D=B\,|F_D|^2 n_s v . \tag{13}$$

Equation (13) explains one of the most important pieces of evidence in the present experiments shown in Fig. 6(a), since it is known that n_s decreases with decreasing temperature and vanishes at T_c. Besides, it has been clarified that the temperature dependence of $|F_D|$ can be evaluated from (13) if that of n_s is available by any means. In other words, the collection of $|F_D|$'s necessary for the structure analysis of the I phase cannot be done without the quantitative evaluation of n_s.

Now it is of particular interest to calculate I_B of the spectra responsible for the BSL's which appear in the low-temperature region of the I phase. Consider that the j-type BSL, which originates at the jth cells of the P phase, contains m_j BSL's in the specimen. Then the diffraction amplitude A_j from this type of domain can be written as

$$A_j=m_jF_B . \tag{14}$$

Therefore the total diffraction amplitude A_B from the specimen is expressed, as there exist p types of domains in all,

$$A_B=\sum_{j=1}^{p} m_jF_Be^{-i(2\pi/p)j} . \tag{15}$$

As has already been noted, there would be no weight on the specific m_j among p types of domains. Therefore it will be reasonable to assume that m_j can be replaced by a constant m, which depends only on the soliton density, viz.,

$$m_j=m=(1-n_s)v/p , \tag{16}$$

and then (15) becomes

$$A_B=[(1-n_s)/p]vF_B\sum_{j=1}^{p} e^{-i(2\pi/p)j} , \tag{17}$$

where it is easy to show that the summation of j vanishes. It follows that A_B is always zero in this case. We thus obtain the solution that the x-ray diffractions cannot take place by the BSL parts in the lower-temperature region of the I phase, although these domains do exist and become predominant as the temperature is lowered. This would be the true reason for our observation that any spectra due to the nearly commensurate lattices do not exist in the I phase.

The integrated reflection I_F of the C phase can be written as

$$I_F=B\alpha'^2\beta'^2(T_c-T)v , \tag{18}$$

where α' and β' are constant. Thus I_F will increase linearly with T. This result can also be confirmed by our experiment [Fig. 6(a)].

C. Temperature change of optical activity

We are now in a position to be able to understand the change of the optical activity of $(NH_4)_2BeF_4$ when it undergoes the transitions among P, I, and C phases. It is reasonable to assume that the gyration tensor g_{13}^P of the plane-wave region in the I phase is proportional to the magnitude of the amplitude mode. Therefore it is written as

$$g_{13}^P=\eta_P(T_i-T)^{1/2} , \tag{19}$$

where η_P is a constant. This relation can be shown to hold, as indicated in Fig. 7, where the square of q_{13} is expressed with respect to T. In the lower-temperature part,

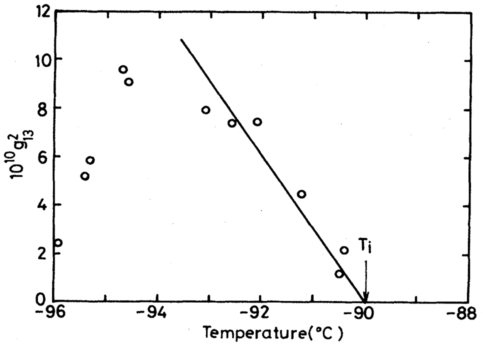

FIG. 7. Temperature change of the square of the gyration tensor of g_{13} of $(NH_4)_2BeF_4$.

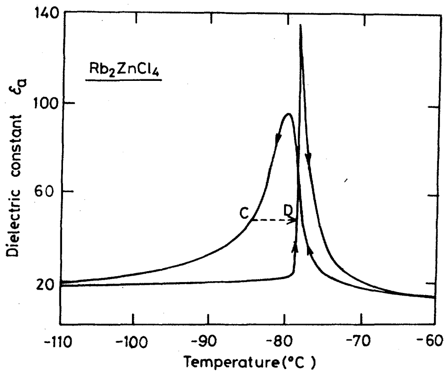

FIG. 8. Anomalous hysteresis in the dielectric constant ϵ_a of Rb_2ZnCl_4 reported by Hamano *et al.* (Ref. 18).

however, there occur BSL domains which are optically inactive. Therefore the BSL domains will dilute the optical activity of the entire specimen. Denoting the gyration tensor of the soliton lattice as g_{13}^D, the observed gyration tensor g_{13}^{ob} is written as

$$g_{13}^{\text{ob}} = g_{13}^D n_s \; . \tag{20}$$

This means that the optical activity should change with n_s, and so we expect that it vanishes at T_c. One of the key points of our optical experiments is thus explained. It is important to note that the soliton density n_s can be derived directly from the measurement of the optical activity in the low-temperature region of the *I* phase, where the magnitude of the amplitude mode is almost saturated to a constant value. In other words, the temperature change of g_{13} in Fig. 1(a) in the lower-temperature region depicts the temperature change of n_s itself. It also follows that the temperature change of $|F_P|$ can be evaluated from (13) by using this result.

In the *C* phase, the gyration tensor g_{13}^F will be increased according to the formula

$$g_{13}^F = \eta_F (T_c - T)^{1/2} \; , \tag{21}$$

where η_F is a constant. This can be apparently confirmed from our experiments [Fig. 1(a)].

V. DISCUSSIONS

We have shown that our experimental results on optical activity and x-ray-diffraction intensities can be qualitatively explained by the proposed mechanism based on the existence of the BSL both in the *I* and *C* phases. Thus measurements of optical activity become particularly useful in the study of the incommensurate phase transitions when they are supplemented by x-ray-diffraction techniques.

Now it will be interesting to review a few problems which have been at issue, from the viewpoint of the present conclusions. Our interpretations indicate that the *I*-*C* transition corresponds to the formation of a single crystal of a BSL from the different types of BSL domains dispersed in the crystalline discommensuration lattice with the definite phase relations. Therefore the *I*-*C* transitions can be compared to the crystallization and decomposition between a BSL and its differently dispersed domains. Therefore it is readily conjectured that the nucleation process would play an essential role in this transition.

It was reported that *I*-*C* transitions are always followed by conspicuous temperature hysteresis phenomena. This is a natural consequence of our model. Hamano *et al.*[18] reported anomalous behavior of hysteresis in dielectric constant ϵ_a along the *a* axis of Rb_2ZnCl_4, which is shown in Fig. 8; when a specimen is cooled down to point *C* in the figure and thereafter heated, ϵ_a is traced at first along the dashed line *CD* and afterwards on the heating curve. This can be explained easily. As in both stages of *C* and *D*, the proportion of single crystal to domains of the BSL's is the same, but directions of temperature changes are opposite, and ϵ_a follows to the different branches.

As to the origin for the disappearance of the polarization of the *I* phase, there has been an explanation that P_s has already occurred together with the onset of the *I* phase at T_i but is hidden by the incommensurate modulation.[19] According to our model, however, the *I* phase is not the result of the modulation of the *C* phase, but of the modulation of the BSL, and, consequently, the ferroelectricity first appears below T_c as a result of improper ferroelectric mechanism. This conclusion is consistent with that derived by van Beest *et al.*[20]

The fact that the Grüneisen constant becomes negative in the *I* phase is closely connected with dispersed domains of the BSL in the body of the soliton scaffolding. In connection with this phenomenon, it is worth noting that the optical birefringence does not reflect the microscopic crystalline structure, but only the difference of the optical densities between the two directions. Therefore it is readily supposed that the birefringence will not be affected by the *I*-*C* transitions when the change of the optical densities between the two states is small. In such cases, the difference will be brought about only through the electrooptic effect of P_s. $(NH_4)_2BeF_4$ is one of the examples where the change of birefringence Δn is extremely small at T_c.

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