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Incommensurate phase transitions and optical activity

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Recent experiments with the high-accuracy universal polarimeter method have revealed optical activity of the incommensurate phases of A_2BX_4 crystals. The origin of this important phenomenon is explained. A pure imaginary perturbation that takes place in the Hermitian dynamical matrix induces two circularly helical lattice waves. One of them is condensed in the same form in the incommensurate phase. This is also the physical picture of the existence of the phason mode. The symmetry of the crystal becomes D_∞, which permits optical activity. The theory is consistent with the Lifshitz condition and with our experimental results.

I. INTRODUCTION

Optical activity (OA) is permitted to occur in a solid that lacks an inversion center. Thus OA is primarily a powerful tool for deciding the symmetry of a solid. Since the symmetry consideration is specifically important for elucidating the mechanism of the incommensurate (IC) phase transitions, there was much interest in investigating whether the IC phases were optically active or not. The HAUP (high-accuracy universal polarimeter)[1] method opened the way for the first time to this study. We measured the temperature dependence of gyrations of A_2BX_4 crystals: $[N(CH_3)_4]_2ZnCl_4$,[2] Rb_2ZnCl_4,[3] $(NH_4)_2SO_4$,[4] and $[N(CH_3)_4]_2CuCl_4$.[5] Meekes and Janner[6] and Dijkatra and Janner[7] were successful in Rb_2ZnBr_4 and $[N(CH_3)_4]_2ZnCl_4$. Thus the occurrence of OA of the A_2BX_4-type ferroelectric and ferroelastic crystals have been established by these workers by using the refined HAUP method.[8,9]

However, it cannot be said that the origin of OA in the IC state has been perfectly understood up to now. Meekes and Janner[6] and Dijkatra and Janner[7] explained the origin of OA on the basis of superspace symmetry and proposed a method of predicting the observable tensor components of various A_2BX_4 crystals. Their theory stems essentially from an idea that the average structures of the IC phases are centrosymmetrical but OA reflects the point-group symmetry of the crystal region within the optical wavelength used. Hardy, Katkanant, and Edwardson[10] studied the crystal structure of IC phases on the basis of molecular dynamics, and claimed the existence of helical structure of atoms. However, the real origin for the formation of the helical structure was elusive to us.

We[11] explained the importance of the study of OA of the IC phase transitions from the viewpoint that OA would provide us with irreplaceable knowledge for the chirality of structure and the characteristic coupling nature of the constituent atoms. We[2,12] ascribed the origin of IC phases to a characteristic dissymmetry which is caused by the existence of the phason mode of the complex order parameter. However, our arguments were qualitative. Since the problem has been so challenging, we feel it necessary to explain our idea in more detail and compare it with experiments. This is the purpose of this paper.

II. STRUCTURE OF INCOMMENSURATE STATE

An essential nature of a crystal of being in the IC state is that the condensed order parameter in the crystal has its own wavelength but modulates an existing lattice period unlimitedly within the specimen. In order that such an IC structure could exist, the order parameter, which was complex before the IC transition, still continues to be complex in the transformed IC phase. If the wave number q, where the complex order parameter was condensed, coincides with any one of the mesh of the Brillouin zone, the wave number must become immediately zero (Γ point) in the new phase; accordingly the order parameter becomes real at once.

Let a complex order parameter at wave number q be defined as Q_q,

$$Q_q = A_q \exp(i\theta_q) , \tag{1}$$

where A_q is the modulus, and θ_q the phase angle. Then the free energy of this system can be expressed by using this order parameter,[13] allowing for the susceptibility to vanish at the transition point T_c,

$$\begin{aligned} G &= G_0 + a(T-T_c)Q_qQ_{-q} + bQ_q^2Q_{-q}^2 \\ &= G_0 + a(T-T_c)A_q^2 + bA_q^4 . \end{aligned} \tag{2}$$

It is important to note that θ_q is not contained in this formula of the free energy. The free energy does not depend on θ_q at all. This fact can be understood more clearly in the following. It is well known that in the irreducible representation of the general point q, a conjugate order parameter Q_q^* is degenerate by an additional symmetry of the time reversal. Thus combining Q_q with Q_q^*, two-dimensional real order parameters P_1 and P_2 can be defined as

$$P_1=\frac{1}{\sqrt{2}}(Q_q+Q_q^*)\ ,$$

and (3)

$$P_2=\frac{i}{\sqrt{2}}(Q_q^*-Q_q)\ .$$

If the free energy is expressed in terms of these parameters, it becomes

$$G=G_0+a(T-T_c)(P_1^2+P_2^2)+b(P_1^2+P_2^2)^2\ . \tag{4}$$

In order to examine this free energy we must note that a general form of the free energy of the two-dimensional space can be written as

$$G=G_0+a(T-T_c)(P_1^2+P_2^2)+b(P_1^2+P_2^2)^2+C(P_1^4+P_2^4). \tag{5}$$

Let us introduce here orientation parameters (ζ_1,ζ_2) with $\zeta_1^2+\zeta_2^2=1$,

$$P_1=P\zeta_1=P\cos\theta\ ,$$

and (6)

$$P_2=P\zeta_2=P\sin\theta\ .$$

Here P is the modulus of the order parameter, and θ represents its orientation angle with respect to the coordinate axes. Then (5) becomes

$$G=G_0+a(T-T_c)P^2+[b+c(\zeta_1^4+\zeta_2^4)]P^4\ . \tag{7}$$

Let B designate a coefficient of the P^4 term,

$$B=b+c(\zeta_1^4+\zeta_2^4)\ . \tag{8}$$

The condensed parameter in the ordered phase will be oriented such that B is kept a positive minimum. The orientation of the order parameter in the new phase can be classified into three types.

(i) When $c<0$, but $b+c>0$. The ordered phase has one of four domains, $\zeta_1=\pm1$, $\zeta_2=0$, or $\zeta_2=\pm1$, $\zeta_1=0$, as depicted in Fig. 1(a).

(ii) When $c>0$, and $B>0$. There are four domains with $\zeta_1=\pm1/\sqrt{2}$, $\zeta_2=\pm1/\sqrt{2}$, as shown in Fig. 1(b).

(iii) When $c=0$, and $b>0$. This corresponds to Eq. (4). The order parameter can occupy any orientation in the space of P_1 and P_2, as shown in Fig. 1(c).

The physical picture of type (iii) can be elucidated by examining the fluctuations of the order parameter. The fluctuation along the existing order parameter, i.e., longitudinal susceptibility η_1, is expressed as

$$\eta_1=\begin{cases}\dfrac{1}{a(T-T_c)}, & T>T_c\\[2ex] \dfrac{1}{2a(T_c-T)}, & T<T_c\ .\end{cases} \tag{9}$$

It is diverged only in the vicinity of T_c. On the other hand, the fluctuation perpendicular to that direction, transverse susceptibility η_2, reads

$$\eta_2=-\frac{b+c}{ac(T_c-T)}\ . \tag{10}$$

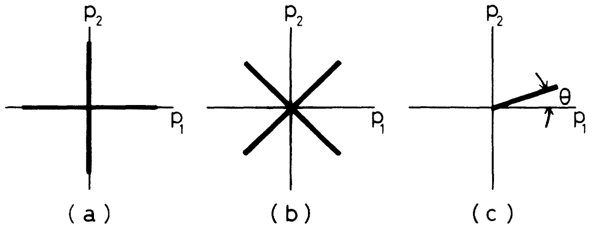

FIG. 1. Orientation of the two-dimensional order parameters. See text.

It is important that as $c=0$ it is always infinite at any temperatures below T_c. In other words, it costs no energy to rotate the order parameter below T_c.

From the discussion above it can be understood that a complex order parameter is condensed in the IC phase accompanying the following two phenomena. (1) The transverse susceptibility is infinite for all $T\leq T_c$. (2) The modulus of the order parameter really comes into existence. In order that the order parameter is consistent with the above conditions, it must rotate with a constant angular velocity below T_c. If condition (1) only is fulfilled, the order parameter will not take place. Because opposite rotations of it can occur with equal probability, the resulting order parameters are canceled by each other. The Hamiltonian of the condensed phase has continuous rotational symmetry in P_1 and P_2. This is the symmetrical condition of the IC state, which permits OA.

The orientation angle θ can be taken as a function of time t and position x. The above condition is expressed as

$$\frac{\partial\theta(t,x)}{\partial t}=\omega\ , \tag{11}$$

where ω is a constant angular velocity. The integration becomes

$$\theta(t,x)=\omega t+\theta_0(x)\ , \tag{12}$$

where θ_0 represents an integration constant. As the Fourier transform of the condensed order parameter takes an IC wave number, $\theta_0(x)$ will change unlimitedly with respect to x. When the linear change is assumed against x, (12) can be expressed as

$$\theta=\omega t+\kappa x\ , \tag{13}$$

taking κ as a constant. This is a direct result followed by the condition that the condensed order parameter is complex. This is the same as the consequence derived from the Lifshitz condition. The Lifshitz term only emphasizes that the order parameter is spatially inhomogeneous within the crystal, viz.,

$$\frac{\partial\theta(t,x)}{\partial x}=\kappa\ . \tag{14}$$

The integration of this term leads to the same result as (13).

Now let us investigate what (13) does mean. For the sake of simplicity, assume that the order parameter takes place below T_c in the (100) plane perpendicular to the x

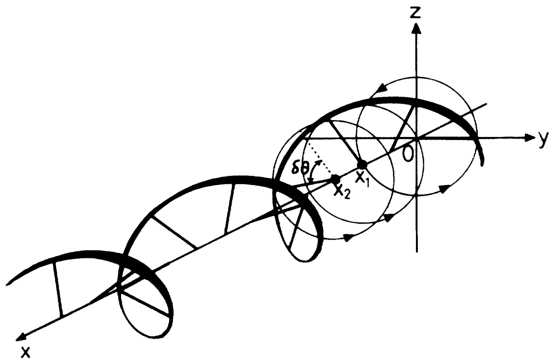

FIG. 2. Helical structure of the complex order parameter in an incommensurate phase.

axis. The schematic representation of the condition (13) is depicted in Fig. 2. θ rotates with a constant angular velocity at each point, but with phases depending linearly on x; e.g., a phase difference $\delta\theta=\kappa(x_2-x_1)$ appearing between two points x_1 and x_2 in the figure. Then it will be seen that the trajectory of a constant θ value at time t forms a helix as indicated by the bold line in the figure. This figure conforms to a symmetry of D_∞, one of the dissymmetric classes which permit OA. This physical picture of (13), viz., the rotation of the helical trajectory of θ, is the phason mode. It has become evident that the excitation of the phason mode in the IC states enhances the symmetry of the crystal as high as D_∞, which forbids the translational symmetry of the crystal. This is one of the characteristic features of the IC phase. The phason cannot be condensed at any temperature below T_c as long as the crystal is in the IC state because the condensation of the phason means the stopping of the rotational motion and the disappearance of the mode itself. The loss of this mode immediately transforms the existing order parameter into a real one. It is necessary to note that the same physical picture can be visualized by using another expression. The rotational motion of the helix is equivalent to the translational motion of the helix with a constant velocity along the x axis. Figure 3 represents the well-known representation between θ and x, but emphasizes the time change of the relation.

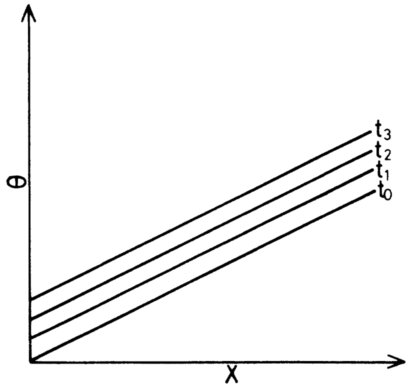

FIG. 3. Spatial variation of the phase mode θ at regular time intervals.

III. FORMATION OF HELICAL STRUCTURE

It was described qualitatively in Sec. II that a complex order parameter appears in a helical form in the condensed IC phase. Here we investigate the reason why and how the complex order parameter can be frozen in an IC point in the Brillouin zone by taking a simple model. Assume that a lattice wave, say, of a transverse-acoustic mode, propagates along the x direction. The wave number is taken at a general point q in the Brillouin zone, and the two orthogonal components of an eigenvector of the dynamical matrix are designated as η_q and ξ_q. As q is a general point, the symmetry of q permits the Lifshitz term to exist in the free energy.

An eigenvalue of the eigenstate of the dynamical matrix is designated as α, where another conjugate state is degenerate by the symmetry of time reversal. Here we define both waves as 1 and 2, and let α decrease linearly with T and vanish at T_c at a rational point q_0. In order that this condition is guaranteed, α must increase quadratically with respect to the wave number,

$$\alpha=a(T-T_c)+b(q-q_0)^2 \ . \tag{15}$$

Here b must be positive and reflects the strength of correlation among atoms in the crystal. The ordinary mean-field theory, where the Landau theory belongs, corresponds to the case where b becomes infinite.

Here it is important to remember that there can exist an internal perturbation which changes the dynamical matrix. It is the occurrence of an antisymmetrical part of the Hermitian dynamical matrix of the crystal. This phenomenon is represented in the free energy as the occurrence of coupling of the existing eigenmodes. The free energy of the system can be expressed as

$$G=G_0+\alpha(\eta_q\eta_q^*+\xi_q\xi_q^*)+\sigma(q)\eta_q^*\xi_q+\sigma^*(q)\eta_q\xi_q^* \ , \tag{16}$$

where $\sigma(q)$ represents a complex coefficient. From this free energy,

$$\frac{\partial G}{\partial\eta_q^*}=\omega^2\eta_q=\alpha\eta_q+\sigma(q)\xi_q \ , \tag{17}$$

and

$$\frac{\partial G}{\partial\xi_q^*}=\omega^2\xi_q=\alpha\xi_q+\sigma^*(q)\eta_q \ , \tag{18}$$

where ω means eigenfrequency. Equations (17) and (18) represent an eigenvalue problem

$$(\alpha-\omega^2)\eta_q+\sigma(q)\xi_q=\omega^2\eta_q \tag{19}$$

and

$$\sigma^*(q)\eta_q+(\alpha-\omega^2)\xi_q=\omega^2\xi_q \ . \tag{20}$$

Here $\sigma(q)$ is expressed by using a coupling constant $\sigma(x)$ between two atoms separated by a vector x,

$$\sigma(q)=\sum_x\sigma(x)\exp(iqx) \ . \tag{21}$$

As x is a small quantity, it can be expanded as

$$\sigma(q)=\sum_{x}\sigma(x)+\sum_{x}\sigma(x)iqx \ . \tag{22}$$

As q is a general point, an inversion center does not exist along the x axis, or $\sigma(x)$ has the symmetry of a vector, i.e., $\sigma(-x)=-\sigma(x)$. This is one of the conditions that the Lifshitz term must be invariant under the symmetry operations of the crystal. Then (21) becomes

$$\sigma(q)=iq\Gamma \ , \tag{23}$$

where

$$\Gamma=\sum_{x}\sigma(x)x \ . \tag{24}$$

Γ stands for the strength of coupling among atoms. Then a secular equation for the above equations becomes

$$\begin{vmatrix} \alpha-\omega^2 & iq\Gamma \\ -iq\Gamma & \alpha-\omega^2 \end{vmatrix}=0 \ . \tag{25}$$

Two solutions for the eigenfrequencies can be obtained,

$$\omega_1^2(q)=\alpha-\Gamma q=a(T-T_c)-\Gamma q+b(q-q_0)^2 \tag{26}$$

and

$$\omega_2^2(q)=\alpha+\Gamma q=a(T-T_c)+\Gamma q+b(q-q_0)^2 \ . \tag{27}$$

Thus it is shown that the degenerate 1 and 2 modes resonate with each other by the effect of a pure imaginary perturbation, and lift to two branches of ω_1^2 and ω_2^2. The wave numbers of the minimum frequencies for each branch can be deduced by a condition of $\partial\omega_1^2/\partial q=\partial\omega_2^2/\partial q=0$,

$$q_1=q_0+\Gamma/2b \tag{28}$$

and

$$q_2=q_0-\Gamma/2b \ . \tag{29}$$

The dispersion of ω_1^2 and ω_2^2 with respect to q are depicted exaggeratively in Fig. 4, where q_1 and q_2 points are symmetrically disposed with respect to q_0. It must be noted that the ratio Γ/b has no relation with the crystalline period along the x axis. Accordingly, q_1 and q_2 will never coincide with any points in the mesh of the Brillouin zone. This is the reason why q_1 and q_2 correspond to IC points in the Brillouin zone.

When (26) is substituted into (19),

$$\eta_q/\xi_q=-i \ . \tag{30}$$

Therefore the 1 wave is a compound wave of η_q and ξ_q, forming a circular right-handed helix with the axis parallel to the x axis. The wavelength or the pitch of this helix is $\lambda_1=2\pi/q_1$. The similar structure of a circular left-handed helix is constructed for the 2 wave, where

$$\eta_q/\xi_q=i \ , \tag{31}$$

and $\lambda_2=2\pi/q_2$.

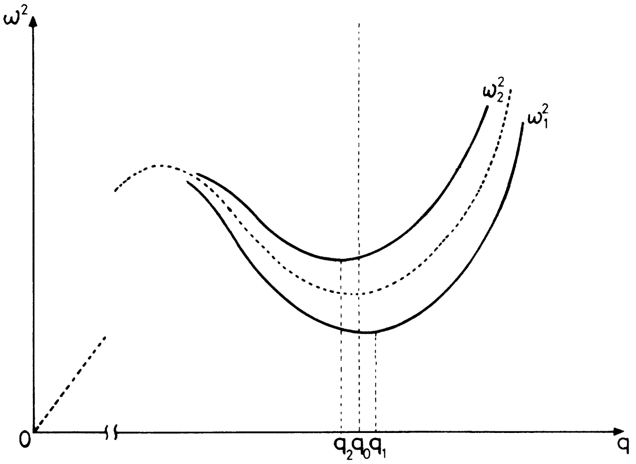

FIG. 4. Splitting of a degenerate mode into two branches, ω_1^2 and ω_2^2 with exaggeration.

The minimum frequencies of the two branches can be obtained by substituting the values of q_1 and q_2 into (26) and (27),

$$^m\omega_1^2=a(T-T_c)-\Gamma q_0-\Gamma^2/4b \tag{32}$$

and

$$^m\omega_2^2=a(T-T_c)+\Gamma q_0-\Gamma^2/4b \ . \tag{33}$$

$^m\omega_1^2$ is always smaller than $^m\omega_2^2$ by $2\Gamma q_0$, and consequently the 1 wave can be condensed earlier than the 2 wave when T is decreased. The transition temperature T_i from the normal to the IC phase can be deduced from the condition of $^m\omega_1^2=0$,

$$T_i=T_c+\frac{\Gamma}{a}q_0+\frac{\Gamma^2}{4ab} \ . \tag{34}$$

Two circular helical waves fluctuate above T_i with an opposite sense of rotation, but with zero mean amplitudes of $\langle|Q_{q_1}|\rangle$ and $\langle|Q_{q_2}|\rangle$. Below T_i, one helical wave, say 1 wave, is condensed with a nonzero amplitude. However, the fluctuation of the phason still continues to be infinite at any temperatures below T_i. This is the physical state of the present model and the same as that already shown in Fig. 2.

The physical state of this system will change in the lower temperature region as depicted in the following. The magnitude of the amplitude mode and, accordingly, the radius of the helix will be increased with decreasing temperature. However, the pitch and the translational velocity of the helix are kept constant. Anisotropy energy of the crystal gradually becomes prevailing, and the helical structure begins to be collapsed. The pitch of the helix is elongated, and commensurate crystalline parts called domains come to exist, where phasons have completely vanished. Such a change of the state in the lower temperature region was also confirmed by our optical activity measurements as will be described later.

IV. ORIGIN OF OPTICAL ACTIVITY IN INCOMMENSURATE PHASES

To reveal a quantitative relation between crystal structure and optical activity was long an important problem of physics and crystallography.[14] Although much progress has been made by Glazer[15] recently, it is still left incomplete due mainly to the lack of the correct knowledge of crystal structures and extreme deficiency of the data of optical activity. However, we believe that a helical structure can produce OA as was elegantly shown by Wood.[16] Here, for the sake of completeness of this paper, we explain briefly how our helical structure of the IC phase can cause OA.

Let us consider that a group of atoms within a pitch of the helix forms a molecule. The molecule contains various kinds of electrons. But we confine our attention simply to a specific one of electrons that are restored to the molecule with a characteristic frequency ω_0, and ignore other electrons. Assume that the number of such electrons in a molecule is n, and N molecules are contained in a unit volume. Electric field $\mathbf{E}=\mathbf{E}^0\exp(i\omega t-\mathbf{k}\cdot\mathbf{r})$, with a frequency ω and wave number $\mathbf{k}$, is applied to this molecular system. In the first step, we disregard the helical structure and assume that the electric field is homogeneous over the molecule. Then the equation of motion of any electron along the x axis is given as

$$m\left[\frac{d^2x}{dt^2}+\omega_0 x\right]=-eE_x=eE_x^0\exp(-i\omega t)\ , \tag{35}$$

where x is the displacement of the electron, and m and e represent its mass and electric charge, respectively. The displacement can be solved as

$$x=-eE_x/m(\omega_0^2-\omega^2)\ . \tag{36}$$

The x component of the induced polarization is given

$$P_x=-eNnx=e^2NnE_x/m(\omega_0^2-\omega^2)\ . \tag{37}$$

Now we take the effect of the helical structure into account. Assume that the electrons are forced to move only along the helical path. A right-handed helix depicted in Fig. 5(a) indicates this limiting path of the electrons. It is essential that under this condition the electrons receive electric force along the x axis not only from the E_x component but also from the E_y and E_z components, when the electric field $\mathbf{E}(E_x,E_y,E_z)$ is applied. To be more precise, an electron located at the lowest position A of the helix in the figure feels the electric force along the positive x direction by E_y, while another electron at the highest position B feels the electric force in the opposite direction by the same field. As a result, the net force will not originate along the x direction by E_y. If E_y changes linearly with respect to the z direction within a molecule, as depicted in Fig. 5(b), where $|E_y|$ is the largest in the lowest and highest parts of the helix, the electrons will be affected by the net force along the x direction by E_y. The same condition holds for E_z when $\partial E_z/\partial y=0$. Instead of Eq. (35), the equation of motion of an electron becomes

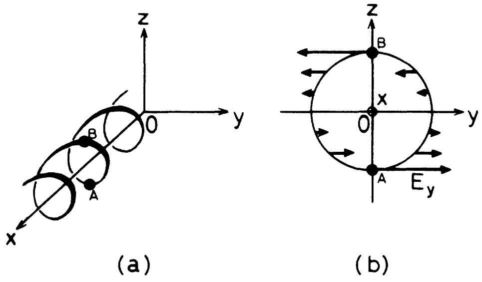

FIG. 5. Schematic demonstration for origin of optical activity. See text.

$$m\left[\frac{d^2x}{dt^2}+\omega_0^2x\right]=-e\left[E_x+c\left[\frac{\partial E_y}{\partial z}-\frac{\partial E_z}{\partial y}\right]\right]\ , \tag{38}$$

where c is a constant. Then, induced P_x is expressed as

$$P_x=[e^2Nn/m(\omega_0^2-\omega^2)][E_x+c(\nabla\times\mathbf{E})_x]\ . \tag{39}$$

The present result can be rewritten into a general form. When the motion of the electrons are confined to a helical path, induced polarization can be expressed as

$$\mathbf{P}=\epsilon_0 x\mathbf{E}+\epsilon_0 g\nabla\times\mathbf{E}\ , \tag{40}$$

where ϵ_0 is the dielectric constant of the vacuum, x the polarizability, and g is a characteristic constant. Accordingly, the electric displacement $\mathbf{D}$ is written as

$$\mathbf{D}=\epsilon_0\mathbf{E}+\mathbf{P}=\epsilon\mathbf{E}+i\epsilon_0\mathbf{G}\times\mathbf{E}\ . \tag{41}$$

Here $\mathbf{G}$ is expressed by

$$\mathbf{G}=G\hat{\mathbf{s}}\ , \tag{42}$$

where $\hat{\mathbf{s}}$ is a unit vector of the wave normal, and G is the gyration. It is readily understood[17] that if the material equation of (40) holds in a crystal it becomes optically active.

V. EXPERIMENTAL RESULTS OF A_2BX_4-TYPE CRYSTALS

We revealed OA of the IC phases of four crystals belonging to A_2BX_4-type crystals as was described before. In Table I, the relevant crystallographic axes and ob-

TABLE I. Crystal orientation and gyration of A_2BX_4 crystals.

Substances	Ferroelectric axis	Incommensurate axis	q_0	g ($\times10^{-6}$) (at 4 °C below Ti)
$[N(CH_3)_4]_2ZnCl_4$	a	c	$\frac{2}{5}$	0.08 (g_{23})
$[N(CH_3)_4]_2CuCl_4$		c	$\frac{1}{3}$	36 (g_{23})
Rb_2ZnCl_4	a	c	$\frac{1}{3}$	1.5 (g_{23})
$(NH_4)_2BeF_4$	b	c	$\frac{1}{2}$	4.0 (g_{13})

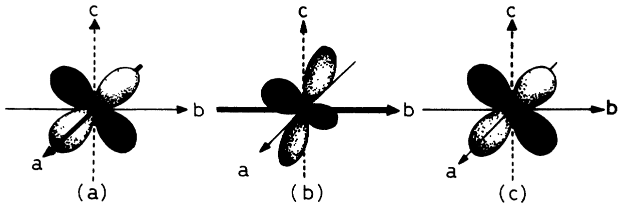

FIG. 6. Gyration surfaces of IC phases of A_2BX_4 crystals.

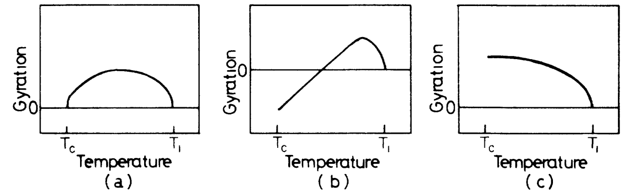

FIG. 8. Modes of temperature dependences of gyration. See text.

served gyrations of these crystals are shown. The orientation of the gyration surfaces of these crystals, with respect to IC and ferroelectric axes, is schematically depicted in Fig. 6 where dotted and bold axes represent IC and polarization axes, respectively. Figure 6(a) represents a gyration surface of the crystals, where g_{23} was measured; $[N(CH_3)_4]_2ZnCl_4$, Rb_2ZnCl_4, and Rb_2ZrBr_4 being contained in this case. Figure 6(b) indicates the case where the g_{13} component was measured, $(NH_4)_2BeF_4$ being the example. Figure 6(c) depicts the case where g_{23} was measured, $[N(CH_3)_4]_2CuCl_4$ being the example, but becoming ferroelastic in the commensurate phase.

In the cases of Figs. 6(a) and 6(b), the gyration surfaces of the IC phases are the same as those in the low-temperature C_{2v} phases, where the crystal becomes ferroelectric. This means that the perturbation which permits optical activity in the IC states is so small that the symmetry of the physical properties conforms to that of the low-temperature form. Even in the case of Fig. 6(c) the gyration surface is quite similar to the two cases, although the low-temperature form is not ferroelectric and optically inactive.

The temperature dependences of gyration tensors of these crystals are shown in Fig. 7: in 7(a) $[N(CH_3)_4]_2ZnCl_4$, in 7(b) Rb_2ZnCl_4, in 7(c) $(NH_4)_2BeF_4$, and in 7(d) $[N(CH_3)_4]_2CuCl_4$. Each gyration tensor increases with decreasing temperature. This clearly reflects the increase of the amplitude mode $\langle |Q_{q_1}| \rangle$. With a further decrease of temperature, the anisotropy term becomes predominant. Then the crystal texture changes as briefly depicted before; segregation into multisoliton regions called discommensurations and domains takes place. The domains are the region where the eigenstates of the symmetrical dynamical matrix are condensed and, accordingly, the order parameters are real. In other words, the phase mode does not exist in the domains, and they must be optically inactive on a basis of our reasoning. This fact has really been demonstrated in $[N(CH_3)_4]_2CuCl_4$.[5] However, it must be noticed that the domains can be optically active through the electrogyration effect when they are ferroelectric.

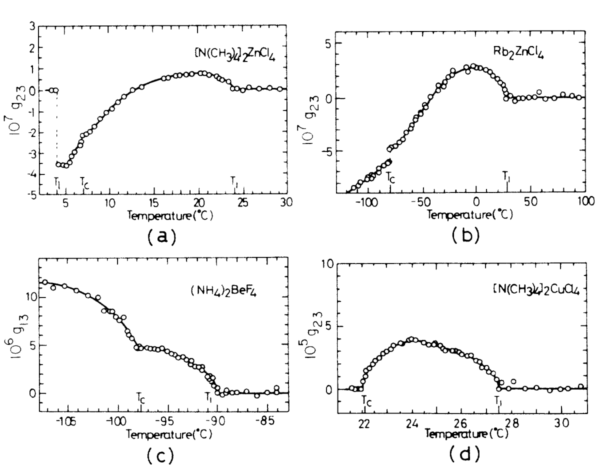

FIG. 7. Temperature dependences of gyration tensors of some A_2BX_4 crystals.

We[8] classified the temperature dependences of gyration of the IC phase into three types under a principle based on our theory. We avoid overlapped descriptions here and only show the schematic representation of the results in Fig. 8. It is clear that all the results shown in Fig. 7 can be perfectly classified into any modes of Fig. 8; $[N(CH_3)_4]_2CuCl_4$ into 8(a), Rb_2ZnCl_4 and $[N(CH_3)_4]_2ZnCl_4$ into 8(b), and $(NH_4)_2SO_4$ into 8(c). This fact also indicates that our interpretation of the origin of OA of the IC phases is correct.

VI. DISCUSSIONS

We have revealed through experimental and theoretical study of OA that the origin of the IC phase transition can be ascribed to a perturbation of the antisymmetrical part of the Hermitian dynamical matrix. It must be noted that the antisymmetrical part is nothing but the Lifshitz term, which appears in the free energy expanded in the real space. However, the present theory which was developed in the Fourier space depicts the outstanding feature of the structure and dynamics of the IC state.

According to our theory, gyration is closely connected with the helical structure of the IC state. Therefore, OA has become a more useful tool than for merely detecting the symmetry in the study of the IC phase transitions. If the pitch of a helix is small, relevant electrons are obliged to make a larger number of revolutions in traveling a given distance along the x axis, and the resultant effect of the y and z components of the electric force is greater than when the pitch is large. Thus the gyration G will be expressed in general

$$G = C\frac{l}{d} , \tag{43}$$

TABLE II. Critical exponents of A_2BX_4 crystals.

Substances	Critical exponents β
$[N(CH_3)_4]_2ZnCl_4$	0.42
$[N(CH_3)_4]_2CuCl_4$	0.44
Rb_2ZnCl_4	0.43
$(NH_4)_2BeF_4$	0.47

where l represents the distance from an atom consisting of the amplitude mode to the helix axis, d is the pitch of the helix, and C is a constant. To be more specific referring to the present case, it becomes

$$G = C\langle |Q_{q_1}| \rangle (q_0 + \Gamma / b) \ . \quad (44)$$

There appears a possibility that the measurements of the OA provide us with the knowledge of a factor of Γ/b, which plays a major role for the transformation into the IC state. However, for obtaining this factor, the amplitude mode must be properly evaluated at first. We found that the temperature dependences of $\langle |Q_{q_1}| \rangle$ of the four crystals are followed to almost the same scaling law, as can be seen in Table II, where the observed critical exponents of the crystals are shown. We are making way for evaluating the absolute value of this quantity. At any rate, the work of OA for the study of IC phase transitions is only a clue. However, this work will be promising and the x-ray work incorporated with OA analysis will be useful.

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