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New view of the two commensurate phases in the typical incommensurate transition sequence (commensurate phase→incommensurate phase→commensurate phase)

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Transition sequence Pr→IF→CF in dielectric substances is dealt with, where Pr, IF, and CF denote prototypic phase, incommensurate ferroic (or distorted) phase, and commensurate ferroic phase, respectively. The transition (or order) parameters are assumed to be two mutually conjugate complex quantities depending only on x, not on y or z. They are denoted by $Q(x)$ and $Q^*(x)$. In general, $Q(x)$ can be expressed as a sum of harmonics of the form $Q_n e^{inhx}$. Commonly, the lowest harmonic adopted is the first harmonic $Q_1 e^{ihx}$. In this paper, however, the zeroth harmonic Q_0 is taken into account. For simplicity, high harmonics are ignored so that $Q(x)=Q_0+Q_1 e^{ihx}$. Three views of CF are possible, i.e., CF may have $\{Q_{\omega s}\neq 0,\ h_s=0\}$, $\{Q_{0s}\neq 0,\ Q_{1s}=0,\ h_s$ indefinite$\}$, or $\{Q_{0s}\neq 0,\ Q_{1s}=0,\ h_s\neq 0\}$, where $Q_\omega \equiv Q_0+Q_1$, and the subscript s means "spontaneous." In the third view, h_s is regarded as definite and assumed not to be nearly zero. The first view is conventional, in essence, while the third is new. Three views of Pr are possible, i.e., Pr may have $\{Q_{\omega s}=0,\ h_s=0\}$, $\{Q_{0s}=0,\ Q_{1s}=0,\ h_s$ indefinite$\}$, or $\{Q_{0s}=0,\ Q_{1s}=0,\ h_s\neq 0\}$. Only one view of IF is possible, i.e., IF has only $\{Q_{0s}=0,\ Q_{1s}\neq 0,\ h_s\neq 0\}$. The transition Pr→IF and the imaginary direct transition Pr→CF are assumed to be second order. The temperatures of the respective transitions are denoted by $T_{\rm tr}$ and $T'_{\rm tr}$. It is found that if the third views of Pr and CF are adopted, the transitions Pr→IF and Pr→CF are *strongly* second order, i.e., even h_s is continuous at $T_{\rm tr}$ and $T'_{\rm tr}$. Let $q_1 \equiv |Q_1|$. Let Φ be the spatially averaged free-energy function. The third views of Pr and CF are thought to be reasonable from the investigation of the T dependence of $(\partial^2\Phi/\partial q_1^2)_s$ in Pr near $T_{\rm tr}$ and in CF near $T'_{\rm tr}$. A full account of this investigation is given.

I. INTRODUCTION

A considerable number of substances are known to undergo the following successive transitions: prototypic phase→incommensurate ferroic phase→commensurate ferroic phase.[1] Sodium nitrite[2,3] and potassium selenate[4–6] are typical examples of such substances. It is convenient to abbreviate the above-mentioned three phases as Pr, IF, and CF, respectively. Pr is a type of commensurate phase. Many authors[7] have thermodynamically investigated the transition Pr→IF or the transition sequence Pr→IF→CF.

Let us assume that the transition (or order) parameters are two mutually conjugate complex quantities, and that they are functions of spatial coordinate x, not depending on y or z. Let them be denoted by $Q(x)$ and $Q^*(x)$. A phase is, obviously, prototypic or ferroic according to whether its $[Q(x)]_s$ (subscript s denotes "spontaneous") is zero independently of x or not. A phase is commensurate or incommensurate according to whether its $[Q(x)]_s$ is x independent or not. For incommensurateness, however, the x dependence should not constitute all of the conditions. A second condition, i.e., the condition that the spatial average of $[Q(x)]_s$ is zero, should be added. This second condition ensures pure incommensurateness. If a phase satisfied only the first condition and not the second, it would be mixed, i.e., both commensurate and incommensurate (in the x direction). In general, $Q(x)$ can be expressed as a sum of harmonics of the form $Q_n e^{inhx}$, where h is the incommensurate wave-number parameter and n is an integer. It is common that the lowest harmonic adopted is the first harmonic $Q_1 e^{ihx}$ (not the zeroth harmonic Q_0). For simplicity, let the second and higher harmonics be ignored. Then,

$$Q(x)=Q_1 e^{ihx}\,. \tag{1.1}$$

Pr, IF, and CF obviously must have

$$Q_{1s}^{\rm Pr}=0\,, \tag{1.2}$$

$$Q_{1s}^{\rm IF}\neq 0\,,\quad h_s^{\rm IF}\neq 0\,, \tag{1.3}$$

$$Q_{1s}^{\rm CF}\neq 0,\quad h_s^{\rm CF}=0\,. \tag{1.4}$$

$Q_{1s}^{\rm Pr}$ stands for the Q_{1s} of Pr.

The lower the harmonic is, the stronger or the less negligible its influence is. This may be a general rule. In the present paper, the zeroth harmonic is taken into account, so that

$$Q(x)=Q_0+Q_1 e^{ihx}\,. \tag{1.5}$$

If $h=0$, the right-hand side of Eq. (1.5) becomes Q_0+Q_1. We set

$$Q_0+Q_1\equiv Q_\omega\,.$$

IF obviously must have

$$Q_{0s}^{\rm IF}=0\,,\quad Q_{1s}^{\rm IF}\neq 0,\quad h_s^{\rm IF}\neq 0\,. \tag{1.6}$$

As for CF, since its $[Q(x)]_s$ is x independent and nonzero, it may have either $\{Q_{\omega s}^{\rm CF}\neq 0,\ h_s^{\rm CF}=0\}$ or $\{Q_{0s}^{\rm CF}\neq 0,\ Q_{1s}^{\rm CF}=0\}$. In the latter case, $h_s^{\rm CF}$ may be regarded either as essentially indefinite or as definite and nonzero. Thus, the following three views of CF are possible:

$$Q_{\omega s}^{\mathrm{CF}} \neq 0 \ , \ \ h_s^{\mathrm{CF}}=0 \ , \tag{1.7}$$

$$Q_{0s}^{\mathrm{CF}} \neq 0, \ Q_{1s}^{\mathrm{CF}}=0, \ h_s^{\mathrm{CF}} \text{ indefinite} \ , \tag{1.8}$$

$$Q_{0s}^{\mathrm{CF}} \neq 0 \ , \ Q_{1s}^{\mathrm{CF}}=0 \ , \ h_s^{\mathrm{CF}} \neq 0 \ . \tag{1.9}$$

In view (1.9), h_s^{CF} is assumed to be not approximately zero, but so large that

$$|h| L \gg 1 \ , \tag{1.10}$$

where L stands for the length of the crystal specimen in the x direction; usually, $1\times 10^{-4} \lesssim L \lesssim 1\times 10^{-2}$ m. (On the other hand, it is assumed that $|h| a_0 \ll 1$, where a_0 stands for the length of the prototype unit cell in the x direction.) Although h_s^{CF} is such a large nonzero, CF is literally a commensurate phase having a lattice constant equal to an integer multiplied by a_0, because Q_{1s}^{CF} is zero or, in other words, the wave $Q_{1s}^{\mathrm{CF}}\exp(ih_s^{\mathrm{CF}}x)$ is zero. Although $Q_{1s}^{\mathrm{CF}}=0$, the definite nonzero value of h_s^{CF} can be really determined by adopting the two-step method (see Sec. II).

The view of CF, (1.7), is essentially the same as the conventional view, (1.4). On the other hand, view (1.9) is new.

As for Pr, since its $[Q(x)]_s$ is zero independently of x, it may have either $\{Q_{\omega s}^{\mathrm{Pr}}=0, \ h_s^{\mathrm{Pr}}=0\}$ or $\{Q_{0s}^{\mathrm{Pr}}=0, \ Q_{1s}^{\mathrm{Pr}}=0\}$. In the latter case, h_s^{Pr} may be regarded either as essentially indefinite or as definite and nonzero. Thus, the following three views of Pr are possible:

$$Q_{\omega s}^{\mathrm{Pr}}=0 \ , \ \ h_s^{\mathrm{Pr}}=0 \ , \tag{1.11}$$

$$Q_{0s}^{\mathrm{Pr}}=0, \ \ Q_{1s}^{\mathrm{Pr}}=0, \ h_s^{\mathrm{Pr}} \text{ indefinite} \ , \tag{1.12}$$

$$Q_{0s}^{\mathrm{Pr}}=0, \ \ Q_{1s}^{\mathrm{Pr}}=0, \ h_s^{\mathrm{Pr}} \neq 0 \ . \tag{1.13}$$

In view (1.13), h_s^{Pr} is assumed to conform to inequality (1.10). Although $Q_{1s}^{\mathrm{Pr}}=0$, the definite nonzero value of h_s^{Pr} can be really determined by adopting the two-step method (see Sec. II). Obviously, the three views of Pr, (1.11), (1.12), and (1.13), correspond to the three views of CF, (1.7), (1.8), and (1.9), respectively.

Only one view of IF is possible, namely view (1.6). h_s^{IF} is definite. For it, inequality (1.10) is assumed.

From the viewpoint of energy, the three views of CF are equally reasonable. They give an equal free energy of CF (see Sec. II). The three views of Pr also give an equal free energy of Pr.

The transition Pr→IF and the imaginary direct transition Pr→CF are both assumed to be second order. (Transition IF→CF is deduced, not assumed, to be first order.) Let T, T_{tr}, and T'_{tr} denote temperature, the Pr→IF transition temperature, and the Pr→CF transition temperature, respectively. That the transition Pr→IF is second order means

$$[Q(x)]_s^{\mathrm{IF}}=0 \text{ independently of } x \text{ at } T_{\mathrm{tr}} \ , \tag{1.14}$$

which amounts to, in net $Q_{1s}^{\mathrm{IF}}=0$ at T_{tr} and, in gross,

$$Q_{0s}^{\mathrm{IF}}=0, \ \ Q_{1s}^{\mathrm{IF}}=0, \ \ h_s^{\mathrm{IF}} \neq 0 \ \text{ at } T_{\mathrm{tr}} \ . \tag{1.15}$$

Although $Q_{1s}^{\mathrm{IF}}=0$ at T_{tr}, h_s^{IF} is still definite. It is still nonzero. (According to observations, $|h_s^{\mathrm{IF}}|$ increases as T approaches T_{tr} from below.) That the transition Pr→CF is second order means

$$[Q(x)]_s^{\mathrm{CF}}=0 \ \text{ at} T'_{\mathrm{tr}} \ , \tag{1.16}$$

which amounts to, in gross,

$$Q_{\omega s}^{\mathrm{CF}}=0, \ h_s^{\mathrm{CF}}=0 \ \text{ at } T'_{\mathrm{tr}} \ , \tag{1.17}$$

$$Q_{0s}^{\mathrm{CF}}=0, \ Q_{1s}^{\mathrm{CF}}=0, \ \ h_s^{\mathrm{CF}} \text{ indefinite at } T'_{\mathrm{tr}} \ , \tag{1.18}$$

$$Q_{0s}^{\mathrm{CF}}=0, \ Q_{1s}^{\mathrm{CF}}=0, \ \ h_s^{\mathrm{CF}} \neq 0 \text{ at } T'_{\mathrm{tr}} \ , \tag{1.19}$$

depending on which view, (1.7), (1.8), or (1.9), is adopted.

A second-order transition is referred to as being *strongly* second order, when not only $[Q(x)]_s$ but its components Q_{0s}, Q_{1s}, and h_s are all continuous at the transition point. An otherwise second-order transition is referred to as being *weakly* second order.

Compare relations (1.15) with relations (1.11)–(1.13). If the third view of Pr, (1.13), is adopted, transition Pr→IF is strongly second order. It holds that $h_s^{\mathrm{Pr}}=h_s^{\mathrm{IF}}$ at T_{tr} (see Sec. II). If either view (1.11) or (1.12) is adopted, transition Pr→IF is weakly second order. As for transition Pr→CF, if the third views of Pr and CF are adopted, the transition is strongly second order. It holds that $h_s^{\mathrm{Pr}}=h_s^{\mathrm{CF}}$ at T'_{tr} (see Sec. II). In summary, the transitions from Pr to the two ferroics are both strongly second order if and only if the third views of Pr and CF are adopted.

Let $q_1 \equiv |Q_1|$, and let Φ be the spatially averaged free-energy function per unit volume. Investigating the T dependence of $(\partial^2\Phi/\partial q_1^2)_s$ in Pr near T_{tr} and in CF near T'_{tr}, I think that the third views of Pr and CF are reasonable. The investigation has been performed on K_2SeO_4 as an example. Its details will be given in Sec. II.

Although the transition sequence Pr→IF→CF is exhibited by $NaNO_2$ as well as by K_2SeO_4, its mechanism is essentially different for the two substances. In K_2SeO_4 it is sufficient that only a pair of soft modes belonging to a single irreducible representation is taken into account, while in $NaNO_2$ it is necessary that, in addition to a soft mode, a hard mode which belongs to a different irreducible representation should be taken into account. The case of $NaNO_2$ is thus more complicated. The third views of Pr and CF will be applied to $NaNO_2$ in Sec. III.

II. THEORY: K_2SeO_4

Upon cooling, potassium selenate[4–6] undergoes transition Pr→IF at 129 K and transition IF→CF at 93 K. Pr has symmetry of the space group *Pnam* (or D_{2h}^{16}). Honestly speaking, the *Pnam* phase is not a prototypic phase, but a ferroic phase (ferroelastic) derived from a certain hexagonal structure.[8] However, for simplicity, the *Pnam* phase is assumed to be prototypic (the present paper does not deal with the hexagonal→*Pnam* transition). CF has symmetry of the space group $Pna2_1$ (or C_{2v}^9), and also has lattice constants equal to $3a_0$, b_0, and c_0, where a_0, b_0, and c_0 stand for the lattice constants of Pr. IF is incommensurately modulated with a wavelength close to $3a_0$ in the x direction. In the y and z directions, IF is commensurate and has lattice constants equal to b_0 and c_0. The transition at 129 K is second order, while the transition at 93 K is first order. Although there exist a few thermodynamical theories on the transitions of potassium selenate,[9,10] a retheorization is necessary for the present subject.

The unmodulated (i.e., x-independent) transition parameters for the transitions of K_2SeO_4 are two mutually conjugate complex quantities, denoted by Q and Q^*. The prototype space group *Pnam* can be generated by three elements, one of which is the pure reflection across the plane through point $(0,0,\frac{1}{4}c_0)$ perpendicular to the z axis. Another is a glide reflection with its reflectional part across the plane through point $(0,\frac{1}{4}b_0,0)$ perpendicular to the y axis and with its translational part along the x axis. The third is the inversion across the origin. By the respective generators, Q and Q^* are transformed as

$$Q\rightarrow -Q,\quad Q^*\rightarrow -Q^*\ , \tag{2.1a}$$

$$Q\rightarrow -e^{i\pi/3}Q,\quad Q^*\rightarrow -e^{-i\pi/3}Q^*\ , \tag{2.1b}$$

$$Q\rightarrow Q^*,\quad Q^*\rightarrow Q\ . \tag{2.1c}$$

From these relations, it immediately follows that the primitive translation along the x axis transforms Q and Q^* as

$$Q\rightarrow e^{i2\pi/3}Q,\quad Q^*\rightarrow e^{-i2\pi/3}Q^*\ ,$$

and the primitive translation along the y or z axis gives $Q\rightarrow Q$ and $Q^*\rightarrow Q^*$. In other words, the wave vectors of Q and Q^* are $(\frac{1}{3},0,0)$ and $(-\frac{1}{3},0,0)$, respectively. Table I shows the sequence of space groups that embodies the set of transformations (2.1).[11] In Table I two phases of rank 1 appear. The phase of space group $P12_1/a1$ (or C_{2h}^5) has

$$\arg Q_s=\tfrac{1}{3}k\pi\quad (k=0,1,\ldots,5)\ , \tag{2.2}$$

while the phase of space group $Pna2_1$ (or C_{2v}^9) has

$$\arg Q_s=\tfrac{1}{6}\pi+\tfrac{1}{3}k\pi\quad (k=0,1,\ldots,5)\ . \tag{2.3}$$

Although either phase may be realized, the $Pna2_1$ phase alone is realized in K_2SeO_4.

TABLE I. Space-group sequence embodying the transformations (2.1) of the unmodulated transition parameters.

Rank 2	Rank 1	Rank 0
Pnam	$P12_1/a1$ $Pna2_1$	$P1a1$

The modulated (i.e., x-dependent) transition parameters are denoted by $Q(x)$ and $Q^*(x)$, which may momentarily be general functions of x not restricted to any special form. $\Phi(x)$, viz., the free energy per unit volume before spatial averaging is assumed to be equatable to a power series in $Q(x)$, $Q^*(x)$, and their first- and second-order derivatives. Duly considering transformation, the free-energy equation is found to take the form

$$\begin{aligned}\Phi(x)=&\tfrac{1}{2}\sum A_{2m,6n}[Q(x)Q^*(x)]^m[Q(x)^{6n}+Q^*(x)^{6n}]\\&-i\tfrac{1}{2}\sum B^{(1)}_{2m,6n+2}[Q(x)Q^*(x)]^m[Q^*(x)^{6n+1}\partial_xQ(x)-Q(x)^{6n+1}\partial_xQ^*(x)]\\&-i\tfrac{1}{2}\sum B^{(2)}_{2m,6n+6}[Q(x)Q^*(x)]^m[Q(x)^{6n+5}\partial_xQ(x)-Q^*(x)^{6n+5}\partial_xQ^*(x)]\\&-\tfrac{1}{2}\sum C^{(1)}_{2m,6n+2}[Q(x)Q^*(x)]^m[Q^*(x)^{6n+1}\partial^2_{xx}Q(x)+Q(x)^{6n+1}\partial^2_{xx}Q^*(x)]\\&-\tfrac{1}{2}\sum C^{(2)}_{2m,6n+6}[Q(x)Q^*(x)]^m[Q(x)^{6n+5}\partial^2_{xx}Q(x)+Q^*(x)^{6n+5}\partial^2_{xx}Q^*(x)]\\&+\tfrac{1}{2}\sum C^{(3)}_{2m,6n+2}[Q(x)Q^*(x)]^m[Q(x)^{6n}+Q^*(x)^{6n}]\partial_xQ(x)\partial_xQ^*(x)\\&-\tfrac{1}{2}\sum C^{(4)}_{2m,6n+4}[Q(x)Q^*(x)]^m\{Q^*(x)^{6n+2}[\partial_xQ(x)]^2+Q(x)^{6n+2}[\partial_xQ^*(x)]^2\}\\&-\tfrac{1}{2}\sum C^{(5)}_{2m,6n+6}[Q(x)Q^*(x)]^m\{Q(x)^{6n+4}[\partial_xQ(x)]^2+Q^*(x)^{6n+4}[\partial_xQ^*(x)]^2\}\ .\end{aligned} \tag{2.4}$$

Here, $\sum$ stands for the double summation from $m=0$ to ∞ and from $n=0$ to ∞. ∂_x and ∂^2_{xx} are abbreviated forms of $\partial/\partial x$ and $\partial^2/\partial x^2$, respectively. The coefficients $A_{2m,6n},\ldots,C^{(5)}_{2m,6n+6}$ are all real.

For simplicity, let us omit from Eq. (2.4) terms of high degree with respect to $Q(x)$ and $Q^*(x)$. The reduced equation is

$$\begin{aligned}\Phi(x)=&\Phi_0+A_{20}Q(x)Q^*(x)+A_{40}[Q(x)Q^*(x)]^2+A_{60}[Q(x)Q^*(x)]^3+\tfrac{1}{2}A_{06}[Q(x)^6+Q^*(x)^6]\\&-i\tfrac{1}{2}B^{(1)}_{02}[Q^*(x)\partial_xQ(x)-Q(x)\partial_xQ^*(x)]-i\tfrac{1}{2}B^{(1)}_{22}Q(x)Q^*(x)[Q^*(x)\partial_xQ(x)-Q(x)\partial_xQ^*(x)]\\&-\tfrac{1}{2}C^{(1)}_{02}[Q^*(x)\partial^2_{xx}Q(x)+Q(x)\partial^2_{xx}Q^*(x)]-\tfrac{1}{2}C^{(1)}_{22}Q(x)Q^*(x)[Q^*(x)\partial^2_{xx}Q(x)+Q(x)\partial^2_{xx}Q^*(x)]\\&+C^{(3)}_{02}\partial_xQ(x)\partial_xQ^*(x)+C^{(3)}_{22}Q(x)Q^*(x)\partial_xQ(x)\partial_xQ^*(x)-\tfrac{1}{2}C^{(4)}_{04}\{Q^*(x)^2[\partial_xQ(x)]^2+Q(x)^2[\partial_xQ^*(x)]^2\}\ .\end{aligned} \tag{2.5}$$

Subscript commas in coefficient symbols have been omitted. A_{00} has been replaced by the conventional symbol Φ_0.

Now, $Q(x)$ and $Q^*(x)$ are specialized to the forms

$$Q(x)=Q_0+Q_1e^{ihx},\quad Q^*(x)=Q_0^*+Q_1^*e^{-ihx}\ , \tag{2.6}$$

the former being the same as Eq. (1.5). We set

$$|Q_0|\equiv q_0,\quad \arg Q_0\equiv\theta_0,\quad |Q_1|\equiv q_1,\quad \arg Q_1\equiv\theta_1$$

The spatial average of $\Phi(x)$ is denoted by Φ, i.e.,

$$\Phi=\frac{1}{L}\int_{-L/2}^{L/2}\Phi(x)dx\ . \tag{2.7}$$

The domain of h is restricted to inequality (1.10). The wave Q_1e^{ihx} is assumed to be coherent over the whole of L. Owing to inequality (1.10), the average of e^{ihx} is approximately zero. The ultimate form of the average of Eq. (2.5) is found to be

$$\begin{aligned}\Phi=\Phi_0&+A_{20}(q_0^2+q_1^2)+A_{40}(q_0^4+4q_0^2q_1^2+q_1^4)+A_{60}(q_0^6+9q_0^4q_1^2+9q_0^2q_1^4+q_1^6)+A_{06}q_0^6\cos6\theta_0\\&+B_{02}hq_1^2+B_{22}h(q_1^4+2q_0^2q_1^2)+C_{02}h^2q_1^2+C_{22}h^2q_1^4+2C'_{22}h^2q_0^2q_1^2\ ,\end{aligned} \tag{2.8}$$

where

$$\begin{aligned}&B_{02}\equiv B_{02}^{(1)},\quad B_{22}\equiv B_{22}^{(1)},\quad C_{02}\equiv C_{02}^{(1)}+C_{02}^{(3)}\ ,\\&C_{22}\equiv C_{22}^{(1)}+C_{22}^{(3)}+C_{04}^{(4)},\quad C'_{22}\equiv C_{22}^{(1)}+\tfrac{1}{2}C_{22}^{(3)}\ .\end{aligned} \tag{2.9}$$

Equation (2.8) does not contain θ_1. We repeat that Eq. (2.8) has been deduced upon the assumption of inequality (1.10). If $|h|L\ll1$, and especially if $h=0$, Eq. (2.8) is invalid.

All coefficients except A_{20} (and Φ_0) are assumed to be T independent. A_{20} is assumed to vanish at a certain temperature T_0 and to depend on T in the form

$$A_{20}=K(T-T_0),\quad K=\text{const}>0\ . \tag{2.10}$$

Coefficients such as A_{40} are assumed to be positive, i.e.,

$$A_{40}>0,\quad A_{60}>0,\quad C_{02}>0,\quad C_{22}>0,\quad C'_{22}>0\ . \tag{2.11}$$

Of the three phases Pr, IF, and CF, let us first consider IF. It has

$$q_{0s}=0,\quad q_{1s}\neq0,\quad h_s\neq0\ , \tag{2.12}$$

which are essentially the same as relations (1.6). For h_s, inequality (1.10) is assumed. Thus Eq. (2.8) can be used. The expressions of h_s and q_{1s} are found to be

$$h_s=-\frac{B_{02}}{2C_{02}}\left[1-\left[\frac{C_{22}}{C_{02}}-\frac{B_{22}}{B_{02}}\right]q_{1s}^2\right]\ , \tag{2.13}$$

$$q_{1s}^2=K(T_1-T)\Bigg/\left[2A_{40}+\frac{B_{02}^2}{2C_{02}}\left[\frac{C_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}\right]\right]\ , \tag{2.14}$$

where T_1 is a characteristic temperature defined by

$$K(T_1-T_0)=B_{02}^2/4C_{02}\ . \tag{2.15}$$

Since $K>0$ and $C_{02}>0$, we have $T_1>T_0$. The inequalities

$$\frac{C_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}>0,\quad \frac{C_{22}}{C_{02}}-\frac{B_{22}}{B_{02}}>0 \tag{2.16}$$

are assumed, the latter of which, however, follows from the former owing to inequalities (2.11). According to Eq. (2.14), T must be lower than T_1; in other words, IF is possible only at $T<T_1$. Substitution of Eq. (2.14) into Eq. (2.13) gives the h_s-vs-T relation. $|h_s|$ decreases with decreasing T. The free energy of IF is found to be

$$\Phi_s-\Phi_0=-[K(T_1-T)]^2\Bigg/\left[4a_{40}+\frac{B_{02}^2}{C_{02}}\left[\frac{C_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}\right]\right]\ . \tag{2.17}$$

As far as IF is concerned, the present theory is the same as the previous theories,[9,10] except that the previous theories ignored the coefficients B_{22} and C_{22} whereas the present theory does not.

Next we consider CF, of which three views are possible. Relations (1.7)—(1.9) can be rewritten as

$$q_{\omega s}\neq0,\quad h_s=0\ , \tag{2.18}$$

$$q_{0s}\neq0,\quad q_{1s}=0,\quad h_s\ \text{indefinite}\ , \tag{2.19}$$

$$q_{0s}\neq0,\quad q_{1s}=0,\quad h_s\neq0\ . \tag{2.20}$$

For view (2.20) since inequality (1.10) is assumed, Eq. (2.8) is valid. On the other hand, for view (2.18), Eq. (2.8) is not valid. However, the more basic equation, (2.5), is valid for all views. The expression of $q_{\omega s}$ in view (2.18) is found to be

$$q_{\omega s}^2=(1/2A_{40})K(T_0-T)\ . \tag{2.21}$$

The expression of q_{0s} in views (2.19) and (2.20) is found to be

$$q_{0s}^2=(1/2A_{40})K(T_0-T)\ . \tag{2.22}$$

According to Eqs. (2.21) and (2.22), T must be lower than T_0. In other words, CF is possible only at $T<T_0$, no matter which view is adopted. What are the expressions of $\theta_{\omega s}$ and θ_{0s}? The inequality

$$A_{06}>0 \tag{2.23}$$

is assumed. Then, in view (2.18),

$$\theta_{\omega s}=\tfrac{1}{6}\pi+\tfrac{1}{3}k\pi\quad(k=0,1,\ldots,5)\ . \tag{2.24}$$

In views (2.19) and (2.20),

$$\theta_{0s}=\tfrac{1}{6}\pi+\tfrac{1}{3}k\pi\quad(k=0,1,\ldots,5)\ . \tag{2.25}$$

The space group of CF is *Pna* 2_1, not *P* $12_1/a\,1$. The free energy is found to be

$$\Phi_s-\Phi_0=-(1/4A_{40})[K(T_0-T)]^2 \tag{2.26}$$

no matter which view is adopted.

What is the expression of h_s in view (2.20)? The usual method of minimizing Φ at point $(q_{0s},\theta_{0s},q_{1s},h_s)$ is to minimize Φ *directly* at that point. By this method, h_s cannot be determined because $q_{1s}=0$. However, if the following *two-step method* is adopted, h_s can be determined. This method is, first, to minimize Φ under a fixed nonzero value of q_1 and, next, to bring q_1 to zero. Let the q_0, θ_0, and h determined in the first process be denoted by q_{0r}, θ_{0r}, and h_r, which are functions of q_1. As $q_1\rightarrow 0$, we have $q_{0r}\rightarrow q_{0s}$, $\theta_{0r}\rightarrow\theta_{0s}$, and $h_r\rightarrow h_s$. For h_r, the right-hand side of Eq. (2.8) is differentiated with respect to h and equated to zero, i.e.,

$$q_1^2[B_{02}+B_{22}(q_1^2+2q_{0r}^2)+2C_{02}h_r+2C_{22}h_rq_1^2+4C'_{22}h_rq_{0r}^2]=0\ .$$

Taking account of $q_1\neq 0$, we obtain

$$h_r=-\frac{B_{02}+B_{22}(q_1^2+2q_{0r}^2)}{2C_{02}+2C_{22}q_1^2+4C'_{22}q_{0r}^2}\ . \tag{2.27}$$

At the limit as $q_1\rightarrow 0$, Eq. (2.27) becomes

$$h_s=-\frac{B_{02}+2B_{22}q_{0s}^2}{2C_{02}+4C'_{22}q_{0s}^2}\ ,$$

which is approximated by

$$h_s=-\frac{B_{02}}{2C_{02}}\left[1-2\left[\frac{C'_{22}}{C_{02}}-\frac{B_{22}}{B_{02}}\right]q_{0s}^2\right]\ . \tag{2.28}$$

This is the h_s of CF in view (2.20). It differs from the h_s of IF expressed by Eq. (2.13). Inequalities

$$\frac{C'_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}>0,\quad \frac{C'_{22}}{C_{02}}-\frac{B_{22}}{B_{02}}>0 \tag{2.29}$$

are assumed, the latter of which, however, follows from the former owing to inequalities (2.11). Substitution of Eq. (2.22) into Eq. (2.28) gives the h_s-vs-T relation. $|h_s|$ decreases with decreasing T.

Following IF and CF, Pr is now considered. Three views of it are possible. Relations (1.11)–(1.13) can be rewritten as

$$q_{\omega s}=0,\ \ h_s=0\ , \tag{2.30}$$

$$q_{0s}=0,\ \ q_{1s}=0,\ \ h_s \text{ indefinite}\ , \tag{2.31}$$

$$q_{0s}=0,\ \ q_{1s}=0,\ \ h_s\neq 0\ . \tag{2.32}$$

The free energy is $\Phi_s-\Phi_0=0$, no matter which view is adopted. As for the expression of h_s in view (2.32), the usual direct method cannot determine it, but the two-step method can. The right-hand side of Eq. (2.8) is differentiated with respect to h under fixed nonzero values of q_0 and q_1, and is equated to zero, i.e.,

$$q_1^2[B_{02}+B_{22}(q_1^2+2q_0^2)+2C_{02}h_r+2C_{22}h_rq_1^2+4C'_{22}h_rq_0^2]=0\ .$$

Solving this equation, we obtain

$$h_r=-\frac{B_{02}+B_{22}(q_1^2+2q_0^2)}{2C_{02}+2C_{22}q_1^2+4C'_{22}q_0^2}\ . \tag{2.33}$$

At the limit as $q_0\rightarrow 0$ and $q_1\rightarrow 0$, Eq. (2.33) becomes

$$h_s=-B_{02}/2C_{02}\ . \tag{2.34}$$

Instead of first assuming that $q_0\neq 0$ (and that $q_1\neq 0$) and next bringing q_0 (and q_1) to zero, we may initially set $q_0=0$. We reach the same result, Eq. (2.34). Equation (2.34) expresses the h_s of Pr in the third view. This h_s is T independent, in contrast with the h_s of IF and the h_s of CF in the third view.

Equations (2.17) and (2.26) indicate that the Pr→IF and Pr→CF transition temperatures are equal to T_1 and T_0, respectively. (In Sec. I the Pr→IF and Pr→CF transition temperatures were denoted by T_{tr} and T'_{tr}, respectively; we now have $T_{\mathrm{tr}}=T_1$ and $T'_{\mathrm{tr}}=T_0$.) If the third views of Pr and CF are adopted, the transitions from Pr to the two ferroics are both strongly second order, because at T_1, Eq. (2.13) becomes $h_s^{\mathrm{IF}}=-B_{02}/2C_{02}=h_s^{\mathrm{Pr}}$ and at T_0, Eq. (2.28) becomes $h_s^{\mathrm{CF}}=-B_{02}/2C_{02}=h_s^{\mathrm{Pr}}$.

Investigating the T dependence of $(\partial^2\Phi/\partial q_1^2)_s$ in Pr near T_1 and in CF near T_0, I think that the third views of Pr and CF are reasonable. Explanations will follow.

Let the second or third views of Pr and CF be adopted. If the second views are adopted, h_s is, for the present, assumed to conform to inequality (1.10) while also being regarded as indefinite. Thus Eq. (2.8) is valid for the second views as well as the third. The equation

$$\tfrac{1}{2}(\partial^2\Phi/\partial q_1^2)_s=A_{20}+2A_{40}(2q_{0s}^2+3q_{1s}^2)+3A_{60}(3q_{0s}^4+18q_{0s}^2q_{1s}^2+5q_{1s}^4)$$
$$+B_{02}h_s+2B_{22}h_s(3q_{1s}^2+q_{0s}^2)+C_{02}h_s^2+6C_{22}h_s^2q_{1s}^2+2C'_{22}h_s^2q_{0s}^2 \tag{2.35}$$

is deduced. First, Pr will considered, and second, CF. In Pr, since $q_{0s}=q_{1s}=0$, Eq. (2.35) reduces to

$$\tfrac{1}{2}(\partial^2\Phi/\partial q_1^2)_s=A_{20}+B_{02}h_s+C_{02}h_s^2\ . \tag{2.36}$$

The parameter h_s is present in Eq. (2.36). Hence, if the second view is adopted, $(\partial^2\Phi/\partial q_1^2)_s$ is essentially indefinite. If the third view is adopted, $(\partial^2\Phi/\partial q_1^2)_s$ is definite. In this latter case, Eq. (2.34) takes effect. That is to say, substitution of it into Eq. (2.36) gives

$$\tfrac{1}{2}(\partial^2\Phi/\partial q_1^2)_s=A_{20}-B_{02}^2/4C_{02}\ , \tag{2.37}$$

which, with the use of Eqs. (2.10) and (2.15), we arrive at the function of T,

$$\tfrac{1}{2}(\partial^2\Phi/\partial q_1^2)_s=K(T-T_1)\ . \tag{2.38}$$

Equation (2.38) is thought to be physically reasonable. It is consistent with the conclusion, drawn from Eq. (2.17), that the Pr→IF transition temperature is T_1. The reason for the consistency might be quite obvious to some readers, but will be set forth, considering a variety of readers. Equation (2.38) indicates the following. Above T_1, $(\partial^2\Phi/\partial q_1^2)_s$ is positive, so that Pr is stable against variation of q_1. Below T_1, $(\partial^2\Phi/\partial q_1^2)_s$ is negative, so that Pr is not stable against variation of q_1. Therefore, at T_1 the transition should take place from Pr to a phase with $q_{1s}\neq 0$.

If the first or second view of Pr is adopted, Eq. (2.38) is not deduced. In other words, Eq. (2.38) is deduced only if transition Pr→IF is strongly second order.

In CF, when the second or third view of CF is adopted, we have $q_{1s}=0$; thus Eq. (2.35) reduces to

$$\tfrac{1}{2}(\partial^2\Phi/\partial q_1^2)_s = A_{20}+4A_{40}q_{0s}^2+9A_{60}q_{0s}^4+B_{02}h_s +2B_{22}h_sq_{0s}^2+C_{02}h_s^2+2C'_{22}h_s^2q_{0s}^2 \; . \quad (2.39)$$

The parameter h_s is present in Eq. (2.39). Hence, if the second view is adopted, $(\partial^2\Phi/\partial q_1^2)_s$ is essentially indefinite. If the third view is adopted, $(\partial^2\Phi/\partial q_1^2)_s$ is definite. In this latter case, Eq. (2.28) takes effect. That is to say, substitution of it into Eq. (2.39) gives

$$\tfrac{1}{2}(\partial^2\Phi/\partial q_1^2)_s = A_{20}-B_{02}^2/4C_{02} + \left[4A_{40}+\frac{B_{02}^2}{2C_{02}}\left[\frac{C'_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}\right]\right]q_{0s}^2 \; , \quad (2.40)$$

which, with the use of Eqs. (2.10) and (2.22), brings us to the function of T,

$$\tfrac{1}{2}(\partial^2\Phi/\partial q_1^2)_s = \left[1+\frac{B_{02}^2}{4A_{40}C_{02}}\left[\frac{C'_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}\right]\right]K(T_2-T) \; . \quad (2.41)$$

A characteristic temperature T_2 appears in Eq. (2.41). It is defined by

$$\frac{1}{K(T_0-T_2)}=\frac{4C_{02}}{B_{02}^2}+\frac{1}{A_{40}}\left[\frac{C'_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}\right] . \quad (2.42)$$

Taking account of inequalities (2.11) and (2.29), the right-hand side of Eq. (2.42) is positive. Hence, $T_2<T_0$. Combination of Eqs. (2.15) and (2.42) gives

$$\frac{T_1-T_0}{T_0-T_2}=1+\frac{B_{02}^2}{4A_{40}C_{02}}\left[\frac{C'_{22}}{C_{02}}-2\frac{B_{22}}{B_{02}}\right] . \quad (2.43)$$

Since the right-hand side of Eq. (2.43) is greater than 1, we have

$$T_0-T_2<T_1-T_0 \; . \quad (2.44)$$

Now, the direct transition Pr→CF is imagined. According to Eqs. (2.22) and (2.26), CF is possible only below T_0, and the Pr→CF transition temperature is T_0. Equation (2.41) is thought to be physically reasonable. It is consistent with the conclusion, drawn from Eqs. (2.15), (2.17), and (2.26), that IF intervenes between Pr and CF (thus the direct transition Pr→CF is not real). The consistency is because Eq. (2.41) indicates the following. Below T_2, $(\partial^2\Phi/\partial q_1^2)_s$ is positive, so that CF is stable against variation of q_1. Between T_2 and T_0, $(\partial^2\Phi/\partial q_1^2)_s$ is negative, so that CF is not stable against variation of q_1. Therefore, a phase with $q_{1s}\neq 0$ should intervene between Pr and CF, covering some temperature range that contains the range $T_2<T<T_0$.

The characteristic temperature T_2 is especially important to CF because, above T_2, CF cannot even be a metastable phase. It is emphasized that this characteristic temperature has been discovered in the investigation of the T dependence of $(\partial^2\Phi/\partial q_1^2)_s$ in CF upon the assumption of the third view of CF. The equations

$$(\partial^2\Phi/\partial q_0^2)_s=4K(T_0-T) \; , \quad (\partial^2\Phi/\partial h^2)_s=0 \; ,$$

$$\begin{vmatrix} (\partial^2\Phi/\partial q_1^2)_s & (\partial^2\Phi/\partial q_1\partial h)_s \\ (\partial^2\Phi/\partial q_1\partial h)_s & (\partial^2\Phi/\partial h^2)_s \end{vmatrix}=0$$

are easily deduced. It is only $(\partial^2\Phi/\partial q_1^2)_s$ that is negative just below T_0. Let T fall from T_2. Immediately below T_2, CF is a metastable phase. The most stable phase is IF. At a certain temperature T_3, the most stable phase is changed from IF to CF, i.e., transition IF→CF takes place. Since CF is metastable above T_3 (and below T_2), transition IF→CF must be first order. Any more discussion of this transition is omitted.

III. THEORY: $NaNO_2$

Upon cooling, sodium nitrite[2,3] undergoes transition Pr→IF at 164 °C and transition IF→CF at 162 °C. Pr belongs to point group *mmm* (or D_{2h}). CF belongs to point group *mm*2 (or C_{2v}) with its twofold axis parallel to the y axis of Pr. The three lattice constants of CF are equal to those of Pr, i.e., a_0, b_0, and c_0. IF is incommensurately modulated with a wavelength of about $8a_0$ in the x direction. In the y and z directions, IF is commensurate and has lattice constants equal to b_0 and c_0. The transition at 164 °C is second order, while the transition at 162 °C is first order. Although there exist a few thermodynamical theories on the transitions of sodium nitrite,[12,13] a retheorization is necessary for the present subject.

The unmodulated transition parameters for the transitions of $NaNO_2$ are two real variables, one of which is transformed according to the zero-wave-number representation B_{2u}, and the other according to the zero-wave-number representation B_{1g} of the prototype point group *mmm*. The B_{2u} transition parameter, denoted by Q, is soft (or a soft-mode coordinate), while the B_{1g} transition parameter, denoted by R, is hard (or a hard-mode coordinate). The former is a leading parameter, while the latter is a supporting parameter.

The modulated transition parameters $Q(x)$ and $R(x)$ may momentarily be general functions of x. The free energy per unit volume, $\Phi(x)$, is assumed to be equatable to a power series in $Q(x)$, $R(x)$, and their first- and second-order derivatives. Duly considering transformation, the free-energy equation is found to take the form

$$\begin{aligned}\Phi(x)={}&\sum A_{2m,2n}Q(x)^{2m}R(x)^{2n}+R(x)\partial_x Q(x)\sum B^{(1)}_{2m+1,2n+1}Q(x)^{2m}R(x)^{2n}\\&+Q(x)\partial_x R(x)\sum B^{(2)}_{2m+1,2n+1}Q(x)^{2m}R(x)^{2n}+Q(x)\partial^2_{xx}Q(x)\sum C^{(1)}_{2m+2,2n}Q(x)^{2m}R(x)^{2n}\\&+R(x)\partial^2_{xx}R(x)\sum C^{(2)}_{2m,2n+2}Q(x)^{2m}R(x)^{2n}+[\partial_x Q(x)]^2\sum C^{(3)}_{2m+2,2n}Q(x)^{2m}R(x)^{2n}\\&+[\partial_x R(x)]^2\sum C^{(4)}_{2m,2n+2}Q(x)^{2m}R(x)^{2n}+Q(x)R(x)\partial_x Q(x)\partial_x R(x)\sum C^{(5)}_{2m+2,2n+2}Q(x)^{2m}R(x)^{2n}\ ,\end{aligned}\tag{3.1}$$

where $\sum$ stands for the double summation from $m=0$ to ∞ and from $n=0$ to ∞.

For simplicity, let us omit from Eq. (3.1) terms of high degree with respect to $Q(x)$ and $R(x)$. The reduced equation is

$$\begin{aligned}\Phi(x)={}&\Phi_0+A_{20}Q(x)^2+A_{02}R(x)^2+A_{40}Q(x)^4\\&+B^{(1)}_{11}R(x)\partial_x Q(x)+B^{(2)}_{11}Q(x)\partial_x R(x)\\&+C^{(1)}_{20}Q(x)\partial^2_{xx}Q(x)+C^{(2)}_{02}R(x)\partial^2_{xx}R(x)\\&+C^{(3)}_{20}[\partial_x Q(x)]^2+C^{(4)}_{02}[\partial_x R(x)]^2\ .\end{aligned}\tag{3.2}$$

Subscript commas in coefficient symbols have been omitted. A_{00} has been replaced by Φ_0. Since the B_{1g} transition parameter is hard, term $R(x)^4$ is dispensable. On the other hand, $Q(x)^4$ is indispensable.

The case of $NaNO_2$ is more complicated than the case of K_2SeO_4 because in $NaNO_2$ the two transition parameters belong to different irreducible representations. In Sec. II the fourth-degree terms with ∂_x and ∂^2_{xx}, such as

$$Q(x)Q^*(x)^2\partial_x Q(x)\ \text{ and }\ Q(x)Q^*(x)^2\partial^2_{xx}Q(x)\ ,$$

were not omitted [see Eq. (2.5)]. However, in this section the corresponding terms are omitted [see Eq. (3.2)] so that this simplification may cancel out the above-mentioned complicacy.

Now, $Q(x)$ and $R(x)$ are specialized to the forms

$$Q(x)=Q_0+Q_1\cos(hx-\theta_Q)\ ,\tag{3.3a}$$

$$R(x)=R_0+R_1\cos(hx-\theta_R)\ .\tag{3.3b}$$

On the assumption that h is large as expressed by inequality (1.10), the average of Eq. (3.2) is found to be

$$\begin{aligned}\Phi={}&\Phi_0+\tfrac{1}{2}A_{20}(2Q_0^2+Q_1^2)+\tfrac{1}{2}A_{02}(2R_0^2+R_1^2)\\&+\tfrac{1}{8}A_{40}(8Q_0^4+24Q_0^2Q_1^2+3Q_1^4)+\tfrac{1}{2}B_{11}hQ_1R_1\sin\Delta\theta\\&+\tfrac{1}{2}C_{20}h^2Q_1^2+\tfrac{1}{2}C_{02}h^2R_1^2\ ,\end{aligned}\tag{3.4}$$

where

$$B_{11}\equiv B^{(1)}_{11}-B^{(2)}_{11}\ ,\quad C_{20}\equiv C^{(3)}_{20}-C^{(1)}_{20},\quad C_{02}\equiv C^{(4)}_{02}-C^{(2)}_{02}\ ,\tag{3.5}$$

and $\Delta\theta\equiv\theta_Q-\theta_R$. Equation (3.4) contains θ_Q and θ_R only as the difference $\Delta\theta$.

All coefficients except A_{20} (and Φ_0) are assumed to be T independent. A_{20} is assumed to vanish at a certain temperature T_0, and to depend on T in the form

$$A_{20}=K(T-T_0),\quad K=\text{const}>0\ .\tag{3.6}$$

Coefficients such as A_{02} are assumed to be positive, i.e.,

$$A_{02}>0,\quad A_{40}>0,\quad C_{20}>0,\quad C_{02}>0\ .\tag{3.7}$$

The allowability of assuming A_{02} to be T independent and positive is what the "hardness" of the B_{1g} transition parameter means.

It is convenient to introduce a quantity ρ defined as

$$\rho=\frac{|B_{11}|}{2(A_{02}C_{20})^{1/2}}\ .$$

Obviously, ρ is dimensionless, T independent, and positive.

Of the three phases Pr, IF, and CF, let us first consider IF. It has

$$Q_{0s}=0,\quad Q_{1s}\neq0,\quad h_s\neq0\ .\tag{3.8}$$

For h_s, inequality (1.10) is assumed. With the use of Eq. (3.4), the expressions of h_s, Q_{1s}, etc. are found to be

$$\Delta\theta_s=\sigma\tfrac{1}{2}\pi,\quad \sigma=\pm1\tag{3.9}$$

$$h_s^2=(A_{02}/C_{02})(\rho-1)\ ,\tag{3.10}$$

$$R_{1s}^2=(C_{20}/C_{02})(\rho-1)Q_{1s}^2\ ,\tag{3.11}$$

$$\sigma B_{11}h_sR_{1s}=-2\frac{A_{02}C_{20}}{C_{02}}\rho(\rho-1)Q_{1s}\ ,\tag{3.12}$$

$$Q_{1s}^2=(2/3A_{40})K(T_1-T)\ ,\tag{3.13}$$

$$\Phi_s-\Phi_0=-(1/6A_{40})[K(T_1-T)]^2\ ,\tag{3.14}$$

and $R_{0s}=0$, where T_1 is a characteristic temperature defined by

$$K(T_1-T_0)=(A_{02}C_{20}/C_{02})(\rho-1)^2\ .\tag{3.15}$$

According to Eq. (3.10), ρ must be greater than 1; in other words, IF is possible only if $\rho>1$. As ρ approaches 1, h_s approaches zero. Throughout this section, ρ is assumed to be so much greater than 1 that h_s satisfies inequality (1.10). According to Eq. (3.13), IF is possible only at $T<T_1$. Equation (3.15) indicates $T_1>T_0$.

As far as IF is concerned, the present theory is the same as Ref. 13.

Next, CF is considered. We set

$$Q_0+Q_1\cos\theta_Q\equiv Q_\omega,\quad R_0+R_1\cos\theta_R\equiv R_\omega\ .$$

The following three views of CF are possible:

$$Q_{\omega s}\neq0,\quad h_s=0\ ,\tag{3.16}$$

$$Q_{0s}\neq0,\quad Q_{1s}=0,\quad h_s\ \text{indefinite}\ ,\tag{3.17}$$

$$Q_{0s}\neq0,\quad Q_{1s}=0,\quad h_s\neq0\ .\tag{3.18}$$

For view (3.18), inequality (1.10) is assumed. The expression of $Q_{\omega s}$ in view (3.16) is found from Eq. (3.2) to be

$$Q_{\omega s}^2=(1/2A_{40})K(T_0-T)\ . \tag{3.19}$$

The expression of Q_{0s} in views (3.17) and (3.18) is found from Eq. (3.2) [or (3.4)] to be

$$Q_{0s}^2=(1/2A_{40})K(T_0-T)\ . \tag{3.20}$$

As regards R, we have $R_{\omega s}=0$ for view (3.16), and $R_{0s}=R_{1s}=0$ for views (3.17) and (3.18). According to Eqs. (3.19) and (3.20), CF is possible only at $T<T_0$, of which view is adopted. The free energy is found to be

$$\Phi_s-\Phi_0=-(1/4A_{40})[K(T_0-T)]^2\ , \tag{3.21}$$

irrespective of which view is adopted.

The expression of h_s in view (3.18) can be determined by the two-step method (this method was explained in Sec. II). It is the same as the expression of h_s^{IF}, (3.10). If, in $\Phi(x)$, some high-degree terms were not omitted, we would have

$$(h_s^{\mathrm{IF}})^2=(A_{02}/C_{02})(\rho-1)[1+\alpha(Q_{1s}^{\mathrm{IF}})^2]\ , \tag{3.22}$$

$$(h_s^{\mathrm{CF}})^2=(A_{02}/C_{02})(\rho-1)[1+\beta(Q_{0s}^{\mathrm{CF}})^2]\ , \tag{3.23}$$

where $\alpha\neq0$, $\beta\neq0$, and $\alpha\neq\beta$. The above-mentioned high-degree terms are

$$\begin{gathered}A_{22}Q(x)^2R(x)^2,\ \ B_{31}^{(1)}Q(x)^2R(x)\partial_xQ(x)\ ,\\ B_{31}^{(2)}Q(x)^3\partial_xR(x),\ \ C_{40}^{(1)}Q(x)^3\partial_{xx}^2Q(x)\ ,\\ C_{40}^{(3)}Q(x)^2[\partial_xQ(x)]^2,\ \ C_{22}^{(1)}Q(x)R(x)^2\partial_{xx}^2Q(x),\\ C_{22}^{(2)}Q(x)^2R(x)\partial_{xx}^2R(x),\ \ C_{22}^{(3)}R(x)^2[\partial_xQ(x)]^2\ ,\\ C_{22}^{(4)}Q(x)^2[\partial_xR(x)]^2,\ \ C_{22}^{(5)}Q(x)R(x)\partial_xQ(x)\partial_xR(x)\ .\end{gathered} \tag{3.24}$$

Equation (3.2) contains none of the terms listed in (3.24). Consequently we have $\alpha=\beta=0$ and $h_s^{\mathrm{IF}}=h_s^{\mathrm{CF}}=(A_{02}/C_{02})(\rho-1)$.

Following IF and CF, Pr is now considered. The following three views of Pr are possible:

$$Q_{\omega s}=0,\ \ h_s=0\ , \tag{3.25}$$

$$Q_{0s}=0,\ \ Q_{1s}=0,\ \ h_s\ \text{indefinite}\ , \tag{3.26}$$

$$Q_{0s}=0,\ \ Q_{1s}=0,\ \ h_s\neq0\ . \tag{3.27}$$

For view (3.27), inequality (1.10) is assumed. As regards R, we have $R_{\omega s}=0$ for view (3.25), and $R_{0s}=R_{1s}=0$ for views (3.26) and (3.27). The free energy is $\Phi_s-\Phi_0=0$, no matter which view is adopted. The expression of h_s in view (3.27) can be determined by the two-step method. It is the same as the expression of h_s^{IF}, (3.10). If the terms (3.24) were not omitted, h_s^{IF} would be expressed by Eq. (3.22) with $\alpha\neq0$, while h_s^{Pr} would still be expressed by Eq. (3.10).

Equations (3.14) and (3.21) indicate that the Pr→IF and Pr→CF transition temperatures are T_1 and T_0, respectively. If the third views of Pr and CF are adopted, the transitions from Pr to the two ferroics are both strongly second order, because the h_s's of the three phases are equal.

It is convenient to set

$$(\partial^2\Phi/\partial Q_1^2)_s\equiv D_{QQ},\ \ (\partial^2\Phi/\partial Q_1\partial R_1)_s\equiv D_{QR}\ ,$$

$$(\partial^2\Phi/\partial R_1^2)_s\equiv D_{RR},\ \ \begin{vmatrix}D_{QQ} & D_{QR}\\ D_{QR} & D_{RR}\end{vmatrix}\equiv D\ .$$

We will investigate the T dependences of D_{QQ}, D_{RR}, and D when the third views of Pr and CF are adopted. It is D rather than D_{QQ} that is most interesting. First, Pr will be considered, and second, CF. In Pr, the equations

$$D_{QQ}=A_{20}+C_{20}h_s^2\ , \tag{3.28}$$

$$D_{RR}=A_{02}+C_{02}h_s^2\ , \tag{3.29}$$

$$D_{QR}=\tfrac{1}{2}B_{11}h_s\sin\Delta\theta_s \tag{3.30}$$

are deduced from Eq. (3.4). Parameters h_s and $\Delta\theta_s$ appear in Eqs. (3.28)–(3.30). The h_s of Pr has already been found to be expressed by Eq. (3.10). The $\Delta\theta_s$ of Pr, however, has not yet been discussed at all.

In Pr, since $Q_{1s}=R_{1s}=0$, $\Delta\theta_s$ cannot be determined by the usual direct method. If $\Delta\theta_s$ is regarded as essentially indefinite, D_{QR} and D are also indefinite. In the third view of Pr, $\Delta\theta_s$ is regarded as definite, in addition to h_s. The definite value of $\Delta\theta_s$ can be found by the two-step method. It is the same as the $\Delta\theta_s$ of IF expressed by Eq. (3.9).

Substitution of Eqs. (3.9) and (3.10) into Eqs. (3.28)–(3.30) gives

$$D_{QQ}=A_{20}+(A_{02}C_{20}/C_{02})(\rho-1)\ , \tag{3.31}$$

$$D_{RR}=A_{02}\rho\ , \tag{3.32}$$

$$D_{QR}^2=(A_{02}^2C_{20}/C_{02})\rho^2(\rho-1)\ . \tag{3.33}$$

[Note that the left-hand side of Eq. (3.33) is not D_{QR} but its square.] From Eqs. (3.31)–(3.33), we obtain

$$D=A_{02}\rho[A_{20}-(A_{02}C_{20}/C_{02})(\rho-1)^2]\ . \tag{3.34}$$

By use of Eqs. (3.6) and (3.15), Eqs. (3.31) and (3.34) are rewritten as functions of T,

$$D_{QQ}=K(T-T_1)+(A_{02}C_{20}/C_{02})\rho(\rho-1)\ , \tag{3.35}$$

$$D=A_{02}\rho K(T-T_1)\ . \tag{3.36}$$

The expression of D_{RR}, (3.32), is T independent.

Equations (3.35), (3.32), and (3.36) are thought to be physically reasonable. They [especially Eq. (3.36)] are consistent with the conclusion, drawn from Eq. (3.14), that the Pr→IF transition temperature is T_1. The reason for the consistency might be quite obvious, but will be set fourth. Equations (3.35), (3.32), and (3.36) indicate the following. D_{QQ} and D_{RR} are positive above T_1 and also just below T_1. D is positive above T_1 and negative below it. Thus, above T_1, Pr is stable against every form of variation of Q_1 and R_1. Just below T_1, Pr is stable against variation of only Q_1 and of only R_1 but it is not stable against every form of simultaneous variation of both Q_1 and R_1. Therefore, at T_1, the transition should take place from Pr to a phase with $Q_{1s}\neq0$ and $R_{1s}\neq0$.

If the first or second view of Pr is adopted, Eq. (3.36) is not deduced. In other words, Eq. (3.36) is deduced only if transition Pr→IF is strongly second order.

In CF, the equation

$$D_{QQ}=A_{20}+6A_{40}Q_{0s}^2+C_{20}h_s^2 \tag{3.37}$$

is deduced from Eq. (3.4). The expressions of D_{RR} and D_{QR} are the same as those in Pr, i.e., Eqs. (3.29) and (3.30). Parameters Q_{0s}, h_s, and $\Delta\theta_s$ appear in Eqs. (3.37), (3.29), and (3.30). The Q_{0s} and h_s of CF have already been found to be expressed by Eqs. (3.20) and (3.10), respectively. In the third view of CF, $\Delta\theta_s$ is regarded as definite, in addition to h_s. The definite value of $\Delta\theta_s$ is found, by the two-step method, to be the same as the $\Delta\theta_s$ of IF expressed by Eq. (3.9). Substitution of Eqs. (3.6), (3.10), and (3.20) into Eq. (3.37) gives

$$D_{QQ}=2K(T_0-T)+(A_{02}C_{20}/C_{02})(\rho-1)\ . \tag{3.38}$$

The ultimate expressions of D_{RR} and D_{QR} are Eqs. (3.32) and (3.33), respectively. From Eqs. (3.38), (3.32), and (3.33), we obtain

$$D=2A_{02}\rho K(T_2-T)\ , \tag{3.39}$$

where T_2 is a characteristic temperature defined by

$$K(T_0-T_2)=\tfrac{1}{2}(A_{02}C_{20}/C_{02})(\rho-1)^2\ . \tag{3.40}$$

Obviously, $T_2<T_0$. The ratio between Eqs. (3.15) and (3.40) is

$$(T_1-T_0)/(T_0-T_2)=2\ . \tag{3.41}$$

Now, the direct transition Pr→CF is imagined. According to Eqs. (3.20) and (3.21), CF is possible only below T_0, and the Pr→CF transition temperature is T_0. Equations (3.38), (3.32), and (3.39) are thought to be physically reasonable. They [especially Eq. (3.39)] are consistent with the conclusion, drawn from Eqs. (3.14), (3.15), and (3.21), that IF intervenes between Pr and CF (thus the direct transition Pr→CF is not real). Equations (3.38), (3.32), and (3.39) indicate the following. D_{QQ} and D_{RR} are positive below T_0. D is positive below T_2 and negative between T_2 and T_0. Thus, below T_2, CF is stable against every form of variation of Q_1 and R_1. Between T_2 and T_0, CF is stable against variation of only Q_1 and of only R_1, but not stable against every form of simultaneous variation of both Q_1 and R_1. Therefore, a phase with $Q_{1s}\neq 0$ and $R_{1s}\neq 0$ should intervene between Pr and CF, covering some temperature range that contains the range $T_2<T<T_0$.

A remark is made upon Eq. (3.41). This equation corresponds to Eq. (2.43) for K_2SeO_4. Equation (2.43) contains the coefficients B_{22} and C'_{22}. In the case of $NaNO_2$, the corresponding coefficients have been omitted. In the case of K_2SeO_4, if analogously B_{22} and C'_{22} are omitted, Eq. (2.43) becomes

$$(T_1-T_0)/(T_0-T_2)=1\ .$$

Compare this equation with Eq. (3.41). It is of interest that their right-hand sides are different integers, 1 and 2. (Instead of 1 or 2, another number may appear for a substance other than either K_2SeO_4 or $NaNO_2$.)

In this paper I have offered new views (i.e., the third views) of CF and Pr, and have explained theoretical grounds for their reasonability. I intend to soon investigate the question of whether there can be any conclusive experimental evidence of the reasonability.

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[1] The concepts of prototype, prototypic phase, and ferroic phase were explained in several papers, including K. Aizu, Phys. Rev. B 2, 754 (1970); 23, 1292 (1981). For convenience the explanation is repeated here. When a prototype is given as a structure, any phase that is a slight distortion (in atomic configuration) of the prototype is a ferroic phase. Distortion implies lowering in symmetry. The prototype itself is not a slight distortion of any other structure. If there exists a phase that is an equisymmetric slight modification of the prototype, it is the prototypic phase. The atomic configuration of the prototypic phase varies with temperature and pressure, while the atomic configuration of the prototype is fixed. If one phase, α, is a slight distortion of another phase, β, and β is a slight distortion of a third phase, γ, then β is not recognized as the prototypic phase of α, but both β and α are recognized as ferroic phases derived from some common prototypic phase, which is γ if γ is not a slight distortion of any fourth structure. Various terms have been used by different authors. Prototypic phase is exactly or roughly synonymous with original phase, initial phase, parent phase, mother phase, normal phase, high-symmetry phase, high-temperature phase, etc. Ferroic phase is exactly or roughly synonymous with distorted phase, final phase, child phase, daughter phase, low-symmetry phase, low-temperature phase, etc. Some of these terms are not very clearly defined.

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[7] One earliest example is A. P. Levanyuk and D. G. Sannikov, Fiz. Tverd. Tela (Leningrad) 18, 423 (1976) [Sov. Phys.—Solid State 18, 245 (1976)].

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[10] D. G. Sannikov and A. P. Levanyuk, Fiz. Tverd. Tela (Leningrad) 20, 1005 (1978) [Sov. Phys.—Solid State 20, 580 (1978)].

[11] The concept of rank was explained in several papers, including K. Aizu, J. Phys. Soc. Jpn. 38, 1592 (1975). For convenience the explanation is repeated here. Let G be a prototype space group, Γ be the irreducible representation of G for a set of transition parameters, N be the dimensionality of Γ, and H be a ferroic space group. When Γ is decomposed into a direct sum of irreducible representations of H, let the identity representation of H appear s times. Then $r\equiv N-s$ is called the rank of the ferroic phase, and s the co-rank.

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