Group Theoretical Analysis of Ferroelastic Phase Transition in Squaric Acid $C_4H_2O_4$

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The ferroelastic phase transition in squaric acid $C_4H_2O_4$ is discussed from the group-theoretical point of view following the Landau theory of phase transition and Birman's extended theory. Observed ferroelastic twin structure is interpreted by the theories.

Introduction

The phase transitions with a change of symmetry are divided into two classes. One is the transition caused at the Brillouin zone center ($k=0$), and the other at the Brillouin zone corner ($k\neq 0$) which accompany the change of the volume of a primitive cell[1]. Recently, much attention has been paid to the incommensurate phase transition, which has a modulated wave vector $k_0+\kappa$ to the particular k, that is, which are accompanied by the changing of the space modulation of crystal[2,3].

The application of group theory to the second order phase transition has been developed by Landau. The method is based on the construction of the free energy from order parameters, which are related to an irreducible representation. The Landau method has been applied to various phase transitions of ferroelectrics and ferroelastics. Birman's extended method based on the Landau theory provides a very useful means for determining the symmetry of the soft mode[4]. Lavrencic and Sigenari applied the theory to the more general second order phase transition[5].

In this paper, a brief commentary for the case of the phase transition in $Gd_2(M_0O_4)_3$ [GMO] is given at first as an example, with the Landau theory[6] and the Birman's extended method[5]. The analysis of the ferroelastic phase transition in squaric acid $H_2C_4O_4$ are discussed at the latter half of this paper.

Landau Theory

The Landau and Lifshitz theory is described shortly as following[1,7,8]. The symmetry of a crystal can be described by means of a density function $\rho_0(r)$, if the crystal consists of particles of several kinds, then one must consider several functions $\rho(r)$ for each kind of atoms. In the following, we shall consider only one function $\rho_0(r)$ keeping in mind that we may understand $\rho_0(r)$ to be a function of several components. The density function $\rho_0(r)$ represents the full symmetry of the crystal, and will be invariant under all operations of the space group of the cryrtal. In a second-order phase transition the density changes continuosly in such a way that the new density function $\rho(r)$ can be written as

$$\rho(r)=\rho_0(r)+\delta\rho(r) \tag{1}$$

where $\delta\rho(r)$ is the small change due to the lowering of symmetry of the crystal. We denote the space symmetry group of the crystal by G_0 for a "high" symmetry phase and by G_1 for a "low" one. Using these symmetry groups G_0 and G_1, $\rho_0(r)$ and $\rho(r)$ are written as

$$\rho_0(r)=g^0{}_i\rho_0(r), \quad (i=1,2,\cdots,d) \tag{2}$$

$$\rho(r)=g^1{}_i\rho(r), \quad (i=1,2\cdots,d') \tag{3}$$

where d and d' are the order of the groups and g's are symmetry operations $\{h|\alpha\}$ of each groups.
The symmetry group of $\rho(r)$ cannot contain symmetry operations which are not contained in the symmetry group of $\rho_0(r)$, that is, the group of $\rho(r)$ is a *subgroup* of the group of $\rho_0(r)$.

The function $\delta\rho(r)$ can be expanded in terms of the basis of the symmetry group G_0 which leaves $\rho(r)$ invariant, that is,

$$\delta\rho(r)=\sum_n{}'\sum_i C^n{}_i\phi^n{}_i \tag{4}$$

where the function $\phi^n{}_i$ form a basis for the n-th irreducible represention of group G_0, and the number of function i for a particular representation n is equal to the dimension of the representation. The prime of the summation denotes omission of the identical representation of the group G_0.

It can be only by accident if two independent types of change would set in at exactly the same transition temperature. Therefore we may consider that a second-order phase transition involves a change of the crystal corresponding to a single irreducible representation. Consequently, one can omit the summation over n in eq. (4).

For small change of $\delta\rho(r)$, therefore small values of the coefficients C_i, the thermodynamic potential is expanded in a power series of C_i. Subtstiuting $C_i=\eta\gamma$ with $\sum_i \gamma^2{}_i=1$, one obtains

$$\Phi=\Phi_0+a\eta f^{(1)}+A\eta^2 f^{(2)}+B\eta^3 f^{(3)}+C\eta^4 f^{(4)}+\ldots, \quad (5)$$

The coefficients a, A,B,C, etc., are functions of the temperature and pressure, and $f^{(l)}$ is a function of order l in the coefficients γ. The thermodynamic potential Φ is, of course, invariant under any symmetry operation. According to eq. (4), this transformation of the basis function $\Phi^n{}_i$ can be treated as a linear transformation of the coefficients $C^n{}_i$. Because first-order invariants exist only for the identical representation, the linear term is omitted in eq. (5).

The actual stable state is found from the conditions for stability $\partial G/\partial\eta=0$, and $\partial G^2/\partial\eta^2>0$. One finds easily that the state $\eta=0$ is stable for $A>0$, whereas for $A<0$ the stable state must have $\eta\neq0$. Therefore a phase transition could occur at the point where $A=0$. However, for the crystal to be stable at the point where $A=0$ and $\eta=0$, Φ must increase both for small positive and negative changes of η. Therefore a second-order phase transition is possible only if third-order terms are zero. It is necessary that no invariant can be formed out of the terms of the third degree [*Landau Condition*].

Furthermore, if in the expression for the density we replace coefficients C_k by certain slowly varying functions of the coordinates, the density ρ will not correspond to a crystal, since it will lose its property of being periodic. It is necessary that the integral of Φ over the volume of the crystal should not contain terms that are linearly dependent on the derivatives $\partial C_k/\partial x_i$. Therefore, the antisymmetric square

$$C_k\frac{\partial C_i}{\partial x}-C_i\frac{\partial C_k}{\partial x} \quad (7)$$

should be omitted in the thermodynamic potential [*Lifshitz condition*].

In terms of the theory of group representations a change of the symmetry of a crystal as a result of a second-order phase transition can be related only to the physically irreducible representations that satisfy the following two conditions:

1. *The antisymmetric square* $\{T^2\}$ *has no common representations with vector representation* V [*Lifshitz Condition*].
2. *The symmetric products* $[T^3]$ *does not contain the identity representation*[*Landau Condition*] (8)

Birman's Subduction condition

It is desirable to use a extended method to avoid the lengthy Landau procedure, knowing the symmetry of the final phase in advance.
Birman pointed out the criterion[4] that

"*the representation* D_k *(m) of* G_0 *subduces the identity representation of* G_1." (9)

This statement, though originally included in the work of Landau, provides a very useful means for determing the symmetry of the soft mode. Lavrencic and Shigenari provided the compatibility relation between different space groups and different k points in the Brillouin zone[5]. The concrete procedure is shown in next chapter.

Structural Phase Transition in $Gd_2(MoO_4)_3$[GMO].

As an example let us discuss $Gd_2(MoO_4)_3$, which exhibits symmetry change from $G_0=D_{2d}{}^3$ to $G_1=C_{2V}{}^8$ at the improper ferroelectric phase transition ($T_C=$ 159°C). The unit cell vectors of $D_{2d}{}^3$ can be chosen as

$$a_1=[a,0,0],\ a_2=[0,a,0],\ a_3=[0,0,c]. \quad (10)$$

The corresponding unit cell vectors in the reciprocal space are

$$b_1=\left(\frac{2\pi}{a},0,0\right),\ b_2=\left(0,\frac{2\pi}{a},0\right),\ b_3=\left(0,0,\frac{2\pi}{c}\right). \quad (11)$$

From X-ray data it follows that in the ferroelectric phase of GMO the unit cell vectors a_1 and a_2 should be rotated by 45° about the z-axis and enlarged by a factor of $\sqrt{2}$. At the ferroelectric phase we can chose as unit cell vectors of $C_{2V}{}^8$

$$a'_1=a_1-a_2,\ a'_2=a_1+a_2,\ a'_3=a_3. \quad (12)$$

The volum of the unit cell after the phase transition will be doubled. It is easily found that the transition occurs at $k=\frac{1}{2}(b_1+b_2)$, M point in the Brillouin zone of the simple tetragonal Bravais lattice Γ_q since exp $(ik_1a_i)=-1$ for $i=1,2$, whereas exp $(ik_1a'_i)=1$ for $i=1,2,3$.

I Landau method

All irreducible representations of $D_{2d}{}^3$ with $k_1=k_1$ are given in the text by Kovalev[9] and they are listed

Table I. The small representation of the space group D_{2d}^3 with $k=\frac{1}{2}(b_1+b_2)$.
The partial translation α is equal to $\alpha=\frac{1}{2}(a_1+a_2)$.

	$\{E\|0\}$	$\{S_4\|0\}$	$\{S_4^2\|0\}$	$\{S_4^3\|0\}$	$\{\sigma'_2\|\alpha\}$	$\{C_{2y}\|\alpha\}$	$\{\sigma'_1\|\alpha\}$	$\{C_{2x}\|\alpha\}$
τ_1	1	i	-1	$-i$	1	$-i$	-1	i
τ_2	1	i	-1	$-i$	-1	i	1	$-i$
τ_3	1	$-i$	-1	i	1	i	-1	$-i$
τ_4	1	$-i$	-1	i	-1	$-i$	1	i
τ_5	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$
T_1	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$
T_2	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$

in Table I. The representation τ_5 is a real two-dimensional representation. T_1 and T_2 are two-dimensional physically meaningful representations constructed from complex-conjugate representations, using the unitary transformation matrix

$$U=\frac{1}{\sqrt{2}}\begin{pmatrix}1&1\\i&-i\end{pmatrix}. \qquad (13)$$

Since the star of $T_i\equiv\tau_5, T_1, T_2$ contains just one vector k_1, the symmetric cube $[T^3_i]$ cannt contain the identity representation[6] [*Landau condition*], The star of T_i^2 contains only $k=0$ and therefore $\{T_i^2\}$ can be reduced in terms of irreducible representions of the point group D_{2d} (Table II). The character of the antisymmetric square calculated from the following

Table II. Character table of irreducible representions of the point group D_{2d}.

D_{2d}	E	$2S_4$	S_4^2	$2C_2$	$2\sigma_d$	polar vector	axial vector	strain
A_1	1	1	1	1	1			x_1+x_2, x_3
A_2	1	1	1	-1	-1		R_z	
B_1	1	-1	1	1	-1			
B_2	1	-1	1	-1	1	z		x_6
E	2	0	-2	0	0	(x, y)	(R_x, R_y)	

equation[7,10]

$$\{\chi^2\}(R)=\frac{1}{2}\{\chi(R)\}^2-\frac{1}{2}\chi(R^2). \qquad (14)$$

Calculating the relation (14), we can easily reduce the representation of $\{T_i^2\}$. After straight forward calculation we get

$$\{\tau_5^2\}=B_1, \quad \{T_j^2\}=A_1 \quad (j=1,2). \qquad (15)$$

Since the vector representation $V(x,y,z)$ is given as

$$V=B_2(z)+E(x,y), \qquad (16)$$

we conclude that τ_5, T_1, T_2 are acceptable representations [*Lifshitz conditon*]. Then we get three active representation τ_5, T_1 and T_2. In order to find out what symmetry change is induced by a particular acceptable representation, we have to minimize the corresponding free energy.

Since the representation T_1 correctly describes symmetry changes connected with the phase transition in GMO at 159°C, it is of interest to write down the corresponding expression for the free energy by the representations.

With aid of eq. (16),

$$[V^2]=A_1(x_1^2+x_2^2)+A_1(z^2)+B_1(x^2-y^2)+B_2(xy)+E(yz, zx), \qquad (17)$$

we get the following reduction of $[T_1^2]$,

$$[T_1^2]=A_1(q_1^2+q_2^2)+B_2(q_1^2-q_2^2)+B_2(q_1q_2). \qquad (18)$$

The density function of the crystal can be written as $\phi=\rho_0+\delta\rho$ using the basis (ϕ_1, ϕ_2), where $\delta\rho$ is given by

$$\delta\rho=q_1\phi_1+q_2\phi_2 \qquad (19)$$

Using the standard thermodynamical procedure it can be shown that a state with spontaneous polarization is possible.

II Birman's extended method

From the character table for the small representation of D_{2d}^3 (M) (Table III), we get three two-dimensional representation τ_5, T_1 and T_2. For a given change of symmetry $G_0\rightarrow G_1$, we denote the symmetry elements of the factor group G_0/T_0 and G_1/T_1 by $g=\{h|\alpha\}$ and $g'=\{h'|\alpha'\}$ respectively. Here T_0 and T_1

Table III. Character table of $D_{2d}{}^3$ at $M=\left(\frac{1}{2}\ \frac{1}{2}\ 0\right)$point.

	$\{E\|0\}$	$\{C_{2z}\|0\}$	$\{\sigma_d\|\alpha\}$	$\{\sigma'_d\|\alpha\}$	$\{S_4\|0\}$	$\{S_4{}^3\|0\}$	$\{C_{2x}\|\alpha\}$	$\{C_{2y}\|\alpha\}$
τ_5	2	2	0	0	0	0	0	0
T_1	2	−2	2	−2	0	0	0	0
T_2	2	−2	−2	2	0	0	0	0

are the translational subgroup of G_0 and G_1, and $\alpha's$ are the non-primitive translations associated with point symmetry operations $h's$. The Birman-Worlock extended theory implies that the soft mode must satisfy the following equation[11],

$$\frac{1}{n}\Sigma_{g'}\chi^j{}_k(g')\chi_\Gamma{}^{(1+)}(q')=\frac{1}{n}\Sigma_{g'}\chi^j{}_k(g')$$
$$=\text{posive integer,} \tag{20}$$

where n is the order of the group G_0/T_0, and $\chi^j{}_k(g')$ is the character of g' in the j-th representation in star k. The translational subgroup T_0 of G_0 is given by

$$T_0=m_1a_1+m_2a_2+m_2a_3\ \ (m_i=0, \pm 1, \cdots). \tag{21}$$

We have to express g' in terms of the element of G_0,

$$g'=\{h'|\alpha\}=\{h|\alpha+t_0\}. \tag{22}$$

The displacement vector t_0, which is defined by eq. (22) should always be an element of T_0. By taking into account the difference between the position of the origin O' of G_1 and O of G_0,

$$t_0=\alpha'(h)-\alpha(h)+s-hs, \tag{23}$$

where s is a vector from O to O'.

Using the equation (22), the character $\chi^j{}_k(g')$ can be easily obtained as a product of $\chi^j{}_k\{h|\alpha\})$ and a multiplication factor $\exp(-ik\cdot t_0)$.

Table IV. Partial character table of $D^3{}_{2d}$. Vector α' are written in terms of $\{a'_i\}$.

	$\{E\|0\}$	$\{C_{2z}\|\frac{1}{2}\ \frac{1}{2}0\}$	$\{\sigma_x\|0\frac{1}{2}0\}$	$\{\sigma_y\|\frac{1}{2}0\ 0\}$	n
$\exp[-ik(t_0+\alpha)]$	1	−1	−1	1	
τ_5	2	−2	0	0	0
T_1	2	2	−2	−2	0
T_2	2	2	2	2	2

The symmetry elements of $C_{2v}{}^8$ are listed in Table Ⅳ. The position of the origin O' concides with O in this case, the vector $s=0$. Therefore for $h'=\sigma_y$, we get $h=\sigma'_d$, $\alpha(\sigma'_d)=\frac{1}{2}a_2$ and $\alpha'(\sigma_y)=\frac{1}{2}a_1+\frac{1}{2}a_2$. From eq. (23), we get $t_0=-a_1$, which give the the multiplication factor $\exp[-ik(t_0+\alpha)]=+1$, for $h'=\sigma_y$. Similar calculations for other elements, the partial character table is given in Table Ⅳ. We can easily obtain the result that the symmetry of the soft mode in GMO is T_1 from the eq. (20), where we used the relation

$$\chi_k{}^j(g')=\exp[-ik\cdot(t_0+\alpha)]\ \ [\sum_\mu \hat{\tau}_{\mu\mu}{}^j(h)] \tag{24}$$

$\tau_{\mu\mu}{}'^j{}_,(h)$ is an (μ,μ') element of the j-th multiplier representation matrix for the operator h. In this theory, we can get the final symmetry representation without examination of the symmetric cubes and the antisymmetric squares.

Ferroelastic phase transition of squaric acid $H_2C_4O_4$ [H_2SQ]

Squaric acid $H_2C_4O_4$ [H_2SQ] is a ferroelastic crystal, which takes the phase transition at 98°C from $C_{4h}{}^5-I4/m$ to $C_{2h}{}^2-P2_1/m$[12]. At the room temperature one can easily observe the ferroelastic twin structure under the polarizing microscope, which move by application of the mechanical stress[13]. The space group of this crystal at a high temperature phase is a body-centered tetragonal system. As is shown in Fig. 1, new primitive translation vector are given by

$$a'_1=-a_1-a_3,\ \ a'_2=a_2+a_3,\ \ a'_3=a_1+a_2. \tag{25}$$

It is easily found that only k vector at z-point in Brillouin zone of the tetragonal body-centered Bravais lattice satisfies the following equations

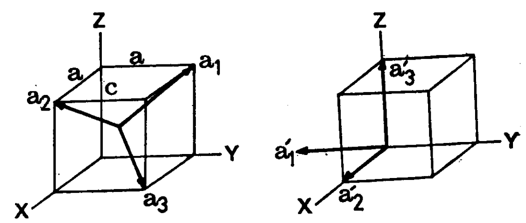

Fig. 1 Primitive translational vectors of tetragonal body-centered lattice $\Gamma_q{}^v$ and monoclinic cell Γ_m.

$$\exp(ik_z\cdot a_i)=-1 \quad (i=1,2,3) \tag{26}$$
$$\exp(ik_z\cdot a'_i)=1 \quad (i=1,2,3)$$

where $k_z=\left(\frac{\bar{1}}{2}\ \frac{1}{2}\ \frac{1}{2}\right)=\frac{1}{2}(-b_1+b_2+b_3)$. The Brillouin zone for $\Gamma_q{}^V$ (a) is shown in Fig. 2. The small representation is shown in Table V. From this table, it is seen that $\hat{\tau}_3=\hat{\tau}_7{}^*$ and $\hat{\tau}_4=\hat{\tau}_8{}^*$ where * denotes a complex representation with a complex conjugate basis. T_1 and T_2 are the physical representations produced by a unitary transformation matrix (13). There are thus four one-dimensional real representation $\hat{\tau}_1, \hat{\tau}_2, \hat{\tau}_5$ and $\hat{\tau}_6$, and two dimensional physically irreducibie representations T_1 and T_2.

The base of the representations $\hat{\tau}_1, \hat{\tau}_2, \hat{\tau}_5$ and $\hat{\tau}_6$ are given by the following, respectively,

$$\Phi_1=\cos\frac{\pi}{a}x\ \cos\frac{\pi}{a}y\ \cos\frac{\pi}{c}z$$

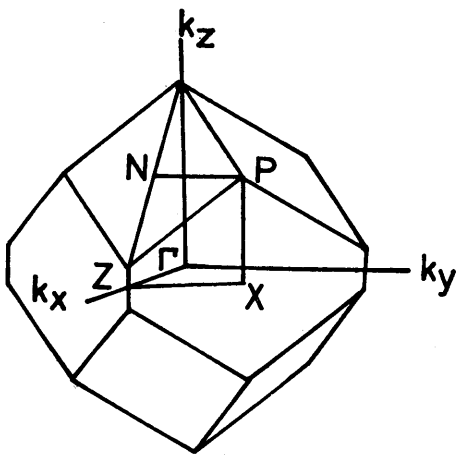

Fig. 2 Brillouin zone for $\Gamma_q{}^V$.

Table V. The small representation of the space group $C_{4h}{}^5$ with $k_z=\frac{1}{2}(-b_1+b_2+b_3)$.

	E	C_4	C_2	$C_4{}^3$	i	$S_4{}^3$	σ_h	S_4
σ_k	1	1	1	1	1	1	1	1
τ_5	1	-1	1	-1	1	-1	1	-1
τ_2	1	1	1	1	-1	-1	-1	-1
τ_6	1	-1	1	-1	-1	1	-1	1
τ_3	1	i	-1	$-i$	1	i	-1	$-i$
τ_7	1	$-i$	-1	i	1	$-i$	-1	i
τ_4	1	i	-1	$-i$	-1	$-i$	1	i
τ_8	1	$-i$	-1	i	-1	i	1	$-i$
T_1	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$
T_2	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}0&1\\-1&0\end{pmatrix}$

$$\phi_2=\cos\frac{\pi}{a}x\ \cos\frac{\pi}{a}y\ \sin\frac{\pi}{c}z$$

$$\phi_5=\sin\frac{\pi}{a}x\ \sin\frac{\pi}{a}y\ \cos\frac{\pi}{c}z$$

$$\phi_6=\sin\frac{\pi}{a}x\ \sin\frac{\pi}{a}y\ \sin\frac{\pi}{c}z. \tag{27}$$

The symmetric product $[T_i{}^3]$ of these one dimensional representation can not have the identity representation.

Table VI. Character Table of irreducible represetnations of the point group C_{4h}.

C_{4h}	E	C_4	C_2	$C_4{}^3$	i	$S_4{}^3$	σ_h	S_4	
A_g	1	1	1	1	1	1	1	1	Rz x^2+y^2, z^2
B_g	1	-1	1	-1	1	-1	1	-1	x^2-y^2 xy
E_g	1	i	-1	$-i$	1	i	-1	$-i$	(R_x, R_y) (xz, yz)
	1	$-i$	-1	i	1	$-i$	-1	i	
A_u	1	1	1	1	-1	-1	-1	-1	z
B_u	1	-1	1	-1	-1	1	-1	1	
Eu	1	i	-1	$-i$	-1	$-i$	1	i	(x, y)
	1	$-i$	-1	i	-1	i	1	$-i$	

One can also show that $\{T_i^2\}(R)=0$ for these one dimensional non-degenerate representations. The characters of irreducible representation of the point group C_{4h} are listed in Table Ⅵ. The vector representation is given as

$$V=A_u(z)+E_u\{x,y\}, \tag{28}$$

$$[V^2]=A_g(x^2+y^2)+A_g(z^2)+B_g(x^2-y^2)+B_g(xy). \tag{29}$$

The antisymmetric squares of $\{T_i^2\}$ for two dimensional representation T_1 and T_2 can be reduced in terms of irreducible representation of the point group C_{4h}. From the eq. (14), we find

$$\{T_i^2\}=A_g \quad (i=1,2). \tag{30}$$

Since the vector representation V is given by eq. (28), and has no common representation, we conclude that these representations are acceptable representations, (that is, *active* representations), In order to find out what symmetry change is induced by a particular acceptable representation, we have to minimize the corresponding free energy.

Since the representation T_2 correctly describes symmetry changes connected with the phase transition in H_2SQ at 97°C, it is of interest to write down the corresponding expression for the free energy. With the following reduction of $[T_2^2]$,

$$[T_2^2]=A_g(q_1^2+q_2^2)+B_g(q_1^2-q_2^2)+B_g(q_1q_2), \tag{31}$$

we get

$$\begin{aligned}F=&\frac{1}{2}\alpha(q_1^2+q_2^2)+\frac{1}{4}\beta_1(q_1^4+q_2^4)+\frac{1}{2}\beta_2q_1^2q_2^2\\&+\frac{1}{3}\beta_3q_1q_2(q_1^2-q_2^2)\\&+\delta_1(q_1^2+q_2^2)(x_1+x_2)+\delta_2(q_1^2+q_2^2)x_3\\&+\delta_3(q_1^2-q_2^2)(x_1-x_2)\\&+\delta_4(q_1^2-q_2^2)x_6+\delta_5q_1q_2(x_1-x_2)+\delta_6q_1q_2x_6\\&+\frac{1}{2}c_{11}(x_1^2+x_2^2)+\frac{1}{2}c_{33}x_3^2+c_{12}x_1x_2+c_{13}(x_1+x_2)x_3\\&+\frac{1}{2}c_{66}x_6^2+c_{16}(x_1-x_2)x_6.\end{aligned} \tag{32}$$

These coefficients $\alpha, \beta_1, \beta_2,$ are functions of pressure and temperature.

From the equilibrium conditions $\partial F/\partial x_i=0$, the strains x_i are given by

$$\begin{aligned}x_1&=f_1(q_1^2+q_2^2)+f_2(q_1^2-q_2^2)+f_3q_1q_2\\x_2&=f_1(q_1^2+q_2^2)-f_2(q_1^2-q_2^2)-f_3q_1p_2\\x_3&=f_4(q_1^2+q_2^2)\\x_6&=f_5(q_1^2-q_2^2)+f_6q_1q_2\end{aligned}\quad, \tag{33}$$

where

$$\begin{aligned}f_1&=\frac{\delta_2c_{13}-\delta_1c_{33}}{c_{33}(c_{11}+c_{12})-2c_{13}^2},\\f_2&=\frac{\delta_4c_{16}-\delta_3c_{66}}{c_{66}(c_{11}-c_{12})-2c_{16}^2},\\f_3&=\frac{\delta_6c_{16}-\delta_5c_{66}}{c_{66}(c_{11}-c_{12})-2c_{16}^2},\\f_4&=\frac{2\delta_1c_{13}-\delta_2(c_{11}+c_{12})}{c_{33}(c_{11}+c_{12})-2c_{13}^2},\\f_5&=\frac{2\delta_3c_{16}-\delta_4(c_{11}-c_{12})}{c_{66}(c_{11}-c_{12})-2c^2_{16}},\\f_6&=\frac{2\delta_5c_{16}-\delta_6(c_{11}-c_{12})}{c_{66}(c_{11}-c_{12})-2c^2_{16}}.\end{aligned} \tag{34}$$

Substituting these x_i into eq. (32), we can rewrite the free energy as

$$\begin{aligned}F=&\frac{1}{2}\alpha(q_1^2+q_2^2)+\frac{1}{4}\beta'_1(q_1^4+q_2^4)+\frac{1}{2}\beta'_2q_1^2q_2^2\\&+\frac{1}{3}\beta'_3q_1q_2(q_1^2-q_2^2),\end{aligned} \tag{35}$$

where the coefficients β'_1, β'_2 and β'_3 can be written in

Table VIⅦ. Partial character table of C_{4h}^5.

g_1 G_1	$\{E\|0\}$	$\{C_2\|\frac{\bar{1}}{2}\frac{\bar{1}}{2}\frac{1}{2}\}$	$\{i\|\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$	$\{\sigma_h\|0\}$	n
g_0 G_0	$\{E\|0\}$	$\{C_2\|0\}$	$\{i\|0\}$	$\{\sigma_h\|0\}$	
τ_1	1	1	1	1	
τ_2	1	1	−1	−1	
τ_5	1	1	1	1	
τ_6	1	1	−1	−1	
T_1	2	−2	2	−2	
T_2	2	−2	−2	2	
$\exp[-ik\cdot(t_0+\alpha)]$	1	−1	−1	1	
τ_1	1	−1	−1	1	0
τ_2	1	−1	1	−1	0
τ_5	1	−1	−1	1	0
τ_6	1	−1	1	−1	0
T_1	2	2	−2	−2	0
T_2	2	2	2	2	2

terms of the coefficients in eq. (32).

It is shown that the free energy given in a form of (35) admits three types of stable solution.

(1) $q_1=q_2=0$. This corresponds to the high temperature phase.

(2) $q^2{}_1\equiv-\alpha/\beta'{}_1=q^2{}_s$, $q_2=0$ (Domain I). The symmetry operations which retain one solution $\rho_\rho=q_s\phi_1$ invariant are the following four elements (Table VII) $\{E|0\}$, $\{C_2|a_i\}$, $\{i|a_i\}$, $\{\sigma_h|0\}$. These are the symmetry elements of the space group $C_{2h}{}^2$.

(3) $q^2{}_{2s}=q^2{}_s$, $q_1=0$ (Domain II)

We get the same symmetry elements of the space group $C_{2h}{}^2$. The spontaneous strains x_{i_s} for each domain can be obtained from eq. (33), that is,

$$x_{6_{\mathrm{I}}}=f_5q^2{}_s \text{ (Domain I)},$$
$$x_{6_{\mathrm{II}}}=-f_5q_s{}^2 \text{ (Domain II)}, \qquad (36)$$

where $q_s{}^2$ is given by $-\alpha/\beta_1'$. It is reasonably assumed that $\bar{x}=a(T-T_c)$ and all other coefficicnts are constant for simplicity. One obtains then the spontaneous strains x_6.

Using the Birman's extended method, the space group have been investigated by Nakashima[14]. The results are shown in Table VII and he showed that T_2 mode at α-point in the paraelectric phase is compatible to B_u mode at Γ point in the ferroeastic phase.

References

1) L.D. Landau and E.M. Lifshitz; *Statistical Physics* (Pergamon Press, London, 1962)
2) A.P. Levanyuk and D.G. Sanikov; Soviet Physics-Solid State **18** 245 (1976)
3) Y. Ishibashi and V. Dvorak; J. Phys. Soc. Jpn **44** 32 (1977)
4) J.L. Birman; Phys. Rev. Lett. **17** 1216 (1966)
5) B.B. Lavrencic and T. Shigenari; Solid State Commun. **13** 1329 (1973)
6) V. Dvorak; Phys. Stat. Sol. (b) **45** 147 (1971)
7) G. Ya. Lyubarskii; *The Application of Group Theory in Physics*, (Pergamon Press, 1960)
8) C. Haas; Phys. Rev. A **140** 863 (1965)
9) O.V. Kovalev; *Irreducible Representations of the Space Groups*, (Gordon and Breach, 1965)
10) A.P. Cracknell and S.J. Joshua; J. Phys. A **1** 40 (1968)
11) J.M. Worlock; *Proc. NATO Advanced Study Institute "Structural Phase Transitions and Soft Modes"*, (Universite Forlaget, Oslo 1971)
12) D. Semmingsen and J. Feder; Solid State Commun. **15** 1369 (1974)
13) I. Suzuki and K. Okada; Solid State Commun. **29** 759 (1979)
14) Nakashima: to be published