Landau description of the calcite-$CaCO_3$(II) phase transition

Dorian M. Hatch and Leo Merrill
Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602
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The calcite-$CaCO_3$(II) phase transition is described within the framework of the Landau criteria for continuous phase transitions. The $\vec{F}$ point is chosen to construct the irreducible representation driving the transition. All Landau conditions are satisfied by the $D^{(*\vec{F},3)}$ representation and the three-component order parameter of $D^{(*\vec{F},3)}$ is shown to correspond to the observed rotations of the CO_3 groups.

I. INTRODUCTION

Single crystals of the mineral calcite undergo a pressure-induced transformation at 15 kbar by a displacive mechanism in which the single-crystal nature of small samples is preserved. The transition is observed to be first order at room temperature. The crystal structure of $CaCO_3$(II), the high-pressure phase of calcite, was solved by Merrill and Bassett[1] from single-crystal x-ray data collected with a miniature diamond-anvil pressure cell. A trigonal space group $R\bar{3}c$ with two molecules per unit cell describes the calcite phase while $CaCO_3$(II) is a monoclinic space group $P2_1/c$ with four molecules per unit cell. The essential features of the $CaCO_3$(II) structure can be obtained mechanistically from the calcite structure by an ordered rotation of the CO_3 groups around the trigonal axis. In a single carbonate layer the CO_3 groups in a row parallel to a hexagonal $\vec{a}$ axis [same as monoclinic $\vec{t}_2$ axis of $CaCO_3$(II)] all undergo the same rotational displacement, while CO_3 groups of adjacent rows undergo the opposite displacements (see Fig. 1). In the appropriate domain,[2] rotations of CO_3 groups in adjacent layers are such as to preserve the $\vec{t}_1$ ($\vec{t}_2$ or $\vec{t}_3$ in other domains) rhombohedral lattice translation vector in the monoclinic cell of $CaCO_3$(II). In correlation with the ordered rotations of the CO_3 groups, two subsets of the calcium atoms undergo antiparallel displacements from their positions of $\bar{3}$ trigonal site symmetry. The above model of carbonate and calcium displacements fits well the x-ray positional parameters and the necessary symmetry features of the new phase.

The phase boundary for the calcite-$CaCO_3$(II) transition was measured to temperatures above 500 °C by Kondo *et al.*[3] In the region of 250 °C they report that the slope of the phase boundary changes from negative to positive. This behavior may be tied to a change of the transition from first to second order as one increases temperature through 200 °C. Such a point has been shown by Griffiths[4] to be characterized by the intersection of three lines of second-order transitions (or critical lines) and hence is called a tricritical point. Recently, Barnett *et al.*[5] have indicated a possibility of critical phenomena at temperatures near 180 °C giving credibility to a change in order of the transition. If such a change in order took place then we would expect descriptions of the structure and its phase changes to be somewhat analogous to that of other materials. For example, perovskite structures and their associated multicriticality have been thoroughly studied. $BaTiO_3$ is a structure with a zone-center soft-mode cubic-to-tetragonal phase transition. Clark and Benguigui[6] have indicated a change in the order of the transition at 32 kbar and room temperature. $SrTiO_3$ is an example of a zone-boundary soft-mode cubic-to-tetragonal transition. When a strain order-parameter

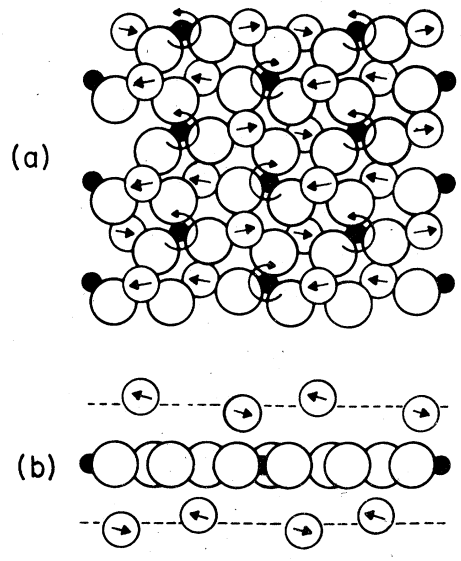

FIG. 1. Essential features of $CaCO_3$(II) structure obtained from the calcite structure. (a) View along the calcite trigonal axis. (b) View along a calcite hexagonal $\vec{a}$ axis.

coupling is considered then $SrTiO_3$ exhibits a rich structure consisting of a bicritical point and a "spin-flop line" in the uniaxial stress—temperature diagram.[7] There is significant theoretical and experimental interest in the nature of such multicritical point phenomena and calcite, due to its noncubic phase, would allow the possibility of a greater range of experimental and formalistic investigation.

In terms of the original calcite rhombohedral basis, the periodicity of the previously described displacive pattern is $\vec{t}_1' = \vec{t}_1$, $\vec{t}_2' = -\vec{t}_2 + \vec{t}_3$, and $\vec{t}_3' = \vec{t}_1 - \vec{t}_2 - \vec{t}_3$ which describes the basis for the monoclinic unit cell. Figure 2 shows the correspondence between the original rhombohedral unit cell and the monoclinic $CaCO_3$(II) unit cell. This new basis corresponds to a cell doubling of the primitive lattice. The transition mechanism will be described in terms of a Brillouin-zone boundary vibrational mode of the crystal which becomes unstable at the transition pressure and temperature. Motivated by the above inference of a change in order of the transition with temperature we will show that within the formalism of Landau (mean field) that it is possible for the $R\bar{3}c$-to-$P2_1/c$ transition to be continuous. A comparison of the rhombohedral and monoclinic space lattices will enable us to identify the wave vector at the $\vec{F}$ point of the rhombohedral Brillouin zone as the one driving the transition. As a result it is antiferroelectric and from the change in space groups would be classified as a pure ferroelastic of the Aizu species $\bar{3}mF2/m$.[8] A single component of the three-component order parameter obtained from the Landau description is associated with a vibrational mode of the structure. By group-theoretical techniques we calculate sets of vibrational modes for each of the irreducible representations of the point group $(2/m)$ of the wave vector $\vec{F}$. From an irreducible representation of the point group a set of modes can be identified which characterizes the displacements of the transition. Thus we describe a noncubic structure for which there is the possibility of observing a tricritical point as well as strain-induced bicritical properties. We stress that experimentally a continuous transition at higher temperatures has not been observed as far as we know.

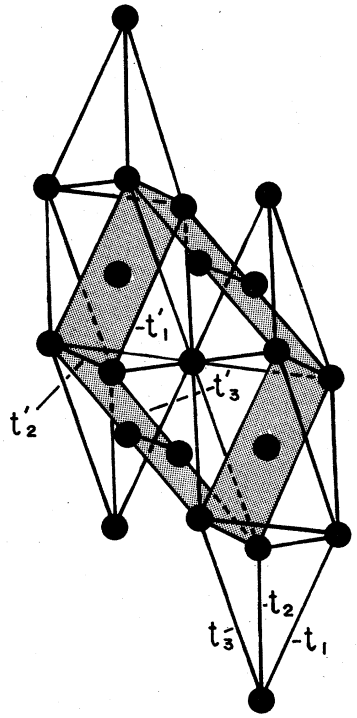

FIG. 2. Correspondence between calcite rhombohedral unit cell and the monoclinic $CaCO_3$(II) unit cell.

II. LANDAU FORMALISM

The most direct mean-field description of phase transitions was formulated by Landau some forty years ago.[9] It is a phenomenological thermodynamic description which has a shortcoming in that it neglects consideration of fluctuations. Necessarily, it often yields incorrect predictions of critical exponents and the continuous nature of the transition may be changed as fluctuations are considered, e.g., renormalization-group methods. However, the symmetry considerations and the *possible* nature of the transition are reliable for wide classes of systems. Moreover, it is felt by some that the group-symmetry considerations when appropriately applied have a reliability beyond the framework of the Landau theory.

The classical formulation of the Landau theory resides in the following conditions:

(a) Near T_c there exists a single "generalized Gibbs potential" $\Phi(P,T,\eta)$. Here T is temperature, P is pressure, and η an initially unconstrained order parameter. The Gibbs potential as well as a probability density fucntion $\rho_0(x,y,z)$ is invariant under all symmetry operations of the higher-symmetry group G^0.

(b) The order parameter η corresponds to the basis of a single irreducible representation of G^0. It is zero in the high-symmetry phase varying from zero continuously into the lower-symmetry phase. The symmetry is therefore changed through an additional contribution to the density function $\rho_0(x,y,z)$ of the form

$$\delta\rho = \sum_\nu c_\nu \phi_\nu(x) \ .$$

Here the c_ν are components of the order parameter and the $\phi_\nu(x)$ are basis functions of the single irreducible representation of G^0. As a result $\rho(x,y,z) = \rho_0 + \delta_\rho$ is invariant under a symmetry group G_1 which is a subgroup of G^0.

(c) The order-parameter components are obtained through a minimization of

$$\Phi(P,T,\eta)=\Phi_0(P,T)+A_1(P,T)\eta^2+A_2(P,T)\eta^4+\cdots$$

with respect to η.

Birman[10] has clarified the Landau formalism by stating some necessary group-theoretical criteria for the transition to be of second order. Strengthening of Birman's original formulation[11] has led to the following conditions: (A) G_1 is a subgroup of G^0. (B) The symmetrized triple Kronecker product of the irreducible representation D of G^0 shall not contain the identity representation Γ_1^+ of G^0, i.e.,

$$([D]^3|\Gamma_1^+(G^0))=0 \ .$$

(C) The antisymmetrized double Kronecker product of D shall not contain the representation of a polar vector, i.e.,

$$(\{D\}^2|\vec{\nabla}(G_0))=0 \ .$$

(D) D of G^0 must subduce into Γ_1^+ (the identity representation) of G_1. (D′) If $G^0\subset G_1\subset G_1'$, and D of G^0 subduces into Γ_1^+ of G_1 $i(G_1)$ times, and D of G^0 subduces into Γ_1^+ of G_1' $i(G_1')=i(G_1)$ times, then the transition $G_0\rightarrow G_1'$ is eliminated as being second order. (Chain-subduction criterion as extended by Jaric.) (E) D of G^0 corresponds to a physical tensor field.

In the typical application of the above conditions an irreducible representation of G^0 is selected and conditions (B), (C), and (E) are then applied to determine the acceptable representations. These representations can be determined with little or no reference to the symmetry group G_1. One then needs to determine the subgroups [condition (A)] corresponding to each acceptable representation and apply conditions (D) and (D′). Jaric has rigorously proven the equivalence of conditions (D) and (D′) to the Landau necessary condition.[12] The actual subgroup selection corresponding to a given physical transition is selected through minimization of $\Phi(P,T,\eta)$ and as a result of knowing the coefficients A_1, A_2, etc., for that structure. Thus this selection cannot be contained within the general symmetry description but only the set of possible representations and transitions.

If we need only decide whether a given symmetry change is possible, i.e., we know G^0 and G_1 such that condition (A) is satisfied, we can select the $\vec{k}$ vector corresponding to G_1 and test conditions (B), (C), and (E) to determine that a representation of G^0 is active. We then check the subduction criterion (D). Finally we form an invariant free energy without the specific functional nature of $A_i(P,T)$, and perform the minimization. There should exist a set of coefficients $A_i(P,T)$ which yield a minimum corresponding to G_1. If all is compatible it is possible within the Landau formalism for the transition to be continuous. This is the process we pursue for the $R\bar{3}c$-to-$P2_1/c$ transition in calcite.

III. APPLICATION TO CALCITE

The symmetry group G^0 of the high-symmetry phase of calcite is $R\bar{3}c$. The origin of the international tables for x-ray crystallography[13] is at $\bar{3}$ and corresponds to the point of the calcium atom. $R\bar{3}c$ is a nonsymmorphic space group whose isogonal point group is $\bar{3}m$ (D_{3d}). We can then express $R\bar{3}c$ as a coset sum with respect to the translations (T) in the form

$$G^0(R\bar{3}c)=\sum_{i=1}^{6}\{R_i|000\}T+\sum_{i=7}^{12}\{R_i|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}T$$

with the numbering in the sum corresponding to the ordering of the symmetry operations of the international tables.

To construct representations of G^0 we must have a specific $\vec{k}$ vector of the Brillouin zone in mind. The lattice constants for calcite correspond to a Brillouin zone as shown in Fig. 3 where we have taken the forms

$$\vec{t}_1=-a\hat{j}+c\hat{k} \ ,$$

$$\vec{t}_2=(a|\bar{3}/2)\hat{i}+(a/2)\hat{j}+c\hat{k} \ ,$$

$$\vec{t}_3=-(a|\bar{3}/2)\hat{i}+(a/2)\hat{j}+c\hat{k}$$

for our primitive translation vectors and

$$\vec{g}_1=2\pi[-(2/3a)\hat{k}_y+(1/3c)\hat{k}_z] \ ,$$

$$\vec{g}_2=2\pi[(1/|\bar{3}a)\hat{k}_y+(1/3c)\hat{k}_z] \ ,$$

$$\vec{g}_3 2\pi[-(1/|\bar{3}a)\hat{k}_x+(1/3a)\hat{k}_y+(1/3c)\hat{k}_z]$$

are the resulting forms of our reciprocal-lattice vectors. A more complete motivation for our selection

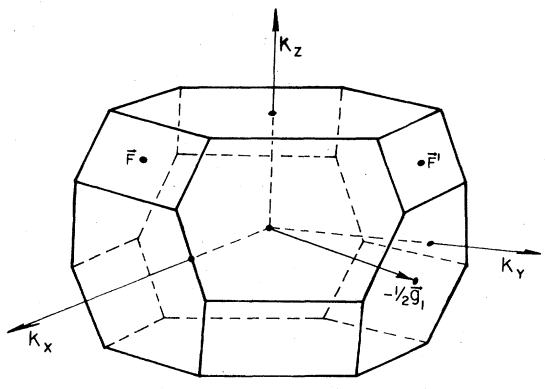

FIG. 3. Brillouin zone for the calcite structure with $\vec{F}$ point and $-\frac{1}{2}\vec{g}_1$ indicated.

of a $\vec{k}$ vector will be apparent as this work is developed but here we point out that the transition is a cell doubling (as seen from x-ray analysis) with the monoclinic phase possessing alternating rows of carbonate groups. The $\vec{k}$ vector must then be a zone-boundary vector and correspond to the monoclinic primitive lattice. We consider then the $\vec{F}$ point $\vec{F}=\frac{1}{2}\vec{g}_1+\frac{1}{2}\vec{g}_2$ as the $\vec{k}$ vector for the description of the transition.

The point group of $\vec{F}$ is $2/m\,(C_{2h})$ having elements

$$G^{\vec{F}}=\{E,C_{23}',I,\sigma_{d3}\}\ .$$

There are three vectors in the star ${}^*\vec{F}=\{\vec{F},\vec{F}',\vec{F}''\}$. The little group is then written in coset form as

$$G^{\vec{F}}=\{E|000\}T+\{I|000\}T+\{C_{23}'|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}T+\{\sigma_{d3}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}T\ .$$

Consideration of the factor system corresponding to these coset representatives reduces to the regular representations for $G^{\vec{F}}$. Among the four representations obtained of the space group we select the representation $D^{({}^*\vec{F},3)}$ indicated below which arises from the one-dimensional representation of $G^{\vec{F}}$, i.e., $1(E),-1(I),1(C_{23}'),-1(\sigma)$. We indicate $D^{({}^*\vec{F},3)}$ for those essential elements of $R\bar{3}c$ from which we can obtain the others:

$$D^{({}^*\vec{F},3)}(\{E|\vec{t}\})=\begin{pmatrix} e^{-i\vec{F}\cdot\vec{t}} & 0 & 0\\ 0 & e^{-iC_3^+\vec{F}\cdot\vec{t}} & 0\\ 0 & 0 & e^{-iC_3^-\vec{F}\cdot\vec{t}}\end{pmatrix},$$

$$D^{({}^*F,3)}(\{I|0\})=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix},$$

$$D^{({}^*\vec{F},3)}(\{C_{23}'|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\})=\begin{pmatrix}-1&0&0\\0&0&-1\\0&-1&0\end{pmatrix},$$

$$D^{({}^*\vec{F},3)}(\{C_3^+|0\})=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}.$$

In checking the antisymmetric square condition we need to consider all possible vectors in ${}^*\vec{F}$ of the form $\vec{k}_i+\vec{k}_j$ for which the sum is equivalent to the vector $\vec{k}=0$. Note that there are three such contributions,

$$\vec{F}+\vec{F}\equiv 0,\quad \vec{F}'+\vec{F}'\equiv 0,\quad \vec{F}''+\vec{F}''\equiv 0\ .$$

The antisymmetric square representation then splits into two portions, for example, T_0 and T_1. T_0 corresponds to that portion with wave vector equivalent to $\vec{k}=0$. Following the development of Lyubarskii[14] we can pick the basis of the representation T_0 as

$$\rho_{jmn'}=e_{jm}\sigma_{j_1m'}-e_{j_1m'}\sigma_{jm}\quad (j\leq j_1)\ .$$

Here j_1 is the label of the vector in star $\vec{k}$ which is equivalent to $-\vec{k}_j$ and m the basis vector of the representation corresponding to $\bar{G}^{\vec{F}}$ ($m=1$ for our case). For ${}^*\vec{F}$ each vector $\vec{k}_j$ is equivalent to $-\vec{k}_j$, so $j_1=j$ and j takes on 3 values.

In order that T_0 have a representation in common with the vector representation,

$$a_v=\frac{1}{N}\sum_f \chi_0(g)\chi(g)$$

should be greater than zero. In this sum N is the order of the isogonal point group $2/m$, f is a rotational element corresponding to the isogonal point group, $g=t_\alpha f\in G^0$, and t_α is a fractional translation. The calculation shows that the antisymmetric square of $D^{({}^*\vec{F},3)}$ (and all four representations of the space group corresponding to $\vec{F}$) does not contain the vector representation of $R\bar{3}c$.

Similarly for the symmetric cube condition we look for triple products of basis vectors of $D^{({}^*\vec{F},3)}$ which are equivalent to the vector $\vec{k}=0$. The only possibility is $\vec{F}+\vec{F}'+\vec{F}'$. As above, T_0 corresponds to that subspace of the symmetric triple product corresponding to $\vec{k}=0$. Checking the character condition

$$a_1=\frac{1}{N}\sum_{f\in F}\chi_0(g)$$

we see that $[D^{({}^*\vec{F},3)}]^3$ does not contain the identity representation ($D^{({}^*F,4)}$ also satisfies this condition).

The components of the order-parameter transform irreducibly under $D^{({}^*\vec{F},3)}$, each component corresponding to one arm of the star. From condition (E) the order-parameter components are to correspond to the components of a physical tensor. We wish to interpret an order-parameter component as an eigenvector of the dynamical matrix and thus specify a normal mode of oscillation. As we show in Sec. IV, our representation $D^{({}^*\vec{F},3)}$ corresponds to a normal mode of oscillation whose pattern of oscillation is that of the rotation pattern described by the x-ray data. We thus assume for now that the condition of "physical tensor" is satisfied.

Next we wish to consider conditions (A) and (D), the subgroup and subduction criteria, respectively. A general form for a character of the $\vec{F}$ point representation $D^{({}^*\vec{F},3)}$ is

$$\chi=(-1)^{n_1+n_2}\chi_1+(-1)^{n_2+n_3}\chi_2+(-1)^{n_1+n_3}\chi_3\ ,$$

where $(-1)^{(\ )}$ arises from lattice translations and χ_i considers the rotational coset forms of $G(R\bar{3}c)$. The cell doubling to a primitive lattice occurs only if one arm of the star contributes to the character con-

siderations. We make such a restriction and consider as an example the $\vec{F}'$ arm. For nonzero contributions to the subduction character sum we obtain primitive lattice vectors of the form

$$\vec{t}_1' = \vec{t}_1, \quad \vec{t}_2' = -\vec{t}_2 + \vec{t}_3$$

and

$$\vec{t}_3' = \vec{t}_1 - \vec{t}_2 - \vec{t}_3$$

with a new cell of twice the volume as well as satisfying the monoclinic relationships between $\vec{t}_1'$, $\vec{t}_2'$, and $\vec{t}_3'$.

Within this selection of lattice translations we can check the correspondence of the symmetry elements of $P2_1/c$ with those of $R\bar{3}c$. Another selection of a single-arm contribution will yield equivalent results and will correspond to a different domain of the structure. Picking the origin of symmetries at $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$ of the international tables we see that $P2_1/c$ is a subgroup of $R\bar{3}c$ with coset representatives of $P2_1/c$ corresponding to transformations

$$\{E|0\}, \quad \{I|-1,+1,0\} ,$$

$$\{C_2|-\tfrac{1}{2}\,-\tfrac{1}{2}\,\tfrac{1}{2}\}, \quad \{\sigma|\tfrac{1}{2}\,-\tfrac{1}{2}\,-\tfrac{1}{2}\} ,$$

as expressed in $R\bar{3}c$. We wish to use the character condition as formulated by Lavrencić and Shigenari[15]:

$$\frac{1}{|G_1|}\sum_{t_1\in G_1}\sum_{g'\in\mathfrak{C}}, \quad \chi_p^{(*k)}(g'\vec{t}_1) = \mathcal{P} ,$$

where $\mathfrak{C}$ is a coset representative of T_1 in G_1 and $\mathcal{P}$ is a positive integer and

$$\chi_p^{(*\vec{k})}(g') = \sum_{i=1}^{\sigma}\exp[-i\vec{k}_i\cdot(\vec{t}_0+\vec{\alpha}+h\vec{\alpha}_i^{(1)}-\vec{\alpha}_i^{(1)})] \times \delta_{h\vec{k}_i,\vec{k}_i}\,\chi_p^{(\vec{k}_1)}((g_i^{(1)})^{-1}hg_i^{(1)}) .$$

In this last expression

$$g \equiv \{h|\vec{\alpha}\} \text{ of } G^0/T^0 ,$$

$$g' \equiv \{h'|\vec{\alpha}'\} \text{ of } G_1/T_1 = \{h|\vec{\alpha}+\vec{t}_0\} \text{ of } G^0 ,$$

$$\vec{t}_0(h) = \vec{\alpha}(h) - \vec{\alpha}(h) - h\vec{S} + \vec{S} ,$$

and

$$g_i \equiv \{g_i^{(1)}|\vec{\alpha}_i^{(1)}\} \text{ for } g_i^{(1)}\vec{k}_1 = \vec{k}_i .$$

We only sum over the one-arm contribution $\vec{F}'$. The above character condition yields the subduction integer 1, so the identity representation of $P2_1/c$ is contained once in $D^{(*\vec{F},3)}$ of $R\bar{3}c$.

The final necessary condition for a continuous phase transition is that $\Phi(P,T,\eta)$ have a minimum corresponding to the above order-parameter selection. Up to fourth order in the order parameter symmetry considerations determine the form for $\Phi(P,T,\eta)$ to be

$$\Phi(P,T,\eta) = A(P,T)\sum_i\eta_i^2 + B_1(P,T)\left[\sum_i\eta_i^2\right]^2 + B_2(P,T)\sum_i\eta_i^4 .$$

Minimization of Φ yields $\eta_i = 0$ in the paraphase and a form in the antiferrophase of $\eta_1 = \eta_3 = 0$, $(\eta_2)^2 = -A/4(B_1+B_2)$. This form corresponds to the above assumption of one arm of the star contributing for the new phase.

IV. PHYSICAL PROPERTY OF ORDER PARAMETER

One of the above conditions for a continuous phase transition was that the order parameter η correspond to a physical tensor field of G^0. In the soft-mode formulation η corresponds to a normal mode of the crystal. In this section we will identify a mode of the crystal which corresponds to the above order-parameter transformation properties.

The lattice modes of a crystal are a direct consequence of its space-group symmetry and its dispersion relations. The calculations of lattice modes can be carried out by a systematic procedure using group theory. A complete description of the normal modes of a crystal must consider (1) the motion of the lattice and (2) motion within a unit cell. According to the soft-mode picture of phase transitions, the eigenvectors of the soft mode are preserved in the lattice of the low-symmetry phase and provide information on the identification of the soft mode and its wave vector.

The wave vector of the soft mode can be identified by an analysis of the atomic displacements $\vec{u}_s(\vec{k},\vec{t})$ and corresponds with the low-symmetry phase. The displacements are given by

$$\vec{u}_s(\vec{k},\vec{t}) = \Gamma\{E|\vec{t}\}u_s(\vec{k},0) .$$

Here $\Gamma\{E|\vec{t}\} = \exp(i\vec{k}\cdot\vec{t})$, $u_s(\vec{k},\vec{0})$ is the displacement of the sth atom at an arbitrary origin, $\vec{k}$ is the wave vector, and $\vec{t} = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3$. Phase factors of the Bloch relation $\Gamma\{E|\vec{t}\}$ have been calculated in terms of the $\vec{k}$ vectors for each of the symmetry points of the rhombohedral Brillouin zone and the three primitive rhombohedral lattice translation vectors. Comparison of these data leads to the conclusion that a wave vector at the $\vec{F}$ point of the rhombohedral Brillouin zone drives the transition.

By starting with the wave vector $\vec{F}$ we can obtain all the unique sublattices of the calcite lattice and see that one of them, T_1, corresponds to the monoclinic

lattice of $CaCO_3$(II), namely,

$$T_{\mathrm{Rh}} = T_1 + \{E \mid \vec{t}_1\} T_1 \ .$$

In the description of the calcite-$CaCO_3$(II) transition the most prominent displacive feature is the rotations of CO_3 groups suggesting the possibility that the soft mode may be composed of CO_3 rotations about the rhombohedral c axis. Since the transition involves a zone-boundary mode it will be necessary to classify the normal modes of calcite according to the irreducible representations of the group of the wave vector. The procedure followed is that of Maradudin and Vosco.[16]

A representation of the symmetry properties of the crystal is constructed in terms of the $(3n \times 3n)$ matrix

$$T^{\kappa\kappa'}_{\alpha\beta}(\vec{\mathrm{F}}, R) = \delta(\kappa, F_0(\kappa', R)) \times \exp\{i\vec{\mathrm{F}} \cdot [\vec{x}(\kappa) - R\,\vec{x}(\kappa')]\} R_{\alpha\beta} \ .$$

The T matrix in general forms a multiplier representation of the point group of the wave vector $\vec{k}$. As previously indicated considerations of the $\vec{\mathrm{F}}$ point of $R\bar{3}c$ lead to regular representations of $\bar{G}^{\vec{\mathrm{F}}}$.

The normal modes of vibration are then classified by assigning them to an irreducible representation of the $\bar{G}^{\vec{\mathrm{F}}}$. The reducible representation D^T can be decomposed by the usual relation

$$a_\rho = -\sum_{f \in \bar{G}^{\vec{\mathrm{F}}}} \chi^T(f)\chi^\rho(f)$$

from which we obtain

$$D^T = 5D^{(1)} + 7D^{(2)} + 10D^{(3)} + 8D^{(4)} \ .$$

Using the projection operator techniques a set of basis functions or symmetry vectors can be calculated for each irreducible representation. For each set of symmetry vectors $\psi(\vec{\mathrm{F}}, \rho, \mu)$ we have constructed possible zone-boundary modes of oscillation.

From the set of symmetry vectors corresponding to the $D^{(^*\vec{\mathrm{F}},3)}$ irreducible representation (see Table I) we have selected a mode corresponding to the CO_3 rotational displacive pattern of the transition. Isolating the rotational displacive pattern, which is a result of the major displacements of the transition, ψ_{rot} can be represented by a linear combination of the symmetry vectors,

$$\psi_{\mathrm{rot}}(\vec{\mathrm{F}}, 3, \mu) = A\,\psi(\vec{\mathrm{F}}, 3, 8) + B\,\psi(\vec{\mathrm{F}}, 3, 9) \ ,$$

where A and B are nonzero constants. Finally, if one considers the zone-center modes of the $CaCO_3$(II) phase, ψ_{rot} is found in the identity representation of G_1; thus the ψ_{rot} mode is Raman active and satisfies the necessary conditions for a zone-boundary soft mode. The translational mode

$$\psi_{\mathrm{trans}}(\vec{\mathrm{F}}, 3, \mu) = C\,\psi(\vec{\mathrm{F}}, 3, 1)$$

TABLE I. Symmetry vectors $\psi(\vec{\mathrm{F}}, 3, \mu)$ of the unit-cell group of $CaCO_3$ for the $D^{(^*\vec{\mathrm{F}},3)}$ irreducible representation.

(1) $X_{\mathrm{Ca}(1)} = -X_{\mathrm{Ca}(2)}$
(2) $Y_{\mathrm{Ca}(1)} = Y_{\mathrm{Ca}(2)}$
(3) $Z_{\mathrm{Ca}(1)} = Z_{\mathrm{Ca}(2)}$
(4) $Y_{\mathrm{C}(1)} = Z_{\mathrm{C}(2)}$
(5) $Z_{\mathrm{C}(1)} = Z_{\mathrm{C}(2)}$
(6) $Y_{\mathrm{O}(1)} = Y_{\mathrm{O}(2)}$
(7) $Z_{\mathrm{O}(1)} = Z_{\mathrm{O}(2)}$
(8) $X_{\mathrm{O}(3)} = X_{\mathrm{O}(4)} = -X_{\mathrm{O}(5)} = -X_{\mathrm{O}(6)}$
(9) $Y_{\mathrm{O}(3)} = Y_{\mathrm{O}(4)} = Y_{\mathrm{O}(5)} = Y_{\mathrm{O}(6)}$
(10) $Z_{\mathrm{O}(3)} = Z_{\mathrm{O}(9)} = Z_{\mathrm{O}(5)} = Z_{\mathrm{O}(6)}$

corresponds to another important displacement of the transition also satisfying the above conditions. What linear combination of ψ_{rot} and ψ_{trans} constitutes the soft mode is not known. We do know that they are the only zone-boundary modes of the $D^{(^*\vec{\mathrm{F}},3)}$ irreducible representation corresponding to the identity representation of $G_1(C_{2h})$. These modes cannot be constructed from the symmetry vectors corresponding to any of the other three irreducible representations of the point group of $\vec{\mathrm{F}}$.

V. CONCLUSIONS

The $R\bar{3}c$ to $P2_1/c$ transition has been described within the framework of the Landau criteria for continuous phase transitions. Motivated by some experimental evidence of x-ray considerations and critical phenomena at temperatures of $\sim$180 °C and 15 kbar the question was formulated as to whether the above transition could be continuous.

The $\vec{\mathrm{F}}$ point was chosen to label the irreducible representation of the transition. It leads to a cell-doubling primitive monoclinic lattice. All Landau conditions *are satisfied* by the $D^{(^*\vec{\mathrm{F}},3)}$ representation. In the analysis of the physical property of the order parameter the observed alternating rotations are seen to arise *only* from the normal mode corresponding to this $D^{(^*\vec{\mathrm{F}},3)}$ representation.

Thus within a Landau formulation it is possible for the transition to be continuous. No experiments have to this date evidenced such a continuous transition at higher termperature, however.

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