Landau free energy form at the F point of the R3c structure

Dorian M. Hatch and D. L. Decker

Citation: The Journal of Chemical Physics **74**, 2518 (1981); doi: 10.1063/1.441321
View online: http://dx.doi.org/10.1063/1.441321
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/74/4?ver=pdfcov
Published by the AIP Publishing

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.187.97.22 On: Thu, 20 Mar 2014 18:27:38

Landau free energy form at the F point of the $R\bar{3}c$ structure

Dorian M. Hatch and D. L. Decker

Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602
(Received 3 September 1980; accepted 6 November 1980)

A free energy form compatible with the F point of the trigonal $D_{3d}^6(R\bar{3}c)$ symmetry is constructed. It is a function of the order parameter, elastic strain, and the stress. The resulting free energy exhibits a close formalistic analogy to the stressed cubic perovskite structures and their associated multicriticality.

I. INTRODUCTION

Over forty years ago Landau phenomenologically treated thermodynamic systems possessing continuous phase transitions.[1] The theory considered symmetry changes as well as thermodynamic functional critical behavior and allowed for descriptions of both second order and first order transitions. The high degree of universality of the formalism was associated with various values of its parameters and gave a description of a type of critical point at which the line of second order transitions changes continuously to a line of first order transitions.

It was only recently Griffiths[2] theoretically showed that the critical point described by Landau occurs at the intersection of three critical (second order) lines and is thus properly termed a tricritical point (TCP). Necessarily, considerations of three thermodynamic field variables are implied and the tricritical point is a "higher order" or multicritical point. There are many systems in which there is a possibility of a TCP and several in which they have been experimentally confirmed.[3]

In addition to tricritical points other types of higher order critical points are known to exist such as bicritical, tetracritical, etc. Many of these higher order critical points can be associated with symmetry breaking fields, e.g., stressed systems.[4] Again there are several structures in which multicritical points arise and $SrTiO_3$ is an example of a structure where a multicritical point arises as a result of a stressing symmetry breaking field.

Usually the initial theoretical approach to the description of such systems is a mean field Landau description from which a valid description is obtained for regions where fluctuations do not significantly contribute. The free energy form together with symmetry compatibilities are then the beginnings for a Landau–Ginsburg–Wilson Hamiltonian to which renormalization group methods can be applied.[5]

Descriptions of continuous transitions within the Landau formalism require the specification of an irreducible representation of the space group. For representations arising from the $\mathbf{k}=0$ point, considerations reduce to point group representations. Recently the classification of possible continuous transitions of the $R\bar{3}c$ structures arising from the Γ, Z, L, and F points was developed.[6]

In this paper we wish to construct a free energy form which is compatible with the trigonal $D_{3d}^6(R\bar{3}c)$ symmetry. The motivation of this work arose from electron spin resonance studies on the $R\bar{3}c$ to $P2_1/c$ calcite transition near 16 kbar.[7] The first order nature of this transition, as interpreted from the discontinuity in the esr spectra of the two phases, was observed to decrease, as the temperature was increased along the phase line, in a manner typical of critical phenomena and approached zero near 200 °C. Thus after showing the compatibility of a continuous transition between these space groups[6] which is necessary for the existence of critical points, the next step is to examine the nature of the possible critical phenomena by a calculation of the form of the free energy. From the Aizu classification[8] the free energy will be a function of the order parameter, the elastic strain, and the stress. From the free energy we indicate a close formalistic analogy with the stressed cubic perovskite structures and their associated multicriticality.

II. FREE ENERGY FORM

The trigonal space group we wish to consider is D_{3d}^6 $(R\bar{3}c)$. Several materials exist in this crystal structure and there is evidence that one or more may exhibit critical phenomena.[7] The first step in the description of points or regions in field space of a continuous phase change is to construct within the formulation of Landau a free energy form compatible with an irreducible representation of the more symmetric phase. We will denote this higher symmetry space group as G_0. The transition then goes to a subgroup G_1 of G_0. In order for the transition to take place continuously a set of necessary conditions on the representation of G_0 as well as the subgroup G_1 need to be checked.[9] Considerations of representations and the construction of the free energy form for zone center points reduce to point group considerations. The group theory and the checking of the Landau conditions for the Z, L, and F points are to be published elsewhere and that work indicates that for the F point three representations together with the appropriate subgroups satisfy the necessary criteria for continuous transitions from the space group $R\bar{3}c(G_0)$. In this development we consider only the F point and the associated representations of $R\bar{3}c$ in the construction of the free energy.

$R\bar{3}c$ 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

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

with the numbering in the sum corresponding to the ordering of the symmetry operations of the *Intenational*

 0021-9606/81/042518-05$01.00 © 1981 American Institute of Physics

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.187.97.22 On: Thu, 20 Mar 2014 18:27:38

Tables for X-Ray Crystallography.[10] We take the forms

$$\begin{aligned} \mathbf{t}_1 &= -a\hat{j} + c\hat{k}\,, \\ \mathbf{t}_2 &= (a\sqrt{3}/2)\hat{i} + (a/2)\hat{j} + c\hat{k}\,, \\ \mathbf{t}_3 &= -(a\sqrt{3}/2)\hat{i} + (a/2)\hat{j} + c\hat{k} \end{aligned} \tag{2}$$

for our primitive translation vectors and

$$\begin{aligned} \mathbf{g}_1 &= 2\pi[-2/3a)\hat{k}_y + (1/3c)\hat{k}_z]\,, \\ \mathbf{g}_2 &= 2\pi[(1/\sqrt{3}a)\hat{k}_x + (1/3a)\hat{k}_y + (1/3c)\hat{k}_z]\,, \\ \mathbf{g}_3 &= 2\pi[-(1/\sqrt{3}a)\hat{k}_x + (1/3a)\hat{k}_y + (1/3c)\hat{k}_z] \end{aligned} \tag{3}$$

are the resulting forms for the reciprocal lattice vectors.

To construct representations of G_0 we must have a specific k vector of the Brillouin zone in mind. Motivated by the correspondence to the transition in calcite we will consider the F point $[\mathbf{F} = (\mathbf{g}_1)/2 + (\mathbf{g}_2)/2]$ as the k vector for the description of the representations. The point group of F is $2/m$ (C_{2h}) with elements

$$\overline{G}^{\mathbf{F}} = \{E,\ C_{23}',\ I,\ \sigma_{d3}\}\,. \tag{4}$$

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

$$G^{\mathbf{F}} = \{E|000\}T + \{I|000\}T + \{C_{23}'|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}T + \{\sigma|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}T\,. \tag{5}$$

Consideration of the factor system corresponding to these coset representatives reduces to the regular representations for $\overline{G}^{\mathbf{F}}$. Among the four representations obtained of the space group consider the representation $D^{(^*\mathbf{F},3)}$ indicated below which arises from the one-dimensional representation of $\overline{G}^{\mathbf{F}}$, i.e., $1(E)$, $-1(I)$, $1(C_{23}')$, $-1(\sigma)$. The above representation along with $D^{(^*\mathbf{F},1)}$ and $D^{(^*\mathbf{F},4)}$ are the representations which satisfy the necessary conditions for continuous transitions and thus the only ones which we consider in the construction of the free energy. For concreteness we indicate for $D^{(^*\mathbf{F},3)}$ those essential elements of $R\bar{3}c$ from which we can obtain the others.

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

$$D^{(^*\mathbf{F},3)}(\{I|0\}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{6}$$

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

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

We will use $D^{(^*\mathbf{F},3)}$ in the following but recognize that $D^{(^*\mathbf{F},4)}$ and $D^{(^*\mathbf{F},1)}$ yield the same form for the free energy. The only difference between these representations and $D^{(^*\mathbf{F},3)}$ is that for the above essential elements of $R\bar{3}c$,

$$D^{(^*\mathbf{F},4)}(C_{23}') = -D^{(^*\mathbf{F},3)}(C_{23}')\ ;\quad D^{(^*\mathbf{F},1)}(I) = -D^{(^*\mathbf{F},3)}(I) \tag{7}$$

and since these matrices appear always as squares in the nonzero sums below the invariants of these three representations are the same.

We first restrict our attention to the construction of the free energy terms which arise *only* from the order parameter contribution. As was done in the original formulation by Landau we interpret the basis functions of $D^{(^*\mathbf{F},3)}$ as local order parameters. The free energy must then be invariant in functional form under the space group transformations of $R\bar{3}c$. The first order invariant term of the free energy is excluded for systems which have an inversion or reflection center. For our group there is thus no first order invariant form.

The second order invariant terms arise from terms of the form $\eta_i\eta_j$ in the order parameters carrying representation $D^{(^*\mathbf{F},3)}$. In terms of group theory an invariant second order form is equivalent to seeking an identity representation of $R\bar{3}c$ within the symmetric squared Kronecker product of the $D^{(^*\mathbf{F},3)}$ representation. We thus need to seek sums of F, F′ and F″ which are equivalent to the zero vector, i.e., equal to $\mathbf{k} = 0$ up to a reciprocal lattice vector. This would assure invariance under all lattice translations. Notice that there are only three such forms, namely

$$\mathbf{F} + \mathbf{F} \equiv 0,\quad \mathbf{F}' + \mathbf{F}' \equiv 0,\quad \mathbf{F}'' + \mathbf{F}'' \equiv 0\,. \tag{8}$$

The symmetric square representation then splits into two portions, say T_0 and T_1, where T_0 corresponds to that portion with wave vector equivalent to $\mathbf{k} = 0$ and thus the only portion we need to consider. We can obtain a basis[11] for T_0 by using

$$\rho_{jmm'} = \eta_{jm}\,\eta_{jm'}\,, \tag{9}$$

with j labeling arms of the star and m, m' labeling the basis vector of the representation of the little group $G^{\mathbf{F}}$ Since $m = m' = 1$ for our case the order parameter functions carrying $D^{(^*\mathbf{F},3)}$ can be labeled η_i with $i = 1, 2, 3$ and they transform under translations as $e^{i\mathbf{F}\cdot\mathbf{t}}$, $e^{i\mathbf{F}'\cdot\mathbf{t}}$, or $e^{i\mathbf{F}''\cdot\mathbf{t}}$. To obtain the second order invariant we can then use the projection operator for the identity representation

$$P^{(1)} = \frac{1}{|G_0|}\sum_g \chi(g)0_g = \frac{1}{|G_0|}\sum_g 0_g\,, \tag{10}$$

and let it act on vectors of T_0. For example,

$$\begin{aligned} P^{(1)}\eta_1\eta_1 &= \frac{1}{|G_0|}\sum_g 0_g(\eta_1\eta_1) \\ &= \frac{1}{|G_0|}\sum_{i,j,g} D_{i1}^{(^*\mathbf{F},3)}(g)\,D_{j1}^{(^*\mathbf{F},3)}(g)\,\eta_i\,\eta_j \\ &= \frac{1}{|T|\,|G_0/T|}\sum_{\substack{f\in\overline{G}^{\mathbf{F}} \\ i,j}} \{D_{i1}^{(^*\mathbf{F},3)}(\overline{g})D_{j1}^{(^*\mathbf{F},3)}(\overline{g})\} \\ &\quad\times\left\{\sum_{t\in T}\exp[i(\mathbf{F}_i + \mathbf{F}_j)\cdot\mathbf{t}\right\}\eta_i\eta_j\,, \end{aligned} \tag{11}$$

where $\overline{g} \equiv \{f|\mathbf{t}_\alpha\}$ are the coset representatives of G_0. The sum over the translations in $R\bar{3}c$ is zero unless $\mathbf{F}_i = \mathbf{F}_j$ for which it gives $|T|$. Thus

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.187.97.22 On: Thu, 20 Mar 2014 18:27:38

$$P^{(1)}\eta_1\eta_1 = \sum_{i=1}^{3}\left\{\frac{1}{|G^{\mathbf{F}}|}\sum_{f\in G^{\mathbf{F}}} D_{i1}^{(*\mathbf{F},3)}(\bar{g})D_{i1}^{(*\mathbf{F},3)}(\bar{g})\right\}\eta_i\eta_i \ . \quad (12)$$

The use of the projection operator on vectors in T_0 yield one invariant of the form $\sum_i \eta_i^2$. This is the usual quadratic form invariant and was to be expected.

To look for cubic invariants we must look for cubic combinations $\eta_i\eta_j\eta_k$ which are invariant under translations. There is only one such symmetric combination, namely $\eta_1\eta_2\eta_3$. The use of the projection operator in this T_0 subspace yields the sum

$$P^{(1)}\eta_1\eta_2\eta_3 = \sum_{i\neq j\neq k}\left\{\frac{1}{|G^{\mathbf{F}}|}\sum_{f\in G^{\mathbf{F}}} D_{i1}^{(*\mathbf{F},3)}(\bar{g})D_{j2}^{(*\mathbf{F},3)}(\bar{g})D_{k3}^{(*\mathbf{F},3)}(\bar{g})\right\}\eta_i\eta_j\eta_k. \quad (13)$$

We obtain no third order invariants and thus representation $D^{(*\mathbf{F},3)}$ satisfies one of the conditions of Landau for a continuous transition. Similar considerations of invariants to sixth order yield the following form for the free energy in terms of the order parameter:

$$\Phi_1(\eta) = \Phi_0 + A\sum_i \eta_i^2 + B_1\sum_i \eta_i^4 + B_2\sum_{i<j}\eta_i^2\eta_j^2 + C_1\left(\sum_i \eta_i^2\right)^3 + C_2\sum_i \eta_i^6 + C_3\eta_1^2\eta_2^2\eta_3^2 \ . \quad (14)$$

This is the same form as was obtained for the cubic perovskite structure.[12]

If we now turn our attention to the free energy contributions solely dependent on elastic strain the lowest order contributions is of the form

$$\Phi_2(e) = \tfrac{1}{2}C_{ij}e_i e_j \ . \quad (15)$$

Here the Voigt notation has been used so the e_i is a second rank symmetric tensor whose components transform as (polar) vector components under symmetry transformations. We choose the Cartesian coordinates for the strain such that the threefold axis is along the z axis and the twofold axis of C_{23}' is along the x axis. At second order in e_i we obtain six strain invariants. Indicating here only the terms of second order (fourth rank tensor forms) we have elastic strain contributions of the form

$$\Phi_2(e) = \tfrac{1}{2}C_{11}(e_1^2+e_2^2+2e_6^2) + C_{12}(e_1e_2-e_6^2) + C_{13}e_3(e_1+e_2) + 2C_{14}(e_4e_1-e_4e_2+2e_5e_6) + \tfrac{1}{2}C_{33}e_3^2 + 2C_{44}(e_4^2+e_5^2) \ . \quad (16)$$

Finally, we consider terms of the free energy which couple strain and order parameter. We will consider only the lowest order contribution consistent with the translation symmetry and the central point property of $R\bar{3}c$. The usual "electrostrictive" contribution $\eta_i\eta_j e_k$ which can be obtained through the use of the projection operator defined earlier is of the form

$$P^{(1)}\eta_{i_0}\eta_{i_0}\epsilon_{j_0k_0} = \frac{1}{|G^{\mathbf{F}}|}\sum_{f\in G^{\mathbf{F}}}\sum_{ijk} \times D_{ii_0}^{(*\mathbf{F},3)}(g)D_{ii_0}^{(*\mathbf{F},3)}(g)D_{jj_0}(f)D_{kk_0}(f)\eta_i^2\epsilon_{jk} \ . \quad (17)$$

Notice we have not used the Voigt notation for strain (ϵ) in the above sum so that the explicit transformation of components can be shown. Here $D_{jj_0}(f)$ corresponds to the matrix elements of the Cartesian vector transformation matrices of the second rank strain tensor. We obtain four possible invariants with the resulting free energy form (Voigt notation)

$$\Phi_3(\eta,e) = \beta_{11}\left(\sum_i \eta_i^2\right)(e_1+e_2) + \beta_{13}\left(\sum_i \eta_i^2\right)e_3 + \beta_{12}\{2\eta_1^2(e_1-e_2) - \eta_2^2(e_1-2\sqrt{3}e_6-e_2) - \eta_3^2(e_1+2\sqrt{3}e_6-e_2)\} + \beta_{14}\{2\eta_1^2e_4 + \eta_2^2(\sqrt{3}e_5-e_4) + \eta_3^2(-\sqrt{3}e_5-e_4)\} \ . \quad (18)$$

III. DISCUSSION

Let us restrict considerations to fourth order in the order parameter, quadratic in e, and add a stress (y_α) strain coupling term. Then

$$\Phi(\eta,\epsilon,y_\alpha) = \Phi_1(\eta) + \Phi_2(e) + \Phi_3(\eta,e) - \sum_\alpha y_\alpha e_\alpha \ . \quad (19)$$

If we now use the condition $(\partial\Phi)/(\partial e_\alpha) = 0$ we can solve for e as a function of η and y_α. The free energy can then be expressed as a function of η and y_α and takes the reduced form

$$\Phi(\eta,y_\alpha) = \frac{r_0}{2}\sum_i \eta_i^2 + u_0\left(\sum_i \eta_i^2\right)^2 + v_0\sum_i \eta_i^4 + L_1\left(\sum_i \eta_i^2\right)(y_1+y_2) + L_2\left(\sum_i \eta_i^2\right)y_3 + L_3\{2\eta_1^2(y_1-y_2) - \eta_2^2(y_1-2\sqrt{3}y_6-y_2) - \eta_3^2(y_1+2\sqrt{3}y_6-y_2)\} + L_4\{2\eta_1^2y_4 + \eta_2^2(\sqrt{3}y_5-y_4) + \eta_3^2(-\sqrt{3}y_5-y_4)\} \ . \quad (20)$$

Under isotropic stress, i.e., $y_i = -p$, $i = 1,2,3$; $y_4 = y_5 = y_6 = 0$ the free energy reduces to

$$\Phi(\eta,p) = \frac{r_0}{2}\sum_i \eta_i^2 + u_0\left(\sum_i \eta_i^2\right)^2 + v_0\sum_i \eta_i^4 - p(2L_1+L_2)\sum_i \eta_i^2 \ . \quad (21)$$

The primary affect of isotropic stress is to renormalize the Curie temperature which is associated with the coefficient of the $\sum_i \eta_i^2$ term. The free energy under these conditions is formalistically the same as for cubic structures, for example, $BaTiO_3$ and $SrTiO_3$.[12] Equilibrium order parameter values can be obtained for this Landau free energy yielding three possibilities:

(a) paraphase $\eta_1 = \eta_2 = \eta_3 = 0$,

(1) for $r_0 > 0$, $v_0 > 0$, $u_0 + v_0/3 < 0$,

(2) for $r_0 > 0$, $v_0 < 0$, $u_0 + v_0 < 0$

(b) ferrophase $\eta_1 = \eta$, $\eta_2 = \eta_3 = 0$,

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.187.97.22 On: Thu, 20 Mar 2014 18:27:38

(1) $r_0<0$, $v_0<0$,

(2) $r_0>0$, $v_0<0$, $u_0+v_0<0$,

(c) ferrophase $\eta_1=\eta_2=\eta_3=\eta$,

(1) $r_0<0$, $v_0>1$,

(2) $r_0>0$, $v_0>0$, $u_0+v_0<0$.

From results to be published elsewhere[6] a continuous transition from the $R\bar{3}c$ paraelastic phase to the $P2_1/c$ ferroelastic phase satisfies Landau's conditions and corresponds to the situation (b) (1) while a continuous transition from $R\bar{3}c$ to $R3c$ satisfies Landau's conditions and corresponds to the situation (c) (1). Other space group possibilities certainly exist within this formalism.

Benguigui[13] has indicated first qualitatively and more recently in a quantitative way[14] for the case of $BaTiO_3$ that a change in order of the transition cannot take place without the presence of either a third order strain contribution e^3 or an $\eta^2 e^2$ term in the initial free energy. From the above reduced free energy we indicate the same additional terms allow for a change in order of the transition for an $R\bar{3}c$ structure.

The application of an anisotropic stress leads to a free energy which generally has a different symmetry than the stress free structure. If we take a uniaxial stress $y_i=-p\delta_{i1}$ the free energy becomes

(I)

$$\Phi(\eta,p)=\frac{r_0}{2}\sum_i\eta_i^2+u_0\Big(\sum_i\eta_i^2\Big)^2+v_0\sum_i\eta_i^4 - p(L_1-L_3)\sum_i\eta_i^2-3pL_3\eta_1^2\,, \tag{22}$$

while for a uniaxial stress $y_i=-p\delta_{i2}$

(II)

$$\Phi(\eta,p)=\frac{r_0}{2}\sum_i\eta_i^2+u_0\Big(\sum_i\eta_i^2\Big)^2+v_0\sum_i\eta_i^4 - p(L_1+L_3)\sum_i\eta_i^2+3pL_3\eta_1^2\,. \tag{23}$$

For the uniaxial stress $y_i=-p\delta_{i3}$ we obtain

(III)

$$\Phi(\eta,p)=\frac{r_0}{2}\sum_i\eta_i^2+u_0\Big(\sum_i\eta_i^2\Big)^2+v_0\sum_i\eta_i^4-pL_2\sum_i\eta_i^2\,. \tag{24}$$

For the asymmetric free energies (I) and (II) above there is a formalistic similarity to that of the stressed perovskite structures, e.g., $SrTiO_3$ and $LaAlO_3$. In the perovskite structure the order parameter components correspond to three orthogonal directions. A stress in the i_0 direction gives a free energy of the form

$$\Phi(\eta,p)=\frac{r_0}{2}\sum_i\eta_i^2+u_0\Big(\sum_i\eta_i^2\Big)^2+v_0\sum_i\eta_i^4 - y_{i_0}(L_1-L_2)\eta_{i_0}^2+y_{i_0}L_2\sum_i\eta_i^2\,. \tag{25}$$

Notice that the asymmetric contribution $y_{i_0}(L_1-L_2)\eta_{i_0}^2$ is of the same form for each of the three directions with the same coefficient (L_1-L_2). In the $R\bar{3}c$ structure the three independent components correspond to the three arms of the star F, F′, and F″. A stress in the x or y direction for $R\bar{3}c$ yields similar asymmetric forms as in (I) and (II) above. However, the coefficient of the asymmetric term in (I) $(-3pL_3)$ is different than in (II) $(+3pL_3)$. Stress in different directions in the x-y plane then yield different strength asymmetric contributions. In addition, there is a directional property asso-

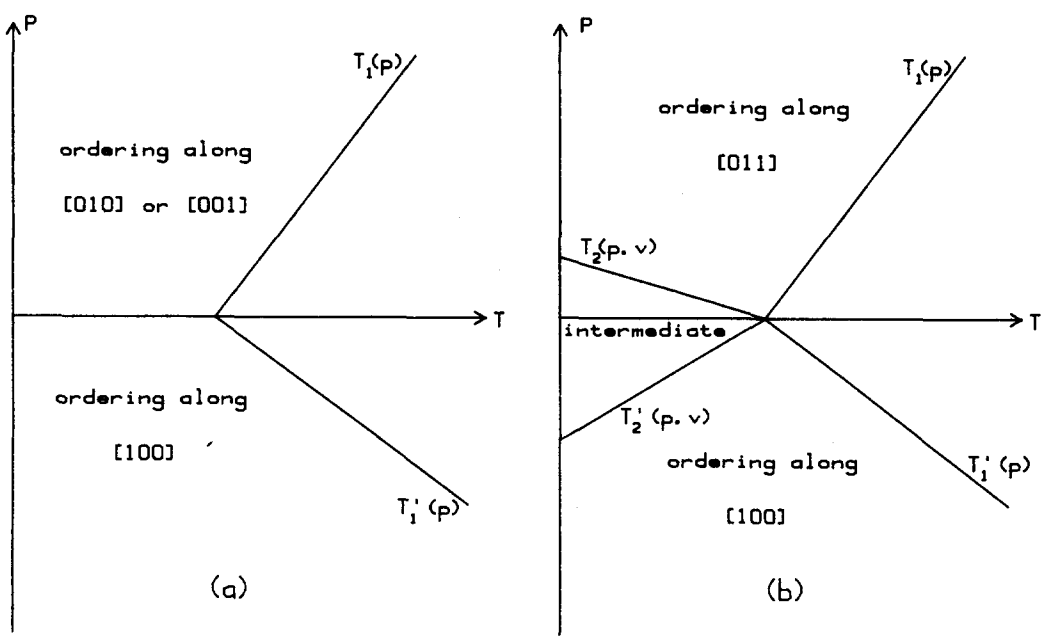

FIG. 1. Phase diagrams of the system with uniaxial anisotropy (a) $v_0<0$, displaying a bicritical point and (b) $v_0>0$, displaying a tetracritical point.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.187.97.22 On: Thu, 20 Mar 2014 18:27:38

ciated with the Curie temperature through $(L_1 - L_3)$ for x direction and $(L_1 + L_3)$ for the y direction. Stress in the z direction is along the trigonal axis and yields a symmetric free energy (III) similar in form to the no stress free energy.

The mean-field theory has been done for this asymmetric free energy.[15] The phase diagrams for $v_0 < 0$ and $v_0 > 0$ are shown in Fig. 1. For $v_0 < 0$ we obtain a bicritical point with ordering along [100] if the coefficient of the η_1^2 term is negative and along [010] or [001] if the coefficient of η_1^2 is positive. For $v_0 > 0$ a tetracritical point may appear with an intermediate phase in which the order parameter continuously changes from the [100] ordering the [011] ordering.

This mean field description is qualitatively correct for stressed perovskites and is changed slightly by renormalmalization group calculations. Because of the formalistic analogy of the stressed trigonal structure we expect the mean field and renormalization group methods to apply and yield the same description for this trigonal system as is found in the stressed perovskites.

[1]L. D. Landau, Phys. Z. Sowjetunion **11**, 26 (1937).
[2]R. B. Griffiths, Phys. Rev. B **7**, 545 (1973).
[3]M. B. Salamon and H. T. Shang, Phys. Rev. Lett. **44**, 879 (1980); A. B. Western, A. G. Baker, C. R. Bacon, and V. H. Schmidt, Phys. Rev. B **17**, 4461 (1978); N. Giordano and W. P. Wolf, Phys. Rev. Lett. **39**, 342 (1977); R. Clarke and L. Benguigui, J. Phys. C **10**, 1963 (1977); J. R. Fox, J. Chem. Phys. **69**, 2231 (1978).
[4]K. A. Müller and W. Berlinger, Phys. Rev. Lett. **35**, 1547 (1975); E. Domany, D. Mukamel, and M. E. Fischer, Phys. Rev. B **15**, 5432 (1977); A. Aharony, Physica (Utrecht) **86–88B**, 545 (1977).
[5]D. Mukamel and S. Krinsky, Phys. Rev. B **13**, 5065 (1976).
[6]D. M. Hatch and L. Merrill, Phys. Rev. B **23**, 368 (1981); also D. M. Hatch, Phys. Rev. (in press).
[7]S. D. Tyagi, "An Investigation of the High Pressure Phase $CaCO_3$(II): Mn^{++} Using Electron Paramagnetic Resonance," Ph. D. dissertation, Brigham Young University, 1976 (unpublished).
[8]K. Aizu, J. Phys. Soc. Jpn. **27**, 387 (1969).
[4]F. E. Goldrich and J. L. Birman, Phys. Rev. **167**, 528 (1968); M. V. Jaric, Ph. D. thesis, CUNY, New York, 1977 (unpublished).
[10]N. F. M. Henry and K. Lonsdayle, *International Tables for X-Ray Crystallography* (Kynoch, Birmingham, 1965), Vol. I.
[11]G. Y. Lyubarskii, *The Application of Group Theory in Physics* (Pergamon, New York, 1960).
[12]A. Aharony and A. D. Bruce, Phys. Rev. Lett. **33**, 427 (1974).
[13]L. Benguigui, Phys. Status Solidi B **60**, 835 (1973).
[14]R. Clarke and L. Benguigui, J. Phys. C **10**, 1963 (1977).
[15]A. D. Bruce and A. Aharony, Phys. Rev. B **11**, 478 (1975).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.187.97.22 On: Thu, 20 Mar 2014 18:27:38