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Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602

Predictions of the possible post-transition symmetries of an $R\,\bar{3}c$ zone center continuous phase transition are made using recent extensions of the Landau theory. The Landau theory is summarized and direct group theoretical methods are applied to the $R\,\bar{3}c$ phase. General techniques for solving systems of nonlinear polynomial equations are reviewed and these techniques are applied to the minimization of the free energy F for the aforementioned possible symmetries. The results of the direct methods and the minimization procedures are shown to be compatible. It is shown that the transition to $R\,3c$ in NaNO$_3$ is consistent with the above results as well as with the observed atomic displacements.

I. INTRODUCTION

Landau theory,[1] as extended by Birman,[2] among others, predicts the symmetry which a crystal can have after a continuous (second order) phase transition. This prediction is based only on a knowledge of the symmetry of the crystal before the transition. This paper briefly explains the most recent version of this process, and applies the theory to the general consideration of a zone center transition of $R\,\bar{3}c$. The transition observed in NaNO$_3$ is a continuous transition[3] from $R\,\bar{3}c$ to $R\,3c$ proceeding from a paraelectric to a ferroelectric phase. The transition occurs at room temperature and 45 kbar and is accompanied by NO$_3^-$ rotations as well as Na$^+$ displacements. Since there is no change in primitive cell size the transition is a k $=$ 0 soft mode. We show compatibility of the theory with the observed experimental evidence.

In Sec. II we review the original Landau theory, making a connection with the more recent developments in the theory, viz., the subduction and chain subduction criteria, and the related concept of an isotropy group. The latter direct group theoretical methods including the Landau and the Lifshitz conditions are then applied to $R\,\bar{3}c$ for the zone center yielding six possible post-transition subgroups.

In Sec. III we consider the additional restriction of minimizing the free energy F. Thus generally a subset of the groups obtained by direct methods correspond to a minimum of F. We review the method of Jarić[4] for solving systems of nonlinear polynomial equations, exploiting the invariance of these equations under relevant symmetry groups. These methods use projection operators to partition solutions of $\nabla F = 0$ into sets according to the symmetry of the vector order parameter, and thereby reduce the degree of the relevant equations. We apply the techniques for the free energy F expanded to fourth order (simple continuous transition).

In Sec. IV using a lattice atomic model, we then indicate the agreement between the predicted order parameter symmetry and experiment for the NaNO$_3$ transition including the determination of the distortion from the average position of the atoms during the transition.

II. LANDAU THEORY AND ISOTROPY GROUPS

The symmetry of a crystal can be defined in terms of a density function, $\rho(x,y,z)$, after Landau.[1] The symmetry group of a crystal is then the set of rotations, reflections, translations, etc., that leave ρ unchanged. Thus, letting r represent an arbitrary transformation, the symmetry group R_0 is the set

$$R_0 \equiv \{r: 0, \rho(x,y,z) = \rho(x,y,z)\}. \tag{1}$$

For the structure of NaNO$_3$, which is of interest here, there are 12 coset representatives which may be selected (cosets with respect to translations) in the space group (see Fig. 1):

E: The identity element. All atoms and coordinates are unchanged. $C_3^{\pm}$: A rotation about the z axis by 120°, clockwise ($-$) or counterclockwise ($+$). C'_{21}: A 180° rotation about the axis along a line from 5 to 3. C'_{22}: Same as C'_{21} only along a line from 7 to 3. C'_{23}: Same as C'_{21} only along a line from 6 to 3. I: Inversion through 2. $S_6^{\pm}: IC_3^{\pm}$ as defined above. $\sigma_{d1}, \sigma_{d2}, \sigma_{d3}$: Reflection through a plane containing the z axis and perpendicular to the C'_{21}, C'_{22}, and C'_{23} axes, respectively, followed by a glide of 1/2 of a unit cell.

This collection of 12 cosets together with trigonal translations, is $R\,\bar{3}c$ in the international notation,[5] and its related point group (G/T) is D_{3d}. The origin of $R\,\bar{3}c$ labeling is at the $\bar{3}$ center, i.e., at the Na atom in NaNO$_3$.

For a quite arbitrary density function ρ it is well known from group theory that the function can be expanded in terms of symmetry functions with respect to $R\,\bar{3}c$, i.e.,

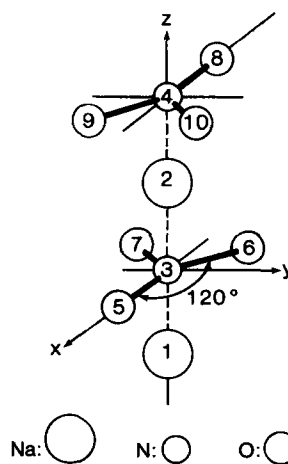$$\rho = \rho_0 + {\sum_m}' \sum_i \eta_i^m \Psi_i^m \equiv \rho_0 + \Delta\rho, \tag{2}$$

FIG. 1. Unit cell of NaNO$_3$ with $R\,\bar{3}c$ symmetry. Origin for $R\,\bar{3}c$ labeling is at the sodium atom 1.

where the prime on the first summation indicates that the identity representation is not included in the sum but is contained in ρ_0. Here m labels the representation and i labels the ith basis function of the mth representation. Thus for a phase transition, we take ρ_0 to be the pretransition density with symmetry $R_0(R\,\bar{3}c)$ and ρ to be the post-transition density. Because ρ contains additional components not invariant under R_0, the symmetry is lowered to a subgroup.

The free energy of the crystal must be at a local minimum for any particular phase of the crystal to be stable. In general, F is a functional of the density function, pressure, temperature, and any external fields. But from Eq. (2), ρ can be expressed in terms of the Ψ_i^m, and therefore an explicit dependence of F on the η_i^m results. It is a characteristic of a continuous phase transition that the coefficients η_i^m vary continuously from zero as one passes through the transition point. This condition allows us to write the free energy in a series expansion of the η_i^m about the transition point. The expansion must satisfy the requirement that it be invariant under an arbitrary symmetry transformation of the space group. To guarantee this invariance the most general form must be combinations of the η_i^m each of which are invariant under transformations of the space group, i.e., transformations of the form $g\eta_i = D_{ij}\eta_j$. We assume a single irrep induces the transition. At fourth order only two such invariants[6] come into play and we exclude representations with third order invariants. Thus ρ has the form

$$\rho = \rho_0 + \sum_i \eta_i \Psi_i, \tag{3}$$

while

$$F = F_0 + A\sum_I \eta_i^2 + \sum_\alpha B_\alpha f_\alpha^4(\eta_i). \tag{4}$$

Here the $f_\alpha^4(\eta_i)$ are fourth order homogenous invariant functions of η_i.

To determine possible symmetries of the post-transition phase, we must find the set of elements which leave ρ invariant. Of course, ρ_0 is invariant under all elements R_0. Also, it is clear that $\Sigma\eta_i\Psi_i$ is invariant under all elements whose corresponding matrix in the irrep Γ is the identity matrix. These elements form a subgroup, the kernel of Γ. The invariance of ρ under the elements of the kernel holds for arbitrary values of η_i. However, for a particular choice of η, say η', the sum $\Sigma\eta_i'\Psi_i$ may be invariant under additional elements, which form a subgroup containing the kernel. The largest group leaving the sum invariant will be called an isotropy group of R_0 in Γ. Because the isotropy groups are the only possible symmetries of $\Delta\rho$, the low-symmetry phase must be an isotropy group corresponding to an irrep of the high-symmetry phase.

Birman[7] saw in the classical formalism of Landau a necessary group theoretical condition on the lower symmetry group. If we let $\chi(r)$ be the character of the $\Gamma(r)$ matrix of a reducible representation corresponding to the transformation r, and let $\chi^p(r)$ be the character of the $\Gamma^p(r)$ matrix corresponding to r of the pth irrep then the number of times Γ^p enters into the reducible representation is given by i, where

$$i = \frac{1}{|R|}\sum_{r\in R}\chi^p(r)\chi(r). \tag{5}$$

The statement that R' be an isotropy group implies that the identity irrep of R' be contained (subduced) in the irrep Γ^m of R_0 (subduction criterion[5]), i.e.,

$$i(R') = \frac{1}{|R'|}\sum_{r\in R'}\chi^m(r) \neq 0. \tag{6}$$

It is worth noting that the kernel is an isotropy group such that $i(R') = \dim\Gamma^m$. Thus, for a continuous phase transition from a high-symmetry to a low-symmetry phase, the only possible post-transition symmetries are those for which $i(R')$ is not equal to zero.

The character of a general space group element is

$$\chi(g) = \sum_\sigma e^{-i\mathbf{k}_\sigma\cdot\mathbf{t}}\chi(\{r_\sigma|\tau_\sigma\}^{-1}g\{r_\sigma|\tau_\sigma\}),$$

where the σ sum is over the arms of the star. For the restriction to the $\mathbf{k} = 0$ point only the representations of the point groups need to be considered and only one arm occurs. Bradley and Cracknel,[8] give the irreps of $D_{3d}(G_{12}^3)$ as A_{1g} (R_1), A_{2g} (R_2), A_{1u} (R_3), A_{2u} (R_4), E_g (R_5), and E_u (R_6). In the case of one-dimensional irreps, the kernel is the only isotropy group. As an example, the character table for the A_{2u} (R_4) irrep of D_{3d} is

E	$2C_3$	$3C_2'$	i	$2S_6$	$3\sigma_d$
1	1	-1	-1	-1	1

By noting which elements correspond to identity matrices for the irrep A_{2u} the elements of the kernel for A_{2u} correspond to C_{3v} and are thus

$$\{E\,|000\}, \quad \{C_3|000\}, \quad \{C_3^-|000\}, \quad \{\sigma_{d1}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\},$$
$$\{\sigma_{d2}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}, \quad \{\sigma_{d3}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\}$$

together with all translations. This space group is the group C_{3v}^6. We have used the notation of Refs. 4 and 8 for the labeling of the symmetry elements above.

To find the isotropy groups of the two-dimensional irreps we use the formula for the subduction frequency. For example, in the case of the E_g irrep, the character table is

E	$2C_3$	$3C_2'$	i	$2S_6$	$3\sigma_d$
2	-1	0	2	-1	0

Applying Eq. (8) to this irrep and using the isomorphism between the isogonal point group and the coset representatives (remember $\mathbf{k} = 0$)

$$i(C_i) = \frac{1}{|C_i|}\{\chi(E) + \chi(i)\} = \tfrac{1}{2}\{2 + 2\} = 2,$$

as C_i is the kernel of the E_g irrep of D_{3d}. By evaluating the subduction frequency of all subgroups of D_{3d} we determine the invariance subgroups of the two-dimensional irreps of D_{3d} which have nonzero subduction frequency for each irrep.

An additional restriction on the possible resultant groups of a continuous phase transition is Birman's chain subduction criterion.[9] This contains the physical statement that the symmetry group must be the largest subgroup which leaves the subspace invariant, i.e., an isotropy group as defined earlier. It takes the following form: Suppose two subgroups, R_1 and R_2, satisfy

$$R_1 \subset R_2, \tag{7a}$$

$$i(R_1) = i(R_2). \tag{7b}$$

Then R_1 is ruled out as a possible post-transition symmetry.

Thus, using the preceeding group theoretical considerations alone, we reduce the number of possible point groups to nine, namely: D_{3d}, C_{3i}, C_i, C_{2h}, D_3, C_3, C_{1h}, C_2, and C_1.

The classical Landau formulation also contains two additional group theoretical conditions.[1] The first condition derives from the condition that the free energy be stable at the origin, i.e., $\eta = 0$. This requires that the third order term in the expansion be absent. Thus the symmetrized triple Kronecker product of the representation Γ^m must not contain the identity representation of R_0, i.e.,

$$[(\Gamma)^3 | \Gamma^+ (R_0)] = 0. \tag{8}$$

The second condition comes from the requirement that the less symmetric phase be stable relative to nonspatially periodic perturbations. This condition requires that the antisymmetrized double Kronecker product of Γ not contain the representation of a polar vector of R_0, i.e.,

$$[\{\Gamma\}^2 | V(R_0)] = 0. \tag{9}$$

Considering the above six representations the A_{1g} and E_g representations must be discarded as they do not satisfy the Lifshitz condition. We thus obtain Table I. The above result is consistent with those obtained in Ref. 10. For the transition of interest in NaNO₃ we see that direct group methods allow the isotropy group $R\,3c$ corresponding to irrep A_{2u}.

III. USE OF SYMMETRY IN SOLVING ∇F = 0

Landau theory places the additional constraint that a phase transition corresponds to a minimum of the free energy at $\eta_i \neq 0$. (Due to the transformation properties of the η, viz., $\eta_i' = D_{ij}\eta_j$, we will consider η_i as a vector representation and denote it as $\boldsymbol{\eta}$.) We thus seek solutions to the equation

$$\nabla F \equiv \mathbf{f}(\boldsymbol{\eta}) = 0, \tag{10}$$

and in particular wish to determine if $R\,3c$ corresponds to a minimum. We will discuss the problem in general terms initially. It is easy to verify that $\mathbf{f}$ has the form

$$f_i(\boldsymbol{\eta}) = \sum_\alpha A_\alpha(\eta)\eta_i^{2\alpha+1}, \tag{11}$$

with $A_\alpha(\eta)$ an invariant function of $\boldsymbol{\eta}$. Because of the large

TABLE I. Isotropy subgroups corresponding to k = 0.

Irrep	Subgroup	Subduction frequency
$A_{1g}{}^a$	$R\bar{3}c(D_{3d}^6)$	1
A_{2g}	$R\bar{3}(C_{3i}^2)$	1
A_{1u}	$R32(D_3^7)$	1
A_{2u}	$R3c(C_{3v}^6)$	1
$E_g{}^a$	$P\bar{1}(C_i^1)$	2
	$C2/c(C_{2h}^6)$	1
E_u	$P1(C_1^1)$	2
	$Cc(C_s^4),\ C_2(C_2^3)$	1

^{a} Representations which do not satisfy the Lifshitz condition.

number of solutions for the general situation as well as the resulting symmetry of the system we would benefit from a systematic approach to finding solutions. A proposed approach was given by Jarić,[3] and is briefly reviewed and applied in this section. Jarić's method exploits the fact that the solutions to Eq. (10) can be selected according to the isotropy groups of R_0.

To begin with, because F was constructed to be invariant under R_0, it follows that:

$$\mathbf{f}(r\boldsymbol{\eta}) = r\mathbf{f}(\boldsymbol{\eta}), \tag{12}$$

where both $\boldsymbol{\eta}$ and $\mathbf{f}$ are n-dimensional vectors. We now define a hyperplane fix R as the set of all vectors which are left invariant by the isotropy group R. Also we can speak of hyperplanes fix R for both $\mathbf{f}$ and $\boldsymbol{\eta}$. Now let $\boldsymbol{\eta}\epsilon$ fix R. From Eq. (12) it follows that $r\mathbf{f}(\boldsymbol{\eta}) = \mathbf{f}(\boldsymbol{\eta})$, because r leaves $\boldsymbol{\eta}$ invariant. Therefore, $\boldsymbol{\eta}\epsilon$ fix R implies $\mathbf{f}(\boldsymbol{\eta})\epsilon$ fix R.

To exploit the symmetry of $\mathbf{f}(\boldsymbol{\eta})$ and $\boldsymbol{\eta}$, we construct the projection operator

$$P(R) = \frac{1}{|R|}\sum_{r\epsilon R} 0_r, \tag{13}$$

which projects an arbitrary vector $\boldsymbol{\eta}$ (or $\mathbf{f}$) onto the hyperplane fix R. We expect $\boldsymbol{\eta}$ to exhibit the symmetry of the post-transition phase. Therefore, $\boldsymbol{\eta}$ will lie in a fix R, where R is one of the possible isotropy groups, e.g., those obtained in Sec. II. Thus, we wish to partition solutions to Eq. (10) according to the hyperplane in which $\boldsymbol{\eta}$ lies, or in other words, according to the symmetry of $\boldsymbol{\eta}$. The equation

$$[1 - P(R)]\boldsymbol{\eta} = 0 \tag{14}$$

restricts us to those values of $\boldsymbol{\eta}$ lying in fix R. For this case $\mathbf{f}(\boldsymbol{\eta})\epsilon$ fix R and we can replace Eq. (10) with

$$P(R)\,\mathbf{f}(\boldsymbol{\eta}) = 0. \tag{15}$$

From Table I, we see that some isotropy groups are subgroups of others but with different subduction frequencies. In fact, a particular nesting of isotropy groups, allows us to exploit the partitioning of solutions in a way that reduces the difficulty of the equations. Suppose two isotropy groups, R and R_k, are related as follows:

$$R \subset R_k \tag{16a}$$

and

$$i(R_k) = i(R) - 1. \tag{16b}$$

Note that from Eq. (16) it follows immediately that fix R $\supset$ fix R_k.

Consider the operator $[P(R) - P(R_k)]$. On an arbitrary vector, this operator yields a vector lying in fix R, but with no component in fix R_k. Also, because the dimension of fix R_k is only one less than that of fix R, any two vectors lying in fix R but having no component in fix R_k must be collinear. Therefore, we can write

$$[P(R) - P(R_k)]\mathbf{f}(\boldsymbol{\eta}) \equiv g_k(\boldsymbol{\eta})[P(R) - P(R_k)]\boldsymbol{\eta}, \tag{17}$$

where $[P(R) - P(R_k)]\mathbf{f}(\boldsymbol{\eta})$ and $[P(R) - P(R_k)]\boldsymbol{\eta}$ are two collinear vectors that differ only by a factor $g_k(\boldsymbol{\eta})$, and where Eq. (17) defines $g_k(\boldsymbol{\eta})$. The condition

$$[P(R) - P(R_k)]\mathbf{f}(\boldsymbol{\eta}) = 0, \tag{18}$$

together with $[P(r) - P(r_k)]\boldsymbol{\eta} \neq 0$ implies

$$g_k(\boldsymbol{\eta}) = 0. \tag{19}$$

This yields all solutions to Eq. (10) for $\boldsymbol{\eta}$ in fix R and yet which have no component lying in fix R_k. Notice that Eq. (19) is of 1° less than Eq. (10), and hence easier to solve.

To summarize the general technique to this point, in seeking solutions to a set of nonlinear equations, we restrict our search to those solutions with a particular isotropy group symmetry, obtain a relevant equation from which we can remove a known factor and thus eliminate spurious solutions, and as a result reduce our equations by 1°.

As Jarić points out, in general there could be several isotropy groups, call them $R_1, R_2, \ldots, R_m$ which satisfy Eqs. (16a) and (16b), and each such isotropy group yields a distinct function $g_1, g_2, \ldots, g_m$. In fact, typically the number of isotropy groups (m) is larger than the dimension $i(r)$ of fix R. Because the normals to the hyperplanes fix $\{R_j\}$ span fix R, the solutions to $g_k = 0$, $k = 1, \ldots, i(r)$, contain all the solutions in fix R and the additional g_k are not linearly independent solutions. To handle this case, additional considerations can be introduced which for our $\mathbf{k} = 0$ case are not necessary.

Thus let us apply the preceeding theory to the $\mathbf{k} = 0$ representations of $R\,\bar{3}c$. One example of the method will be shown explicitly.

Choose R to be C_i, corresponding to the E_g irrep. R_k is then C_{2h}. For a two-dimensional irrep we represent the vector $\boldsymbol{\eta}$ with two components, η_1 and η_2. Then the free energy to fourth order is

$$F = F_0 + A(\eta_1^2 + \eta_2^2) + C(\eta_1^2 + \eta_2^2)^2$$

and

$$\mathbf{f}(\boldsymbol{\eta}) = [2A + 4C(\eta_1^2 + \eta_2^2)]\begin{pmatrix}\eta_1\\\eta_2\end{pmatrix},$$

which is seen to have the general form of Eq. (11). To separate all solutions with C_i symmetry we construct

$$P(C_i) = 1/2\left[\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} + \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}\right] = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}.$$

Equation (14) becomes

$$\left[\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} - \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}\right]\begin{pmatrix}\eta_1\\\eta_2\end{pmatrix} = 0,$$

which admits all values of $\begin{pmatrix}\eta_1\\\eta_2\end{pmatrix}$. We now determine $P(C_{2h})$:

$$P(C_{2h}) = \frac{1}{4}\left[\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} + \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} + \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\right.$$
$$\left. + \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\right] = \begin{pmatrix}1 & 0\\0 & 0\end{pmatrix}$$

and construct

$$[P(C_i) - P(C_{2h})] = \begin{pmatrix}0 & 0\\0 & 1\end{pmatrix}.$$

Thus a vector $\boldsymbol{\eta}$ contained in fix C_i but not in fix C_{2h} will have only an η_2 component. Equation (17) becomes

$$\begin{pmatrix}0 & 0\\0 & 1\end{pmatrix}\left\{[2A + 4C(\eta_1^2 + \eta_2^2)]\begin{pmatrix}\eta_1\\\eta_2\end{pmatrix} = g_{C_{2h}}\left[\begin{pmatrix}0 & 0\\0 & 1\end{pmatrix}\begin{pmatrix}\eta_1\\\eta_2\end{pmatrix}\right]\right\}.$$

Solving for $g_{C_{2h}}$, while requiring $[P(C_i) - P(C_{2h})]\boldsymbol{\eta} \neq 0$ yields

$$g_{C_{2h}} = 2A + 4C\eta_2^2 = 0.$$

Therefore,

$$\eta_2 = \pm\left[\frac{-A}{2(C)}\right]^{1/2}$$

is a solution corresponding to symmetry C_i but not the higher symmetry C_{2h}. Minima for the other isotropy groups can be obtained in a similar fashion. It is easily seen that all isotropy groups obtained in Sec. II correspond to minima of the corresponding free energy to fourth order in $\boldsymbol{\eta}$. Our interest is mainly in A_{2u} and $R\,\bar{3}c$ and one sees that $R\,\bar{3}c$ does correspond to a minimum of the generalized free energy $F = F_0 + A\eta_1^2 + B\eta_1^4$ with $\eta_1 = \pm\sqrt{(-A/2B)}$ and $A < 0$, $B > 0$.

IV. LATTICE DESCRIPTION

Obtaining a simple form for the density function yields additional insight into the movement of atoms during the phase transition. We will assume an average equilibrium position for each atom: $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n)$. Also displacements from equilibrium u_i are assumed to be small. Then $\rho(\mathbf{x} - \mathbf{r} - \mathbf{u}) \approx \rho(\mathbf{x} - \mathbf{r}) - \nabla\rho\cdot\mathbf{u} \equiv \rho_0 - \nabla\rho\cdot\mathbf{u}$. Consistent with the Landau philosophy the displacements from equilibrium must correspond to the single irrep of the transition.

Perhaps the simplest coordinate system for describing the displacements from equilibrium $\mathbf{u}$ is a set of Cartesian coordinates, one set being attached to each atom. Then the arbitrary displacements can be written $\mathbf{u}_1 = \mathbf{u}_{1x}\mathbf{i}_1 + u_{1y}\mathbf{j}_1 + u_{1z}\mathbf{k}_1$ similarly for each $\mathbf{u}_i$ where i labels an atom of the unit cell.

We could equivalently write a column matrix which represents a vector in a vector space spanned by the basis functions $\mathbf{i}_1, \mathbf{j}_1, \mathbf{k}_1, \ldots, \mathbf{k}_n$. The fact that any arbitrary displacement $\mathbf{u}$ can be written as a linear combination of basis functions allows us to know the effect of 0_r on a general displacement $\mathbf{u}$ simply by knowing its effect on each of the basis functions $\mathbf{i}_1, \mathbf{j}_1, \mathbf{k}_1, \ldots, \mathbf{k}_n$. This then allows us to represent each operator by a matrix $\Gamma_{ij}(r)$. Thus, if

$$0_r\mathbf{r} = 0_r(\mathbf{r}_0 + \mathbf{u}) = 0_r\mathbf{r}_0 + 0_r\mathbf{u} = \mathbf{r}_0 + \mathbf{u}',$$

then

$$\sum_j \Gamma_{ij}u_j = u_i'.$$

The ten-atom set of $NaNO_3$ has a set of 30×30 dimensional matrices to represent transformations on the unit cell. From Fig. 1 and the description of the symmetry tranformations the matrices corresponding to the various elements of R_0 are easily determined. The matrices form a reducible representation Γ of $R\,\bar{3}c$ and therefore, we can reduce the representation in terms of the irreducible representations of $\mathbf{k} = 0$. Recall that the number of times an irrep enters a given reducible representation is given by Eq. (7). The results of the calculation are $A_{1g}:1$, $A_{2g}:3$, $E_g:4$, $A_{1u}:2$, $A_{2u}:4$, $E_u:6$. Remembering that each E_g or E_u irrep has two basis functions associated with it, we can see that the above reduction agrees with the dimension of the original matrix.

In changing the original 30×30 matrix to a set of irreducible component representations we also must change the basis functions. These new functions must transform as basis

functions of the respective irreps. A systematic method for obtaining these basis function makes use of projection operators.

The formula for the ith basis function of the mth irrep is

$$P_i^m(R)\Psi = \frac{\dim I^m}{|R|}\sum_{r\epsilon R}\Gamma_{ij}^m(r)0_r\Psi, \qquad (16)$$

where ψ is an arbitrary vector and j is fixed. Here we represent Ψ by its components in the 30-dimensional Cartesian space and the operator 0_r is the corresponding matrix in the 30-dimensional space. An example calculation, using the projection operator, is sketched below for A_{2u}.

$$P_1^{A}2u(D_{3d})\Psi = \frac{1}{|D_{3d}|}\{\Gamma_{11}^{A_{2u}}(E)\,E\,\Psi + \Gamma_{11}^{A_{2u}}(C_3^+)C_3^+\,\Psi$$

$$+\cdots+\Gamma_{11}^{A_{2u}}(\sigma_{d3})\sigma_{d3}\Psi\}.$$

Because the operators 0_r are linear we can separate out the sum of matrices:

$$P_1^{A}2u(D_{3d})\Psi = \frac{1}{|D_{3d}|}\left[\sum_r \Gamma_{11}^{A_{2u}}(r)\,0_r\right]\Psi. \qquad (17)$$

The sum of matrices, with the appropriate coefficients, is shown in the Appendix. If we choose y_5 for our initial Ψ, then

$$A_1^{A_{2u}}(D_{3d})y_5 = 2y_5 + 2\gamma x_6 - y_6 - 2\gamma x_7 - y_7 + 2y_8$$

$$+ 2\gamma x_9 - y_9 - 2\gamma x_{10} - y_{10},$$

$$\gamma = (3/2)^{1/2},$$

which represents an alternating rotation of the nitrate groups. A similar procedure choosing z_2 as an initial Ψ yields $z_1 + z_2$ corresponding to a displacement of the Na atoms along k.

In determining basis functions for the irreps we find, e.g., that one possible basis function for A_{2u} is $z_1 + z_2 + \cdots + z^{10}$, which is simply a translation of the entire unit cell. Such a vector says nothing about the internal symmetry of the crystal. We eliminate this function and corresponding ones for translation in the x-y plane, and we are left

with 27 basis functions, sufficient to describe any relative displacements of atoms within the crystal. The remaining irreps then enter as follows: A_{1g}: 1, A_{2g}: 3, E_g: 2, A_{1u}: 3, A_{2u}: 4, E_u: 5.

In general, for the displacement vector to transform as a given irrep it can be a linear combination of the vector basis functions. This is in fact the case for the 45 kbar transition in NaNO₃. Barnett[3] reported that this transition involves the rotation of alternating nitrate groups by 15° around the z axis, coupled with a translation of the sodium atoms along the z axis. Thus a linear combination of the two basis functions indicated above does in fact correspond to the experimental displacements and it transforms according to the A_{2u} irrep. This irrep is the same one which obtains the lower symmetry phase $R\,3c$. The group theoretical description then does yield a compatible description of the experimental results for the NaNO₃ transition.

CONCLUSIONS

We have shown that direct group theoretical methods appropriate to the description of continuous phase transitions yield six possible lower symmetry phases corresponding to the $k = 0$ irreps of $R\,\bar{3}c$. We used general techniques of solving polynomial equations to find solutions corresponding to the extrema of the free energies to fourth order for these six phases. Although the full use of these techniques is not needed here it is shown that all phases correspond to minima. We have also shown that the A_{2u} representation drives the transition $R\,\bar{3}c$ to $R\,3c$ in NaNO₃ and yields the appropriate equilibrium distortions of the atoms as the system goes through the transition.

ACKNOWLEDGEMENTS

APPENDIX

The form for the projection operator $P_1{}^{A_2u}$ (D_{3d}) of Eq. (17). It is a 10x10 block matrix where each entry is a 3x3 matrix of the form listed below.

$E+C_3'$ $+C_3^- -i$ $-s_6^+ -s_6^-$	$\sigma_1+\sigma_2$ $+\sigma_3-C_{21}$ $-C_{22}-C_{23}$								
$\sigma_1+\sigma_2$ $+\sigma_3-C_{21}$ $-C_{22}-C_{23}$	$E+C_3^+$ $+C_3^- -i$ $-s_6^+-s_6^-$								
		$E+C_3^+$ $+C_3^- - C_{21}$ $-C_{22}-C_{23}$	$\sigma_1+\sigma_2$ $+\sigma_3-i$ $-s_6^+-s_6^-$						
		$\sigma_1+\sigma_2$ $+\sigma_3-i$ $-s_6^+ -s_6^-$	$E+C_3^+$ $+C_3^- -C_{21}$ $-C_{22}-C_{23}$						
				$E-C_{21}$	$C_3^+-C_{22}$	$C_3^--C_{23}$	σ_1-i	$\sigma_2-s_6^-$	$\sigma_3- s_6^+$
				$C_3^--C_{22}$	$E-C_{23}$	$C_3^+-C_{21}$	$\sigma_2-s_6^+$	σ_3-i	$\sigma_1-s_6^-$
				$C_3^+-C_{23}$	$C_3^--C_{21}$	$E-C_{22}$	$\sigma_3-s_6^-$	$\sigma_1-s_6^+$	σ_2-i
				σ_1-i	$\sigma_2-s_6^-$	$\sigma_3-s_6^+$	$E-C_{21}$	$C_3^+-C_{22}$	$C_3^--C_{23}$
				$\sigma_2-s_6^+$	σ_3-i	$\sigma_1-s_6^-$	$C_3^--C_{22}$	$E-C_{23}$	$C_3^+-C_{21}$
				$\sigma_3-s_6^-$	$\sigma_1-s_6^+$	σ_2-i	$C_3^+-C_{23}$	$C_3^--C_{21}$	$E-C_{22}$

$$i=\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad S_6^+=\begin{pmatrix} 1/2 & -\gamma & 0 \\ \gamma & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad S_6^-=\begin{pmatrix} 1/2 & \gamma & 0 \\ -\gamma & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$\sigma_{d1}=\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_{d2}=\begin{pmatrix} 1/2 & \gamma & 0 \\ \gamma & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_{d3}=\begin{pmatrix} 1/2 & -\gamma & 0 \\ -\gamma & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$C_{21}^1=\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad C_{22}^1=\begin{pmatrix} -1/2 & -\gamma & 0 \\ -\gamma & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad C_{23}^1=\begin{pmatrix} -1/2 & \gamma & 0 \\ \gamma & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$C_3^+=\begin{pmatrix} -1/2 & -\gamma & 0 \\ \gamma & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad C_3^-=\begin{pmatrix} -1/2 & \gamma & 0 \\ -\gamma & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad E=\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\gamma=\frac{(3)^{1/2}}{2}.$$

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