Phase transitions in the grandite garnets

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Abstract

Birefringence among the grandite garnets (grossular-andradite solid-solution series) is common and has been found previously to result, at least in some cases, from ordering of Al and Fe^{3+} on the octahedral (a) sites of space group $Ia3d$, lowering the symmetry to $Fddd$ or $I\bar{1}$; other possible space groups, all of them subgroups of $Ia3d$, have been suggested. A group theoretical analysis, based on the Landau formalism and including the theory of induced representations, has been carried out for order-parameter transitions from $Ia3d$ to subgroup symmetries, in which the primitive unit cell is preserved. It is found that only one irreducible representation of $Ia3d$, namely T_{2g}, leads to space group $Fddd$, and it yields $R\bar{3}c$, $C2/c$, and $I\bar{1}$ as permissible subgroups as well. Elastic strain, domain formation, and domain-wall orientations are discussed for the transitions from $Ia3d$. Further, a function that transforms under the identity representation of $\bar{3}$ and that is associated with the (0,0,0) site of $Ia3d$ induces the T_{2g} representation of $Ia3d$, and that function is interpreted as an ordering function. Extension to the remaining 15 octahedral (a) sites in the conventional (nonprimitive) cubic unit cell produces ordering functions (i.e., basis functions of T_{2g}) that can be applied to any of the above subgroups. The ordering functions for $Fddd$ and for $I\bar{1}$ correctly predict the relative ordering of Al and Fe^{3+} observed in grandite garnets of those space groups. It is concluded that for birefringent garnets with compositions between grossular and andradite, ordering schemes that have been observed to date could have occurred as homogeneous phase transformations from $Ia3d$, driven by a *single* T_{2g} order parameter, as well as by crystal-growth phenomena as suggested by other authors.

Introduction

Nearly all naturally occurring crustal garnets are cubic, and crystal-structure investigations (e.g., Menzer, 1926; Euler and Bruce, 1965; Prandl, 1966; Gibbs and Smith, 1966; Novak and Gibbs, 1971; Meagher, 1975; Lager et al., 1987) have shown that they crystallize in space group $Ia3d$. In the general garnet formula ${X}_3[Y]_2(Z)_3O_{12}$ (notation of Geller, 1967), ${X}$ = eight-coordinated Ca, Fe^{2+}, Mg, or Mn, $[Y]$ = six-coordinated Al, Fe^{3+}, Cr, V, or Ti, and (Z) = tetahedrally coordinated Si, for common rock-forming varieties; all atoms except oxygen are on special positions. Despite the evident chemical complexity of the family, as long as the symmetry is $Ia3d$ there are rather simple relationships between the average sizes of the ${X}$, $[Y]$, and (Z) atoms on the one hand, and the cubic unit-cell dimension and oxygen positional parameters on the other (Novak and Gibbs, 1971; Hawthorne, 1981).

Among the intermediate grandites (minerals with compositions between those of grossular, $Ca_3Al_2Si_3O_{12}$, and andradite, $Ca_3Fe_2^{3+}Si_3O_{12}$), however, are a substantial number of observed garnets that exhibit optical anisotropy. An early explanation for this (attributed to Brewster in Dana, 1900) was that these garnets consisted of complexly twinned triclinic individuals arranged so as to yield average cubic symmetry. Later, birefringence was generally attributed to local strain in the crystal lattice rather than to a change in overall symmetry. Yoder (1950) was the first to suggest that birefringence might be a consequence of ordering of the octahedrally coordinated Al and Fe^{3+} in these garnets, and subsequent crystal-structure of refinements by Takéuchi et al. (1982) have shown such ordering to exist. Of the three ordered grandite structures they determined, two were found to be orthorhombic, space group $Fddd$, and one was found to be triclinic, $I\bar{1}$. Hirai and Nakazawa (1986) observed inequalities in intensities on X-ray precession photographs of a grandite that suggested possible $C2/c$ symmetry; although no structure refinement was done, it seems possible that ordering of octahedral cations could be the cause of this reduction from cubic symmetry, also. [All birefringence in garnets might not be caused by ordering; that in some chemically zoned and twinned grandites may result from coherency strain across boundaries separating zones of disparate lattice dimensions (Chase and Lefevre, 1960; Verkaeren, 1971; Lessing and Standish, 1973).]

In a careful study of a sector-twinned, birefringent $Gro_{90.2}And_{5.5}Alm_{4.3}$ (Alm = almandine, $Fe_3^{2+}Al_2Si_3O_{12}$),

Allen and Buseck (1988) found a noncubic distribution both of metal atoms and of hydroxyl groups, the latter presumably replacing silicate oxyanions by the substitution $4(OH^-) = SiO_4^{4-}$ (e.g., Aines and Rossman, 1984). Consideration of their garnet is complicated somewhat by nongrandite chemistry, namely the presence of both OH and Fe^{2+}. Heating specimens to 800 and 870 °C resulted in dehydration, but only the higher temperature produced isotropy; thus it appears that the (OH^-) distribution contributes to the birefringence in this garnet, but is not likely the primary cause of it.

The experimental confirmation of cation ordering as one cause of low symmetry in some birefringent grandites is clear, but the reason for the ordering itself is not as evident. Gali (1983) and Akizuki (1984) used similar approaches to show that anisotropy could result from ordering of Al and Fe^{3+} on growth steps of {110} faces during crystal formation. Gali (1983) considered that the different orientations of the [Y] sites render them crystallographically inequivalent and that the symmetry under any single growth step is $I\bar{1}$; he further showed that fragments containing portions of appropriate growth steps from a single growth pyramid of a dodecahedral crystal can show the symmetry of any centrosymmetric subgroup of *Fddd*, and that portions of different growth pyramids can be superimposed to yield any centrosymmetric subgroup of *Ia3d*. Thus all of the space groups so far observed for natural noncubic silicate garnets could result from combinations of triclinic domains in the crystals investigated.

Heating experiments (e.g., Hariya and Kimura, 1978) have shown that birefringent grandites (or near-grandites in the case of Allen and Buseck, 1988) are homogenized (that is, made isotropic—presumably by disordering the [Y] cations) by heating at temperatures between 800 and 1000 °C. Some remain isotropic even after they are annealed at lower temperatures for long periods, and this is at least consistent with a growth-step origin of anisotropy, although it does not constitute proof. Some grandites, however, regain their birefringence after annealing (Hariya and Kimura, 1978), and this seems inconsistent with origin of low symmetry during crystal growth. Rather, the successful reversal of the optical character of these garnets suggests that the observed low symmetry might result from a temperature-induced order-disorder phase transformation. Even if the original octahedral ordering of birefringent garnets was imposed during crystal growth, it is clear that disordering by heating followed by ordering on annealing constitutes a phase transformation.

The transition of a homogeneous phase from one space group to a subgroup of lower symmetry can be described within the context of Landau theory. This group theoretical treatment of phase transitions is usually applied to continuous transformations and was originally formulated by Landau (1937a, 1937b). Extensions by Birman (1966), Goldrich and Birman (1968), Jaric and Birman (1977), Hatch (1981a, 1981b), and Hatch and Stokes (1985, 1986) have been made to the original theory. The theory is a mean-field description and necessarily neglects

fluctuations near the critical transition. In spite of the resulting limitations in predicting critical exponents or changes in the order of transitions caused by fluctuations, the theory has proven reliable in delineating the possible natures of phase transformations, order-parameter characteristics, thermodynamic potentials, and allowed subgroup symmetries for a wide variety of systems (e.g., Hatch, 1981a, 1981b; Hatch and Merrill, 1981; Stokes and Hatch, 1984, and references therein) and is applicable to discontinuous, as well as continuous, transitions. Our purpose here is to use Landau theory to investigate the possible nature of a phase transformation in grandite garnets. We then use additional group-theoretical techniques to obtain domain characteristics and to describe the microscopic changes at the transition.

REVIEW OF GENERAL LANDAU THEORY

Consider a phase transition between two crystal structures, one of which has higher symmetry than the other, and take $\rho(\mathbf{r})$ to be the density function that gives the probability distribution of atomic positions in the crystal. The space group G of the crystal is the set of all symmetry operators g that leaves $\rho(\mathbf{r})$ invariant, i.e.,

$$\mathrm{T}(g)\rho(\mathbf{r}) = \rho(\mathbf{r}). \tag{1}$$

Each symmetry operator g is a coordinate transformation that consists of a point operator R followed by a translation, τ, denoted by $\{R|\tau\}$. Denote the space group of the higher-symmetry phase by G_0, with $\rho_0(\mathbf{r})$ invariant under G_0, and let G be the space group of the lower-symmetry phase. We can decompose $\rho(\mathbf{r})$ into a linear combination of basis functions of the physically irreducible representations of G_0:

$$\rho(\mathbf{r}) = \Sigma\Sigma\eta_i^{(m)}\phi_i^{(m)}(\mathbf{r}), \tag{2}$$

where $\phi_i^{(m)}(\mathbf{r})$ is the ith basis function of the mth irreducible representation and $\eta_i^{(m)}$ are the numbers that give the amplitude of each basis function in its contribution to $\rho(\mathbf{r})$.

The set of numbers $\eta_1^{(m)}$, $\eta_2^{(m)}$, $\eta_3^{(m)}$ . . . is called the *order parameter,* and it represents the contributions (coordinates) of the basis functions $\phi_i^{(m)}(\mathbf{r})$ to the density $\rho(\mathbf{r})$. If the matrices of the mth representation are n-dimensional ($n \times n$ square matrices), this order parameter has n components $[\eta_1^{(m)}, \eta_2^{(m)}, \ldots, \eta_n^{(m)}]$ and forms a vector η in an n-dimensional representation space. Usually only one irreducible representation appears at the transition, i.e., only one geometrical or physical property becomes nonzero at the transition. [From this point on, we will consider only the irreducible representation that causes the transition, and we will drop the superscript (m) from our notation.] The density function $\rho(\mathbf{r})$ is thus written

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \Sigma\eta_i\phi_i(\mathbf{r}). \tag{3}$$

In the higher-symmetry phase, $\boldsymbol{\eta} = 0$, and thus $\rho(\mathbf{r}) = \rho_0(\mathbf{r})$ with symmetry G_0. In the lower-symmetry phase, $\boldsymbol{\eta} \neq 0$, and now only a subset of the operators $g \in G_0$ will leave $\rho(\mathbf{r})$ invariant. Symmetry is lost in the transition,

TABLE 1. Subgroups of $Ia3d$ allowed by the T_{2g} representation

Sub-group*	Origin	Basis vectors	Direction of vector η
$R\bar{3}c$ (167)	(0,0,0)	$(-1,1,0),(0,-1,1),(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	(η_1,η_1,η_1)
$Fddd$ (70)	(0,0,0)	$(1,1,0),(-1,1,0),(0,0,1)$	$(\eta_1,0,0)$
$C2/c$ (15)	(0,0,0)	$(0,-1,0),(1,0,-1),(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	(η_1,η_1,η_3)
$P\bar{1}$ (2)	(0,0,0)	$(-\frac{1}{2},\frac{1}{2},\frac{1}{2}),(\frac{1}{2},-\frac{1}{2},\frac{1}{2}),(\frac{1}{2},\frac{1}{2},-\frac{1}{2})$	(η_1,η_2,η_3)

* Numbers in parentheses are space-group numbers from *International Tables for X-ray Crystallography* (1983).

TABLE 2. Matrices for the T_{2g} representations of $Ia3d$

Element	Matrix representation		
$\{C_{4z}^+\mid\frac{1}{4},\frac{3}{4},\frac{1}{4}\}$	-1 0 0		
	0 0 1		
	0 -1 0		
$\{C_{31}^+\mid0,0,0\}$	0 0 1		
	1 0 0		
	0 1 0		
$\{I\mid0,0,0\}$	1 0 0		
	0 1 0		
	0 0 1		
$\{E\mid t_1,t_2,t_3\}$*	1 0 0		
	0 1 0		
	0 0 1		

Note: Matrices represent the transformation properties of the functions ϕ_1, ϕ_2, ϕ_3. Only generating elements of $Ia3d$ are shown.
* Translations t_1, t_2, t_3 apply to any and all lattice points.

and the new symmetry is the maximal set of operators leaving $\rho(\mathbf{r})$ invariant (the isotropy group of η).

For a given set of basis functions $\{\phi_i(\mathbf{r})\}$, the crystal structure is completely determined by the value of the order parameter η. Thus, we write the thermodynamic potential Φ (the free energy) as a function of pressure P, temperature T, and order parameter η, i.e., $\Phi = \Phi(P,T,\eta)$. In a continuous phase transition, η changes continuously from zero to a nonzero value. Thus, near the transition, η is small, and we can expand Φ in powers of η. The form of the expansion is determined by the requirements of symmetry. Since Φ is a scalar function, it must be invariant under all operations $g \in G_0$, i.e., $T(g)\Phi = \Phi$. The expansion of Φ to fourth degree looks like

$$\Phi(P,T,\eta) = \Phi_0(P,T) + A(P,T)\eta^2 + \Sigma B_\alpha(P,T)I_\alpha^{(4)}(\eta), \quad (4)$$

where

$$\eta^2 = \Sigma\eta_i^2 \quad (5)$$

and where $I_\alpha^{(4)}(\eta)$ represents the independent fourth-degree polynomials (in $\eta_1, \eta_2, \ldots, \eta_n$) that are individually invariant under all operators $g \in G_0$, i.e., $T(g)I_\alpha^{(4)} = I_\alpha^{(4)}$. The coefficients $A(P,T)$ and $B_\alpha(P,T)$ carry the P and T dependency of Φ. In a discontinuous parametric transition, it may be required that Φ be expanded to higher-order terms, but Φ must still be invariant under all operations $g \in G_0$.

ORDER PARAMETER AND FREE ENERGY FOR THE INTERMEDIATE GRANDITES

In order to interpret the characteristics of the possible transitions in the grossular-andradite minerals, we now formulate a detailed Landau description of space-group changes and the associated order parameters. Given the work of Takéuchi et al. (1982), one important space-group change to consider is from $Ia3d$ to $Fddd$, which is classified as a pure ferroelastic transition by Aizu (1969); that is, the transition could be caused by the onset of macroscopic strain. From experiment, it is seen that the transformation preserves the (nonconventional) primitive unit cell, so it must arise from the gamma (Γ) point (zone center) of the Brillouin zone.

There are ten representations of the space group $Ia3d$ associated with the Γ point. Our approach in obtaining the subgroups of $Ia3d$ is to allow contributions to the density function (as shown in Eq. 3) from each representation, one at a time. Then by considering arbitrary di-

rections for the order parameter η of that representation, the subgroups that leave η unchanged are the only possible lower-symmetry subgroups allowed by the onset of this order parameter. This is a specific use of the Curie principle and is a result of the physical statement that a quantity which becomes nonzero below the transition and which has the irreducible representation symmetry reduces the symmetry of the structure to that of the resulting subgroup; that is, the transition is a parameter-driven transition. Investigation of the allowed subgroups (Stokes and Hatch, 1988) indicates that the three-dimensional T_{2g} representation leads to the subgroups $R\bar{3}c$, $Fddd$, $C2/c$, and $P\bar{1}$ (see Table 1), and is the *only* cell-preserving representation that leads to the subgroup $Fddd$. The subgroup $Fddd$ is the symmetry group of a crystal in which only one component of the order parameter η is nonzero (for example, $(\eta_1,0,0)$ or $(0,\eta_2,0)$, etc.). However as the order parameter varies more freely, the other subgroups listed above correspond to the space group of the crystal. Notice that for an arbitrarily oriented order parameter, the subgroup is $P\bar{1}$.

The space group $Ia3d$ can be generated by successive operations of the space-group elements $\{C_{4z}^+\mid\frac{1}{4},\frac{3}{4},\frac{1}{4}\}$, $\{C_{31}^+\mid0,0,0\}$, $\{I\mid0,0,0\}$, and translations (notation of Bradley and Cracknell, 1972). The matrices representing these operations in the three-dimensional order-parameter space of T_{2g} are shown in Table 2. (Note that, in general, these are not the same matrices that represent these operations in physical space.)

The three nonzero macroscopic spontaneous strains (ϵ_{12}, ϵ_{23}, ϵ_{13}) transform according to the representation T_{2g} and could therefore be a candidate for the order parameter of the transition. Particular sublattice atomic displacements could also serve as the order parameter for the transition. However, our choice for the primary order parameter in the intermediate grandites is the ordering of the octahedrally coordinated Al and Fe^{3+} at the sixteen (a) sites. This sublattice ordering can couple linearly with the strain components as well as with appropriate symmetrized atomic displacements. Thus, strain and atomic displacements could be induced by the onset of the primary order parameter.

The free energy to fourth order is of the form

$$\Delta F = (a/2)(\eta_1^2 + \eta_2^2 + \eta_3^2) + (b/3)(\eta_1\eta_2\eta_3)$$
$$+ (c_1/4)(\eta_1^2 + \eta_2^2 + \eta_3^2)^2 + (c_2/4)(\eta_1^4 + \eta_2^4 + \eta_3^4)$$
$$+ (\lambda/2)(\eta_1 q_1 + \eta_2 q_2 + \eta_3 q_3) + (\alpha/2)(q_1^2 + q_2^2 + q_3^2). \quad (6)$$

Here η_i are the components of the primary order parameter (the Al,Fe^{3+} ordering) and the q_i are the strain components [namely $(\epsilon_{12}, \epsilon_{23}, \epsilon_{13})$], which transform in the same manner as the primary order parameter. Note that Equation 6 contains a third-order term in η and thus does not satisfy the Landau condition that requires that the symmetrized triple Kronecker product of the irreducible representation of G_0 not contain the identity representation of G_0; the transformation must therefore be discontinuous (first-order). The bilinear coupling of the primary order parameter with the shear strain implies that for the subgroup $Fddd$ with order-parameter components $(\eta_1, 0, 0)$, only the macroscopic shear strain ϵ_{12} should be induced. Thus a change in the γ angle of the cubic lattice is expected. As other order-parameter contributions occur, additional shear strains could be induced. In particular, a transition to the $R\bar{3}c$ subgroup can be accompanied by shear strain of the form $\epsilon_{12} = \epsilon_{23} = \epsilon_{13}$; a transition to the $C2/c$ subgroup can be accompanied by shear strain of the form $\epsilon_{12} = \epsilon_{23} \neq \epsilon_{13}$; and a transition to the $P\bar{1}$ subgroup can be accompanied by shear strain of the form $\epsilon_{12} \neq \epsilon_{23} \neq \epsilon_{13}$.

TWIN DOMAIN FORMATION DUE TO THE PHASE TRANSITION

As the coefficients of the free-energy change (for example, as temperature is lowered), the transition from a cubic to an orthorhombic structure may result. For orientation $\eta = (\eta_1, 0, 0)$, which gives $Fddd$, there are other orientations that are crystallographically equivalent and have the same free-energy minimum. Such a transition will result in six twin domains having crystallographically equivalent subgroup symmetries. Thus, as stated by Takéuchi et al. (1982), many twin laws are possible in the lower-symmetry phase. For $Fddd$ (in the "first" domain), the symmetry elements of the parent group that are preserved are $\{E\,|\,0,0,0\}$, $\{C_{2z}\,|\,\frac{1}{2},0,\frac{1}{2}\}$, $\{C_{2a}\,|\,\frac{3}{4},\frac{1}{4},\frac{1}{4}\}$, $\{C_{2b}\,|\,\frac{3}{4},\frac{3}{4},\frac{3}{4}\}$, $\{I\,|\,0,0,0\}$, $\{\sigma_{da}\,|\,\frac{1}{4},\frac{3}{4},\frac{3}{4}\}$, $\{\sigma_{db}\,|\,\frac{1}{4},\frac{1}{4},\frac{1}{4}\}$, $\{\sigma_{dz}\,|\,\frac{1}{2},0,\frac{1}{2}\}$, and all multiples of primative translations. The resolution of $Ia3d$ into left cosets with respect to the subgroup $Fddd$ is then

$$Ia3d = \{E\,|\,0,0,0\}Fddd + \{C_{2x}\,|\,\frac{1}{2},\frac{1}{2},0\}Fddd$$
$$+ \{C_{2c}\,|\,\frac{1}{4},\frac{3}{4},\frac{3}{4}\}Fddd + \{C_{2d}\,|\,\frac{1}{4},\frac{3}{4},\frac{1}{4}\}Fddd$$
$$+ \{C_{2e}\,|\,\frac{3}{4},\frac{3}{4},\frac{3}{4}\}Fddd + \{C_{2f}\,|\,\frac{3}{4},\frac{3}{4},\frac{3}{4}\}Fddd. \quad (7)$$

The coset representative specifies the orientation of each domain relative to the first domain and allows six distinct orientations, all of which are energetically equivalent. In Table 3 we show explicity the coset members and the six associated order-parameter directions. Because $Ia3d$ is a nonsymmorphic space group, coset representations in the table must also include the appropriate fractional translations.

Following the procedure described by Janovec (1972,

1974), the orientation of permissible domain walls in the $Ia3d$-to-$Fddd$ transition can be straightforwardly obtained. First, the double coset decomposition of $Ia3d$ with respect to the subgroup $Fddd$ must be determined. For this case, we find

$$Ia3d = Fddd\{E\,|\,0,0,0\}Fddd + Fddd\{C_{2x}\,|\,\frac{1}{2},\frac{1}{2},0\}Fddd.$$

Thus there are two nonequivalent sets of domain pairs. In Table 3 we have collected the left cosets corresponding to the six relative domain orientations $(D^{(1)}, D^{(j)})$ into these equivalent sets. The horizontal spaces in the table delineate the sets, one of which consists of domain 1 and domain 2, whereas the other consists of domain 1 and domains 3, 4, 5, and 6. Following Janovec, there are two permissible domain walls separating domains 1 and 2. With respect to the cubic lattice, these walls are perpendicular to the diad axes C_{2x} and C_{2y} and are thus rational planes (W). For the domain pairs $(D^{(1)}, D^{(j)})$, $j = 3, 4, 5, 6$, one wall (W) is perpendicular to the diad axis shown in the table, whereas the other wall (S) is noncrystallographic. The latter wall is determined by spontaneous strain in the orthorhombic phase, but is perpendicular to the W wall. Realizing that each of the six domains could be chosen as the "first" domain, we obtain a total of 21 permissible domain-wall orientations. This is consistent with the results of Sapriel (1975).

Depending upon which lower-symmetry subgroup is obtained, different twinning will result. The above discussion is for the subgroup $Fddd$ and gave six possible distinct twin domains in the lower-symmetry phase. For the subgroup $R\bar{3}c$, 4 distinct domains are possible; for $C2/c$, 12 possible; and for $P\bar{1}$, 24 are possible. In each case, the overall average symmetry, assuming equal probability of domains, is the symmetry $Ia3d$.

No domain-wall orientations in grandites have been experimentally determined to date, but the above development defines the possible orientations for each subgroup. These predicted orientations will serve as another check of consistency for the ordering mechanism we have proposed.

MICROSCOPIC ORIGIN OF PHASE TRANSITIONS IN GRANDITES

As mentioned earlier, the order parameter is assumed to be the Al-Fe^{3+} ordering at the (a) sites. Up to this point however, we have considered the transformation only in terms of the symmetry properties of the $Ia3d$-to-$Fddd$ transition, particularly representation properties, and we have not attempted any detailed microscopic description of changes in cation distribution that cause the loss in symmetry. We now wish to describe the qualitative changes in octahedral site occupancies that bring about the previously described space-group change.

The 16 (a) sites have site-symmetry $\bar{3}$; consequently, each of the (a) sites $(0,0,0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, $(\frac{1}{4},\frac{1}{4},\frac{3}{4})$, $(\frac{1}{4},\frac{3}{4},\frac{1}{4})$, plus the body-centered translations of these, is left unchanged by a subgroup of $Ia3d$ that is isomorphic to the point group $\bar{3}$. For example, the point $(0,0,0)$ is left unchanged under the group

of transformations $(E|000)$, $(C_{31}^+|000)$, $(C_{31}^-|000)$, $(I|000)$, $(S_{61}^-|000)$, and $(S_{61}^+|000)$. Other (a) sites are invariant under other subgroups isomorphic to $\bar{3}$, some of which involve translations as well as rotations. In a manner similar to the way in which lattice modes are calculated, we can assign a distortion to the $(0,0,0)$ site and then obtain the distortions of other equivalent points by determining the effects of the symmetry elements of $Ia3d$ that map $(0,0,0)$ into those equivalent points. This process is a well-defined method of group theory and leads to an induced representation of $Ia3d$ (see Hatch et al., 1987, for details). The induced representation theory we use here is not part of the usual Landau theory since it focuses on more than just the general symmetry properties of the order parameter η.

Depending upon the symmetry of the distortion at the (a) sites, only certain space-group representations are induced. For example, it can be shown that a displacement of an atom at the $(0,0,0)$ site in the [111] direction can induce the A_{1u}, A_{2u}, T_{1u}, and T_{2u} representations, but cannot induce the T_{2g} representation. Thus a displacement in the [111] direction cannot be the order parameter of the T_{2g} representation, which is the representation associated with the $Ia3d$-to-$Fddd$ transition. Detailed calculations show, however, that a function that transforms under the identity representation of $\bar{3}$ and is associated with the $(0,0,0)$ site can induce the T_{2g} representation of $Ia3d$. We interpret this function as a probability function expressing the relative concentrations (that is, ordering) of Fe^{3+} and Al at the $(0,0,0)$ site. Extension to symmetrically equivalent sites by projection-operator methods then yields the following $\phi_i(\mathbf{r})$ (see Eq. 3) for the T_{2g} representation:

$$\phi_1 = \begin{bmatrix} 1 \\ 1 \\ -1 \\ -1 \\ 1 \\ 1 \\ -1 \\ -1 \end{bmatrix} \quad \phi_2 = \begin{bmatrix} 1 \\ -1 \\ -1 \\ 1 \\ -1 \\ 1 \\ 1 \\ -1 \end{bmatrix} \quad \phi_3 = \begin{bmatrix} 1 \\ -1 \\ 1 \\ -1 \\ -1 \\ 1 \\ -1 \\ 1 \end{bmatrix}.$$

The elements of each basis function correspond to the eight equivalent non–body-centered (a) sites of $Ia3d$ listed, from top to bottom, in the same order as the *International Tables for X-ray Crystallography* (1983)—that is, $(0,0,0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, $(\frac{1}{4},\frac{1}{4},\frac{3}{4})$, and $(\frac{1}{4},\frac{3}{4},\frac{1}{4})$; they also apply in the same sequence to the other eight (a) sites, obtained by adding the body-centering vector $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ to the original set. The elements of these functions represent the relative weighting at the eight equivalent positions of a localized ordering function transforming as the identity under $\bar{3}$.

Ordering in orthorhombic garnets

For the $Ia3d$-to-$Fddd$ transition, only the first component, η_1, of the order parameter is nonzero (Table 1), and so the ordering function $(\eta_i\phi_i)$ is

TABLE 3. Cosets and order-parameter directions

Domain	Left cosets	Order-parameter directions	Domain walls
(1)	E, C_{2z}, C_{2a}, C_{2b}, I, σ_z, σ_{da}, σ_{db}	$(\eta_1,0,0)$	
(2)	C_{2x}, C_{2y}, C_{4z}^-, C_{4z}^+, σ_x, σ_y, S_{4z}^-, S_{4z}^+	$(-\eta_1,0,0)$	W, W
(3)	C_{2c}, C_{4y}^+, C_{33}^+, C_{32}^-, σ_{dc}, S_{4y}^-, S_{63}^-, S_{62}^+	$(0,-\eta_2,0)$	
(4)	C_{2d}, C_{4x}^-, C_{34}^-, C_{32}^+, σ_{dd}, S_{62}^+, S_{64}^-, S_{4x}^-	$(0,0,-\eta_3)$	W, S
(5)	C_{2e}, C_{4y}^-, C_{34}^+, C_{31}^-, σ_{de}, S_{4y}^+, S_{64}^-, S_{61}^-	$(0,\eta_2,0)$	
(6)	C_{2f}, C_{4x}^+, C_{33}^-, C_{31}^-, σ_{df}, S_{4x}^-, S_{63}^+, S_{61}^+	$(0,0,\eta_3)$	

Note: Horizontal spaces divide domains into two inequivalent sets, one consisting of domains 1 and 2, the other of domains 1 and 3 through 6. See text for full explanation.

$$\begin{bmatrix} \eta_1 \\ \eta_1 \\ -\eta_1 \\ -\eta_1 \\ \eta_1 \\ \eta_1 \\ -\eta_1 \\ -\eta_1 \end{bmatrix},$$

where η_1 is an arbitrary multiple of ϕ_1 with magnitude determined by the degree of Al-Fe^{3+} ordering. The positive and negative values signify two different states of ordering at the respective sites of an ordered phase, referred to the (disordered) cubic lattice; each state of ordering differs from the disordered state by the same amount as the other, but in the opposite sense. Thus, two sets of ordered sites emerge, one consisting of $(0,0,0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ and their body-centered equivalents [the 16(c) sites of $Fddd$], and the second consisting of $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{4},\frac{1}{4},\frac{3}{4})$, $(\frac{1}{4},\frac{3}{4},\frac{1}{4})$ and their body-centered equivalents [the 16(d) sites of $Fddd$]. Within one set of sites, Fe^{3+} is enriched relative to a disordered distribution, and in the other set, it is depleted by the same amount.

Comparison of our results with those of Takéuchi et al. (1982) obviously requires that the group theoretical and experimental treatments both be referred to the same crystallographic origin and axial orientation in both the higher- and lower-symmetry phases. The ordering of Al and Fe^{3+} removes the degeneracy inherent in the cubic lattice, and the naming of the axes of the face-centered orthorhombic lattice relative to the those of the body-centered cubic one is arbitrary. In the transition to domain 1 (Table 3), η_2 and η_3 are zero, and thus the only shear strain induced is ϵ_{12} (see Eq. 6), and our analysis predicts that the cubic γ angle will become different from 90°; Takéuchi et al. (1982) chose that angle to be β. Their choice corresponds to shear ϵ_{13}, or to an order parameter with only the third component being nonzero, that is, $(0,0,\eta_3)$. Such a transformation is a transition to domain 6 (or 4) of our listing and is crystallographically equivalent to the one we describe. Notice that if only the third component η_3 of the order parameter is nonzero, the site-distribution $(\eta_i\phi_i)$ should be

$$\begin{bmatrix} \eta_3 \\ -\eta_3 \\ \eta_3 \\ -\eta_3 \\ -\eta_3 \\ \eta_3 \\ \eta_3 \\ -\eta_3 \end{bmatrix},$$

and the two sets of ordered sites become $(0,0,0)$, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, $(\frac{1}{4},\frac{1}{4},\frac{3}{4})$, and $(\frac{1}{2},0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{1}{4},\frac{3}{4},\frac{1}{4})$, respectively. This is just the ordering pattern found by Takéuchi et al. (1982). Thus the two assumptions built into our description—namely (1) an order parameter leading to an *Fddd* subgroup and (2) the transition being driven by an (a)-site ordering process—predict the correct ordering scheme, although we cannot predict which set of octahedra would be Fe richer or Fe poorer.

Ordering in other subgroups of *Ia3d*

From Table 1 it is seen that a transition from *Ia3d* to $R\bar{3}c$ can occur only if all three components of the order parameter are equal. Thus the ordering function at the eight non–body-centered (a) sites (which are based on the *pseudocubic* unit cell) would be of the form

$$\begin{bmatrix} 3\eta_1 \\ -\eta_1 \\ -\eta_1 \\ -\eta_1 \\ -\eta_1 \\ 3\eta_1 \\ -\eta_1 \\ -\eta_1 \end{bmatrix}.$$

For a transition to $C2/c$, the ordering function would be of the form

$$\begin{bmatrix} 2\eta_1 \\ 0 \\ -2\eta_1 \\ 0 \\ 0 \\ 2\eta_1 \\ -2\eta_1 \\ 0 \end{bmatrix} + \begin{bmatrix} \eta_3 \\ -\eta_3 \\ \eta_3 \\ -\eta_3 \\ -\eta_3 \\ \eta_3 \\ \eta_3 \\ -\eta_3 \end{bmatrix} = \begin{bmatrix} 2\eta_1 + \eta_3 \\ -\eta_3 \\ -2\eta_1 + \eta_3 \\ -\eta_3 \\ -\eta_3 \\ 2\eta_1 + \eta_3 \\ -2\eta_1 + \eta_3 \\ -\eta_3 \end{bmatrix}.$$

A transition to the subgroup $P\bar{1}$ (or $I\bar{1}$, if the pseudocubic cell is retained) would have arbitrary contributions of η_1, η_2, and η_3:

$$\begin{bmatrix} \eta_1 + \eta_2 + \eta_3 \\ \eta_1 - \eta_2 - \eta_3 \\ -\eta_1 - \eta_2 + \eta_3 \\ -\eta_1 + \eta_2 - \eta_3 \\ \eta_1 - \eta_2 - \eta_3 \\ \eta_1 + \eta_2 + \eta_3 \\ -\eta_1 - \eta_2 + \eta_3 \\ -\eta_1 + \eta_2 - \eta_3 \end{bmatrix}.$$

Transitions governed by other representations

Takéuchi et al. (1982), in their Figure 6, included all of the centrosymmetric subgroups of *Ia3d* containing the same translational group and predicted inversion paths on the basis of group-subgroup relationships alone. In failing to consider the constraints that a single parameter (representation) transition would impose (that is, the assumption that a single mechanism drives the transition), they predicted four series of transitions from *Ia3d* to *I*$\bar{1}$ that mixed space groups deriving from different representations. Consideration of each of the subgroups in light of the Landau approach (Stokes and Hatch, 1988), leads to the following: The T_{2g} representation can result in transitions from *Ia3d* to $R\bar{3}c$, *Fddd*, *I2/c*, and *I*$\bar{1}$; the T_{1g} representation accounts for transitions to $R\bar{3}$, $I4_1/a$, *I2/c*, and *I*$\bar{1}$; and the E_g representation governs transitions to $I4_1/acd$ and *Ibca*. Figure 1 summarizes these results and is topologically distinct from Figure 6 of Takéuchi et al. (1982). Notice that transformation to *I2/c* and *I*$\bar{1}$ can occur along two different paths governed by different irreducible representations, and the ordering patterns that result from the two paths will necessarily be different. (Note also that *I2/c* is the same as *C2/c* with a different choice of *a* axis, and our previous discussions that involved space group *C2/c* could as well have been stated in terms of *I2/c*.)

Consideration of the *I*$\bar{1}$ Munam garnet of Takéuchi et al. (1982) provides a good illustration of the power of the group theoretical formalism (induced representation theory) we have used in dealing with phase transformations. Table 4 shows the eight unique triclinic sites, with atomic coordinates referred to the pseudocubic unit cell. Also given are the ordering functions for the T_{2g} and the T_{1g} representations—that is, the two representations that can lead to this space group in the context of our study. The ordering function for T_{2g} shows that the sites must, if the transition is governed by this representation, divide into four sets of two equivalently ordered sites each; in the orientation of Takéuchi et al. (1982), these are M(11) and M(13), M(12) and M(14), M(22) and M(23), and M(21) and M(24). The ordering function for T_{1g} predicts that each site should have a unique Fe^{3+} concentration and that some must be the negatives of each other (in the sense that one is as much above the mean Fe^{3+} concentration as the other is below it). The last column of Table 4 shows that the Fe^{3+} concentrations observed by Takéuchi et al. (1982) conform closely to the first prediction; although the two values of each pair are not precisely identical, they are statistically indistinguishable from their mean, and so the differences can be attributed to experimental error.

Homogeneous phase transformation or crystal-growth phenomenon?

We have shown that, if the transition is governed by a single order parameter that belongs to the T_{2g} representation, ordered (or partially ordered) *Fddd* grandites, as

Fig. 1. Possible phase transitions from $Ia3d$ to subgroup symmetry, assuming that only cell-preserving transitions driven by a single order parameter are permissible. $I2/c$ is used for consistency with Fig. 6 of Takéuchi et al. (1982), but is identical to $C2/c$ used in the text, with the a axis chosen differently.

TABLE 4. Ordering in $I\bar{1}$ Munam grandnite

Site*	Site name**	Ordering function for T_{2g}	Ordering function for T_{1g}	Observed Fe^{3+} (%)**
(0,0,0)	M(11)	$\eta_1 + \eta_2 + \eta_3$	$\eta_1 + \eta_2 + \eta_3$	41
(½,0,½)	M(12)	$\eta_1 - \eta_2 - \eta_3$	$\eta_1 - \eta_2 - \eta_3$	45
((0,½,½)	M(22)	$-\eta_1 - \eta_2 + \eta_3$	$-\eta_1 - \eta_2 + \eta_3$	29
(½,½,0)	M(21)	$-\eta_1 + \eta_2 - \eta_3$	$-\eta_1 + \eta_2 - \eta_3$	15
(¾,¼,¼)	M(14)	$\eta_1 - \eta_2 - \eta_3$	$-\eta_1 + \eta_2 + \eta_3$	49
(¾,¾,¾)	M(13)	$\eta_1 + \eta_2 + \eta_3$	$-\eta_1 - \eta_2 - \eta_3$	45
(¼,¼,¾)	M(23)	$-\eta_1 - \eta_2 + \eta_3$	$\eta_1 + \eta_2 - \eta_3$	27
(¼,¾,¼)	M(24)	$-\eta_1 + \eta_2 - \eta_3$	$\eta_1 - \eta_2 + \eta_3$	16

* Coordinates based on our unit-cell orientation.
** Site names and Fe concentrations from Takéuchi et al. (1982).

well as grandites of three other subgroups of $Ia3d$, can result from a homogeneous phase transformation from the cubic space group. Moreover, our treatment has predicted specific ordering functions that can be tested by crystal-structure refinement.

As previously mentioned, Gali (1983) and Akizuki (1984) have suggested that ordering can occur as a result of crystal-growth processes, yielding grandites that are triclinic ($I\bar{1}$) at formation, but may appear to have higher symmetries owing to superposition of variously oriented triclinic growth sectors. Gali (1983), in particular, has predicted four possible ordering schemes that result from the superposition of his growth sectors numbered I and II, from numbers I and III, from numbers I and IV, and from numbers I, II, III, and IV together. The first three each yield average $C2/c$ structures, but each one has a qualitatively unique ordering scheme. The fourth, superposition of all four sectors, yields an average $Fddd$ structure.

In Table 5 we compare the ordering schemes predicted by our analysis and by that of Gali (1983) for the monoclinic polymorph. We have used letters simply to indicate which sites must be equivalently occupied in each case, with no implication that the same letters used for different structures represent the same degree of ordering. Combining Table 5 with our previous discussion, several observations are pertinent. First, we have shown above that our approach correctly predicts the ordering observed by Takéuchi et al. (1982) in both of their orthorhombic garnets, and this is the same ordering scheme predicted by Gali (1983) as a superposition of four growth sectors. Second, because Gali assumed $I\bar{1}$ to be the fundamental space group, with higher symmetries being artifacts of the presence of various growth sectors, he necessarily restricts apparent $Ia3d$ symmetry to only those

fragments with equal numbers of appropriate domains; we take $Ia3d$ to be the starting fundamental symmetry and on that basis have correctly predicted the qualitative nature of ordering in the lone refined $I\bar{1}$ grandite. Third, our treatment leads to a unique monoclinic polymorph, whereas Gali's predicts that three different monoclinic ordering patterns should be observed; so far, only one report of a possible monoclinic garnet has been published (Hirai and Nakazawa, 1986), and the structure was not determined, but it is noteworthy that none of Gali's three monoclinic ordering patterns is the same as the one we predict for the $C2/c$ polymorph.

We note here that Allen and Buseck (1988) also refined an anisotropic garnet in space group $I\bar{1}$ and found a cation distribution different from the one we predict. The composition of their specimen (given above) is nearly end-member grossular, but it contains almost as much almandine component as andradite component. They found partial ordering in not only the octahedral sites, but also the dodecahedral sites. Thus, if ordering in their specimen resulted from a phase transition, it must have been driven by a different mechanism than discussed in the present treatment, which is limited to garnets of strictly grandite composition with (a)-site ordering.

CONCLUSIONS

The agreement between our predictions based on group theory and the ordering scheme found by Takéuchi et al. (1982) in two orthorhombic grandites and one triclinic grandite supports the following conclusions:

1. Evidence that all three of the garnets of Takéuchi et al. (1982) might have experienced a phase transition from $Ia3d$ to $Fddd$ or $I\bar{1}$ via the T_{2g} representation is strong. Thus, these garnets could have originally grown as cubic phases in space group $Ia3d$.

2. If this was the case, the harmony between the group theoretical and the experimental results indicates that these garnets would have experienced a (primitive) cell-preserving transition that was governed by a single order parameter.

3. The order-parameter mechanism for the transition

TABLE 5. Comparison of predicted ordering patterns in $C2/c$ grandites

	M(11)	M(12)	M(13)	M(14)	M(21)	M(22)	M(23)	M(24)
This work	a	b	a	b	b	c	c	b
Gali no. 1	a	b	a	c	d	c	b	d
Gali no. 2	a	b	c	b	c	d	d	a
Gali no. 3	a	b	c	d	a	b	d	c

Note: Letters indicate equality or inequality of site occupancies only within a given structure, and not between structures.

would have been the ordering of Al-Fe^{3+} at the (a) sites of the cubic phase.

4. The validity of the assumption that this single order-parameter mechanism is sufficient for the complete description of existing experimental data is evident. Moreover, additional predicted characteristics (e.g., domain-wall orientations and monoclinic and rhombohedral site ordering) are also provided.

5. From symmetry arguments alone, we cannot tell whether the rhombohedral ordering pattern was ever present in any of these garnets, or whether the Munam garnet passed through the monoclinic Al-Fe^{3+} distribution before becoming triclinic.

There is ample evidence that some synthetic birefringent garnets, particularly some nonsilicate species, exhibit growth-induced anisotropy (e.g., Callen, 1971; Pfeiffer, 1977; Kitamura et al., 1986). Their properties are highy dependent on the conditions of growth, however, and it seems unlikely that the conditions required for those growth mechanisms would often be duplicated in nature. Nonetheless, if ordered grandite garnets do grow as primary phases in nature, then a correct theoretical treatment of an asymmetric growth process resulting from the $\bar{3}$ symmetry of (a) sites should yield the same distributions we have predicted for the $C2/c$ subgroup, and not those of Gali (1983). Obviously, much more work, including the crystal-structure refinements of many other anisotropic grandite garnets, is required before more general conclusions can be drawn concerning the relative importance of phase transitions and growth mechanisms in producing anisotropic grandites.

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