LETTER

Symmetry analysis of the phase transition and twinning in MgSiO$_3$ garnet: Implications to mantle mineralogy

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INTRODUCTION
The (Mg,Fe)SiO$_3$ (majorite) garnet phase is considered to be a major constituent of the transition zone of the Earth’s mantle between the 400- and 670-km discontinuities (Ringwood, 1967; Liu, 1977; Akaogi and Akimoto, 1977; Ito and Takahashi, 1987). The addition of Al to the MgSiO$_3$ system stabilizes the cubic (Ia$3d$) pyrope-type garnet, whereas for the MgSiO$_3$ composition, the symmetry is reduced to tetragonal (I$_4$/a) primarily because of the ordering of the Mg and Si atoms in the octahedral sites (Kato and Kumazawa, 1985; Sawamoto, 1987). The MnSiO$_3$ garnet phase also shows tetragonal symmetry and nearly complete ordering of $^{6}$Mn and $^{6}$Si in the octahedral sites (sixfold coordination indicated by the superscript [6]; Fujino et al., 1986) (cf. CaGeO$_3$ and GdGeO$_3$ garnets, Prewitt and Sleight, 1969). Because of the geophysical importance of the MgSiO$_3$ garnet phase, a possible cubic to tetragonal phase transition in the MgSiO$_3$ garnet and the associated cation ordering in the octahedral sites are of great interest from the thermodynamic point of view. This transition also has important implications on the seismic velocities in the transition zone. Recently, tetragonal single crystals of MgSiO$_3$ garnet have been synthesized at 17 GPa and 1800°C (Angel et al., 1989); these show partial $^{6}$Mg-$^{6}$Si ordering in the octahedral sites and two different types of twinning: (1) merohedric twinning with irregular twin boundaries and (2) pseudomerohedric twinning with twin lamellae parallel to (110) related by a 3 rotation parallel to (111). Remarkably, both sets of twins are found in leucite (KAI$_2$Si$_2$O$_7$) crystals of volcanic origin, which have crystallized with the cubic (Ia$3d$) symmetry and subsequently undergone a sequence of closely spaced phase transitions, Ia$3d$ → I$_4$/acd → I$_4$/a, at approximately 605 and 590°C, respectively (see Lange et al., 1986). High-temperature electron-microscope experiments on leucite show that the pseudomerohedric (110) twins result from the cubic (Ia$3d$) to tetragonal (I$_4$/acd) transition, where the 3 operation of the cubic point group is lost, and the merohedric twins result from the tetragonal (I$_4$/acd) to tetragonal (I$_4$/a) transition, where the diagonal mirror plane (110) of the high-temperature tetragonal phase is lost (Palmer et al., 1988; Heany and Veblen, 1988). That these twins in leucite are transformation twins and not growth twins is further confirmed by the fact that the tetragonal leucite crystals grown hydrothermally at 500°C (considerably below the temperature of the phase transitions) show no signs of twinning (Friedel and Friedel, 1890; Wyart, 1940). On the basis of similar twinning found in MgSiO$_3$ garnet crystals, we suggest that as in leucite these are also transformation twins and that the MgSiO$_3$ garnet synthesized at 17 GPa and 1800°C has undergone a cubic to tetragonal phase transition on cooling. In this letter, we analyze the cubic to tetragonal phase transition in MgSiO$_3$ garnet in terms of group theory. We consider the $^{6}$Mg-$^{6}$Si ordering in the octahedral sites as the primary order parameter, which drives the phase transition.

ORDER-PARAMETER DESCRIPTION
The phase transition in MgSiO$_3$ garnet from Ia$3d$ to I$_4$/a is driven by the onset of a primary order parameter at the transition temperature. From the tables of Stokes and Hatch (1988), it can be seen that a primary order parameter transforming according to the three-dimensional $o^*(2,2)$ representation of Ia$3d$ can induce the cubic to tetragonal transition being considered. The transformation is an improper ferroelastic transition, and thus the strain cannot serve as the primary order parameter. The cubic to tetragonal transition could be continuous since the representation satisfies the Landau and Lifschitz conditions and it results from the order parameter taking on the restricted form (a, 0, 0). In Table I we show the new basis vectors of the tetragonal phase as well as the location of the origin of this phase relative to the original cubic origin. The location (0, $\frac{t}{2}$, 0) is expressed in terms of the basis vectors of the original cubic structure.

The transition Ia$3d$ ↔ I$_4$/a is a translationengleich transition, i.e., no translations are lost at the transition. There are a number of ways of selecting the fourfold axis from Ia$3d$, and each selection determines an equivalent domain of I$_4$/a. The number of such equivalent tetragonal domains for the lower-symmetry phase can be obtained by simply considering the change in the orders of
the point groups \( m3m \) and \( 4/m \), which are 48 and 8, respectively. Thus there are six equivalent domains in the lower-symmetry phase, and all are orientational (twin) domains. Table I gives basis vectors of each of the domains, their origin locations, the generators of each corresponding equivalent symmetry subgroup, and the order-parameter direction for each domain.

From Tables 9 and 10 of Stokes and Hatch (1988), the free energy for the \( \Gamma_2 \) representation is easily obtained. The free energy is an expansion of the order parameter in invariant polynomial forms. The expansion to the fourth degree is

\[
\Phi = a_1 (\eta^2 + \zeta^2 + \zeta) + a_2 (\eta^2 + \zeta^2 + \eta) + a_3 (\eta^2 + \zeta^2 + \eta) + a_4 \eta^2 + \zeta^2 + \eta^2, \tag{1}
\]

A transition to \( I4_1/a \) and the third domain would correspond to an order parameter value of \((0, 0, \eta)\). This value of \( \eta \) corresponds to a range of coefficients \( a_1, a_2, a_3 \) that makes \( \Phi \) a minimum. Other equivalent domain orientations with the same subgroup symmetry would give the same value of \( \Phi \) and are thus energetically degenerate with \((0, 0, \eta)\).

In Table 2 we show other subgroup possibilities and their description as given in Stokes and Hatch (1988). Phase transitions from cubic to trigonal, monoclinic, and triclinic phases are possible by parametric distortions of the \( \Gamma_2 \) parameter. For each phase, order-parameter directions are shown for one representative domain. A given phase will occur only if the coefficients of the free-energy expansion in Equation 1 are such that they minimize the free energy for that direction of the order parameter.

The primary order parameter \( \eta = (0, 0, \eta) \) (domain three) determines the lower-symmetry phase \( I4_1/a \). The subgroup is obtained by keeping all symmetry elements of \( Ia3d \) that leave invariant the order parameter \( \eta \) (which transforms according to \( \Gamma_2 \)). In most transitions, atomic distortions (either atomic displacements or atomic ordering) for more than one Wyckoff position transform according to \( \Gamma_2 \) and can contribute to the distortion allowed by \( \Gamma_2^+ \). Any one of these allowed distortions could be used as a primary order parameter. There are also additional distortions that could occur and that do not destroy the symmetry of the \( I4_1/a \)-subgroup phase. These secondary distortions, which we take as secondary order parameters, do not transform according to \( \Gamma_2^+ \) but will couple linearly to it. Since the coupling terms between the secondary and primary order parameters are linear in the secondary order parameter, distortions transforming according to the secondary order parameter must occur at the transition, even if they are small. For \( I4_1/a \), the additional distortions are of the form \( Q = (q, 0, 0) \), which arises from the two-dimensional irreducible representation \( \Gamma_2 (E_2) \), and \( P = (p, 0) \), which arises from the one-dimensional irreducible representation \( \Gamma_2 (A_1) \). From symmetry considerations it follows that only these two irreducible representations can couple linearly with \( \Gamma_2^+ \).

As can be seen from Table 4 of Stokes and Hatch (1988), certain strain components transform according to \( \Gamma_2^+ \) and \( \Gamma_2^+ \), and no strain components transform according to \( \Gamma_2 \). Specifically, the strain combination \((\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})\) transforms according to \( \Gamma_2^+ \), whereas the combinations \((\varepsilon_{11} + 2\varepsilon_{22} + 2\varepsilon_{33})\) transform according to the two-dimensional \( \Gamma_2^+ \). Thus (1) a volume dilation (contraction) can appear at the transition because of coupling of \( \Gamma_2^+ \) with the primary order parameter and (2) a tetragonal and/or orthorhombic distortion can also appear because of the first and second component, respectively, of \( \Gamma_2^+ \). The distortions of \( \Gamma_2^+, \Gamma_2^+ \) resulting from coupling with the primary order parameter \( \Gamma_2^+ \) will be considered in more detail below.

**MICROSCOPIC DISTORTIONS**

In several previous publications, the method of induced representations has been discussed (Hatch et al., 1987; Hatch and Griffen, 1989; Ghose et al., 1989; Hatch and Ghose, 1989; Hatch and Stokes, 1989a, 1989b). The method determines which microscopic distortions (displacements, orderings, etc.) are consistent with order parameters appearing at the transition. For the MgSiO\(_3\) garnets, the Wyckoff positions of the atoms and their site symmetry in the cubic phase are given in Table 3. From the tables of Putnam (1983) (or Kovalev, 1986), the possible orderings and/or displacements attributed to these atomic positions can be obtained. All orderings and/or displacements are defined relative to the (cubic) high-symmetry equilibrium distributions or positions. Table 3 presents those results. There, under column three, the induction frequency of a local displacive distortion from the cubic position is shown, followed by the induction frequency of an ordering distortion for each occupied cubic position of MgSiO\(_3\). These two frequencies are separated by a hyphen. If a zero entry appears, it signifies that

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**TABLE 1. The six possible domain orientations for the subgroup \( I4_1/a \)**

<table>
<thead>
<tr>
<th>Domain</th>
<th>Basis vectors</th>
<th>Origin</th>
<th>Generators</th>
<th>Direction vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((0, 1, 0), (0, 0, 1), (1, 0, 0))</td>
<td>((0, 0, 0))</td>
<td>((C_{4h}</td>
<td>\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (l</td>
</tr>
<tr>
<td>2</td>
<td>((0, 1, 0), (0, 0, 1), (-1, 0, 0))</td>
<td>((0, 0, 0))</td>
<td>((C_{4h}</td>
<td>\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}), (l</td>
</tr>
<tr>
<td>3</td>
<td>((1, 0, 0), (0, 0, 1), (0, 0, 1))</td>
<td>((0, 0, 0))</td>
<td>((C_{4h}</td>
<td>-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (l</td>
</tr>
<tr>
<td>4</td>
<td>((1, 0, 0), (0, -1, 0), (0, 0, 1))</td>
<td>((0, 0, 0))</td>
<td>((C_{4h}</td>
<td>-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}), (l</td>
</tr>
<tr>
<td>5</td>
<td>((0, 0, 1), (1, 0, 0), (0, 1, 0))</td>
<td>((0, 0, 0))</td>
<td>((C_{4h}</td>
<td>\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}), (l</td>
</tr>
<tr>
<td>6</td>
<td>((0, 0, 1), (1, 0, 0), (-1, 0, 0))</td>
<td>((0, 0, 0))</td>
<td>((C_{4h}</td>
<td>\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}), (l</td>
</tr>
</tbody>
</table>

*Note: The basis vectors, origin locations, and generators are specified relative to the high-symmetry \( Ia3d \) phase. Order-parameter directions for each domain are also listed.*
we obtain the following \( r \) functions for the \( \Gamma^+ \) representation induced from the \( \Gamma \) representation of \( 3 \):

\[
\phi_1 = [1, 1, -1, 1, -1, 1, 1, 1], \\
\phi_2 = [1, -1, 1, 1, -1, 1, 1, 1], \\
\phi_3 = [1, 1, -1, 1, 1, 1, 1, 1].
\]

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, \((a, a, 0), (a, 0, 0), (0, a, 0), (0, 0, a)\). The basis-function elements are then repeated in the same sequence for the points obtained by adding the body-centering vector \((1/2, 1/2, 1/2)\) to the above set. The elements of these functions give the relative weighting of the \((a)\)-site ordering demanded by the \( \Gamma^+ \) representation. To be specific, if at \((0, 0, 0)\) we take the ordering probability \( p \) becomes nonzero at \((1/2, 1/2, 1/2)\), etc. Notice that for the transition from \( Ia3d \) to \( I4/a \), only the single function \( \phi_3 \) contributes for a transition to domain three (see Table 1).

A similar calculation for the grandite garnets was performed where the \( 16(a) \) sites of \( Ia3d \) were also considered (Hatch and Griffen, 1989). There, however, the cation ordering transformed according to the \( \Gamma^+ (T_{2g}) \) representation. As can be seen by comparing Equation 2 with the results of Hatch and Griffen (1989), the relative ordering, as expected, is different for the two distinct representations.

**Domain-wall formation**

As discussed above, the transition from \( Ia3d \) to \( I4/a \) is driven by the primary order parameter \( \Gamma^+ \), which gives the \( \text{[Mg-Si]} \) ordering at the \( 16(a) \) sites. The \( \Gamma^+ \) representation can also couple with the \( \Gamma^+ \) and \( \Gamma^+ \) representations so that at the transition, additional distortions appear but they do not destroy the symmetry of the tetragonal \( I4/a \) phase. Because of the linear-quadratic coupling between \( \Gamma^+ \) and \( \Gamma^+ \) and the linear-quadratic coupling between \( \Gamma^+ \) and \( \Gamma^+ \), contributions from strain must appear at the transition. The symmetry change at the transition and the spontaneous onset of strain will lead to

**Table 3.** Assignment of atomic positions for MgSiO\(_3\) in the \( Ia3d \) phase

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Position</th>
<th>Site symmetry</th>
<th>( \Gamma^+ (T_{2g}) )</th>
<th>( \Gamma^+ (A_{1g}) )</th>
<th>( \Gamma^+ (E_g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{[Mg-Si]} )</td>
<td>24(c)</td>
<td>222</td>
<td>3-0</td>
<td>0-1</td>
<td>1-1</td>
</tr>
<tr>
<td>( \text{[Mg-Si]} )</td>
<td>16(a)</td>
<td>3</td>
<td>0-1</td>
<td>0-1</td>
<td>0-0</td>
</tr>
<tr>
<td>( \text{[Si]} )</td>
<td>24(d)</td>
<td>4</td>
<td>2-1</td>
<td>0-1</td>
<td>1-1</td>
</tr>
<tr>
<td>O</td>
<td>96(h)</td>
<td>1</td>
<td>1-1</td>
<td>1-1</td>
<td>1-1</td>
</tr>
</tbody>
</table>

Note: The Wyckoff position and site symmetry for each distinct set of atoms are listed. In columns four, five, and six, the induction frequency for displacements followed by the induction frequency for ordering is listed for each Wyckoff position and each representation \( \Gamma^+, \Gamma^+, \Gamma^+ \).
to twinning in the lower-symmetry phase. There are six energetically equivalent domains for the phase 14'/a that can be viewed as resulting from the loss of the threefold axes along (111) (pseudomerohedric twins) and the loss of the diagonal mirror planes (110) (merohedric twins). Both types of twinning were observed through electron microscopy by Angel et al. (1989).

The loss of symmetry in going from the (cubic) $Ia3d$ phase to the low-temperature phase can be used to determine domain-wall orientations resulting from the minimization of elastic strain. The $T^3$ representation leads to a volume expansion or contraction and will not lead to orientational domains. The $T^3$ representation, however, leads to orientational domains, and their description can be broken into two parts. (1) The first symmetry change results from the loss of the (111) threefold axis. This symmetry change would be $3m3m$ to $4/mmm$ and would be a ferroelastic change. From the work of Sapriel (1975), the domain walls are parallel to (110). (2) The second part, the loss of the mirror planes, implies that the two domains are related by the lost symmetry element, i.e., the (110) mirror plane. This symmetry loss gives rise to the merohedric twinning.

Since the transition is improper ferroelastic and the coupling of the primary order parameter to elastic strain is linear-quadratic, there is no effect on the elastic constants of the cubic phase above the transition temperature, but there will be a decrease in selected elastic constants below the transition (Lüthi and Rehwald, 1981). The $T^3$ mode will affect the stiffness constants $c_{11} + 2c_{12}$, whereas the $T^1$ mode will affect $c_{11} - c_{12}$ in the tetragonal phase (Chan, 1988).

**Conclusions**

We suggest that the rapid Mg-Si ordering in the octahedral sites of MgSiO$_3$ (majorite) garnet during quenching from 17 GPa and 1800 °C results in a cubic to tetragonal phase transition. This implies that under mantle conditions the majorite garnet is cubic (with complete octahedral Mg-Si disorder) and not tetragonal as is currently believed.

**Acknowledgments**

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**References Cited**

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