

Static disorders of atoms and experimental determination of Debye temperature in pyrope: Low- and high-temperature single-crystal X-ray diffraction study—Discussion

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INTRODUCTION

Pyrope, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, being an important phase in the interior of the Earth, has been investigated many times. However, there is long-standing disagreement on the behavior of the Mg cation located in the triangular dodecahedron of the garnet crystal structure. Two interpretations have been advanced: (1) that the Mg cation has a large amplitude of thermal vibration (i.e., shows dynamic disorder or a “rattling” motion) and (2) that the Mg cation is statically disordered positionally around the special $24c$ Wyckoff position. Nakatsuka et al. (2011) presented X-ray single-crystal diffraction results on pyrope and argued for interpretation (2). However, their proposal is contradicted by a number of published studies, some of which are not cited in their report. The physical behavior of Mg in pyrope can be analyzed using various approaches (details are found in the studies cited below), that is: (1) through X-ray and neutron diffraction, (2) by various spectroscopic measurements, (3) by computational modeling, and (4) using thermodynamic considerations.

RESULTS AND ANALYSIS

In terms of diffraction (point 1), a main contention centers on analyzing the behavior (i.e., the mean square displacements) of the Mg cation as described by its large atomic displacement parameters (adp's) as obtained in structure refinements. It is clear from all the conflicting interpretations in the literature that this is not a simple matter. The key, here, is in making measurements as a function of temperature and evaluating the adp's in a physically interpretable manner, as attempted by Nakatsuka et al. (2011) and other workers (Armbruster et al. 1992; Armbruster and Geiger 1993; Pavese et al. 1995; Artioli et al. 1997). In short (see Nakatsuka et al. for details), if the adp's for Mg decrease in magnitude with decreasing temperature and extrapolate close to a value of 0 \AA^2 approaching 0 K, this would indicate thermal or dynamic disorder. Nakatsuka et al. (2011) made a series of measurements over a range of temperatures from 97 to 973 K and, together with an analysis of residual electron density at and around the $24c$ site, concluded that *all atoms* in pyrope have static disorder and especially Mg. The analysis is not simple, because several factors can come into play and affect the adp values, including possible zero-point motion.

I cannot comment on the soundness of the complex model refinement of Nakatsuka et al., but it must be noted that other relatively recent diffraction investigations, including one with neutrons (Artioli et al. 1997), made as a function of temperature

concluded that the Mg cation shows dynamic and not static positional disorder. Moreover, it is important to note that the studies of Armbruster et al. (1992) and Armbruster and Geiger (1993) used a different experimental strategy. They analyzed the *difference adp's* (ΔU_{ij} values) for the different cation-oxygen bonding vectors in the pyrope structure as a function of temperature (this same type of analysis was also done in other studies for the garnets almandine, spessartine, grossular, and andradite). The use of difference adp's is powerful for differentiating between static and dynamic atomic disorder, because ΔU values are less affected by certain experimental errors, such as absorption, extinction, and thermal diffuse scattering, in the diffraction data set used in the structure refinement procedure (see Chandrasekhar and Bürgi 1984; Bürgi 2000 and references therein). Armbruster and Geiger concluded that the SiO_4 and AlO_6 groups in pyrope vibrate as essentially rigid polyhedra. Furthermore and importantly, they observed that the ΔU values for the longer Mg-O4 bond increase with temperature, whereas the ΔU values for the shorter Mg-O2 bond remain approximately constant. This *argues strongly for thermal disorder of the Mg cation* within the plane given by the Mg-O4 bonds of the MgO_8 dodecahedron (i.e., Mg shows anisotropic thermal motion). It *cannot be ruled out* that a small degree of Mg positional disorder, as could arise from local variations in structure (e.g., defects, slight cation disorder over sites), makes a minor contribution to the ΔU values. The amplitudes of thermal vibration for Mg and the surrounding O atoms, obtained from the difference in their U_{ij} values at 100 and 500 K, are shown in Figure 1 (top). This analysis shows that the strongest vibration is for the central Mg cation and within the plane of the longer Mg-O4 bonds.

In terms of spectroscopy (point 2), Kolesov and Geiger (1998, 2000) measured the Raman single-crystal spectrum of pyrope (the 2000 work was not cited by Nakatsuka et al. 2011) and addressed directly the question of the behavior of Mg. Kolesov and Geiger (2000) wrote: “The spectra are consistent with the proposal that the Mg cation is dynamically disordered and not statically distributed over subsites in the large triangular-dodecahedral E-site in pyrope. A low-energy band at about 135 cm^{-1} softens and shows a large decrease in its line width with decreasing temperature. The presence of a weak, broad band at about 280 cm^{-1} may be due to anharmonic effects, as could be the one at 135 cm^{-1} . The latter is assigned to the rattling motion of Mg in pyrope in the plane of the longer Mg-O4 bonds.” The observed changes in line width of a Mg-translational mode would be difficult to explain if Mg is positionally disordered statically rather than thermally. Additional spectroscopic indications are

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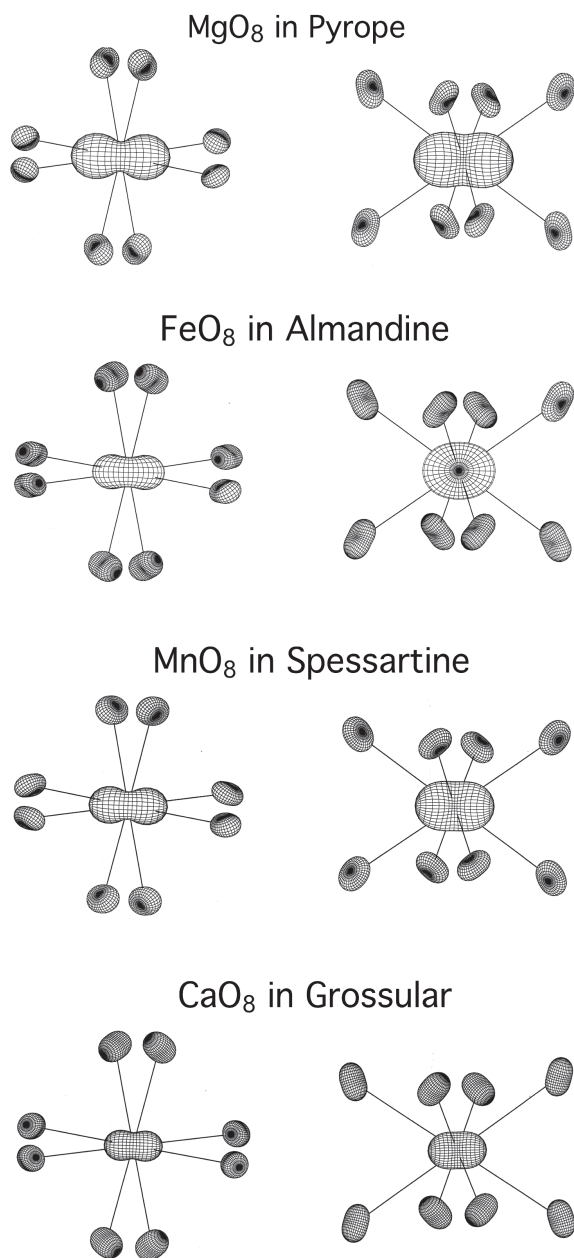


FIGURE 1. Atomic amplitudes of vibration for a given EO_8 coordination for different end-member garnets as calculated from the difference between their atomic mean-square displacements at 500/550 and 100 K. The projections are approximately along twofold axes and those in the right-hand column are rotated approximately 90° from the projections in the left-hand column. The E-cation shows anisotropic thermal vibration (i.e., dynamic disorder) with the largest amplitude in the plane of the longer E-O4 bonds. The eight surrounding oxygen anions have smaller vibrational amplitudes (from Geiger et al. 1992; Armbruster et al. 1992; Armbruster and Geiger 1993; Geiger and Armbruster 1997).

given by EXAFS results measured on the Mg *K*-edge of pyrope (Quartieri et al. 2008). They fit the spectra using a model with two Debye-Waller terms to describe the anisotropic vibrational behavior of Mg. Finally in terms of spectroscopy and on a related note, the observation of anisotropic recoil free fraction (i.e.,

the Gol'danskii-Karyagin effect) for Fe in the ^{57}Fe Mössbauer spectrum of structurally similar almandine requires anisotropic vibration of Fe^{2+} and not static disorder (Geiger et al. 1992).

In terms of computational studies (point 3), there are a series of empirical pair potential lattice dynamic investigations (Pilati et al. 1996; Gramaccioli 2002; Gramaccioli et al. 2002; Gramaccioli and Pilati 2003), a couple of which are cited by Nakatsuka et al. (2011), proposing positional subsite disorder for Mg as well as for Fe^{2+} in almandine and Mn^{2+} in spessartine. The conclusions of Gramaccioli and coworkers arguing for static subsite disorder of the divalent cations in garnet have already been criticized (Winkler et al. 2000; Geiger 2008; Dachs et al. 2009, 2012). Problems with their model-dependent calculations and resulting analysis are both numerous and serious. For pyrope, their model adp values for Mg are very small and they do not agree with any diffraction-measured adp's—including those of Nakatsuka et al. (2011)! It is therefore no surprise, then, that their calculated low-energy vibrational modes in garnet (Gramaccioli and Pilati 2003) do a poor job of reproducing published Raman and IR spectra and thus also ultimately give incorrect thermodynamic C_p results at low temperatures. The difficulty in modeling the behavior of Mg and its related modes in the vibrational spectra of pyrope was stated earlier in Kolesov and Geiger (2000): “The successful modeling of the anisotropic motion of the Mg cation in pyrope, which has an anharmonic character, provides a valuable test of the validity of empirical or semi-empirical lattice-dynamic calculations for silicates.” It is finally noted that a quantum mechanical study specifically addressing the behavior of Mg in pyrope was made (Winkler et al. 2000). They wrote: “the potential which the Mg experiences is highly anisotropic and in one direction is strongly anharmonic.” They found no evidence for subsite positional disordering. Their proposal for dynamic disorder of Mg at the $24c$ site was confirmed by further ab initio calculations of Freeman et al. (2006).

In terms of thermodynamics (point 4), if there were static positional Mg disorder over say four different sub-sites, as proposed (e.g., Pilati et al. 1996; Gramaccioli and Pilati 2003; Nakatsuka et al. 2011), it should be reflected in a configurational entropy term as given by $S^{\text{conf}} = 3R \ln 4 = 34.5 \text{ J}/(\text{mol} \cdot \text{K})$. This term would have to be added to the vibrational entropy to give the total entropy of pyrope. However, the standard third-law entropy of pyrope measured by low-temperature calorimetry (Haselton and Westrum 1980), together with C_p data at $T > 298 \text{ K}$, can be used to calculate various high P - T reactions involving pyrope and reproduce well experimental phase equilibrium results without the need for any ad hoc S^{conf} contribution. Indeed, internally consistent thermodynamic databases do not consider any S^{conf} term in their analysis of pyrope's properties (i.e., Berman 1988; Chatterjee et al. 1998; Holland and Powell 2011). Furthermore, claims that static disorder of Mg can account for the large low-temperature heat capacity of pyrope (Nakatsuka et al. 2011) have no physical basis. On the contrary, the best explanation is that low-energy phonons related to the large amplitude Mg vibrations are responsible for the large observed heat capacities (Haselton and Westrum 1980; Dachs and Geiger 2006; Geiger 2008; and references therein).

In closing, the behavior of the divalent cations (Mg, Fe, Mn, Ca) in the four aluminosilicate garnets pyrope, almandine,

spessartine, and grossular give a “consistent picture” (Fig. 1). These cations are characterized by anisotropic thermal vibration, whereby their amplitudes are largely a function of cation mass and size (Geiger and Armbruster 1997; Geiger 2008 and references therein), as illustrated and summarized earlier in Geiger (2004, Fig. 3). Anisotropic thermal (dynamic) disorder for Mg in pyrope better explains the overwhelming bulk of the published experimental and computational results than a model based on static sub-site positional disorder.

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