

1 **Static disorders of atoms and experimental determination of Debye temperature in pyrope:**  
2 **Low- and high-temperature single-crystal X-ray diffraction study -- Comment**

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### INTRODUCTION

10 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  
11 investigated many times. However, there is longstanding disagreement on the behavior of the Mg  
12 cation located in the oxygen-coordinated dodecahedron of the garnet crystal structure. Two  
13 interpretations have been advanced: (i) that the Mg cation has large amplitude of thermal vibration  
14 (shows dynamic disorder or a “rattling” motion) and (ii) that the Mg cation is statically disordered  
15 positionally around the special 24c Wyckoff position. Nakatsuka et al. (2011) presented X-ray  
16 single-crystal diffraction results on pyrope and argued for (ii). However, their proposal is  
17 contradicted by a number of published studies, some of which are not cited in their report. The  
18 physical behavior of Mg in pyrope can be analyzed using various approaches (details are found in  
19 the studies cited below). That is: (1) through X-ray and neutron diffraction, (2) by various  
20 spectroscopic measurements, (3) by computational modeling and (4) using thermodynamic  
21 considerations.

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### RESULTS AND ANALYSIS

24 In terms of (1), a main contention centers on analyzing the behavior (i.e. the mean square  
25 displacements) of the Mg cation as described by its large atomic displacement parameters (adps) as  
26 obtained in diffraction-based structure refinements. It is clear from all the conflicting interpretations

27 in the literature that this is not a simple matter. The key, here, is in making measurements as a  
28 function of temperature and evaluating the adps in a physically interpretable manner, as attempted  
29 by Nakatsuka et al. (2011) and other workers (Armbruster et al. 1992; Armbruster and Geiger 1993;  
30 Pavese et al. 1995; Artioli et al. 1997). In short (see Nakatsuka et al. for details), if the adps for Mg  
31 decrease in magnitude with decreasing temperature and extrapolate close to a value of  $0 \text{ \AA}^2$   
32 approaching 0 K, this would indicate thermal or dynamic disorder. Nakatsuka et al. (2011) made a  
33 series of measurements over a range of temperatures from 97 K to 973 K and, together with an  
34 analysis of residual electron density at and around the  $24c$  site, concluded that *all atoms* in pyrope  
35 have static disorder and especially Mg. The analysis is not simple, because a number of factors can  
36 come into play and affect the adps, including possible zero-point motion.

37 I cannot comment on the soundness of the complex model refinement of Nakatsuka et al.,  
38 but it must be noted that other relatively recent diffraction investigations, including one with  
39 neutrons (Artioli et al. 1997), made as a function of temperature concluded that the Mg cation  
40 shows dynamic and not static positional disorder. Moreover, it is important to note that the studies  
41 of Armbruster et al. (1992) and Armbruster and Geiger (1993) used a different experimental  
42 strategy. They analyzed the *difference adps* ( $\Delta U_{ij}$ 's) for the different cation-oxygen bonding vectors  
43 in the pyrope structure as a function of temperature (this same type of analysis was also done in  
44 other studies for the garnets almandine, spessartine, grossular and andradite). The use of difference  
45 adps is powerful for differentiating between static and dynamic atomic disorder, because  $\Delta U$ 's are  
46 less affected by certain experimental errors, such as absorption, extinction, and thermal diffuse  
47 scattering, in the diffraction data set used in the structure refinement procedure (see Chandrasekhar  
48 and Bürgi 1984; Bürgi 2000 and references therein). Armbruster and Geiger concluded that the  
49  $\text{SiO}_4$  and  $\text{AlO}_6$  groups in pyrope vibrate as essentially rigid polyhedra. Furthermore and  
50 importantly, they observed that the  $\Delta U$  values for the longer Mg-O(4) bond increase with  
51 temperature, whereas the  $\Delta U$  values for the shorter Mg-O(2) bond remain approximately constant.  
52 This *argues strongly for thermal disorder of the Mg cation* within the plane given by the Mg-O(4)  
53 bonds of the  $\text{MgO}_8$  dodecahedron (i.e. Mg shows anisotropic thermal motion). It *cannot be ruled*

54 *out* that a small degree of Mg positional disorder, as could arise from local variations in structure  
55 (e.g., defects, slight cation disorder over sites), makes a minor contribution to the  $\Delta U$  values. The  
56 thermal amplitudes of vibration for Mg and the surrounding O atoms, obtained from the difference  
57 in their  $U_{ij}$ 's values at 100 K and 500 K, are shown in Fig. 1 (top). This analysis shows that  
58 strongest vibration is for the central Mg cation and within the plane of the longer Mg-O(4) bonds.

59 In terms of spectroscopy (2), Kolesov and Geiger (1998; 2000) measured the Raman single-  
60 crystal spectrum of pyrope (the 2000 work was not cited by Nakatsuka et al. 2011) and addressed  
61 directly the question of the behavior of Mg. Kolesov and Geiger (2000) wrote "The spectra are  
62 consistent with the proposal that the Mg cation is dynamically disordered and not statically  
63 distributed over subsites in the large triangular-dodecahedral E-site in pyrope. A low-energy  
64 band at about  $135\text{ cm}^{-1}$  softens and shows a large decrease in its line width with decreasing  
65 temperature. The presence of a weak, broad band at about  $280\text{ cm}^{-1}$  may be due to  
66 anharmonic effects, as could the one at  $135\text{ cm}^{-1}$ . The latter is assigned to the rattling motion of  
67 Mg in pyrope in the plane of the longer Mg-O(4) bonds". The observed changes in line width of a  
68 Mg-translational mode would be difficult to explain if Mg is positionally disordered rather than  
69 thermally. Additional spectroscopic indications are given by EXAFS results measured on the Mg K-  
70 edge of pyrope (Quartieri et al. 2008). They fit the spectra using a model with two Debye-Waller  
71 terms in order to describe the anisotropic vibrational behavior of Mg. Finally in terms of  
72 spectroscopy and on a related note, the observation of anisotropic recoil free fraction (i.e. the  
73 Gol'danskii-Karyagin effect) for Fe in the  $^{57}\text{Fe}$  Mössbauer spectrum of structurally similar  
74 almandine requires anisotropic vibration of  $\text{Fe}^{2+}$  and not static disorder (Geiger et al. 1992).

75 In terms of computational studies (3), there are a series of *empirical* pair potential lattice  
76 dynamic investigations (Pilati et al. 1996; Gramaccioli 2002; Gramaccioli et al. 2002; Gramaccioli  
77 and Pilati 2003), a couple of which are cited by Nakatsuka et al. (2011), proposing positional  
78 subsite disorder for Mg - as well as for  $\text{Fe}^{2+}$  in almandine and  $\text{Mn}^{2+}$  in spessartine. The conclusions  
79 of Gramaccioli and coworkers arguing for static subsite disorder of the divalent cations in garnet  
80 have already been criticized (Winkler et al. 2000; Geiger 2008; Dachs et al. 2009; Dachs et al.

81 2012). Problems with their model-dependent calculations and resulting analysis are both numerous  
82 and serious. For pyrope, their model adp values for Mg are very small and they do not agree with  
83 *all* diffraction-measured adps - including those of Nakatsuka et al. (2011)! It is therefore no  
84 surprise, then, that their calculated *low-energy* vibrational modes in garnet (Gramaccioli and Pilati  
85 2003) do a poor job of reproducing published Raman and IR spectra and thus also ultimately give  
86 incorrect thermodynamic  $C_p$  results at low temperatures. The difficulty in modeling the behavior of  
87 Mg and its related modes in the vibrational spectra of pyrope was stated *earlier* in Kolesov and  
88 Geiger (2000) “The successful modeling of the anisotropic motion of the Mg cation in pyrope,  
89 which has an anharmonic character, provides a valuable test of the validity of empirical or semi-  
90 empirical lattice-dynamic calculations for silicates.” It is finally noted that a *quantum mechanical*  
91 study specifically addressing the behavior of Mg in pyrope was made (Winkler et al. 2000). They  
92 wrote “the potential which the Mg experiences is highly anisotropic and in one direction is strongly  
93 anharmonic”. They found no evidence for subsite positional disordering. Their proposal for  
94 dynamic disorder of Mg at the 24c site was confirmed by the further ab initio calculations of  
95 Freeman et al. (2006).

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

108 vibrations are responsible for the large observed heat capacities (Haselton and Westrum 1980;  
109 Dachs and Geiger 2006; Geiger 2008; and references therein).

110 In closing, the behavior of the divalent cations (Mg, Fe, Mn, Ca) in the four aluminosilicate  
111 garnets pyrope, almandine, spessartine, and grossular give a consistent “picture” (Fig. 1). These  
112 cations are characterized by anisotropic thermal vibration, whereby their amplitudes are largely a  
113 function of cation mass and size (Geiger and Armbruster 1997; Geiger 2008 and references therein),  
114 as illustrated and summarized earlier in Geiger (2004 - Fig. 3). Anisotropic thermal (dynamic)  
115 disorder for Mg in pyrope better explains the overwhelming bulk of the published experimental and  
116 computational results than a model based on sub-site positional disorder.

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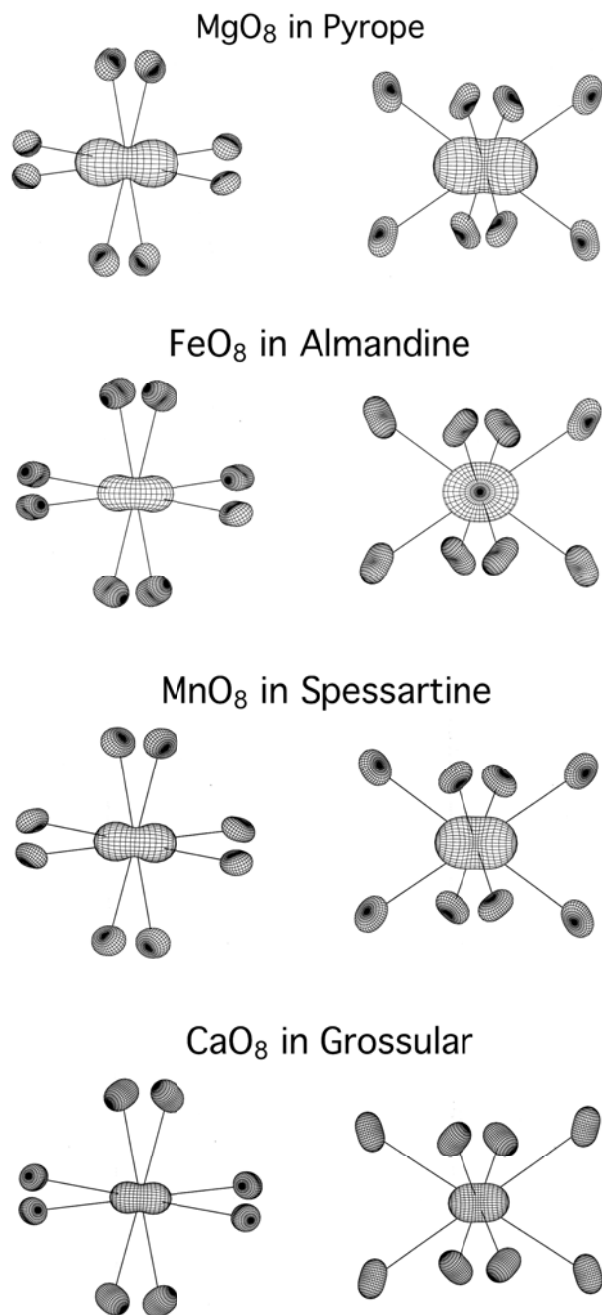
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199 Figure 1. Atomic amplitudes of vibration for a given **E**O<sub>8</sub> coordination for different end-member  
200 garnets as calculated from the difference between their atomic mean-square displacements at  
201 500/550 and 100 K. The projections are approximately along two-fold axes and those in the right-  
202 hand column are rotated approximately 90° from the projections in the left-hand column. The **E**-  
203 cation shows anisotropic vibration (i.e., dynamic disorder) with the largest amplitude in the plane of  
204 the longer **E**-O(4) bonds. The eight surrounding oxygen anions have smaller vibrational amplitudes  
205 (from Geiger et al. 1992; Armbruster et al. 1992; Armbruster and Geiger 1993; Geiger and  
206 Armbruster 1997).