

20 Geiger (2012) argues that the large mean square displacement (MSD) of Mg in the
21 dodecahedral site in pyrope, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, originates in the dynamic disorder of Mg due to
22 its large anisotropic thermal vibration, including anharmonic contribution, and refutes our
23 findings that the Mg static disorder is present. His argument is based on the diffraction,
24 spectroscopic, thermodynamic and computational studies made mainly by him and his
25 co-workers. However, these investigations only suggested the large anisotropy of the Mg
26 thermal vibration, and do not necessarily prove that there is no Mg static disorder. What we
27 must obtain is conclusive experimental proof as to whether the Mg static disorder exists or
28 not.

29 A “direct” method to solve this problem is to observe a splitting of electron density
30 maxima around the Mg site from the structure analysis. As shown in Nakatsuka et al. (2011),
31 we successfully observed the residual electron density maxima around the Mg site (24c site)
32 in the difference Fourier map at a low temperature of 97 K. In addition, the refinements
33 assigning Mg to these electron density maxima (split-atom model refinements) yielded “the
34 Mg positional parameters deviating significantly from the 24c site” and provided “the atomic
35 displacement parameters (ADPs) of Mg significantly smaller than the ones in the
36 normal-model refinements”, assigning Mg to the 24c site, as a consequent of the removal of
37 the static disorder components. These are direct evidence for the presence of the Mg static
38 disorder.

39 In the anharmonic refinements, several of the higher-rank tensor coefficients of Mg,
40 Al, Si, and O atoms deviated significantly from zero even at a low temperature of 97 K [Fig.
41 10 in Nakatsuka et al. (2011)]. In “rigid crystals such as pyrope”, the anharmonic contribution
42 to atomic thermal vibrations should be in principle absent at such a low temperature.
43 Therefore, it is unreasonable that the non-zero higher-rank tensor coefficients (the
44 deformation of the probability density functions from ellipsoidal distributions) are attributed
45 to the anharmonic contribution to atomic thermal vibrations. Indeed, none of them showed
46 systematic temperature dependence below at least 800 K, where a sign of the anharmonic

47 contribution to atomic thermal vibrations begins to appear [Fig. 10 in Nakatsuka et al. (2011)].
48 It should be noted from this point of view that the residual electron density maxima observed
49 in Figure 7 in Nakatsuka et al. (2011) almost entirely disappeared in the difference Fourier
50 map after the anharmonic refinement [Fig. 11 in Nakatsuka et al. (2011)]. The maxima should
51 thus be due to the Mg static disorder, and indeed the split-atom model refinements
52 successfully fitted the maxima as described above.

53 In Nakatsuka et al. (2011), MSDs (or ADPs) over the wide temperature range were
54 fitted directly to the Debye equation (Debye model fitting). This least-squares fitting is
55 performed including zero-point motion contribution in dynamic disorder component and
56 optimizes static disorder component and Debye temperature. It should be noted, therefore,
57 that the obtained static disorder component is not influenced by zero-point motion. Thus, the
58 Debye model fitting can more exactly determine static disorder component and Debye
59 temperature than the conventional method, i.e., the linear extrapolation of high-temperature
60 MSDs to 0 K. To extract still more reliable static disorder components by the Debye model
61 fitting, we paid special attention to the measurements of diffraction intensities and the
62 procedure for structure refinements as follows: (1) all possible corrections for the effects
63 affecting diffraction intensities, including “thermal diffuse scattering effect”, were made; (2)
64 in the structure refinements, low-angle reflections with $(\sin\theta)/\lambda < 0.24 \text{ \AA}^{-1}$ were eliminated to
65 reduce the secondary extinction effects and to avoid dependence on atomic charge as far as
66 possible in the choice of atomic scattering factors; (3) the reflections affected by a multiple
67 scattering were also eliminated; (4) the data corrections at the 20 temperature-points were
68 performed including the measurements at the 6 temperature-points of $T > 700 \text{ K}$,
69 corresponding the Debye temperature of pyrope [698(16) K (Suzuki and Anderson 1983)].
70 The item (4) is especially important to still more exclude the influence of zero-point motion
71 on the determination of the static disorder components. Such more precise and careful
72 treatments revealed the presence of the significant static disorder components for all the
73 atoms (Mg, Al, Si and O), which agrees with the observation that these atoms have the

74 significantly non-zero higher-rank tensor coefficients at the low temperature. It is also
75 noteworthy that the average of the microscopic Debye temperatures for each atom determined
76 by the Debye model fitting [$\Theta_D = 731(1)$ K (Nakatsuka et al. 2011)] agrees well with the
77 macroscopic Debye temperatures of pyrope estimated from other properties such as
78 volumetric thermal expansion [$\Theta_D = 717(20)$ K (Nakatsuka et al. 2011), 698(16) K (Suzuki
79 and Anderson 1983)]. This indicates that the resulting microscopic Θ_D values, related to the
80 slope of MSD vs. T curve, are reliable and hence the resulting static disorder components are
81 temperature-independent. Thus, the resulting static disorder components are not influenced by
82 the dynamic disorder such as zero-point motion. Recently, in the same way, we determined
83 the static disorder components of atoms in some vanadate garnet compounds and perovskite
84 compounds “without any possibility of static disorder”. The resulting values were zero within
85 error; thus, we confirmed the validity of the static disorder components determined by this
86 method. These researches will be published somewhere in the near future. Moreover, the fact
87 that the displacement quantity between the 24c and the disordered Mg sites obtained from the
88 split-atom refinement agrees with the one estimated from the Mg static disorder components
89 (Nakatsuka et al. 2011) successfully explains the presence of the Mg static disorder.

90 To examine the model dependence of the determination of static disorder components,
91 we also performed the fitting of the equivalent isotropic displacement parameters U_{eq} to the
92 Einstein model, more drastic approximation than the Debye model. The static disorder
93 components obtained from this fitting are $1.38(10) \times 10^{-3} \text{ \AA}^2$ for Mg, $0.59(4) \times 10^{-3} \text{ \AA}^2$ for Al,
94 $0.62(6) \times 10^{-3} \text{ \AA}^2$ for Si and $0.47(5) \times 10^{-3} \text{ \AA}^2$ for O, and those from the Debye model fitting
95 [Table 4 in Nakatsuka et al. (2011)] are $1.43(10) \times 10^{-3} \text{ \AA}^2$ for Mg, $0.64(5) \times 10^{-3} \text{ \AA}^2$ for Al,
96 $0.68(6) \times 10^{-3} \text{ \AA}^2$ for Si and $0.57(4) \times 10^{-3} \text{ \AA}^2$ for O. No essential difference in the resulting
97 static disorder components could be found between the Debye and Einstein models, although
98 there is the large difference in the approximation of DOS (density of states) between both
99 models. This means that the difference in their approximation does not have an essential
100 influence on the extraction of the static disorder components. From the fact that the Debye

101 model agrees well with specific heats of various solids (especially in low- and
102 high-temperature regions), even if a perfect modeling of MSD were established, the obtained
103 static disorder components would little differ from those from the Debye model as seen
104 between the Einstein and Debye models.

105 The diffraction studies on the atomic displacements of pyrope were also reported in
106 Pavese et al. (1995) and Artioli et al. (1997), as cited also in Geiger (2012). These studies
107 tried the estimation of the static disorder components by the linear extrapolation of ADP data
108 to 0 K. However, these studies were based on a limited number of ADP data (4 points for the
109 former study; 6 points for the latter study), and moreover the number of data points above the
110 Debye temperature were only 2 points for the former study and only 3 points for the latter
111 study. In addition, their extrapolations were performed including the data down to much
112 lower temperatures than the Debye temperature; the static disorder components obtained by
113 this way could therefore include some zero-point motion contributions. Consequently, the
114 former study resulted in a large uncertainty of the extrapolated values to 0 K. The latter study
115 showed that the extrapolated values to 0 K were significantly positive in Mg and O atoms, but
116 the structure refinements based on possible split-atom models resulted in failure. Thus, their
117 claim that the Mg static disorder is unlikely is only because they failed to find its evidence.

118 From the above, it is clear that the Mg static disorder is present. In particular, we
119 successfully observed the residual electron density maxima due to the Mg static disorder as
120 the direct evidence. Geiger (2012) could not make any comments on this evidence. The
121 presence of static disorder is strongly suggested also for Al, Si and O atoms from their
122 significant static disorder components obtained by the Debye model fitting; the reason for this
123 was reasonably explained in terms of crystal chemistry (Nakatsuka et al. 2011). Meanwhile,
124 as shown in Figure 6 in Nakatsuka et al. (2011), we confirmed that Mg has the large
125 anisotropy of thermal vibration (dynamic disorder) even after removal of the static disorder
126 components; namely, the dynamic disorder components of Mg along its displacement
127 ellipsoid axes become larger in order of $[100] \ll [01\bar{1}] \ll [011]$. This may corresponds to

128 “dynamic disorder of the Mg cation within the plane given by Mg–O(4) bonds” stated by
129 Geiger (2012). We explained this large anisotropy of Mg based on the effect of Mg-Si
130 repulsion (Nakatsuka et al. 2011), in the connection with our previous studies (Nakatsuka et al.
131 2005, 2004, 2003, 1999a, 1999b, 1995; Yoshiasa et al. 1997). Thus, we agree with Geiger
132 (2012) in the point that Mg has the large anisotropy of thermal vibration, but disagree as to
133 whether the Mg static disorder exists or not.

134 In conclusion, the studies that claimed the absence of the Mg static disorder, such as
135 suggested by Geiger (2012), only failed to find evidence for the presence of the Mg static
136 disorder. We proved the presence of the Mg static disorder, together with its large anisotropy
137 of thermal vibration (Nakatsuka et al. 2011).

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