

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

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### INTRODUCTION

Geiger (2013) argues that the large mean square displacement (MSD) of Mg in the dodecahedral site in pyrope, Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, originates from the dynamic disorder of Mg due to its large anisotropic thermal vibration, including anharmonic contribution, and refutes our findings that the Mg static disorder is present. His argument is based on the diffraction, spectroscopic, thermodynamic, and computational studies made mainly by him and his co-workers. However, these investigations only suggested the large anisotropy of the Mg thermal vibration, and do not necessarily prove that there is no Mg static disorder. What we must obtain is conclusive experimental proof as to whether the Mg static disorder exists or not. In the present paper, a reply to his comment (Geiger 2013), we discuss the validity of our findings (Nakatsuka et al. 2011).

### DISCUSSION

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

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

dependence below at least 800 K, where a sign of the anharmonic contribution to atomic thermal vibrations begins to appear (Fig. 10 in Nakatsuka et al. 2011). It should be noted from this point of view that the residual electron density maxima observed in Figure 7 in Nakatsuka et al. (2011) almost entirely disappeared in the difference Fourier map after the anharmonic refinement (Fig. 11 in Nakatsuka et al. 2011). The maxima should thus be due to the Mg static disorder, and indeed the split-atom model refinements successfully fitted the maxima as described above.

In Nakatsuka et al. (2011), MSDs (or ADPs) over the wide temperature range were fitted directly to the Debye equation (Debye model fitting). This least-squares fitting is performed including the zero-point motion contribution for the dynamic disorder component and optimizes the static disorder component and the Debye temperature. It should be noted, therefore, that the obtained static disorder component is not influenced by zero-point motion. Thus, the Debye model fitting can more exactly determine static disorder component and Debye temperature than the conventional method, i.e., the linear extrapolation of high-temperature MSDs to 0 K. To extract still more reliable static disorder components by the Debye model fitting, we paid special attention to the measurements of diffraction intensities and the procedure for structure refinements as follows: (1) all possible corrections for the effects affecting diffraction intensities, including “thermal diffuse scattering effect,” were made; (2) in the structure refinements, low-angle reflections with  $(\sin\theta)/\lambda < 0.24 \text{ \AA}^{-1}$  were eliminated to reduce the secondary extinction effects and to avoid dependence on atomic charge as far as possible in the choice of atomic scattering factors; (3) the reflections affected by multiple scattering were also eliminated; and (4) data corrections at the 20 temperature-points were performed including the measurements at the 6 temperature-points of  $T > 700 \text{ K}$ , corresponding to the Debye temperature of pyrope [698(16) K (Suzuki and Anderson 1983)]. Item 4 is especially important to further exclude the influence of zero-point motion on the determination of the static disorder components. This very precise and careful treatment revealed the presence of significant static disorder components for all the atoms (Mg, Al, Si, and O), which agrees with the observation that these atoms have significant non-zero higher-rank tensor coefficients even at low temperature. It is also noteworthy that the average of the microscopic Debye temperatures for each atom determined by the Debye model fitting [ $\Theta_D = 731(1) \text{ K}$  (Nakatsuka et al. 2011)] agrees well with the macroscopic Debye temperatures of pyrope

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estimated from other properties such as volumetric thermal expansion [ $\Theta_D = 717(20)$  K (Nakatsuka et al. 2011),  $698(16)$  K (Suzuki and Anderson 1983)]. This indicates that the resulting microscopic  $\Theta_D$  values, related to the slope of MSD vs.  $T$  curve, are reliable and hence the resulting static disorder components are temperature-independent. Thus, the resulting static disorder components are not influenced by the dynamic disorder such as zero-point motion. Recently, in the same way, we determined static disorder components of atoms in some vanadate garnet compounds and perovskite compounds “without any possibility of static disorder.” The resulting values were zero within error; thus, we confirmed the validity of the static disorder components determined by this method. These results will be published somewhere in the near future. Moreover, the fact that the displacement quantity between the  $24c$  and the disordered Mg sites obtained from the split-atom refinement agrees with the one estimated from the Mg static disorder components (Nakatsuka et al. 2011) successfully explains the presence of the Mg static disorder.

To examine the model dependence of the determination of static disorder components, we also performed the fitting of the equivalent isotropic displacement parameters  $U_{eq}$  to the Einstein model, a more drastic approximation than the Debye model. The static disorder 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,  $0.62(6) \times 10^{-3} \text{ \AA}^2$  for Si, and  $0.47(5) \times 10^{-3} \text{ \AA}^2$  for O, and those from the Debye model fitting (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,  $0.68(6) \times 10^{-3} \text{ \AA}^2$  for Si, and  $0.57(4) \times 10^{-3} \text{ \AA}^2$  for O. No essential difference in the resulting static disorder components could be found between the Debye and Einstein models, although there is the large difference in the approximation of density of states (DOS) between both models. This means that the difference in their approximation does not have an essential influence on the extraction of the static disorder components. From the fact that the Debye model agrees well with specific heats of various solids (especially in low- and high-temperature regions), even if a perfect modeling of MSD were established, the obtained static disorder components would differ little from those from the Debye model as seen between the Einstein and Debye models.

The diffraction studies on the atomic displacements of pyrope were also reported in Pavese et al. (1995) and Artioli et al. (1997), as cited also in Geiger (2013). These studies tried the estimation of the static disorder components by the linear extrapolation of ADP data to 0 K. However, these studies were based on a limited number of ADP data (4 points for the former study; 6 points for the latter study), and moreover the number of data points above the Debye temperature were only 2 points for the former study and only 3 points for the latter study. In addition, their extrapolations were performed including the data down to much lower temperatures than the Debye temperature; the static disorder components obtained by this way could therefore include some zero-point motion contributions. Consequently, the former study resulted in a large uncertainty of the extrapolated values to 0 K. The latter study showed that the extrapolated values to 0 K were significantly positive in Mg and O atoms, but the structure refinements based on possible split-atom models resulted in failure. Thus, their claim that the Mg static disorder is unlikely is only because they failed to find its evidence.

From the above, it is clear that the Mg static disorder is present. In particular, we successfully observed the residual electron density maxima due to the Mg static disorder as the direct evidence. Geiger (2013) could not make any comments on this evidence. The presence of static disorder is strongly suggested also for Al, Si, and O atoms from their significant static disorder components obtained by the Debye model fitting; the reason for this was reasonably explained in terms of crystal chemistry (Nakatsuka et al. 2011). Meanwhile, as shown in Figure 6 in Nakatsuka et al. (2011), we confirmed that Mg has the large anisotropy of thermal vibration (dynamic disorder) even after removal of the static disorder components; namely, the dynamic disorder components of Mg along its displacement ellipsoid axes become larger in order of  $[100] \ll [01\bar{1}] \ll [011]$ . This may correspond to “dynamic disorder of the Mg cation within the plane given by Mg-O4 bonds” stated by Geiger (2013). We explained this large anisotropy of Mg based on the effect of Mg-Si repulsion (Nakatsuka et al. 2011), in the connection with our previous studies (Nakatsuka et al. 2005, 2004, 2003, 1999a, 1999b, 1995; Yoshiasa et al. 1997). Thus, we agree with Geiger (2013) in the point that Mg has the large anisotropy of thermal vibration, but disagree as to whether the Mg static disorder exists or not.

In conclusion, the studies that claimed the absence of the Mg static disorder, such as suggested by Geiger (2013), only failed to find evidence for the presence of the Mg static disorder. We proved the presence of the Mg static disorder, together with its large anisotropy of thermal vibration (Nakatsuka et al. 2011).

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