Symmetry and Its Change in Reciprocal Space of a Crystal Simulated by Molecular Dynamics: Application to Quartz

AKIRA MIYAKE,[a]* HIROYUKI HASEGAWA,[a] KATSUYUKI KAWAMURA[b] AND MASAO KITAMURA[a]

[a]*Department of Geology and Mineralogy, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-01, Japan, and* [b]*Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152, Japan. E-mail: miya@mine.kueps.kyoto-u.ac.jp*

Abstract

The Fourier transformation to calculate structure factors was applied to a crystal simulated by the molecular-dynamics (MD) method to clarify crystallographic symmetry (point group and space group) of the crystal and its change during phase transition. The crystal symmetry and phase transition of quartz as a trial material were studied. The behavior of structure factors in reciprocal space, such as systematic extinction, shows that a MD-simulated crystal of quartz has the same symmetry and it changes during the phase transition as a real crystal. The present study clearly shows that the symmetry change of the arrangement of Si and O atoms occurs simultaneously at the phase transition.

1. Introduction

The molecular-dynamics (MD) simulation using appropriate interatomic potentials between two atoms has been widely used for investigating the physical properties of materials and in particular the structures of crystals, liquids and gases. The primary information given by MD simulation is the positions and the velocities of atoms as a function of time. The accuracy of any MD calculation depends mainly on the accuracy of the interatomic potential models, which can be justified by reproducibility of cell parameters, atomic coordinates and the physical properties of real crystals. The crystal symmetry and phase transition of a MD-simulated crystal have been compared with those of real crystals using atomic trajectories or mean atomic positions in real space (*e.g.* Tsuneyuki *et al.*, 1990; Matsui & Price, 1992; Yamahara *et al.*, 1995).

On the other hand, the symmetry and atomic arrangements of crystal structures of real crystals can be determined using methods such as X-ray diffraction. Phase transitions of real crystals have also been studied extensively using data from diffraction methods. Structure factors in reciprocal space change only by the relative displacement of atoms that changes the length and direction of vectors connecting atoms. The diffraction patterns calculated from a MD-simulated crystal can, therefore, give clearer information about the relative displacement of atoms than conventional diagrams of trajectories including all kinds of atomic movement in real space. Therefore, crystal symmetry and phase transitions can be discussed by comparing the diffraction patterns obtained from MD-simulated crystals with those of real crystals in a more direct manner than the usual procedures, such as the comparison of mean atomic positions in real space.

In the present study, accordingly, a computer program to calculate the Fourier transform of atomic positions of a MD-simulated crystal was developed and the crystal symmetry and phase transition of a MD-simulated crystal were studied in reciprocal space. Quartz (SiO_2) was selected as a trial material among minerals whose crystal structure and phase transition have been studied extensively. Quartz transforms from the low-temperature form (α-quartz, point group 32 and space group $P3_121$ or $P3_221$) to the high-temperature form (β-quartz, point group 622 and space group $P6_222$ or $P6_422$) at around 864 K under atmospheric pressure. The crystal structures of both α- and β-quartz and the transition between them have been studied in detail by X-ray diffraction methods (*e.g.* Wright & Lehmann, 1981; Zarka *et al.*, 1988; Kihara, 1990, 1993) and by MD simulations (Tsuneyuki *et al.*, 1990). The change of structure factors calculated from the Fourier transform of MD-simulated quartz will be described and discussed in relation to the phase transition in the present study.

2. MD simulation and structure-factor calculation

2.1. MD simulation

In the present MD simulation of the crystal structure of quartz, we employed an interatomic potential model, where the interatomic potential function (Φ_{ij}) between two atoms (i, j) consists of the Coulombic, the short-range repulsion, the van der Waals attraction and the

Table 1. *Potential parameters used in the present MD simulation*

Ion	z (e)	a (Å)	b (Å)	c ($kJ^{0.5}$ $Å^3$ $mol^{0.5}$)	Ion pair	D (kJ mol^{-1})	β ($Å^{-1}$)	r^* (Å)
O	−1.2	1.926	0.160	40.92	Si–O	17.7	2.0	1.510
Si	2.4	0.945	0.090	0.0	Others	0.0	0.0	0.0

Table 2. *Cell parameters of quartz obtained by an X-ray diffraction method (Wright & Lehmann, 1981) and by the present MD simulation at 300 K, 1 atm*

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	ρ (g cm^{-3})
X-ray diffraction	4.9134	4.9134	5.4052	90.00	90.00	120.00	2.6489
MD simulation	4.9362	4.9372	5.4118	89.99	90.02	119.97	2.6200

Morse potential terms, as given by

$$\Phi_{ij}(r_{ij}) = z_i z_j e^2 / r_{ij} + f_0 (b_i + b_j)$$
$$\times \exp(a_i + a_j - r_{ij}/b_i + b_j) - c_i c_j / r_{ij}^6$$
$$+ D_{ij} \{ \exp[-2\beta_{ij}(r_{ij} - r_{ij}^*)]$$
$$- 2 \exp[-\beta_{ij}(r_{ij} - r_{ij}^*)] \}, \qquad (1)$$

where r_{ij} is an interatomic distance, f_0 (= 6.9511 × 10^{-11} N) a constant, e the electronic charge, z, a, b and c parameters for each atomic species, and D_{ij}, β_{ij} and r_{ij}^* parameters for cation–anion pairs. These parameters were newly determined by trial-and-error procedures based on the published data (Kawamura, 1992). The electrostatic valences of the ions, z, were then chosen to be 60% of the full charges and the Morse term was applied only to Si–O pairs. The parameters used in the present study are shown in Table 1.

MD simulations were carried out by using a MD program (*MXDTRICL*) produced by one of the authors (Kawamura, 1993). The Ewald method was applied for the summations of Coulombic interactions. Integration of motions of ions was carried out using Verlet's algorithm (Δt = 2.0 fs). Temperature and pressure were controlled by scaling particle velocities and simulation of the cell parameters, respectively. In this study, a temperature range of 300–1000 K was investigated, while pressure was kept around 1 atm throughout the MD calculations. The unit cell used in the present MD calculation (MD cell) is a parallelepiped but has a similar shape to a hexagonal cell ($a_{MD} \approx b_{MD}$, $\alpha \approx \beta \approx$ 90° and $\gamma \approx$ 120°) and the number of atoms in the system is 576 (containing 64 crystallographic unit cells of quartz; $a_{MD} = 4a_{Qz}$, $b_{MD} =$ $4a_{Qz}$, $c_{MD} = 4c_{Qz}$). Starting from the atomic positions of α-quartz experimentally determined by Wright & Lehmann (1981), a MD-simulated crystal of quartz was annealed for 20 ps (10 000 steps) at 300 K so as to obtain an equilibrium atomic configuration at the particular temperature. This MD-simulated crystal was also used as a starting MD-simulated crystal for further MD calculations at all other temperatures. After raising the temperature of the system to the required level, the resulting MD-simulated crystal was 'annealed' for at

least 20 ps (10 000 steps) to obtain an equilibrium atomic configuration. After attaining equilibration, a production run of 10 ps (5000 steps) was performed and various properties and atomic positions were then evaluated.

2.2. Calculation of structure factors of a MD-simulated crystal

The structure factor of real crystals is defined by using coordinates of atoms in a unit cell. Because a periodic boundary condition is employed in MD calculations, atomic arrangements in a MD-simulated crystal repeat regularly with the period of the MD cell. Structure factors of a MD-simulated crystal, $F_{MD}(h_{MD}, k_{MD}, l_{MD})$ are, therefore, calculated by taking a MD cell as the basic cell. Since the MD cell in the present study has cell edges four times larger than the unit cell of the real crystal, the indices h, k and l of a real crystal correspond to $4h_{MD}$, $4k_{MD}$ and $4l_{MD}$, respectively. In the following, $F_{MD}(4h_{MD}, 4k_{MD}, 4l_{MD})$ is expressed as $F_{MD}(hkl)$ for simplicity. In the calculation of structure factors, we used the atomic scattering factors of O^{1-} and Si^{4+} (Maslen *et al.*, 1992).

The structure factors of a real crystal that are observed in diffraction experiments are space and time averaged. The MD basic cell is, in contrast, at most 2 or 3 nm in diameter and therefore too small to calculate a space average. If an average was taken over a sufficiently long time, the system would go through all possible states and in some cases the time average can be considered equivalent to the space average. If this assumption is adequate, each structure factor would converge to a constant value with an increase of sampling number. To verify this hypothesis, the change of structure factors with sampling number was examined as described below. In the present study, $\langle x \rangle$ denotes the time average of x. Thus, $|\langle F_{MD}(hkl) \rangle|$ denotes the absolute value of time-averaged $F_{MD}(hkl)$ and $\langle |F_{MD}(hkl)| \rangle$ the time average of structure amplitude $|F_{MD}(hkl)|$, respectively.

Calculated cell parameters and atomic positions fluctuate with changing number of MD steps under any given temperature and pressure, even after annealing of

10^4 steps. To obtain the time averages of cell parameters and structure factors, we first examined how many steps were required for these values to become constant. The interval of sampling was fixed at every 25 MD steps (50 fs) after annealing. Cell parameters oscillated significantly for small sampling numbers (<60) and then became stable and almost constant. Changes in $|\langle F_{MD}(hkl)\rangle|$ with sampling number showed similar behavior to the change of cell parameters. In the present study, time averages over 200 samples (corresponding to 5 ps) were used for cell parameters, structure factors and other physical properties of a MD-simulated crystal of quartz.

3. Results and discussion

3.1. Cell parameters of a MD-simulated quartz crystal

Cell parameters derived from the present MD calculation at 300 K are compared with those determined by an X-ray diffraction method (Table 2). For this calculation, we employ a parallelepiped MD cell and do not impose trigonal symmetry on the MD-simulated crystal. The lengths of a_1 and a_2 axes are therefore not exactly equal to each other and the angles among crystallographic axes are not fixed in the calculation. As seen in Table 2, the cell parameters at 300 K show a good agreement with those of a real crystal. Temperature dependency of the length of the a axis by MD calculation is then compared with that of quartz measured by an X-ray single-crystal method (Kihara, 1990) (Fig. 1). With increasing temperature, the length of the a axis by the MD calculation increases gradually up to 780 K and abruptly at 780 K, and then becomes almost constant above around 800 K. This tendency is similar to that of a real quartz crystal measured by an

X-ray method. The transition temperatures (T_c) from α- to β-quartz of a real crystal and a MD-simulated crystal are estimated based on the abrupt change of the cell parameters at 846 and 780 K, respectively, with a difference of only 66 K between these two T_c's.

3.2. Translation symmetry of a MD-simulated quartz crystal

To elucidate the relationship between the periodic atomic arrangements of real and MD-simulated crystals, the structure factors of a MD-simulated crystal with indices other than $h = 4h_{MD}$, $k = 4k_{MD}$, $l = 4l_{MD}$ are examined. The result shows that all of these time-averaged structure factors are actually zero. This fact suggests that the atomic arrangements of the MD-simulated crystal repeats with periods of $a_{MD}/4$, $b_{MD}/4$ and $c_{MD}/4$, i.e. the length of the unit cell of the real crystal, and therefore that the MD cell in the present study is large enough to study the crystal structure of a real quartz crystal. In the following, only structure factors with indices of hkl, $|\langle F_{MD}(hkl)\rangle|$, are compared with those of a real crystal. Intensities of a MD-simulated crystal, $I_{MD}(hkl)$, at 500 K are compared with those of a real crystal, $I_{obs}(hkl)$, observed by the X-ray single-crystal method (Kihara, 1990, 1997) in Fig. 2. As seen in the figure, with increasing value of $I_{MD}(hkl)$, the ratio of $I_{MD}(hkl)/I_{obs}(hkl)$ tends to increase. This nonlinearity can be explained by an extinction effect expressed approximately by

$$I_{obs}(hkl) = I_{MD}(hkl)/\{k + (a/\mu)I_{MD}(hkl)\},$$

where k is the scaling factor, a a constant, and μ the absorption factor. The least-squares fitting of the data gives $k = 4.4 \times 10^{-3}$ and $a/\mu = 7.0 \times 10^{-6}$ (Fig. 2).

The temperature dependence of $I_{obs}(hkl)$ has been measured by a single-crystal X-ray diffraction method
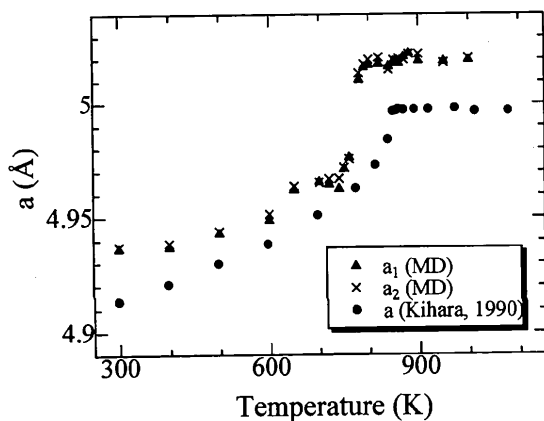

Fig. 1. Length of the a axis of a real quartz and a MD-simulated crystal at different temperatures. The transition temperatures of a real quartz and a MD-simulated crystal are estimated to be 840 and 780 K, respectively. Solid triangles and crosses represent the length of the a_1 and a_2 axes of a MD-simulated crystal, respectively. Solid circles represent the length of the a axis of a real quartz measured by Kihara (1990).
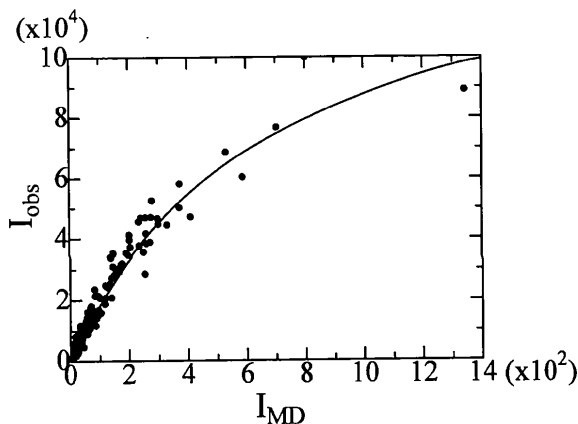

Fig. 2. Intensities of a MD-simulated crystal, $I_{MD}(hkl)$, are plotted against those of a real crystal, $I_{obs}(hkl)$, at 500 K. The correlation between them can be explained by an extinction effect. The least-squares fitting of all data gives $I_{obs}(hkl) = I_{MD}(hkl)/\{4.4 \times 10^{-3} + 7.0 \times 10^{-6}I_{MD}(hkl)\}$ with the correlation $|r| = 0.98$.

(Kihara, 1997). As an example, the values of $I_{MD}(003)$ are compared in Fig. 3 with that of experimental $I_{obs}(003)$ (Kihara, 1997) after correction for the extinction effect mentioned above. The value of $I_{MD}(003)$ decreases up to the transition temperature of 780 K, estimated from the abrupt change of the cell parameters. Above this temperature, $I_{MD}(003)$ is almost constant with increasing temperature. This tendency and the absolute value show good agreement with those of a real quartz crystal. The good correlation between two kinds of intensities (Figs. 2 and 3) gives a basis for further discussion of crystal symmetry and phase transition by using structure factors of a MD-simulated quartz crystal.

3.3. Crystal symmetry and structure factors of a MD-simulated crystal

The phase-transition temperature of a MD-simulated crystal has been estimated by the change of cell parameters and the symmetry of the crystal has been determined by using the trajectory of atomic positions in real space [e.g. quartz: Tsuneyuki et al. (1990); zeolite: Yamahara et al. (1995)]. In the present study, the transition temperature and crystal symmetry were also estimated based on the change of structure factors and symmetry in reciprocal space as described below.

Space groups of α- and β-quartz are $P3_121/P3_221$ and $P6_222/P6_422$, respectively. The extinction rules of both phases are the same: conditions for possible reflections are no restrictions for hkl and $l = 3n$ for $00l$ reflections, except for an extinction rule for the special positions of the Si atom in β-quartz. Calculation of structure factors of a MD-simulated crystal shows that $|\langle F_{MD}(003)\rangle|$ and $|\langle F_{MD}(006)\rangle|$ are more than 3 but all of $|\langle F_{MD}(00l)\rangle|$ with $l \neq 3n$ are less than 0.01 at every temperature (from 300 to 1000 K), which is consistent with the extinction rule described above. The systematic absences of $00l$ with $l \neq 3n$ then suggest the existence of 3_1 (or 3_2) or 6_2 (or 6_4) in the present MD-simulated quartz.

In order to distinguish 3_1 (or 3_2) from 6_2 (or 6_4) in reciprocal space, the amplitudes of structure factors (or Laue symmetry) and the phase differences among structure factors must be examined. The space group of α-quartz is $P3_121$ or $P3_221$, and therefore three structure factors with indices of hkl, $-h-k,h,l$ and $k,-h-k,l$ are symmetrically equivalent. These structure factors have a phase difference of $2n/3$: $F(-h-k,h,l) = F(hkl)\exp(2\pi l/3)$ and $F(k,-h-k,l) = F(hkl)\exp(-2\pi l/3)$. In addition, because of a screw axis of 3_1 or 3_2, a structure factor with indices of hkl is not crystallographically equivalent to that with indices of $-h,-k,l$, that is, these two structure factors have different amplitudes and phase differences. Similarly, β-quartz with a space group of $P6_222$ or $P6_422$ has the same extinction rule and has the same relationship among three structure factors with indices of hkl,

$-h-k,h,l$ and $k,-h-k,l$ as α-quartz. In β-quartz, however, an (hkl) plane is crystallographically equivalent to a $(-h,-k,l)$ plane and then $F(hkl) = F(-h,-k,l)$ with no phase difference.

In order to check whether a MD-simulated quartz crystal has the symmetry relationships mentioned above, structure factors, $F_{MD}(hkl)$, are plotted in the Gaussian coordinates system. The behavior of structure factors changing with temperature can be divided into three types corresponding to below 760 K, above 800 K and in a temperature range between them. One of the examples is shown in Figs. 4(a)–(c), where $F_{MD}(012)$, $F_{MD}(1\bar{1}2)$, $F_{MD}(\bar{1}02)$, $F_{MD}(0\bar{1}2)$, $F_{MD}(\bar{1}12)$ and $F_{MD}(102)$ at 500, 780 and 900 K are plotted. $|\langle F_{MD}(012)\rangle - \langle F_{MD}(0\bar{1}2)\rangle|$ [defined as $\Delta F(012)$] is plotted against temperature in Fig. 4(d) because $\langle F_{MD}(012)\rangle$ is not equal to $\langle F_{MD}(0\bar{1}2)\rangle$ in α-quartz and $\langle F_{MD}(012)\rangle$ is exactly equal to $\langle F_{MD}(0\bar{1}2)\rangle$ in β-quartz as described above.

As seen in Fig. 4, some structure factors at every temperature have imaginary parts with nonzero values, indicating that both low- and high-temperature forms of a MD-simulated crystal have no center of symmetry. $\Delta F(012)$ decreases abruptly around 780 K and then becomes almost zero above 800 K. The transition temperature from α- to β-quartz of a MD-simulated crystal is estimated based on the abrupt change of $\Delta F(012)$ at 780 K, which is the same as those estimated from the cell parameters.

Below 780 K (Fig. 4c), there are two groups of structure factors: one group of $F_{MD}(012)$, $F_{MD}(1\bar{1}2)$ and $F_{MD}(\bar{1}02)$ and another group of $F_{MD}(0\bar{1}2)$, $F_{MD}(\bar{1}12)$ and $F_{MD}(102)$. Each group consists of three structure factors with the same amplitude and phase difference of $2\pi/3$ between them and has a phase difference of $\pi/2$ with another group. $\Delta F(012)$ is, therefore, not equal to zero (Fig. 4d). The behavior of the structure factors
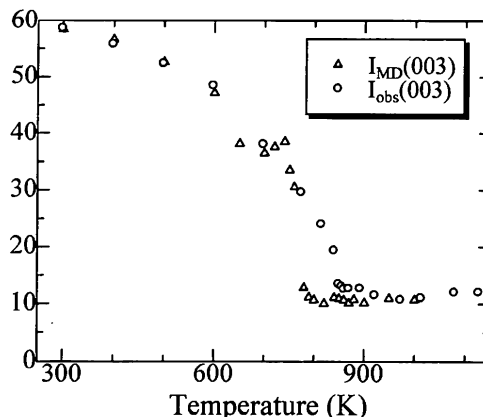

Fig. 3. Temperature variation of intensities of a real quartz crystal, $I_{obs}(003)$, observed by the X-ray single-crystal diffraction method (Kihara, 1990) and those of a MD-simulated crystal, $I_{MD}(003)$. $\triangle$: $I_{MD}(003)$; $\circ$: $I_{obs}(003)$.

indicates that a MD-simulated crystal must have 3_1 (or 3_2) along the c axis.

Above 800 K (Fig. 4a), the six structure factors have the same amplitude and are plotted in three regions with phase differences of $2\pi/3$. $F(hkl)$ and $F(-h, -k, l)$ are plotted in the same region in this temperature range, while they are plotted in different regions below 780 K. $\Delta F(012)$ is, therefore, equal to zero (Fig. 4d). The distribution of structure factors indicates that a MD-simulated crystal has 6_2 (or 6_4) along the c axis of β-quartz.

Based on the behavior of structure factors as described above, it can be concluded that the transition temperature is 780 K and the space groups of low- and high-temperature forms of MD-simulated quartz are confirmed as $P3_121/P3_221$ and $P6_222/P6_422$, respectively, as those of natural α- and β-quartz.

In the intermediate temperature range (Fig. 4b), the six structure factors are plotted in three elongated regions. To investigate the fluctuation of structure factors in the elongated regions, we calculated for a further 50 000 steps (120 ps) at 780 K and the temporal variations of the real part of the structure factors of $F_{MD}(012)$ and $F_{MD}(0\bar{1}2)$, whose imaginary parts are almost zero, are given in Fig. 5. The vibration of the real part of $F_{MD}(012)$ defined as Re(012) synchronizes with the vibration of the real part of $F_{MD}(0\bar{1}2)$ defined as Re(0$\bar{1}$2). In the range from 10 000 (20 ps) to 35 000 (70 ps) steps, Re(012) takes a negative value around -5; at the same time, Re(0$\bar{1}$2) takes a positive value around 13. After about 5000 steps [from 40 000 (80 ps) to 50 000 (100 ps) steps], Re(012) takes the positive value, whereas Re(0$\bar{1}$2) takes the negative value. This shows that Re(012) and Re(0$\bar{1}$2) became interchanged with time, although no particular periodicity was
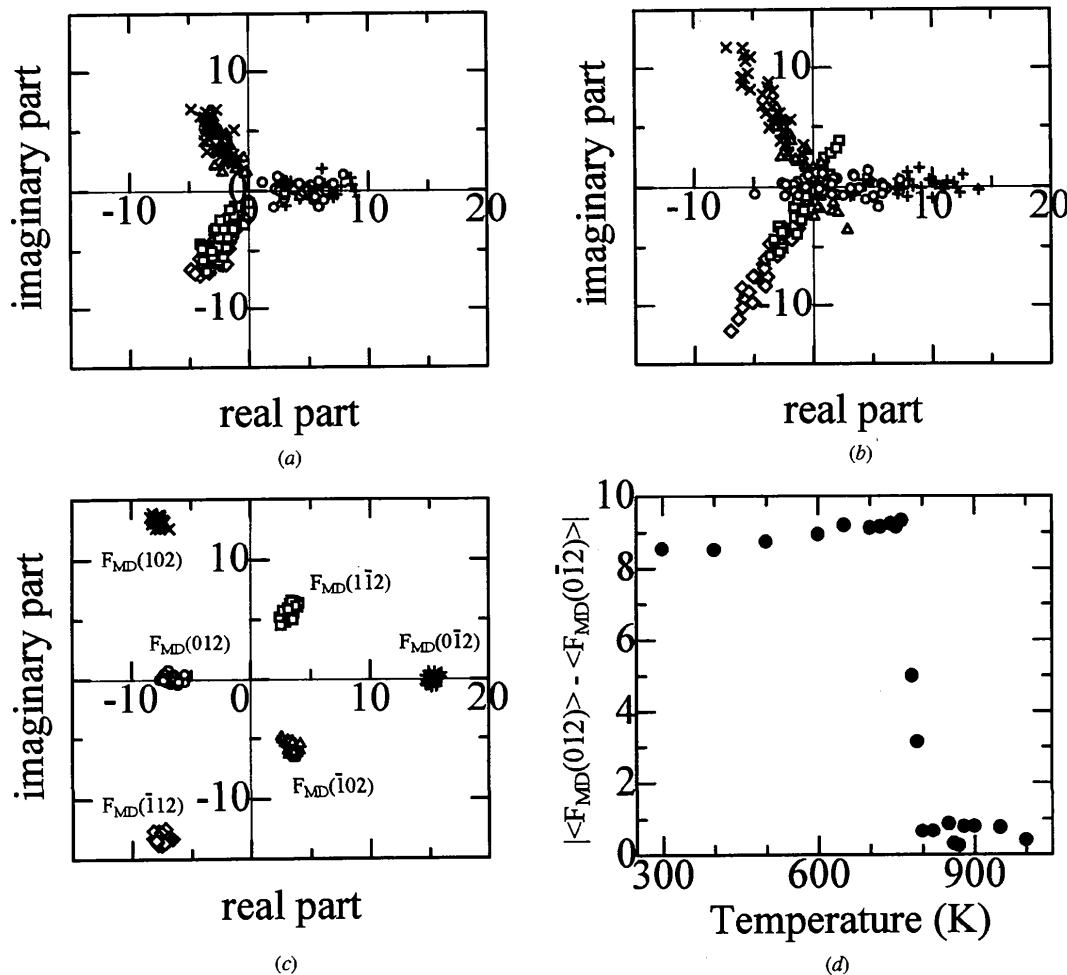

Fig. 4. Six structure factors, $F_{MD}(012)$, $F_{MD}(1\bar{1}2)$, $F_{MD}(\bar{1}02)$, $F_{MD}(0\bar{1}2)$, $F_{MD}(\bar{1}12)$ and $F_{MD}(102)$, plotted with the Gaussian coordinates, at (a) 900, (b) 780 and (c) 500 K. For clarity, every sixth sampling point of the data (33 samples) is plotted. $\Diamond$: $F_{MD}(\bar{1}12)$; $\square$: $F_{MD}(1\bar{1}2)$; $\triangle$: $F_{MD}(\bar{1}02)$; $\times$: $F_{MD}(102)$; $+$: $F_{MD}(0\bar{1}2)$; $\circ$: $F_{MD}(012)$. (d) Temperature dependence of the amplitudes of the structure factor, $|\langle F_{MD}(012)\rangle - \langle F_{MD}(0\bar{1}2)\rangle|$.

observed. In the present study, it is also confirmed by the behavior of the structure factors that the two states (α_1 and α_2) with the positive and negative values in Fig. 5 are related by a 180° rotation of the structure around the c axis, *i.e.* in the Dauphiné twin relationship, as reported by the previous study (Tsuneyuki *et al.*, 1990).

3.4. Behavior of Si and O atoms during phase transition

An arrangement of certain atoms in a crystal can have higher symmetry than the crystal symmetry. For instance, part of the constituent atoms preserves the arrangements with higher symmetry specific to a high-temperature form during phase transition, while the arrangements of the other atoms have the lower symmetry of its low-temperature form. Such behavior of the atoms during phase transition can be studied by the change of structure factors calculated only with definite atoms. Partial structure factors of the Si atoms, $F_{MD}^{Si}(hkl)$, and of the O atoms, $F_{MD}^{O}(hkl)$, were calculated with the atomic coordinates in a MD-simulated quartz crystal.

Space groups of the low- and high-temperature forms of MD-simulated quartz crystals are confirmed to be $P3_121/P3_221$ and $P6_222/P6_422$, respectively, as described above. Therefore, Si atoms at $(x,0,0)$ in α-quartz occupy the $3(c)$ positions $(\frac{1}{2},0,0)$ in β-quartz (Wright & Lehmann, 1981). Therefore, $F_{MD}^{Si}(hkl)$ in β-quartz satisfies an extinction rule ($h = 2n$, $k = 2n$ and $l = 3n$ for hkl reflections). One of the examples is shown in Fig. 6, where $F_{MD}^{Si}(222)$, $F_{MD}^{Si}(223)$ and $F_{MD}^{Si}(224)$ are plotted. Above 780 K (Fig. 6a), the averaged amplitudes of $F_{MD}^{Si}(222)$ and $F_{MD}^{Si}(224)$ are at the origin, while that of $F_{MD}^{Si}(223)$ remains far from the origin. This
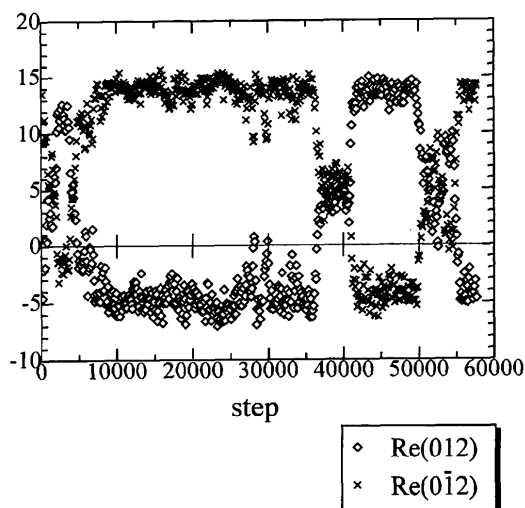
(a)

(b)

step

Re(012) ⋄
Re(01̄2) ×

Fig. 5. Temporal variation of the real part of the structure factors of $F_{MD}(012)$ and $F_{MD}(01\bar{2})$ [$Re_{MD}(012)$ and $Re_{MD}(01\bar{2})$] at 780 K. For clarity, every fourth sampling point of the data (576 samples) is plotted. ⋄: $Re_{MD}(012)$; ×: $Re_{MD}(01\bar{2})$.
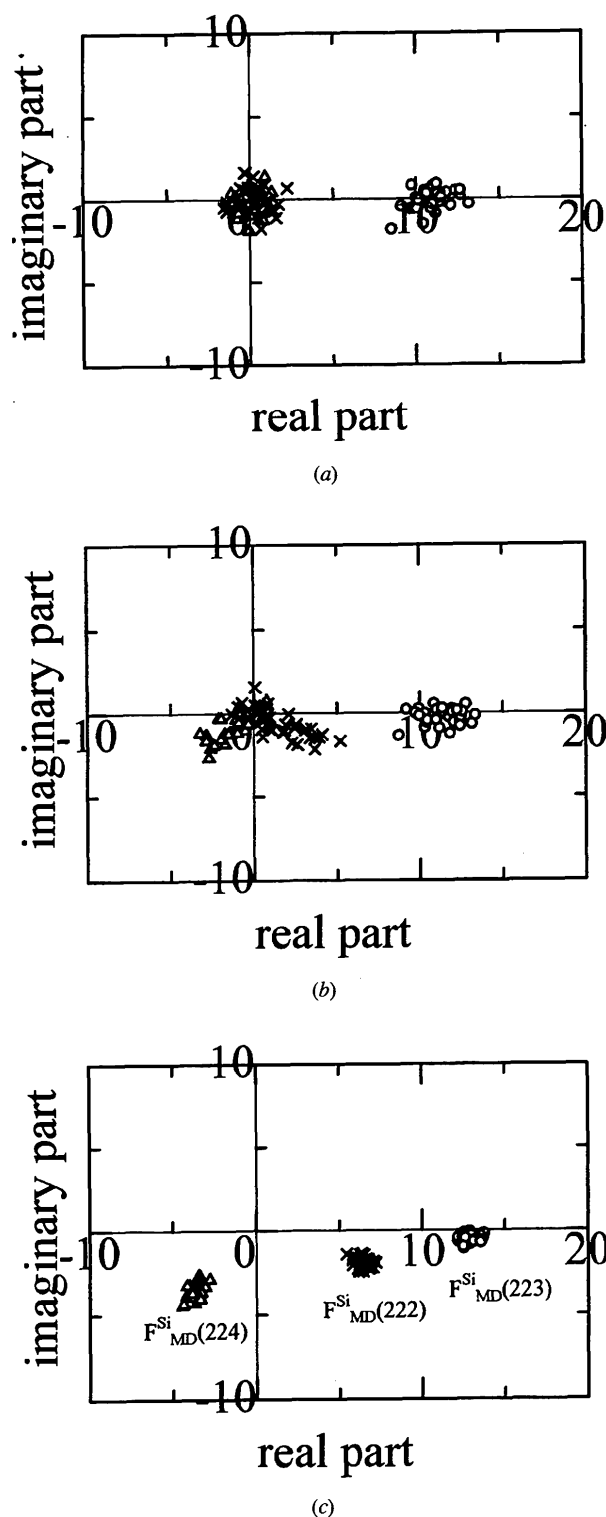
(c)

Fig. 6. Three structure factors, $F_{MD}^{Si}(222)$, $F_{MD}^{Si}(223)$ and $F_{MD}^{Si}(224)$, plotted with the Gaussian coordinates, at (a) 900, (b) 780 and (c) 500 K. For clarity, every sixth sampling point of the data (33 samples) is plotted. ◇: $F_{MD}^{Si}(224)$; o: $F_{MD}^{Si}(223)$; ×: $F_{MD}^{Si}(222)$.

suggest that Si atoms in β-quartz occupy the $3(c)$ position as expected.

On the other hand, Si atoms in α-quartz occupy the positions of $(x, 0, 0)$ even with $x = \frac{1}{2}$ without violating the space group $P3_121$. Below 780 K (Fig. 6c), none of the three structure factors are plotted on the origin and the extra extinction does not appear. This fact indicates that Si atoms occupy the position $(x, 0, 0)$ with $x \neq \frac{1}{2}$.
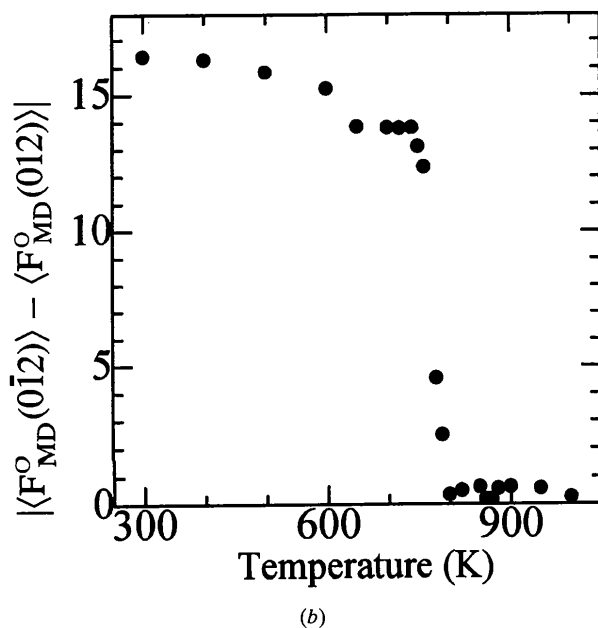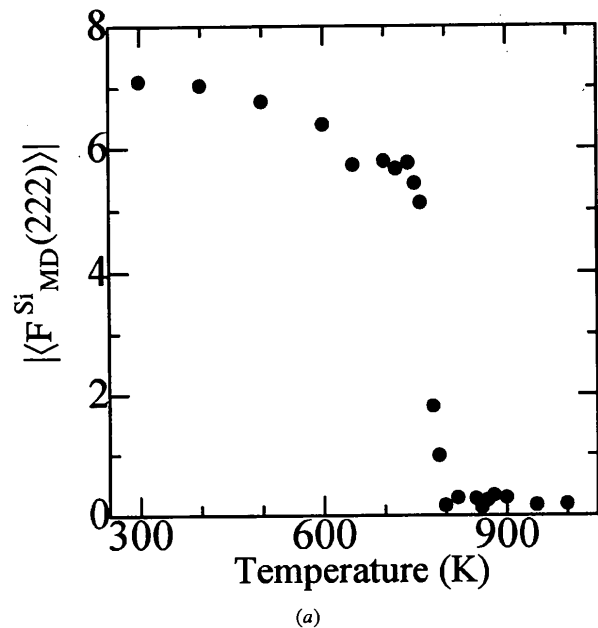

(a)

(b)

Fig. 7. Temperature dependence of the amplitudes of the structure factor, (a) $|\langle F_{MD}^{Si}(222)\rangle|$ and (b) $|\langle F_{MD}^{O}(012)\rangle - \langle F_{MD}^{O}(0\bar{1}2)\rangle|$. The abrupt decreases of the amplitudes occur simultaneously around the transition temperature of 780 K, indicating the simultaneous change of symmetry of the arrangements of Si and O atoms.

below 780 K. The change of $|\langle F_{MD}^{Si}(222)\rangle|$ is plotted against temperature in Fig. 7. As seen in the figure, the symmetry change of the arrangements of Si atoms occurs around the transition temperature of 780 K.

No extinction rules for O atoms are expected in the space groups of both the low- and high-temperature forms of quartz. However, it can be shown that the amplitudes of the difference between structure factors, $|\langle F_{MD}^{O}(012)\rangle - \langle F_{MD}^{O}(0\bar{1}2)\rangle|$, should be zero for the high-temperature form. The amplitudes are plotted against temperature in Fig. 7. The drastic change of the amplitude to zero is observed around the transition temperature, indicating the symmetry change of the arrangements of the O atoms. The symmetry change of the arrangements of Si and O atoms is, therefore, concluded to occur simultaneously at the phase transition. This fact suggests that the movement of atoms during the phase transition can be approximated to the movement of SiO_4 tetrahedra.

4. Concluding remarks

(i) A computer program was written for the Fourier transformation to calculate structure factors of a MD-simulated crystal. The details of symmetry of a MD-simulated crystal and its change can be studied by using this Fourier transformation method. In particular, symmetry changes of an arrangement of specific atoms during phase transitions can be studied in detail. Using this method, the symmetry (point group and space group) and its change in reciprocal space of quartz was studied in the present paper.

(ii) A MD-simulated crystal of quartz was shown to have the same crystal structures and symmetries as those of matural low- and high-temperature forms of quartz. Around the phase-transition temperature, the MD structure fluctuates temporarily between two states related by a 180° rotation of the structure around the c axis, i.e. in the Dauphiné twin relationship.

(iii) The symmetry change of arrangements of Si and O atoms in the MD-simulated crystal of quartz occurs simultaneously at the phase transition, suggesting that the movement of atoms during the phase transition can be approximated to the movement of SiO_4 tetrahedra.

References

Kawamura, K. (1992). *Molecular Dynamics Simulations*, edited by F. Yonezawa, pp. 88–97. *Springer Series in Solid-State Sciences* No. 103. Berlin: Springer-Verlag.

Kawamura, K. (1993). *MXDTRICL*. Japan Chemistry Program Exchange, No. 077.

Kihara, K. (1990). *Eur. J. Mineral.* **2**, 63–77.

Kihara, K. (1993). *Phys. Chem. Miner.* **19**, 492–501.

Kihara, K. (1997). Personal communications.

Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, Section 6.1.1. Dordrecht: Kluwer Academic Publishers.

Matsui, M. & Price, G. D. (1992). *Phys. Chem. Miner.* **18**, 365–372.

Tsuneyuki, S., Aoki, H., Tsukada, M. & Matsui, Y. (1990). *Phys. Rev. Lett.* **64**, 776–779.

Wright, A. F. & Lehmann, S. (1981). *J. Solid State Chem.* **36**, 371–380.

Yamahara, K., Okazaki, K. & Kawamura, K. (1995). *Catal. Today*, **23**, 397–402.

Zarka, A., Capelle, B. & Petit, M. (1988). *J. Appl. Cryst.* **21**, 72–73.