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Paper

Anisotropic Thermal Expansion and Phase Transition in $Sc_2(MoO_4)_3$

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$Sc_2(MoO_4)_3$の異方性熱膨張と相転移

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Lattice deformation in monoclinic $Sc_2(MoO_4)_3$, induced by both thermal expansion and phase transition, has been investigated by a matrix algebra analysis. From 4 K to 178 K, one of the principal distortions of the monoclinic lattice (λ_1) invariably showed a positive coefficient of thermal expansion, while the other two distortions λ_2 and λ_3 showed negative thermal expansion in the temperature region of $T<55$ K (λ_2) and $T<35$ K (λ_3). Because of the bidimensional shrinkage along the latter two axes, volumetric contraction occurred below 30 K. The λ_2-axis coincides with the crystallographic *b*-axis. The intersection angle between the λ_1-axis and the crystallographic *c*-axis was ~78.8° at 11 K, and it steadily decreased to ~20.1° with increasing temperature up to 178 K. The magnitude of lattice deformation nearly along [$\bar{3}02$] is negligibly small. Therefore, the lattice deformation induced by the monoclinic-to-orthorhombic phase transition at 178 K was accompanied essentially by bidimensional expansion along [010] and nearly along [$\bar{2}05$], the magnitudes of which are, respectively, ~0.6 and ~0.9%. [Received May 11, 2001; Accepted August 9, 2001]

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1. Introduction

When a crystal is uniformly heated, it homogeneously deforms and uniformly expands. Because the crystals, except for the cubic system, are anisotropic, the thermal deformation depends on direction. If the initial crystal is spherical in shape, the resulting crystal after heating will be ellipsoidal. There are three directions perpendicular to each other along which the expansion is, respectively, a maximum, intermediate or minimum.[1),2)] These three mutually perpendicular directions form the principal axes of the resulting ellipsoid.

With crystals belonging to the tetragonal, trigonal, hexagonal and orthorhombic systems, the principal axes of deformation are exactly parallel to the crystallographic axes. However, with crystals belonging to the monoclinic system, one of the principal axes is parallel to the monoclinic axis (*b*-axis for second setting), and the two others do not necessarily coincide with the crystallographic axes. Accordingly, the temperature dependence of the principal distortions would be indispensable for a comprehensive understanding of the thermal expansion behavior of monoclinic crystals. Both the magnitudes and directions of the principal distortions are readily determined from calculations based on matrix algebra analysis.[3),4)]

Several oxides have been recently reported to show negative, or very low, thermal expansion behavior.[5)-8)] Evans and Mary[5)] have investigated the thermal expansion and monoclinic-to-orthorhombic phase transition of $Sc_2(MoO_4)_3$ by diffractometry from 4 K to 300 K. Despite the great similarity of crystal structure between the two phases, the contributions of thermal expansion anisotropy have been in marked contrast to each other. Below 178 K $Sc_2(MoO_4)_3$ was monoclinic (space group $P2_1/a$). As long as the temperature was below 30 K, the monoclinic phase showed slight negative thermal expansion, while, above 30 K, it had a positive coefficient of thermal expansion. It underwent a displacive phase transition at 178 K and the resulting orthorhombic phase definitely had a negative coefficient of thermal expansion up to 300 K; the *a* and *c* parameters showed a negative coefficient of thermal expansion, and the *b* parameter showed a positive coefficient. The relative magnitudes of these coefficients were such that the bulk volume steadily shrinks with increasing temperature.

In the present study, the thermal deformation anisotropy of the monoclinic phase has been evaluated by matrix algebra analysis to determine the temperature dependence of the principal distortions. A similar analytical procedure (i.e., the phenomenological analysis as used in displacive phase transitions) has been applied to the monoclinic-to-orthorhombic phase transition. A close relationship has been demonstrated between the principal distortions induced by the thermal expansion and those by the phase transition.

2. Theory

2.1 Anisotropic thermal expansion in a monoclinic crystal

The initial monoclinic crystal at T_0 will be, when heated at higher temperature T, homogeneously distorted into the new monoclinic crystal. The homogeneous distortion is generally characterized by the existence of three mutually orthogonal directions known as the principal axes of distortion. They remain orthogonal to each other after the distortion. The directions and magnitudes of the principal distortions upon heating from T_0 to T are, respectively, the eigenvectors and eigenvalues (λ_i) of the following equation:[3),4)]

$$|\mathsf{G}(T)-\lambda_i^2\mathsf{G}(T_0)|=0 \qquad (1)$$

where G is the metrix for the monoclinic phase, which is given by

$$\mathsf{G}(T)=\begin{bmatrix} a_T^2 & 0 & a_Tc_T\cos\beta_T \\ 0 & b_T^2 & 0 \\ a_Tc_T\cos\beta_T & 0 & c_T^2 \end{bmatrix}$$

where a_T, b_T, c_T and β_T are the cell dimensions at T. In the orthonormal basis defined by the principal axes, the matrix (D), which represents the lattice deformation, takes the simple form as follows:

$$\mathsf{D}=\begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}.$$

2.2 Lattice deformation induced by the monoclinic-to-orthorhombic phase transition

We assume that, upon low-high transition, the monoclinic phase lattice is homogeneously distorted into the or-

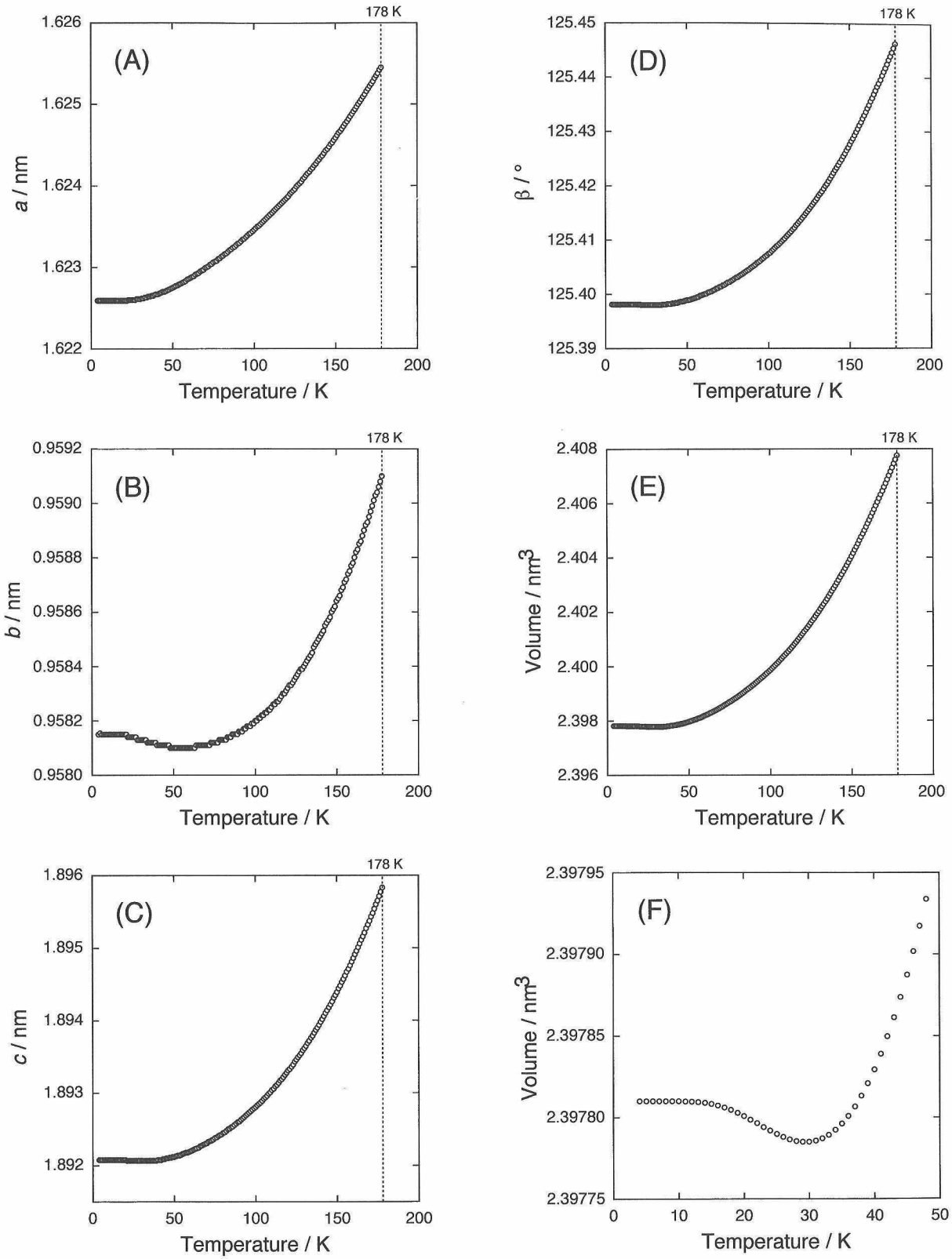

Fig. 1. Variation in unit-cell dimensions with temperature from 4 K to 178 K at 1 K intervals for monoclinic $Sc_2(MoO_4)_3$ [(A) a, (B) b, (C) c, (D) β, (E) volume, and (F) enlargement of a part of the figure (E)]. The volume shrinks below 30 K. The dimensions determined from calculation based on the regression analysis by Evans and Mary.[5]

thorhombic phase lattice. The magnitudes and directions of the principal distortions (ξ_i) are given by the eigenvalues and eigenvectors of the following equation:[9)-11)]

$$|(MC'O)(O^*GO)(OCM) - \xi_i^2(M^*GM)| = 0 \quad (2)$$

The matrix (OCM) represents the lattice correspondence between the monoclinic phase (M) and the orthorhombic phase (O). The matrix (MC'O) is the transpose of (OCM). The metrix (O*GO) is for the orthorhombic phase and that

of (M*GM) is for the monoclinic phase. Each metrix is determined from the individual cell dimensions at the transition temperature. In the orthonormal basis parallel to the principal axes, the lattice distortion matrix takes the simple form of a diagonal matrix, consisting of the three eigenvalues (ξ_1, ξ_2 and ξ_3).

3. Results and discussion

3.1 Change in cell dimensions of monoclinic $Sc_2(MoO_4)_3$ with temperature

Evans and Mary[5] determined the temperature dependence of the cell dimensions for monoclinic $Sc_2(MoO_4)_3$ from 4 K to 178 K. Based on the results of their regression analysis, we determined the cell dimensions by calculation at 1 K intervals, and plotted them as ordinate and the temperature as abscissa (Fig. 1). The *b*-axis showed negative thermal expansion below ~60 K, and the *a*- and *c*-axes showed a zero or positive coefficient of thermal expansion above 4 K. These are in fair agreement with the experimental results.[5]

Neither the magnitudes nor directions of the principal distortions, induced by thermal expansion, are currently available. Thus, it is still uncertain why the monoclinic phase was slightly negative below 30 K (Fig. 1(F)).

3.2 Principal distortions (λ_i) induced by thermal expansion in monoclinic $Sc_2(MoO_4)_3$

We have determined the directions and magnitudes of the principal distortions upon heating from 4 K up to 178 K by solving the Eq. (1). The magnitudes, together with the volume change V/V_{4K} ($=\lambda_1\lambda_2\lambda_3$), are plotted in Fig. 2. In the entire temperature ranges, the magnitudes of the principal distortions bore the relationship $\lambda_1>\lambda_3>\lambda_2$. The magnitude of λ_1 steadily increased with increasing temperature; the λ_1-axis invariably had a positive coefficient of thermal expansion. On the other hand, λ_3 as well as λ_2, the latter of which is parallel to the *b*-axis, showed negative thermal expansion in the temperature region of $T<35$ K for λ_3 and $T<55$ K for λ_2. The relative magnitudes of these principal distortions are such that the volume showed negative thermal expansion below 30 K.

Orthorhombic $Sc_2(MoO_4)_3$ exhibited bidimensional shrinkage with increasing temperature.[5] This would essentially lead to the contraction in volume. The volumetric contraction of monoclinic $Sc_2(MoO_4)_3$ below 30 K may be interpreted in the same way; the bidimensional shrinkage along λ_2 and λ_3 would be indispensable for the negative thermal expansion.

The λ_2-axis necessarily coincides with the crystallographic *b*-axis. The directions of λ_1 and λ_3 are simply represented by the acute angle $\lambda_1 \wedge c$ (Fig. 3). With increasing temperature from 11 K to 178 K, the angle steadily decreased from ~78.8° to ~20.1° (Fig. 4). For example with the lattice deformation at 178 K, the directions of the three principal distortions, which are expressed in the orthonormal basis defined by the unit vectors i, j and k, are given in Table 1.

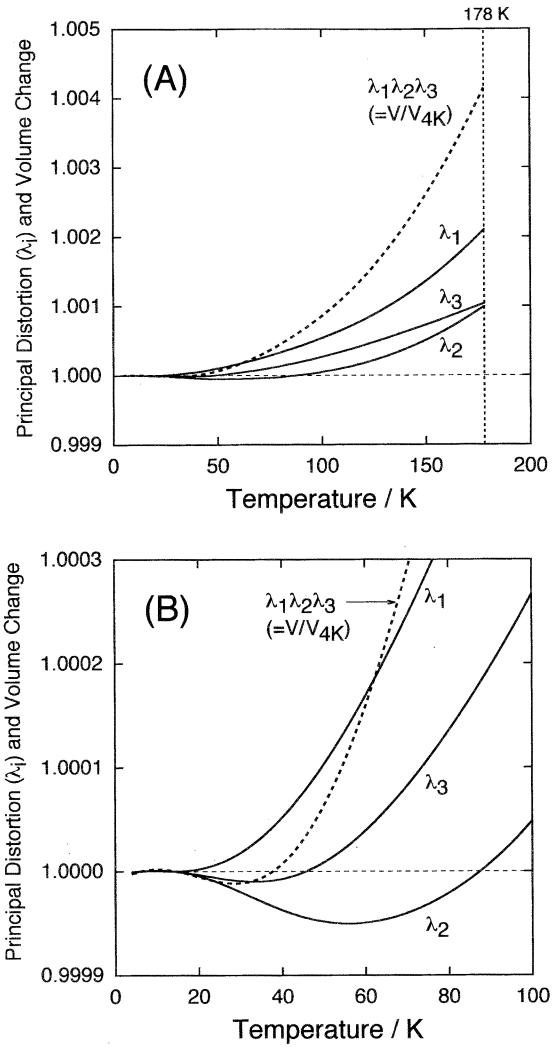

Fig. 2. Temperature dependence of principal distortions (λ_i) and volume change ($\lambda_1\lambda_2\lambda_3$). One of the distortions, λ_1, is almost invariably larger than unity, while the others, λ_2 and λ_3, are less than unity below ~88 K for the former and below ~45 K for the latter. The relative magnitudes of the three distortions are such that, due to the contraction in both λ_2 and λ_3, volumetric shrinkage occurs below ~30 K.

Table 1. Principal Distortions (λ_i) of Monoclinic $Sc_2(MoO_4)_3$ upon Heating from 4 to 178 K

λ_1	λ_2	λ_3
$\lvert\lambda_1\rvert = 1.0021$	$\lvert\lambda_2\rvert = 1.0010$	$\lvert\lambda_3\rvert = 1.0010$
$\lambda_1 = -0.3432\mathbf{i} + 0.9393\mathbf{k}$	$\lambda_2 = \mathbf{j}$	$\lambda_3 = -0.9393\mathbf{i} - 0.3432\mathbf{k}$

i, j and **k** are the unit vectors in the orthonormal basis defined by **i** ∥ a^*, **j** ∥ *b* and **k** ∥ *c*.

a, *b* and *c* are crystallographic axes of the monoclinic cell at 4 K.

λ_1, λ_2 and λ_3 are the unit vectors along the principal axes.

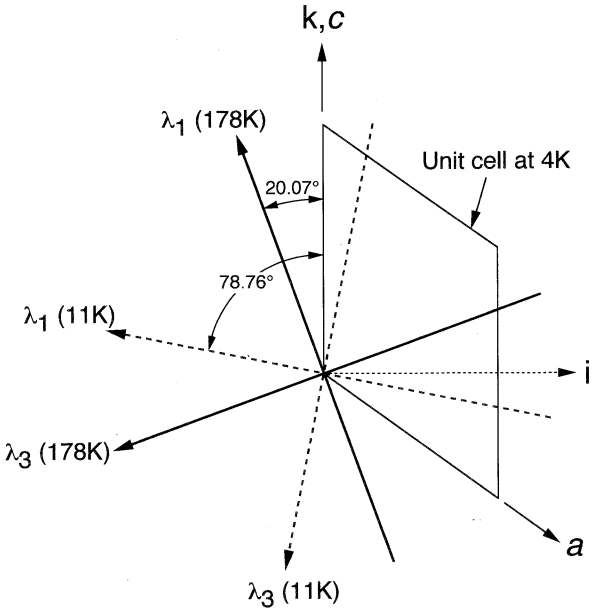

Fig. 3. Superposition of the principal axes λ_1 and λ_3 on the monoclinic unit cell at 4 K. The intersection angle $\lambda_1 \wedge c$ is used to define the orientation of λ_1 and λ_3. The λ_2-axis coincides with the *b*-axis. The λ_i(11 K) and λ_i(178 K) are the principal axes upon heating from 4 K to, respectively, 11 K and 178 K. The orthonormal basis defined by the unit vectors i (//a^*), j (//b) and k (//c).

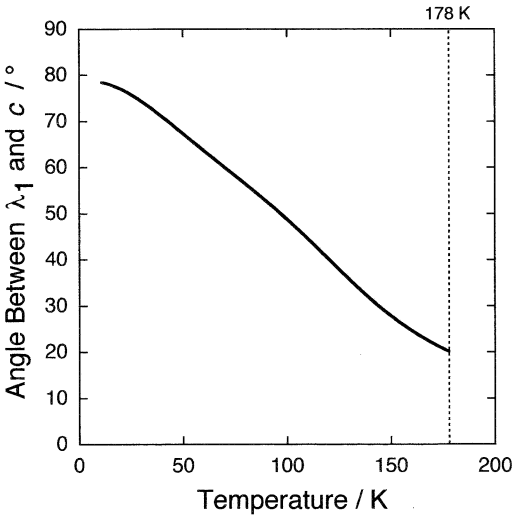

Fig. 4. Temperature dependence of the intersection angle $\lambda_1 \wedge c$, which defines the orientation of the principal axes λ_1 and λ_3. The angle steadily decreases from ~78.8° to ~20.1° with increasing temperature from 11 K to 178 K.

The magnitudes of the relevant principal distortions indicate that the initial lattice at 4 K expands in all directions when heated at 178 K. The maximum expansion of ~0.2% occurred along the λ_1-axis. Both expansion magnitudes along the other principal axes λ_2 and λ_3 were ~0.1%. During subsequent heating, the monoclinic-to-orthorhombic phase transition, as mentioned below, will immediately occur.

3.3 Principal distortions (ξ_i) induced by the monoclinic-to-orthorhombic phase transition

The cell parameters of the monoclinic phase at the transition temperature (178 K) are given in Table 2. With the orthorhombic phase, we have determined the cell parameters at 178 K by linear extrapolation; this calculation is based on the cell parameters at 200 K and the coefficients of linear thermal expansion along the *a*-, *b*- and *c*-axes, all of which are given by Evans and Mary.[5] The matrix representing the lattice correspondence between the two phases (OCM) is given by

$$(\mathrm{OCM}) = \begin{bmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 1 & 0 & \bar{2} \end{bmatrix}$$

Equation (2) has been solved with the cell parameters and the lattice correspondence to determine the magnitudes and directions of the three principal distortions (Table 3). One of the principal distortions ξ_3 was very close to unity, and the others were larger than unity. This implies that the lattice deformation upon low–high transition is such that, assuming $\xi_3 = 1$, bidimensional expansion essentially occurs along the ξ_1- and ξ_2-axes, the magnitudes of which are ~0.9% for the former and ~0.6% for the latter.

The direction of ξ_1, together with that of ξ_3, is superimposed on the schematic diagram of the monoclinic unit cell at 178 K (Fig. 5). The ξ_1-axis and *c*-axis intersect at an angle of ~12.60°. Thus, the directions of ξ_1 and ξ_3 are, respectively, nearly parallel to $[\bar{2}05]$ and $[\bar{3}0\bar{2}]$ of monoclinic $Sc_2(MoO_4)_3$ ($\xi_1 \wedge [\bar{2}05] = \sim 0.52°$ and $\xi_3 \wedge [\bar{3}0\bar{2}] = \sim 1.03°$). Since the lattice deformation along $[\bar{3}0\bar{2}]$ is negligibly small, the structural change before and after the transition could be clearly demonstrated by the atomic arrangements when viewed along $[\bar{3}0\bar{2}]$, which corresponds to [031] of the orthorhombic phase.

The monoclinic-to-orthorhombic phase transition occurs as the result of the thermal deformation of the monoclinic phase during heating. Comparing the principal distortions induced by the thermal expansion at 178 K (λ_i(178 K)) and those by the phase transition (ξ_i) shows there is little difference in orientation; the intersection angle between λ_1(178 K) and ξ_1 is only 7.47° (=20.07°−12.60°). In addition, the λ_1 (178 K) is, among the three distortions of λ_i(178 K), the largest in magnitude, and so is the ξ_1. Accordingly, it may be concluded that there is a close relationship in both magnitude and orientation between λ_i(178 K) and ξ_i. Detailed clarification of this relationship as well as of the negative thermal expansion mechanism is a subject for the future. In this respect, a comparative investigation of the monoclinic and orthorhombic structures at around 178 K would en-

Table 2. Cell Parameters of the Monoclinic and Orthorhombic $Sc_2(MoO_4)_3$ at 178 K

Crystal System	*a* (nm)	*b* (nm)	*c* (nm)	β (°)	Volume (nm^3)
Monoclinic	1.62545	0.95910	1.89583	125.446	2.4078
Orthorhombic	0.96485	1.32367	0.95564	———	1.2205

Table 3. Principal Distortions (ξ_i) and Volume Change ($\xi_1\xi_2\xi_3$) upon Monoclinic-to-Orthorhombic Lattice Deformation at 178 K

Principal distortions			Volume change
ξ_1	ξ_2	ξ_3	$\xi_1\xi_2\xi_3$
$\lvert\xi_1\rvert = 1.0086$	$\lvert\xi_2\rvert = 1.0060$	$\lvert\xi_3\rvert = 0.9992\ (\approx 1)$	1.014
$\xi_1 = -0.2182\mathbf{i} + 0.9759\mathbf{k}$	$\xi_2 = \mathbf{j}$	$\xi_3 = -0.9759\mathbf{i} - 0.2182\mathbf{k}$	

i, **j** and **k** are the unit vectors in the orthonormal basis defined by **i** ∥ a^*, **j** ∥ b and **k** ∥ c.

a, b and c are crystallographic axes of the monoclinic cell at 178 K.

ξ_1, ξ_2 and ξ_3 are the unit vectors along the principal axes.

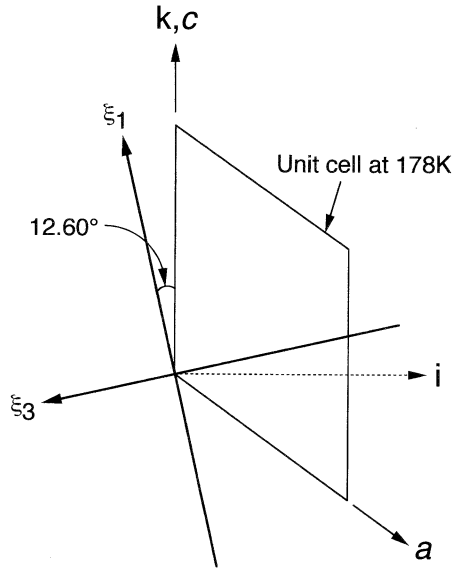

Fig. 5. Superposition of the principal axes ξ_1 and ξ_3 on the monoclinic unit cell at 178 K. The ξ_2-axis coincides with the b-axis. The orthonormal basis defined by the unit vectors i (//a^*), j (//b) and k (//c).

hance our understanding of the unusual thermal behavior of $Sc_2(MoO_4)_3$.

4. Conclusions

(1) With thermal expansion of monoclinic $Sc_2(MoO_4)_3$, one of the principal distortions λ_1 was invariably larger than unity; the magnitude steadily increased with increasing temperature. The other distortions, λ_2 and λ_3, showed negative thermal expansion in the temperature region of $T<55$ K for λ_2 and $T<35$ K for λ_3. Because of the bidimensional shrinkage along the latter two axes, volumetric contraction occurred below 30 K.

(2) The λ_2-axis coincides with the crystallographic b-axis. The intersection angle between λ_1 and c was ~78.8° at 11 K; it steadily decreased to ~20.1° with increasing temperature to 178 K.

(3) The lattice deformation, induced by the monoclinic-to-orthorhombic phase transition at 178 K, was essentially accompanied by the bidimensional expansion along [010] and nearly along [$\bar{2}$05], the magnitudes of which are respectively ~0.6 and ~0.9%.

(4) Since the lattice deformation along [$\bar{3}0\bar{2}$] is negligibly small, the structural change before and after the transition could be clearly demonstrated when viewed along [$\bar{3}0\bar{2}$], which corresponds to [031] of the orthorhombic phase.

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