Crystal structure of a $P2_1/m$ ferromagnesian cummingtonite at 140 K

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ABSTRACT

We report a structure refinement of a $P2_1/m$ ferromagnesian cummingtonite crystal with Fe/(Mg + Fe) = 0.37 at 140 K; this crystal was inverted from the $C2/m$ structure, which is stable at room temperature. The phase-transition temperature is ~240 K. The most significant structural changes associated with the $C2/m$-to-$P2_1/m$ phase transition are as follows: (1) one crystallographically independent O-rotated silicate chain becomes two, with the A chain S rotated and the B chain O rotated; (2) the M4 site collapses, with a marked decrease (0.020 Å) in the average M4-O6 bond distance; and (3) the largest decrease in the isotropic displacement factor is for the M4 cation. From 295 to 140 K, total changes of 14 and 11° occur in the O5-O6-O5 kinking angles of the A and B chains, respectively. The volume of the M1 octahedron decreases more than that of the other three MO_6 polyhedra, whereas the volume of the M3 octahedron is essentially unchanged. All four MO_6 polyhedra become more regular as a result of the $C2/m$-to-$P2_1/m$ transformation. These results provide new evidence that the effective size of the M4 cation controls the relative stability of the $C2/m$ and $P2_1/m$ structures. The results also provide a new explanation for the unresolved broadening of the cummingtonite Raman spectra measured at low temperatures by Wang et al. (1988).

INTRODUCTION

The details of the crystal structure of cummingtonite, $(Mg,Fe,Mn)_7Si_8O_{22}(OH)_2$, are essential in understanding various spectroscopic data and the nature of cation distributions, which are closely related to the thermodynamic mixing properties of the cummingtonite solid solution and to the cooling rates of host rocks. Cummingtonite may crystallize in space groups $C2/m$ or $P2_1/m$. Although $P2_1/m$ cummingtonite is restricted to Mg-rich compositions (Hirschmann et al. 1994, and references therein), it represents an important link between the two most abundant amphibole structure types, namely the monoclinic $C2/m$ structure and the orthorhombic *Pnma* structure (Ross et al. 1968, 1969; Papike et al. 1969; Prewitt et al. 1970; Maresch and Czank 1988). Structure refinements of $P2_1/m$ cummingtonite have been reported by several workers (Papike et al. 1969; Ghose 1982; Hirschmann et al. 1994; Yang and Hirschmann 1995). The $C2/m$ and $P2_1/m$ cummingtonite structures are both characterized by double silicate chains of six-membered tetrahedral rings parallel to *c*, each chain consisting of two nonequivalent SiO_4 tetrahedra, T1 and T2. The silicate tetrahedral chains form layers parallel to (100) and are linked together by strips of cations occupying four different sites: the octahedrally coordinated M1, M2, and M3 sites and a very

distorted sixfold-coordinated M4 site. Structural differences between $C2/m$ cummingtonite and $P2_1/m$ cummingtonite include the existence of one crystallographically distinct silicate chain in the $C2/m$ structure, whereas there are two, designated as A and B chains, in the $P2_1/m$ structure; and the presence of four M cations on twofold axes in the $C2/m$ structure but not in the $P2_1/m$ structure, although the M3 site in $P2_1/m$ cummingtonite remains on a mirror plane. Yang and Hirschmann (1995) found that the A chain in $P2_1/m$ ferromagnesian cummingtonite is S rotated and the B chain O rotated (see Fig. 1 of Yang and Hirschmann 1995), in contrast to the results reported by Papike et al. (1969) for $P2_1/m$ manganoan cummingtonite, in which both chains are O rotated.

The relative stabilities of $P2_1/m$ vs. $C2/m$ cummingtonite have been previously considered in terms of bulk composition (e.g., Yakovleva et al. 1978; Ghose 1982; Hirschmann et al. 1994) and the M4-cation occupancies (Ross et al. 1968, 1969; Papike et al. 1969; Prewitt et al. 1970; Sueno et al. 1972; Hawthorne 1983; Yang and Hirschmann 1995). Yang and Hirschmann (1995) showed that ferromagnesian cummingtonite crystals with X_{Mg}^{M4} (the site populations of Mg in the M4 site) > 0.15 ± 0.02 have $P2_1/m$ symmetry and those with X_{Mg}^{M4} < 0.15 have $C2/m$ symmetry. The $P2_1/m$-to-$C2/m$ symmetry change also occurs on heating of $P2_1/m$ cummingtonite (Prewitt et al. 1970; Sueno et al. 1972); the transition was found to be reversible and unquenchable and thought to be

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TABLE 1. Crystal data and cation site occupancies for cummingtonite sample NMNH 118125 at 295 and 140 K

	295 K	140 K
a (Å)	9.502(1)	9.492(2)
b (Å)	18.126(2)	18.093(2)
c (Å)	5.309(1)	5.292(1)
β (°)	102.07(1)	102.11(1)
Space group	$C2/m$	$P2_1/m$
Total refls.	2836	2813
Refls. >4 σ_F	1091	1690
Refls. >4 σ_F but violate $C2/m$	11	608
R_w (%)	4.4	4.0
R (%)	4.3	4.4
X_{Fe}^{M1}	0.200(5)	0.203(5)
X_{Fe}^{M2}	0.089(5)	0.087(4)
X_{Fe}^{M3}	0.169(7)	0.163(6)
X_{Fe}^{M4}	0.906	0.908

TABLE 2. Atomic positional coordinates and equivalent isotropic displacement factors for cummingtonite sample NMNH 118125 at 295 and 140 K

Parameter		295 K	140 K A chain	140 K B chain
M1	x	0		−2496(2)
	y	869(1)		3369(1)
	z	5000		4888(3)
	B	0.54(4)		0.31(3)
M2	x	0		−2053(2)
	y	1772(1)		4270(1)
	z	0		9886(3)
	B	0.55(4)		0.37(3)
M3	x	0		−2491(3)
	y	0		2500
	z	0		9905(4)
	B	0.59(6)		0.36(4)
M4	x	0		−2522(1)
	y	2591(1)		5094(1)
	z	5000		4848(1)
	B	0.77(2)		0.38(2)
T1	x	2877(1)	385(2)	5378(2)
	y	841(1)	3346(1)	8335(1)
	z	2744(2)	2626(2)	2874(2)
	B	0.43(2)	0.26(2)	0.31(2)
T2	x	2977(1)	460(2)	5494(2)
	y	1689(1)	4200(1)	9175(1)
	z	7811(2)	7688(2)	7937(2)
	B	0.40(2)	0.32(2)	0.29(2)
O1	x	1138(3)	−1352(5)	3647(5)
	y	871(2)	3368(2)	8374(2)
	z	2094(5)	1992(6)	2194(6)
	B	0.53(5)	0.34(6)	0.42(6)
O2	x	1240(3)	−1280(5)	3750(4)
	y	1724(2)	4222(2)	9223(2)
	z	7194(5)	7057(6)	7316(6)
	B	0.62(5)	0.45(6)	0.39(6)
O3	x	1143(4)	−1336(7)	3613(6)
	y	0	2500	7500
	z	7088(7)	6986(9)	7171(9)
	B	0.69(5)	0.57(9)	0.40(8)
O4	x	3803(3)	1280(4)	6329(5)
	y	2453(2)	4977(2)	9929(2)
	z	7696(5)	7811(6)	7613(6)
	B	0.90(5)	0.40(6)	0.68(6)
O5	x	3517(3)	1010(4)	6032(4)
	y	1312(2)	3733(2)	8871(2)
	z	645(5)	341(6)	905(6)
	B	0.85(5)	0.50(5)	0.41(5)
O6	x	3500(3)	1035(4)	5974(4)
	y	1184(2)	3783(2)	8605(2)
	z	5588(5)	5313(6)	5827(6)
	B	1.13(6)	0.60(6)	0.51(6)
O7	x	3433(5)	948(6)	5925(6)
	y	0	2500	7500
	z	2710(8)	2917(9)	2579(9)
	B	0.85(7)	0.60(9)	0.40(8)

Note: Atomic positional coordinates are shown times 10⁴; isotropic displacement factors are shown in squared angstroms.

driven by the differential expansion of octahedra and tetrahedra. Cummingtonite has been studied at temperatures below 295 K by Mössbauer spectroscopy (Hafner and Ghose 1971; Ghose and Weidner 1972) and Raman spectroscopy (Wang et al. 1988). In this study, we report the structure refinement of a $P2_1/m$ ferromagnesian cummingtonite crystal at 140 K, which was inverted from the $C2/m$ structure, which is stable at room temperature. Our results confirm the importance of the M4 site in the $C2/m$-to-$P2_1/m$ phase transition in ferromagnesian cummingtonite and provide a new explanation for the unresolved broadening of the cummingtonite Raman spectra measured at low temperatures by Wang et al. (1988).

EXPERIMENTAL PROCEDURES

The sample used in this study, NMNH 118125, is from the collection of the Smithsonian Institution, Washington, DC. A nearly cube-shaped crystal (0.12 × 0.12 × 0.10 mm), which was previously studied by Yang and Hirschmann (1995) (labeled as UH1), was extracted from the polished thin section and mounted on a glass fiber with Super Glue. The crystal has the composition $(Ca_{0.09}Mn_{0.07}Fe_{2.48}Mg_{4.35}Al_{0.01})Si_8O_{22}(OH)_2$ and $C2/m$ symmetry at room temperature (Yang and Hirschmann 1995). The experiment was performed on a Siemens P4 automated X-ray diffractometer equipped with a graphite monochromator and a molybdenum rotating anode generator operating at 50 kV and 200 mA. The low temperature was achieved with a Siemens cooling device by a steady flow of cold nitrogen gas over the crystal. The device was calibrated by placing a Cu/Cu-Ni thermocouple at the crystal position; the temperature stability is within ±2 K at temperatures below ~240 K.

Unit-cell dimensions and X-ray diffraction intensities of the crystal were measured at 295 and 140 K. Unit-cell dimensions were determined by the least-squares refinement of 26 reflections with $15° < 2\theta < 30°$. X-ray intensity data of one quadrant of reciprocal space with $2° < 2\theta$ < 60° were collected using variable scan speeds and a constant-precision θ-2θ scan mode. Three standard reflections were checked after every 97 reflections; no significant or systematic variations in the intensities of the

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[1] A copy of Table 3 may be ordered as Document AM-96-611 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 4. Si-O bond distances (Å) and other geometric parameters for SiO₄ tetrahedra in cummingtonite sample NMNH 118125 at 295 and 140 K

	295 K	140 K	
		A chain	B chain
T1-O1	1.616(3)	1.612(5)	1.608(5)
T1-O5	1.620(3)	1.615(4)	1.638(4)
T1-O6	1.626(3)	1.631(4)	1.622(4)
T1-O7	1.615(2)	1.618(3)	1.615(3)
Avg.	1.619	1.619	1.621
TV	2.178(5)	2.176(7)	2.185(6)
TQE	1.000(2)	1.000(1)	1.000(1)
TAV	1.2(1)	1.6(1)	0.8(1)
T2-O2	1.616(3)	1.616(4)	1.621(4)
T2-O4	1.599(3)	1.601(4)	1.605(5)
T2-O5	1.634(3)	1.628(3)	1.642(3)
T2-O6	1.649(3)	1.653(4)	1.653(4)
Avg.	1.625	1.625	1.630
TV	2.187(6)	2.180(7)	2.210(7)
TQE	1.005(2)	1.006(3)	1.004(2)
TAV	18.3(4)	25.2(5)	15.74(4)

Note: TV = tetrahedral volume in cubic angstroms, TQE = tetrahedral quadratic elongation, and TAV = tetrahedral angle variance (Robinson et al. 1971).

TABLE 5. M-O bond distances (Å) and other geometric parameters for MO₆ polyhedra in cummingtonite sample NMNH 118125 at 295 and 140 K

	295 K	140 K	
		A chain	B chain
M1-O1	2.061(3) × 2	2.056(4)	2.070(4)
M1-O2	2.138(3) × 2	2.115(4)	2.141(4)
M1-O3	2.095(3) × 2	2.099(4)	2.074(4)
Avg. of 6	2.098	2.093	
OV	12.13(2)	12.03(3)	
OQE	1.010(2)	1.010(3)	
OAV	33.3(3)	32.6(4)	
M2-O1	2.138(3) × 2	2.141(4)	2.125(4)
M2-O2	2.085(3) × 2	2.079(4)	2.082(4)
M2-O4	2.045(3) × 2	2.025(4)	2.054(4)
Avg. of 6	2.089	2.084	
OV	11.99(2)	11.92(3)	
OQE	1.010(2)	1.009(2)	
OAV	31.7(3)	30.3(3)	
M3-O1	2.096(3) × 4	2.087(4)	2.104(4)
M3-O3	2.067(4) × 2	2.073(6)	2.054(6)
Avg. of 6	2.086	2.085	
OV	11.85(2)	11.84(3)	
OQE	1.015(1)	1.014(3)	
OAV	47.2(3)	44.8(5)	
M4-O2	2.155(3) × 2	2.160(4)	2.144(4)
M4-O4	2.007(3) × 2	2.021(4)	2.001(4)
M4-O6	2.691(3) × 2	2.485(4)	2.856(4)
M4-O5	3.150(3) × 2	3.393(4)	2.923(4)
Avg. of 6	2.284	2.278	
OV	11.61(2)	11.53(3)	
OQE	1.258(8)	1.253(9)	
OAV	477.8(7)	455.0(7)	
Avg. of 8 (Å)	2.501	2.498	
V of 8 (Å³)	24.89(4)	24.23(4)	

Note: OV = octahedral volume in cubic angstroms, OQE = octahedral quadratic elongation, and OAV = octahedral angle variance (Robinson et al. 1971).

standard reflections were observed. Before the low-temperature experiment started, seven strong reflections violating $C2/m$ symmetry ($h + k = 2n + 1$) ($\overline{7}04$, $\overline{3}02$, $\overline{3}65$, $\overline{1}04$, $\overline{1}63$, $\overline{1}67$, and 506) were selected from the X-ray diffraction data of Yang and Hirschmann (1995) to monitor the $C2/m$-to-$P2_1/m$ phase transition. These reflections are hereafter referred to as primitive reflections. Their intensities and peak profiles were measured at intervals of 10 K as the temperature was decreased. At 295 K no significant X-ray diffraction intensities were detected at the positions of the seven primitive reflections, but at 235 K these reflections showed weak intensities and relatively broad peak profiles, indicating that the $C2/m$-to-$P2_1/m$ transition had taken place between 245 and 235 K. The crystal was then cooled to 140 K, at which all seven primitive reflections had strong intensities and sharp peak shapes.

All X-ray intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied because of the crystal's relatively small size and relatively low absorption coefficient (29.2 cm⁻¹). Yang and Hirschmann (1995) showed that empirical absorption corrections do not significantly affect the refined structural parameters and site occupancies of cummingtonite, at least for crystal compositions similar to that of sample NMNH 118125. Reflections having intensities $> 4\sigma_F$ were considered as observed and included in the refinements, where σF is the standard deviation determined from the counting statistics. Eleven weak observed reflections violate the $C2/m$ space group in the data set collected at 295 K, possibly because they stem from microscopic exsolution lamellae of actinolite (Hirschmann et al. 1994) or chain-width disorder (e.g., Veblen 1985; Maresch and Czank 1988). The structures were refined with the bulk composition constrained to that determined from microprobe analysis (Yang and Hirschmann 1995). Procedures of structure refinements are similar to those described by Hirschmann et al. (1994). Unit-cell dimensions, final R and R_w factors, and refined cation-site occupancies are presented in Table 1. Atomic positional coordinates and isotropic displacement parameters from the final cycles of refinements are listed in Table 2 and anisotropic displacement factors in Table 3.[1] Selected bond lengths for SiO₄ tetrahedra and MO₆ octahedra are given in Tables 4 and 5, respectively, and bond angles are presented in Table 6. The structure of the crystal at room temperature was refined by Yang and Hirschmann (1995), but for internal consistency and better comparison with the low-temperature data, we recollected and refined the data at room temperature to avoid any systematic differences owing to the different procedures used to obtain the structure factors in two laboratories. The atomic positional coordinates and cation-site occupancies determined in this study are similar to those reported by Yang and Hirschmann (1995) (within experimental errors), but the isotropic displacement factors determined in this study are systematically smaller. As expected, our data indicate that the low-temperature $C2/m$-to-$P2_1/m$ phase transition has no effect on the cation distribution in the structure.

TABLE 6. Selected interatomic angles (°) in tetrahedral chains in cummingtonite sample NMNH 118125 at 295 and 140 K

	295 K	140 K	
		A chain	B chain
O1-T1-O5	110.5(2)	110.7(2)	109.7(2)
O1-T1-O6	110.1(2)	110.7(2)	109.6(2)
O1-T1-O7	110.6(2)	110.3(3)	110.7(3)
O5-T1-O6	108.7(2)	108.2(2)	109.4(2)
O5-T1-O7	108.6(2)	108.4(3)	108.7(2)
O6-T1-O7	108.4(2)	108.6(2)	108.7(2)
O2-T2-O4	116.6(2)	117.0(2)	116.0(2)
O2-T2-O5	108.3(2)	108.7(2)	108.1(2)
O2-T2-O6	108.9(2)	109.9(2)	108.1(2)
O4-T2-O5	109.6(2)	110.8(2)	109.0(2)
O4-T2-O6	103.3(2)	101.4(2)	104.3(2)
O5-T2-O6	110.1(2)	108.7(2)	111.2(2)
O5-O6-O5	170.0(2)	176.0(2)	159.3(2)
O5-O7-O6	169.2(2)	175.5(2)	159.3(2)
T1-O5-T2	139.7(2)	140.3(3)	136.4(3)
T1-O6-T2	140.5(2)	139.4(3)	138.5(3)
T1-O7-T1	141.5(3)	142.2(4)	138.5(4)

RESULTS AND DISCUSSION

One of the most significant structural changes associated with the $C2/m$-to-$P2_1/m$ phase transition is the rearrangement of the silicate chain configurations. In the $C2/m$ structure the tetrahedral chains are O rotated with a O5-O6-O5 kinking angle of 170°, whereas in the $P2_1/m$ structure the A chain is S rotated with a kinking angle of 184° and the B chain O rotated with a kinking angle of 159° [See Fig. 1 of Papike and Ross (1970) for illustrations of S and O rotations]. Note that to maintain the analogy with pyroxenes (Smyth 1974; Sueno et al. 1976; Hugh-Jones et al. 1994), the kinking angle of S-rotated chains is calculated as $360° - \angle O5A\text{-}O6A\text{-}O5A$. The B chain therefore undergoes an additional 11° of kinking at the transition, whereas the A chain reverses its sense of kinking and undergoes a total change of 14°. Similar structural changes in silicate chain configurations have also been found in the $P2_1/c$-to-$C2/c$ phase transition in pigeonite (Brown et al. 1972), clinohypersthene (Smyth 1974), clinoenstatite (Angel et al. 1992), and clinoferrosilite (Hugh-Jones et al. 1994). Our results for the $P2_1/m$ structure are similar to those reported by Hirschmann et al. (1994) and Yang and Hirschmann (1995) for other ferromagnesian cummingtonite crystals, but different from those of Papike et al. (1969) for a $P2_1/m$ manganoan cummingtonite crystal, in which the A and B chains are O rotated. Despite the fact that both A and B chains in the $P2_1/m$ structure at 140 K are both more kinked by ~3° than the corresponding chains in $P2_1/m$ cummingtonite crystals with similar compositions at room temperature, the average value of the kinking angles of the two chains remains approximately 171°, as found in other ferromagnesian cummingtonite crystals (Yang and Hirschmann 1995).

The T2 tetrahedron in the $C2/m$ structure and the T2A and T2B tetrahedra in the $P2_1/m$ structure show relatively large distortion of the tetrahedral angle variance (TAV) (Robinson et al. 1971) (Table 4). This is because these tetrahedra each share an edge (O4-O6) with the M4 polyhedron. As a result, the bond angles of O4-T2-O6 in the $C2/m$ structure and those of O4A-T2A-O6B and O4B-T2B-O6B in the $P2_1/m$ structure are the smallest in each tetrahedron to which they belong. In the $P2_1/m$ structure, the T2A-O4A and T2B-O4B bond lengths are the shortest (1.601 and 1.605 Å, respectively) of all T-O bonds, and the difference between them (0.004 Å) is within 1σ; thus, the T2A and T2B tetrahedra show similar distortion in terms of the tetrahedral quadratic elongation (TQE) (Robinson et al. 1971). However, the T2A-O4A bond distance in the $P2_1/m$ manganoan cummingtonite studied by Papike et al. (1969) is only 1.575 Å, and the difference between the T2A-O4A and T2B-O4B distances is as large as 0.035 Å. Thus, the T2A tetrahedron in $P2_1/m$ manganoan cummingtonite is far more distorted than the T2B tetrahedron in terms of TQE. On the basis of bond-valence calculations, Hawthorne (1983) showed that the M4 cation in the $P2_1/m$ manganoan cummingtonite contributes a much greater bond valence to the T2B tetrahedron than to the T2A tetrahedron; accordingly, the T2B-O4B bond length is greater than the T2A-O4A bond length, and hence the T2B tetrahedron is less distorted than the T2A tetrahedron.

The most significant change in the octahedral strips associated with the $C2/m$-to-$P2_1/m$ transformation is the coordination change or the collapse of the M4 site. In the $C2/m$ structure the M4 cation is coordinated by six O atoms forming a highly distorted polyhedron, with four O atoms (two O2 and two O4) at an average distance of 2.081 Å and two (O6) at 2.691 Å. The M4 cation in the $P2_1/m$ structure can also be regarded as sixfold coordinated, but it actually has a 4 + 1 + 1 coordination: four O atoms (O2A, O2B, O4A, and O4B) at an average distance of 2.081 Å, one (O6A) at 2.485 Å, and one (O6B) at 2.856 Å. In comparison with the M4-O6 distance in the $C2/m$ structure, the average M4-O6 distance (2.671 Å) in the $P2_1/m$ structure is shorter, giving a tighter coordination around the M4 cation. Thus, if only the six nearest O atoms are considered, the M4 polyhedral volume in the $C2/m$ structure (11.61 Å³) is larger than that in the $P2_1/m$ structure (11.53 Å³). The relatively small volume of the M4 polyhedron in the $P2_1/m$ structure results from the independent adjustments of the S-rotated A chain and the O-rotated B chain. Because of the small temperature range we studied, the average M-O bond distances of four MO₆ polyhedra do not decrease appreciably, the decreasing rate being in the order M4-O (0.31%) > M2-O (0.24%) = M1-O (0.24%) > M3-O (0.05%). Owing to the $C2/m$-to-$P2_1/m$ symmetry change, all four MO₆ polyhedra become slightly more regular (Table 5). The volume decrease (0.82%) of the M1 octahedron from 295 to 140 K is greater than that of the other MO₆ polyhedra, whereas the M3 octahedral volume is essentially unchanged. The observation that the size of the M3 octahedron is least affected by temperature may be related to the position of the M3 octahedron in the middle of the

octahedral strip in the amphibole structure. Similar results were found in other amphiboles, such as manganoan cummingtonite (Sueno et al. 1972) and tremolite (Sueno et al. 1973), as a function of temperature. It should be pointed out that the effective coordination number of the M4 site in cummingtonite has been controversial (e.g., Hawthorne 1983). If the M4 cation is considered as sixfold coordinated, the M4 polyhedron in the $C2/m$ and $P2_1/m$ structures has the smallest volume of all M-cation polyhedra, and its volume decreases only by 0.70% due to the $C2/m$-to-$P2_1/m$ phase transition. On the other hand, if the M4 cation is considered as eightfold coordinated, then the M4 polyhedral volume is the largest in the structure and decreases most (2.67%) from 295 to 140 K.

Isotropic displacement factors of all atoms in the $P2_1/m$ structure at 140 K are noticeably smaller than those of the corresponding atoms in the $C2/m$ structure at 295 K. The B parameter for the M4 cation decreases by 51%, whereas the B factors for the M1, M2, and M3 cations decrease by only 35–37%. In fact, the decrease in the B factor for the M4 cation is the largest of all atoms in the $P2_1/m$ structure. In contrast, Sueno et al. (1972) found that from room temperature to 543 K the increase in the B factor for the M4 cation in a manganoan cummingtonite is anomalously smaller than that for the M1, M2, or M3 cation, which was interpreted as a result of an average effect of increased thermal vibration with decreased positional disorder. Because the crystal we studied contains mainly Fe²⁺ and Mg in the M4 site, the positional disorder may not be a major factor affecting the B parameter of the M4 cation; hence, the considerably larger decrease in the B factor for the M4 cation than for the M1, M2, or M3 cation is likely to result primarily from the decreased thermal vibration.

Yang and Hirschmann (1995) found that the $P2_1/m$-to-$C2/m$ phase transition in cummingtonite is a function of cation site occupancies in the M4 site; they also concluded that the phase transition from the unheated $C2/m$ structure to the heated $P2_1/m$ structure probably occurs during quenching from high temperature. In this process, the high Mg/Fe ratios in the M4 site induced by disordering at high temperatures were preserved, but the thermal vibration amplitude of the M4 cation was greatly reduced, resulting in the collapse of the M4 site and the $C2/m$-to-$P2_1/m$ transformation. Our results not only confirm these conclusions, but also suggest that the thermal behavior of the M4 cation plays a critical role in the $C2/m$-to-$P2_1/m$ phase transition. The effect of decreasing temperature on the structure is similar to that of the substitution of smaller cations into the M4 site. In other words, depending on chemical composition and temperature, the change of the effective mean size of the M4 cation is a primary driving force for the $P2_1/m$-to-$C2/m$ phase transition in cummingtonite.

Our results on the $C2/m$-to-$P2_1/m$ phase transition in the NMNH 118125 cummingtonite also provide a better understanding of the Raman spectra of a DH7–482 ferromagnesian cummingtonite crystal measured at low temperatures by Wang et al. (1988). In general, infrared and Raman spectra of intermediate ferromagnesian cummingtonite crystals show four bands of the O-H stretching vibration in the range 3600–3700 cm⁻¹; these bands are normally labeled as the A, B, C, and D bands from high to low frequency [see Hawthorne (1983) for a review of the nomenclature and assignment of bands]. The spectra obtained by Wang et al. (1988) in the O-H stretching region show that the line widths of the B and C bands increase significantly as temperature decreases to 83 K; however, Wang et al. (1988) could not determine the temperature dependence of the A and D bands owing to their low intensities. Wang et al. (1988) interpreted their observations as a result of the interaction between M cations and O atoms becoming stronger when the sample temperature decreases, which causes the separation between the components of the B band and those of the C band; nevertheless, the splitting of the components is much smaller than the spectral resolution of the instrument. Thus, the greater separation between the components at low temperature appears as an apparent increase in the band line widths. However, the interpretation of Wang et al. (1988) was based on the assumption that their cummingtonite sample retained $C2/m$ symmetry between 293 and 83 K. According to our study, the cummingtonite crystal investigated by Wang et al. (1988) probably underwent a $C2/m$-to-$P2_1/m$ phase transition between 293 and 83 K because their sample is only slightly more Fe-rich [Fe/(Fe + Mg) = 0.39, Hirschmann et al. (1994)] than the cummingtonite crystal studied here. Therefore, the significantly wider line widths of the cummingtonite Raman spectra measured by Wang et al. (1988) at low temperatures are probably related to the $C2/m$-to-$P2_1/m$ symmetry change. In the $P2_1/m$ cummingtonite structure there are two crystallographically distinct OH positions; the slightly different environments of two OH positions lead to the slight differences in the stretching frequency, which is sufficient to broaden each band but not to split it into two resoluble components. Burns and Law (1970) referred to this as "chain broadening" on the basis of their infrared spectra measured on anthophyllite and gedrite, the structures of which also contain two nonequivalent OH positions. Likewise, cummingtonite samples DH7–482 and NMNH 118125 studied by Hafner and Ghose (1971) and Ghose and Weidner (1972) using Mössbauer spectroscopy at 77 K may also have undergone a $C2/m$-to-$P2_1/m$ structural transformation. Therefore, caution should be exercised in future low-temperature research on intermediate ferromagnesian cummingtonite.

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