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NEUTRON DIFFRACTION STUDY OF A ONE-LAYER MONOCLINIC CHLORITE

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Abstract—A monoclinic II*b*-2 clinochlore from the Achmatov mine, Ural Mountains, U.S.S.R., was investigated by neutron diffraction. The formula, based on electron microprobe and wet chemical analyses, is $(Mg_{4.54}Al_{0.97}Fe^{2+}_{0.28}Fe^{3+}_{0.18}Mn_{0.01})(Si_{2.85}Al_{1.15})O_{10}(OH)_8$. A refinement based on 512 unique reflections converged in space group $C2/m$ to a final R = .066. Cation disorder was found in the two octahedral positions of the 2:1 layer, whereas partial Mg and Al ordering occurs in the interlayer sheet. The two hydroxyl dipoles are roughly perpendicular to the interlayer sheet, forming weak to medium hydrogen bonds with O. . .O distances of 2.859 and 2.881 Å. The OH-dipole of the 2:1 layer is perpendicular to the (001) plane.

Key Words—Cation ordering, Chlorite, Crystal structure, Hydrogen bonding, Neutron diffraction.

Zusammenfassung—Die Struktur eines monoklinen II*b*-2 Klinochlors von der Achmatov-Mine, Ural, UdSSR, wurde mit Neutronenbeugung untersucht. Mikrosondenanalyse und naßchemische Methoden ergaben die Zusammensetzung: $(Mg_{4.54}Al_{0.97}Fe^{2+}_{0.28}Fe^{3+}_{0.18}Mn_{0.01})(Si_{2.85}Al_{1.15})O_{10}(OH)_8$. Die Verfeinerung mit 512 symmetrisch unabhängigen Reflexen konvergierte in Raumgruppe $C2/m$ zu einem R = 0,066. Die Kationen der beiden oktaedrischen Positionen der 2:1-Schicht sind vollständig ungeordnet, während in der Zwischenschicht teilweise eine Ordnung von Mg und Al beobachtet wird. Die beiden Hydroxyl-Dipole stehen senkrecht auf der Zwischenschicht und bilden schwache bis mittelstarke Wasserstoffbrücken mit O. . .O-Abständen von 2,895 und 2,881 Å. Der OH-Dipol der 2:1-Schicht ist senkrecht zur 001-Fläche.

INTRODUCTION

Natural chlorites occur commonly as one-layer triclinic polytypes (Steinfink, 1958; Brown and Bailey, 1963; Joswig *et al.*, 1980). Considerable disorder is present in most specimens; only a few samples (apart from higher order stacking sequences) show one-layer monoclinic symmetry, but the crystal quality is distinctly inferior compared with the triclinic polytype. A monoclinic chlorite was first refined structurally by film data (Steinfink, 1958) into space group $C2$. Steinfink concluded that Si and Al tetrahedral ordering and partial octahedral ordering was present. His crystals from Mtito Andei, Kenya, were intergrown with triclinic polymorphs.

More recently, Zheng and Bailey (1989) reinvestigated material from the same location and determined a random Si/Al distribution in $C2/m$ symmetry. Another refinement of a monoclinic II*b*-2 polytype from Washington, D.C., was reported by Rule and Bailey (1987). Here also, no ordering in the T-site was observed. Partial ordering of Mg and Fe in the octahedral sites of the 2:1 layer, a complete ordering of Al in one of the octahedral sites of the interlayer sheet, and a preference of Mg and Fe in the other two octahedral sites was found. The octahedral positions of the interlayer sheet are given here as $M_b(1)$ and $M_b(2)$ and those in the 2:1 layer as $M_t(1)$ and $M_t(2)$. The correspondence with Rule and Bailey (1987) is $M_t(1) = M(1)$, $M_t(2) = M(2)$, $M_b(1) = M(3)$ and $M_b(2) = M(4)$.

The purpose of the present neutron diffraction study was to determine the hydrogen-bonding pattern and a cation-ordering scheme in a monoclinic polytype. The sample also contained triclinic II*b*-4 clinochlores. One of them was investigated by X-ray diffraction; the results were reported by Joswig and Fuess (1989).

EXPERIMENTAL

The chlorite sample examined was from the Achmatov mine, Ural Mountains, U.S.S.R. Besides occasional triclinic and higher stacking polytypes, only two ordered monoclinic crystals were found among many crystals of disordered and semi-random stacking. Precession photographs of the monoclinic crystal indicated a II*b*-2 polytype (Bailey and Brown, 1962). The

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Table 1. Electron microprobe analysis of clinochlore, Achmatov mine, Ural Mountains, U.S.S.R.

	Weight percent	Calculation for 28 positive charges		
SiO_2	29.31	Si	2.85	4.00 IV
Al_2O_3	18.50	$Al^{(IV)}$	1.15	
		$Al^{(VI)}$	0.97	
FeO	3.43[1]	Fe^{2+}	0.28	
Fe_2O_3	2.52[1]	Fe^{3+}	0.18	5.98 VI
MgO	31.32	Mg	4.54	
MnO	0.13	Mn	0.01	
K_2O	0.04			
Na_2O	0.11			
Cr_2O_3, PO_4 TiO_2, CaO	<0.05			

[1] By wet chemical analysis.

crystal used here for neutron work was 0.8 × 0.5 × 0.3 mm. The lattice constants, refined by X-ray diffraction data using 25 reflections from a smaller crystal, are: a = 5.327(2), b = 9.227(2), c = 14.327(5) Å, β = 96.81(3)°.

Microprobe analyses from eight locations on a different grain and a wet chemical analysis gave the bulk chemical composition listed in Table 1. Based on 28 positive charges the structural formula is:

$$(Mg_{4.54}Al_{0.97}Fe^{2+}{}_{0.28}Fe^{3+}{}_{0.18}Mn_{0.01})$$
$$(Si_{2.85}Al_{1.15})O_{10}(OH)_8.$$

The composition indicates that the sample is clinochlore (Bayliss, 1978). Microprobe analyses also indicated that grains had Mg/Fe compositional zones, in which Mg was concentrated in the core and Fe near the grain edges.

The intensity data were collected on the newly commissioned four-circle neutron diffractometer D19 of the Institute Laue-Langevin, Grenoble, France. This instrument has a vertically curved position-sensitive detector subtending 4° horizontally and 64° vertically. Because of the small unit-cell size, most reflections were scanned with equatorial-plane geometry. At a neutron wavelength of λ = 1.547 Å, 1219 reflections were measured to a maximum $\sin\theta/\lambda$ of 0.57 $Å^{-1}$. Of these, 398 were measured once only. The remaining 821 reflections were registered twice or more times on the position sensitive detector. They were averaged and 184 unique reflections were obtained. The 184 averaged reflections, together with the 398 that were measured only once, resulted in a set of 582 unique reflections. The R-factor of the 184 averaged reflections on F^2 was R = .022 (R_w = .029), showing that high-quality neutron diffraction data can be obtained from small samples using a position sensitive detector. Crystals of this size have never been measured before with conventional neutron equipment. The three-dimensional arrays of counts around each reflection were corrected for background. The reduction to structure amplitudes (F^2) followed the integration method of Wilkinson and Khamis (1983). Corrections for absorption and extinction were not made due to the small sample volume. Further details on the instrument and on the data reduction procedure were given by Renault *et al.* (1987).

Least-squares refinement based on 512 reflections with $F_0 \geq 2\sigma(F_0)$ and using programs from Stewart *et al.* (1975) were made. Starting parameters were taken from Rule and Bailey (1987) for the monoclinic II*b*-2 polytype in the ideal *C*2/*m* space group. Scattering lengths were from Koester (1977). Numerical values are (in Fermi = 10^{-15} m): b(Fe) = 9.54, b(Al) = 3.449, b(Mg) = 5.375, b(Si) = 4.149, b(O) = 5.803, b(Mn) = −3.73, and b(H) = −3.74.

A weighting scheme, $w(F_0) = [2\sigma^2 + 0.001 \cdot F_0^2 + 0.5]^{-1}$, with $\sigma(F_0)$ from counting statistics, was used, and a correction for contamination of $\lambda/2$ harmonics was introduced. Hydrogen positions (with negative scattering density) were located from difference Fourier

Table 2. Atomic coordinates, neutron scattering lengths, population parameters, and anisotropic thermal parameters of clinochlore, Achmatov mine, Ural Mountains, U.S.S.R.

Atom	Neutron scatter. length b(10^{-15} m)	Population	Atomic coordinates x	y	z	Anisotropic thermal parameters (U_{ij} × 10^{-2}) U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$M_t(1)$	5.87(16)		.00	.00	.00	0.2(4)	1.3(4)	1.8(4)	0.0	0.3(3)	0.0
$M_t(2)$	5.86(10)		.00	.3323(5)	.00	1.3(3)	0.6(2)	2.1(3)	0.0	0.1(2)	0.0
T	3.84(7)		.2283(7)	.1665(5)	.1925(3)	0.6(2)	0.6(2)	1.2(2)	0.1(2)	0.2(2)	−0.3(2)
O(1)	5.803		.1917(5)	.1668(4)	.0773(2)	1.4(2)	1.3(1)	1.0(2)	0.1(2)	0.3(1)	−0.2(1)
O(2)			.2052(9)	.00	.2344(3)	2.6(3)	1.3(2)	2.1(3)	0.0	0.5(2)	0.0
O(3)			.5103(6)	.2306(3)	.2335(2)	1.7(2)	2.0(2)	2.0(2)	−0.5(2)	0.1(1)	0.2(1)
O(4)		.98(3)	.1900(9)	.50	.0728(5)	1.0(3)	1.0(3)	1.1(5)	0.0	0.0(2)	0.0
H(1)	−3.74	.98(4)	.2138(19)	.50	.1401(9)	5.2(6)	3.7(5)	0.9(9)	0.0	−0.3(5)	0.0
$M_b(1)$	5.45(10)		.00	.1676(6)	.50	1.3(3)	1.5(3)	1.9(3)	0.0	0.2(2)	0.0
$M_b(2)$	4.46(16)		.00	.50	.50	1.0(6)	0.7(4)	1.7(6)	0.0	0.8(4)	0.0
O(5)	5.803		.1535(10)	.00	.4308(5)	2.6(3)	1.3(2)	1.4(3)	0.0	0.6(3)	0.0
O(6)			.1394(6)	.3370(4)	.4297(3)	1.6(2)	2.0(2)	1.5(2)	0.1(2)	0.1(2)	0.0(2)
H(2)	−3.74	.97(4)	.1425(19)	.00	.3634(8)	4.0(6)	3.3(5)	1.1(7)	0.0	−0.5(4)	0.0
H(3)		.98(2)	.1117(12)	.3331(7)	.3634(5)	3.8(4)	3.5(3)	1.8(4)	−0.4(4)	0.6(3)	0.1(3)

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Table 3. Interatomic distances (Å) and bond angles (°) of clinochlore, Achmatov mine, Ural Mountains, U.S.S.R.

		Tetrahedra	
T–O(1)	1.639(4)		
–O(2)	1.660(5)		
–O(3)	1.656(5)		
–O(3)	1.661(5)		
Mean	1.654		
Edge lengths		Bond angles	
O(1)–O(2)	2.721(5)	O(1)–T–O(2)	111.2(3)
–O(3)	2.709(4)	–O(3)	110.6
–O(3)	2.712(4)	–O(3)	110.6
O(2)–O(3)	2.678(4)	O(2)–T–O(3)	107.8
–O(3)	2.693(4)	–O(3)	108.4
O(3)–O(3)	2.687(4)	O(3)–T–O(3)	108.2
		Octahedra	
$M_t(1)$		$M_t(2)$	
$M_t(1)$–O(1)	2.090(3) × 2	$M_t(2)$–O(1)	2.081(4)
–O(4)	2.055(6)	–O(1)	2.087(3)
		–O(4)	2.063(5)
Mean	2.078	Mean	2.077
$M_b(1)$		$M_b(2)$	
$M_b(1)$–O(5)	2.058(6)	$M_b(2)$–O(6)	2.001(4) × 2
–O(6)	2.046(6)	–O(5)	1.989(6)
–O(6)	2.061(3)	Mean	1.997
Mean	2.055		
		OH dipole (2:1 layer)	
O(4)–H(1)	0.957(15)	<OH, (001)	89.3(4)°

syntheses. The refined atomic and thermal parameters are listed in Table 2, together with occupancy factors and scattering lengths for the cation positions. The final reliability factors for space group $C2/m$ were R = .066 and R_w = .047. Possible tetrahedral and further octahedral cation ordering in subgroups $C2$ and Cm were tested in refinement procedures. The parameters returned within three standard deviations to those of $C2/m$. The ideal space group is the correct one.

RESULTS AND DISCUSSION

One independent tetrahedron exists in space group $C2/m$; it has a mean T–O distance of 1.654 Å. This value reflects a tetrahedral composition of Al^{IV} = 1.15 (per 4 sites) compared with 1.655 for Al^{IV} = 0.944 found by Zheng and Bailey (1989) for the II*b*-2 polytype and 1.668 Å found by Rule and Bailey (1987).

The octahedral sites in the 2:1 layer $M_t(1)$ and $M_t(2)$ are nearly identical in size, having mean bond lengths of 2.078 Å ($M_t(1)$) and 2.077 Å ($M_t(2)$), slightly shorter (vs. 2.086 and 2.082 Å) than those reported by Zheng and Bailey (1987). The refined scattering lengths of the two octahedral sites in the 2:1 layer, together with identical bond lengths, indicate complete cation disorder. The refined scattering length $b(M_t(1))$ = 5.87(16) and $b(M_t(2))$ = 5.86(10) are matched approximately by a composition $Mg_{2.75}Fe_{0.25}$ (b_{calc} = 5.72).

The two octahedral cation sites in the interlayer sheet are characterized by partial ordering based on the analysis of refined scattering lengths ($M_b(1)$ of b = 5.45(10) vs. $M_b(2)$ = 4.46(16)) and $M_b(1)$–O = 2.055 Å vs. $M_b(2)$–O = 1.997 Å). These values are consistent with a site occupancy of $M_b(1)$ of $Mg_{1.25}Al_{0.5}Fe_{0.25}$ (b_{calc} = 5.41) and $Mg_{0.5}Al_{0.5}$ (b_{calc} = 4.41) for $M_b(2)$.

HYDROGEN BONDING SYSTEM

The two symmetrically independent OH dipoles linking the interlayer sheet with the 2:1 layer form weak to medium hydrogen bonds based on the O. . .O distances of 2.859 and 2.881 Å (Table 4). The dipoles are nearly perpendicular to the interlayer sheet with a small inclination to the respective acceptor oxygen. The observed angles are 3.1° and 3.3°. The geometry of the hydrogen bonds (given in Figure 1) shows essentially the same pattern as the neutron study of the triclinic chlorite structure (Joswig *et al.*, 1980).

Table 4. Hydrogen-bonding pattern in chlorite, Achmatov mine, Ural Mountains, U.S.S.R.

O–H···O	O–H	O···O	H···O	O–H···O	H–O···O
O(5)–H(2)···O(2)	0.960(13) Å	2.859(8) Å	1.917(12) Å	166.6(9)°	9.0(6)°
O(6)–H(3)···(3)	0.944(8) Å	2.881(5) Å	1.965(7) Å	163.0(6)°	11.5(4)°

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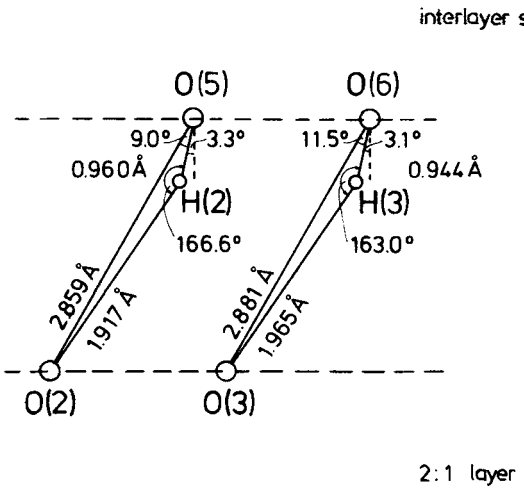


Figure 1. Hydrogen bonding system of the II*b*-2 chlorite, Achmatov mine, Ural Mountains, U.S.S.R.

The OH dipole of the 2:1 layer is perpendicular to the sheet. This arrangement is common in other octahedral phyllosilicates containing similar octahedral cations (Joswig, 1972; Joswig *et al.*, 1986).

SUMMARY AND CONCLUSIONS

The cation ordering pattern of the monoclinic II*b*-2 chlorite is similar to those described earlier for monoclinic specimens from different localities. Complete disorder was established for the tetrahedral and octahedral sites of the 2:1 layer for the sample studied here. The interlayer cations are partially ordered, with Al in the $M_b(2)$ position.

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