Fiedlerite: revised chemical formula [Pb₃Cl₄F(OH)·H₂O], OD description and crystal structure refinement of the two MDO polytypes

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Abstract

The chemical formula of fiedlerite, a rare hydrated lead halide, has been revised. The mineral is now known to contain also fluorine, and the new, correct formula is $Pb_3Cl_4F(OH)\cdot H_2O$. X-ray diffraction studies on fiedlerite from Laurion, Greece (the type locality), and from Baratti, Italy (the second known occurrence), revealed its Order-Disorder (OD) character. All structures within this OD family can be built up by layers of the same kind. The two polytypes with Maximum Degree of Order (MDO) display triclinic and monoclinic symmetry, with one and two OD layers, respectively, in the unit cell. On these grounds the nomenclature of fiedlerite has been revised, and the mineral is designated together with the polytype suffix (i.e. fiedlerite-1A, fiedlerite-2M). The crystal structures of the two MDO polytypes of fiedlerite have been solved and refined: fiedlerite-1A: $P\bar{1}$, $a = 8.574(3)$ Å, $b = 8.045(4)$, $c = 7.276(2)$, $\alpha = 89.96(4)°$, $\beta = 102.05(4)$, $\gamma = 103.45(4)$, $R = 0.092$; fiedlerite-2M: $P2_1/a$, $a = 16.681(4)$ Å, $b = 8.043(3)$, $c = 7.281(2)$, $\beta = 102.56(4)°$, $R = 0.061$. In both structures Pb is eight-coordinated by different ligands [Cl^-, F^-, $(OH)^-$, H_2O] that define bicapped trigonal prisms.

KEYWORDS: OD structures, fiedlerite-1A, fiedlerite-2M, lead halides, chemical data, crystal structure.

Introduction

FIEDLERITE is a rare mineral which previously has been described as a lead hydroxychloride with chemical formula $Pb_3Cl_4(OH)_2$, on the basis of a chemical analysis (de Schulten, 1905; Lacroix and de Schulten, 1908) carried out on fiedlerite from Laurion, Greece, the only known occurrence (vom Rath, 1887; Lacroix, 1896) until very recently.

A second occurrence of the mineral has now been reported from the Etruscan iron slags of Baratti, southern Tuscany, Italy by Franzini *et al.* (1992). Here fiedlerite was found together with a number of lead and copper oxy- and hydroxy-chlorides, sulfates and carbonates. In this locality fiedlerite is rarely associated with penfieldite, $Pb_2Cl_3(OH)$, and phosgenite, $Pb_2Cl_2(CO_3)$.

Fiedlerite was assigned to the monoclinic system, on the basis of a careful morphological study on crystals from Laurion, by Palache (1934), who updated the earlier data by vom Rath (1887)

and Smith (1899). The following unit cell parameters were later determined by the Weissenberg method: $a = 16.59$ Å, $b = 8.00$, $c = 7.19$, $\beta = 102.2°$, space group $P2_1/a$ (Palache *et al.*, 1951). To keep consistency with data in the literature, this non-standard orientation has been maintained in the present work.

A systematic inspection by single crystal X-ray diffraction of selected crystals of fiedlerite from Baratti revealed that the mineral displays two distinct modifications, with triclinic and mono-clinic symmetry respectively. These two polytypes belong to a family of Order-Disorder structures (OD-Structures) built up by layers of one kind.

Besides the recognition of the OD relationships between these two polytypes, the primary goal of our study was to solve their crystal structures, to compare and to describe them in terms of the OD theory. Unexpectedly, during the refinement of the structure of the triclinic polytype, we gained

compelling evidence that the chemical formula so far accepted for fiedlerite was incorrect, and that fluorine was present as a major element. An electron microprobe analysis carried out on fiedlerite from both Laurion and Baratti confirmed our suspicions, leading to the chemical formula $Pb_3Cl_4F(OH)\cdot H_2O$.

The Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association has accepted our proposal to redefine the mineral species fiedlerite on the basis of our new chemical and structural data. The present paper deals with both the structural characterization and the revision of the chemical formula of fiedlerite. Even if it does not correspond to the chronological achievement of the results, the data are presented in their logical order, first the chemical analysis, followed by the crystal structure refinements and the OD description. The type material has been deposited at the Museo di Storia Naturale e del Territorio, University of Pisa.

Chemical study

Chemical analyses of fiedlerite from both Laurion and Baratti were carried out by wavelength-dispersive electron microprobe, operated at 15 kV accelerating voltage, with a sample current of 15 nA, and a beam size of 10 μm. The standards used were metallic Pb, natural sodalite and CaF_2 for Pb, Cl and F, respectively. Moreoever, as an additional standard, a previously tested crystal fragment of matlockite from Baratti was used, assuming for it the ideal stoichiometry PbClF. All data, corrected for the different standards, are reported in Table 1, and indicate $Pb_3Cl_4F(OH)\cdot H_2O$ as the correct chemical formula, instead of $Pb_3Cl_4(OH)_2$, that is reported in all previous mineralogical treatises.

The experimental data for fiedlerite from Baratti, even if the atomic ratios seem correct, give a total wt.% of atoms in the range 100.78–103.66, depending on the standards, which is too high, considering that the contributions from oxygen and hydrogen are missing. It cannot be excluded that either a minor intergrowth of fiedlerite with another phase presenting higher Pb/Cl ratio — for instance phosgenite — or alteration products may be present.

To complete our analytical data, the hydrogen content of fiedlerite was measured on a grain concentrate (about 2 mg) of fiedlerite from Laurion by means of a Carlo Erba 1104 elemental micro-analyser. The H content of fiedlerite is 0.35 wt.%, very close to the expected value (0.37) for the ideal stoichiometry $Pb_3Cl_4F(OH)\cdot H_2O$. The previously accepted chemical formula $Pb_3Cl_4(OH)_2$ would have implied 0.25 wt.% of H. The presence of fluorine in fiedlerite could also be the reason why Edwards *et al.* (1992) did not succeed in synthesizing that phase: in fact fluorine

TABLE 1. Microprobe analyses for fiedlerite from Laurion and from Baratti (average of 5 points for both).

	Fiedlerite from Laurion			Fiedlerite from Baratti		
	1	2	3	1	2	3
	wt.% element					
Pb	76.17	75.37	76.97	82.36	81.49	83.22
Cl	17.30	16.54	17.87	17.46	16.70	18.04
F	2.10	2.17	2.01	2.51	2.59	2.40
Σ	95.57	94.08	96.85	102.33	100.78	103.66
	atoms per formula unit					
Pb	3.00	3.00	3.00	3.00	3.00	3.00
Cl	3.98	3.85	4.07	3.72	3.59	3.80
F	0.90	0.94	0.85	1.00	1.04	0.94

Ideal $Pb_3Cl_4F(OH)\cdot H_2O$: Pb 76.03 %, Cl 17.37, F 2.32, O 3.91, H 0.37.
1. Standards: metallic Pb + matlockite (Pb), sodalite + matlockite (Cl), CaF_2 + matlockite (F)
2. Standards: metallic Pb (Pb), sodalite (Cl), CaF_2 (F)
3. Standards: matlockite (Pb, Cl, F)

TABLE 2. Experimental data for the crystal structure analyses of fiedlerite.

	1A	2M
Polytype	1A	2M
Sample locality	Baratti, Italy	Laurion, Greece
Dimensions of crystal (mm)	0.3 × 0.3 × 0.1	0.2 × 0.1 × 0.1
Space group	$P\bar{1}$	$P2_1/a$
a(Å)	8.574(3)	16.681(4)
b	8.045(4)	8.043(3)
c	7.276(2)	7.281(2)
α(°)	89.96(4)	90
β	102.05(4)	102.56(4)
γ	103.45(4)	90
V(Å^3)	476.8(5)	953.5(4)
Diffractometer	Ital Structures	
Radiation	Mo-$K\alpha$ (λ = 0.71069 Å)	
Monochromator	Graphite crystal	
Scan mode	ω–2θ	
Scan range (2θ)	4°–60°	
Minimum scan speed	2.0°/min	1.5°/min
Scan width (ω)	±(0.7 + 0.15tanθ)°	
Measured intensities	3116	3369
Observed intensities ($I > 3\sigma$)	2364	1370
Unique reflections	2073	1156
Absorption correction	DIFABS (Walker & Stuart, 1983)	
Corrective factors	0.73–1.36	0.74–1.54
R	0.092	0.061

was lacking from all experimental runs they carried out, at different temperatures, with varying concentrations of lead and chloride ions.

Single crystal X-ray diffraction study

The first suggestion of the OD character of fiedlerite was given by the preliminary Weissenberg photographs, which displayed the characteristic features of OD structures. In fact the diffraction patterns of fiedlerite typically consisted of two class of reflections:

(a) family reflections, which are independent, in both their position and intensity, of the stacking sequence of the OD layers, and which define a common sub-cell;

(b) superstructure reflections, which are generally weaker than the preceding ones and depend on the particular stacking sequence.

A systematic inspection of several, long-exposed, single-crystal X-ray diffraction patterns of selected crystals of fiedlerite from both Laurion and Baratti revealed the presence, at both occurrences, of the two simplest and regular structures, the former with monoclinic, the latter with triclinic symmetry, and of a number of more complex or disordered sequences. Among all tested crystals, we were lucky enough to find two

suitable crystals, consisting of almost pure fiedlerite-1A (from Baratti) and fiedlerite-2M (from Laurion). With these crystals we carried out the collection of the X-ray diffraction intensity data for the structural analyses. As a first step the crystal structure of the 1A polytype was solved by direct methods (SHELXS86 computer program package; Sheldrick, 1986). At the end of the refinement of fiedlerite-1A (SHELX76 least-squares refinement program; Sheldrick, 1976), the starting coordinates (x_m, y_m, z_m) for the refinement of the 2M polytype were obtained from the coordinates (x_a, y_a, z_a) in the 1A polytype, on the basis of the OD relationships (see below) between the two polytypes, namely:

$$x_m = x_a/2$$
$$y_m = -x_a/4 + y_a$$
$$z_m = z_a$$

In Table 2 miscellaneous experimental data (unit cell parameters, data collection parameters, R factors) are reported. Tables of the observed and calculated structure factors, and the anisotropic thermal parameters, may be obtained from one of the authors (MP) upon request.

Although the structural model was firmly assessed for both polytypes, a minor problem remained unsolved for the 2M polytype, because of the strong correlation coefficients between pairs

TABLE 3. Fractional coordinates and B (Å^2) thermal parameters for fiedlerite-1A and fiedlerite-2M. The e.s.d.'s are given in parentheses and refer to the last digit. For lead and chlorine B is the equivalent isotropic parameter converted from the anisotropic ones [$B_{eq} = 8\pi^2(U_{11}U_{22}U_{33})^{1/3}$].

		FIEDLERITE-1A		
	x	y	z	B
Pb1	0.3700(2)	0.2145(2)	0.3251(2)	1.28(3)
Pb2	0.8954(2)	0.3521(2)	0.2727(2)	1.08(3)
Pb3	0.9011(2)	0.8463(2)	0.2595(2)	1.09(3)
Cl1	0.192(1)	0.421(1)	0.083(1)	1.4(2)
Cl2	0.345(1)	0.459(1)	0.634(1)	1.5(2)
Cl3	0.195(1)	0.923(1)	0.090(1)	1.4(2)
Cl4	0.349(1)	0.966(1)	0.636(1)	1.7(2)
F	0.931(3)	0.857(3)	0.611(3)	1.3(3)
(OH)	0.947(3)	0.361(3)	0.613(3)	0.6(3)
H_2O	0.505(4)	0.753(4)	0.995(4)	1.8(4)

		FIEDLERITE-2M		
	x	y	z	B
Pb1	0.1848(1)	0.1259(4)	0.3252(2)	1.10(4)
Pb2	0.4473(1)	0.122(3)	0.2741(2)	1.13(5)
Pb3	0.4510(1)	0.630(3)	0.2584(2)	1.07(8)
Cl1	0.0955(8)	0.362(5)	0.082(1)	1.3(6)
Cl2	0.1725(9)	0.363(8)	0.637(2)	1.3(4)
Cl3	0.0982(7)	0.862(5)	0.092(1)	1.1(5)
Cl4	0.1748(8)	0.868(8)	0.634(2)	1.5(3)
F	0.467(2)	0.609(4)	0.612(3)	0.6(4)
(OH)	0.472(2)	0.105(4)	0.613(4)	0.9(6)
H_2O	0.247(3)	0.610(9)	0.987(6)	2.7(9)

of atoms related through a pseudo-translation of $b/2$. The pairs involved are Pb2 and Pb3, Cl1 and Cl3, Cl2 and Cl4, F and (OH). This caused the e.s.d.'s of the y coordinates of such atoms to assume anomalously high values.

Description of the structure

The final fractional coordinates and thermal parameters for both polytypes are included in Table 3, and selected bond distances are given in Table 4. The crystal structures of the two
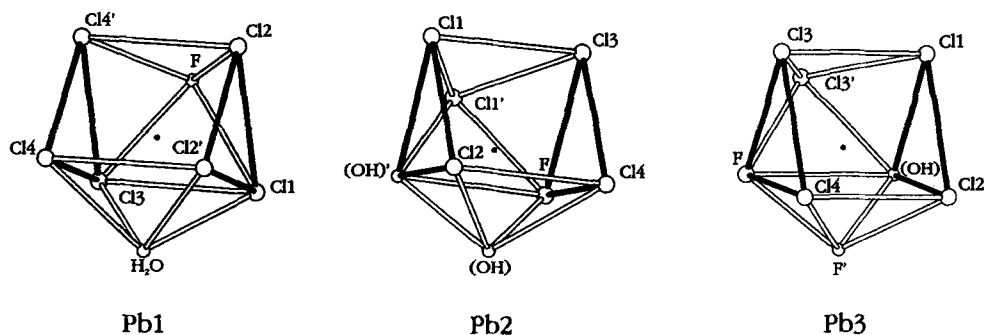

FIG. 1. Coordination polyhedra of the three independent lead atom sites that occur in fiedlerite-1A and fiedlerite-2M. Lead atoms are indicated by small filled circles. For each polyhedron, the triangular bases of the prism are outlined.

TABLE 4. Selected interatomic distances (Å) for fiedlerite-1*A* and fiedlerite-2*M*.

		1*A*	2*M*
Pb1	- Cl1	2.87(1)	2.80(3)
	- Cl2	3.06(1)	3.01(4)
	- Cl2'	3.111(9)	3.15(5)
	- Cl3	2.825(9)	2.91(3)
	- Cl4	3.03(1)	3.01(5)
	- Cl4'	3.06(1)	3.09(5)
	- F	2.65(2)	2.67(3)
	- H_2O	2.75(3)	2.75(5)
Pb2	- Cl1	3.08(1)	3.09(1)
	- Cl1'	3.23(1)	3.29(3)
	- Cl2	3.01(1)	3.05(5)
	- Cl3	3.290(9)	3.25(3)
	- Cl4	3.08(1)	3.01(5)
	- F	2.53(2)	2.63(4)
	- (OH)	2.42(2)	2.32(4)
	- (OH)'	2.44(2)	2.42(3)
Pb3	- Cl1	3.137(9)	3.07(3)
	- Cl2	3.056(9)	3.00(5)
	- Cl3	2.97(1)	2.96(1)
	- Cl3'	3.23(1)	3.31(3)
	- Cl4	3.10(1)	3.18(5)
	- F	2.51(2)	2.43(4)
	- F'	2.55(2)	2.54(2)
	- (OH)	2.41(3)	2.57(4)

polytypes of fiedlerite are characterized by the same coordination polyhedra. In fact, in both structures the three independent lead atoms lie at the centre of an 8-coordinated polyhedron, which may be described as either a distorted cubic antiprism or, more appropriately, as a bicapped trigonal prism. Such coordination is frequently displayed by Pb atoms in lead halides and other lead minerals (e.g. see Cannillo *et al.*, 1969; Kampf, 1991; Merlino *et al.*, 1993).

It is noteworthy that the nature of the bonding anions is different for the three independent lead atom sites (cf. Fig. 1): Pb1 is linked to 6 Cl, 1 F and 1 H_2O; Pb2 is linked to 5 Cl, 2 (OH) and 1 F; and Pb3 is linked to 5 Cl, 2 F and 1 (OH). As stated above, a pseudo *b*/2 translation occurs in the 2*M* polytype. Such a translation also involves Pb2 and Pb3, though they differ in the nature of the coordinating anions. Although F⁻ and (OH)⁻ have different crystal chemical roles, as explained below, they have similar dimensions. Therefore, we can regard Pb2 and Pb3 to be similar, in that they are linked to 5 larger Cl⁻ anions and 3 smaller (F,OH)⁻ anions. In contrast, the nature of the Pb1-centered polyhedron is markedly different.

Obviously, the positions of F⁻ and (OH)⁻ cannot be arbitrarily interchanged. In fact fluorine

is tetrahedrically linked to 4 lead atoms, whereas the oxygen of the (OH) group is linked to 3 lead atoms on one side, having the hydrogen pointing towards the opposite side. It was our discovery of an anion at the centre of a tetrahedron formed by 4 lead atoms that led us hypothesize the occurrence of fluorine instead of hydroxyl, which would be unlikely to be located within a lead tetrahedron. The chemical analysis we carried out confirmed our idea that 1 F and 1 (OH) per formula unit were present.

The crystal structure of both modifications of fiedlerite is characterized by the following structural units, alternately stacked along [100] (Fig. 2):

(*a*) Layers, parallel to (100), formed by Pb2- and Pb3-centered polyhedra. These polyhedra regularly alternate by sharing of triangular faces, and give rise to columns running along [010].

(*b*) Layers, also parallel to (100), formed by Pb1-centered polyhedra. Such polyhedra give rise, along [010], to zigzag chains by sharing of edges. Within these layers the polyhedral packing is less dense with respect to the (*a*) type layers, and water molecules are accommodated in the cavities of this layer.

OD description of fiedlerite

Following the basic statements of the OD theory (Dornberger-Schiff, 1964, 1966, 1979), those structures are to be considered OD structures, in which neighbouring layers can be arranged in two or more geometrically equivalent ways. The existence of two or more different ways of connecting neighbouring layers makes it possible to obtain a family of structures with variable degrees of order, which, taken as a whole, build up a family of OD structures. The symmetry features common to all members are dealt with by the OD theory, which focuses attention on the space transformations which convert any layer into itself or into the adjacent one. Such space transformations are the so-called λ- and σ-POs (partial operations) which, as suggested by their name, are not necessarily valid for the whole structure. A thorough account of the symmetry aspects of OD structures consisting of equivalent layers may be found in Dornberger-Schiff and Fichtner (1972).

The single layer in fiedlerite (Fig. 3) displays the layer group symmetry P (1) $2_1/m$ 1, and it is periodic in two dimensions ($b_0 = b_m \approx 8.0$, $c_0 = c_m \approx 7.3$ Å), the other parameters being $a_0 = 1/2$ $a_m \approx 8.3$ Å, $\beta_0 = \beta_m \approx 102°$. Pairs of adjacent layers are related through a screw axis parallel to *b*
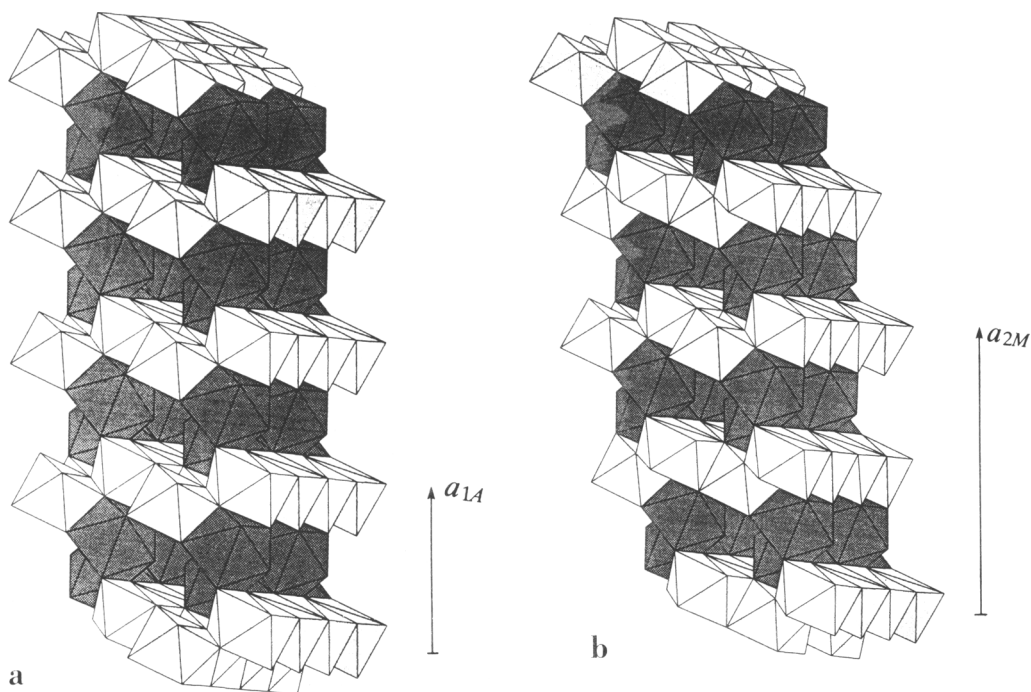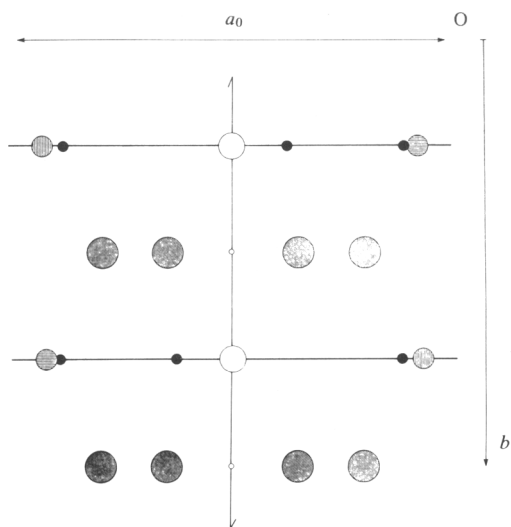
FIG. 2. Polyhedral packing in (*a*) fiedlerite-1*A*, and (*b*) fiedlerite-2*M*. The drawings are viewed down [021] (with [100] vertical). Pb1-, Pb2- and Pb3-centered polyhedra are denoted by dotted patterns with high, low and medium density respectively.

P (1) $2_1/m$ 1

with translational component $+b/4$, indicated by the symbol $2_{1/2}$, and a glide normal to b with translational component a_0, indicated by the symbol a_2. The presence of a mirror m among the λ-POs makes it possible for neighbouring layers to be related, besides the $2_{1/2}$ screw axis, also by the $2_{\bar{1}/2}$ screw axis, in which the translational component has the opposite direction ($-b/4$). The OD groupoid family symbol

$$P \ (1) \ 2_1/m \ 1$$
$$(1) \ 2_{1/2}/a_2 \ 1$$

accounts for the symmetry properties of the whole family of OD structures. As stated above, the pair of layers related through the $2_{1/2}$ operator is geometrically — and energetically — equivalent to

FIG. 3. The OD layer in fiedlerite. Atoms are denoted by circles with the following patterns: full (Pb), horizontal lines (OH), vertical lines (F), diagonal lines (Cl), dots (H$_2$O). The layer group symmetry is also given.
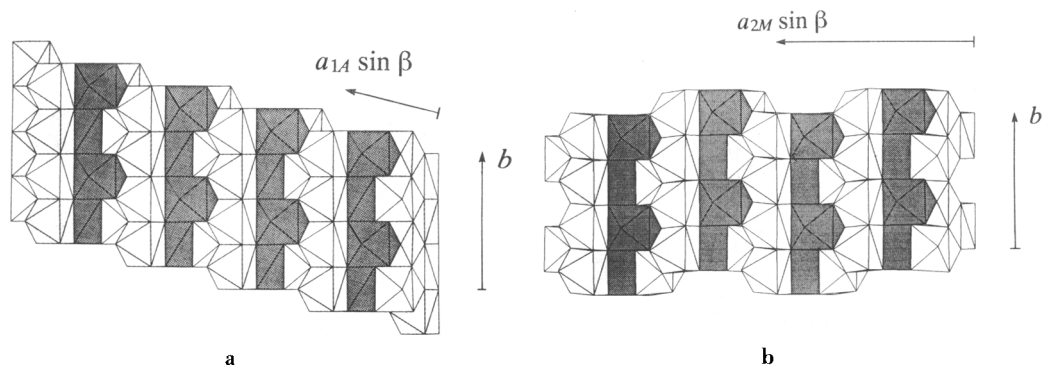
FIG. 4. Schematical drawing of (a) fiedlerite-1A and (b) fiedlerite-2M, as seen in [001] projection, featuring the different stacking of the OD layers.

the pair of layers related through the $2_{\bar{1}/2}$ operator. Different sequences of $2_{1/2}$ and $2_{\bar{1}/2}$ operators give rise to an infinite number of different polytypes and to disordered structures as well.

Among them the two simplest polytypes, the so-called polytypes with maximum degree of order (MDO-polytypes), are obtained (Fig. 4):

(a) from a sequence of operators all of the same kind, either $2_{1/2}$ or $2_{\bar{1}/2}$, which give rise to two structures with triclinic symmetry in twin relationships (MDO1 and MDO1');

(b) from a regular alternation of $2_{1/2}$ and $2_{\bar{1}/2}$ operators, which gives rise to a structure with monoclinic symmetry (MDO2).

In this latter case the λ-PO 2_1 and the σ-PO a_2 become total symmetry operators for the MDO2 structure, which has space group $P2_1/a$: the translational component of the σ-PO a_2 is just half of
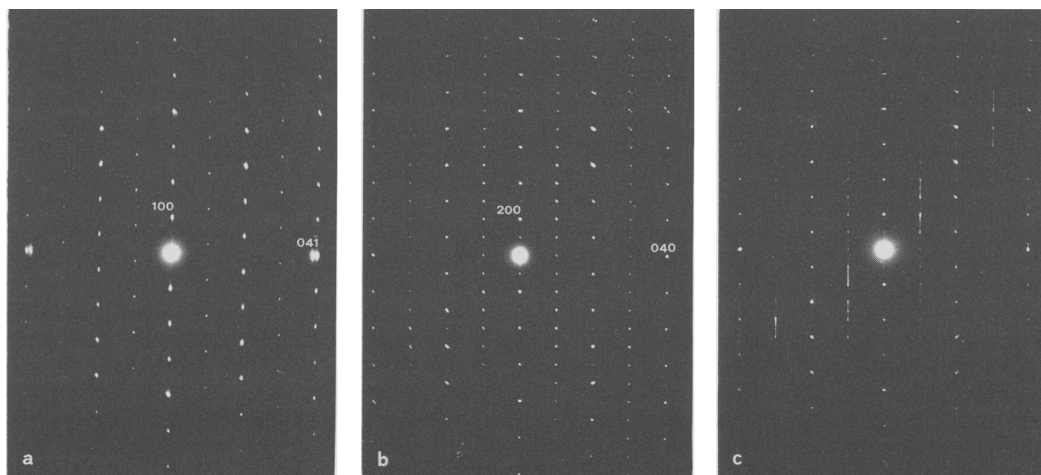

FIG. 5. Selected area electron diffractions of the two MDO polytypes: (a) fiedlerite-1A (zone axis [014]), (b) fiedlerite-2M (zone axis [001]), and of (c) a disordered crystal (zone axis [001]$_{2M}$). In all structures the 'family reflections' (i.e. those with k even) are independent of the stacking of the layers. A few forbidden reflections (i.e. $h00$ with h odd) are present in the 2M polytype, due to dynamical effects. In the k-odd rows of Fig. 5c weak streaked reflections indicate the presence of disordered stacking sequences, in addition to the presence of both MDO polytypes.

the cell parameter a of the MDO2 structure, and a_2 becomes a normal a glide in a structure which contains two layers within the unit cell.

In the former case only the inversion centers are maintained as total symmetry operators for the MDO1 structure, which in fact has space group $P\bar{1}$.

The two MDO structures just correspond to the two polytypes fiedlerite-$1A$ and fiedlerite-$2M$.

Nomenclature

Fiedlerite has been found to date in two occurrences (Laurion, Greece, and Baratti, Italy). Fiedlerites from both localities display OD character and the two MDO polytypes $1A$ and $2M$ were found. Therefore, together with the proposal of revision of the chemical formula of fiedlerite, discussed above, we submitted a proposal on nomenclature of the mineral to the I.M.A. CNMMN. Due to its OD character, the I.M.A. CNMMN approved the proposal to rename fiedlerite and, from now on, the denote the mineral together with the polytype suffixes (i.e. fiedlerite-$1A$, fiedlerite-$2M$), according to the accepted rules set out in Guinier et al. (1984). A range of non-MDO fiedlerite polytypes are likely to exist.

To this aim we examined specimens from both localities by transmission electron microscopy. Our purpose was to obtain high-resolution electron micrographs that would enable us to identify and characterize more complex polytypes within this OD family. Unfortunately, fiedlerite has proven to be highly sensitive to the electron beam, and this prevented us from obtaining any direct lattice images of it. However, we recorded a number of selected-area electron diffraction patterns. Among these we identified patterns from each of the MDO polytypes, and we recorded evidence for the occurrence of polytypes characterized by more disordered sequences of layers (see Fig. 5).

Acknowledgements

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