

## GJERDINGENITE-Fe FROM NORWAY, A NEW MINERAL SPECIES IN THE LABUNTSOVITE GROUP: DESCRIPTION, CRYSTAL STRUCTURE AND TWINNING

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### ABSTRACT

Gjerdingenite-Fe occurs as yellow prisms or laths up to 1 mm long in miarolitic cavities of a sodic granite ("ekerite") at Gjerdingselva, Lunner, Oppland, Oslo Region, Norway. The simplified formula is  $K_2[(H_2O)_2(Fe,Mn)][(Nb,Ti)_4(Si_4O_{12})_2(OH,O)_4] \cdot 4H_2O$ , *i.e.*, the mineral is an analogue of those with root name kuzmenkoite, which have  $Ti > Nb$ . The mineral is monoclinic,  $C2/m$ , with  $a$  14.529(2),  $b$  13.943(2),  $c$  7.837(2) Å,  $\beta$  117.61(1)°,  $V$  1406.8(9) Å<sup>3</sup>,  $Z = 2$ . The crystal structure was refined to  $R = 0.054$  on the basis of 1677 observed reflections; twinning on {001} simulates an orthorhombic  $F$ -centered lattice. The partitioning of cations and H<sub>2</sub>O molecules in the sites  $B$ ,  $B'$ ,  $C$  (occupying channels of the zeolite-like structure) is discussed; for the refined crystal, the following crystal-chemical formula is established by comparison of chemical and structure-refinement data:  $\{[K_{1.20}Na_{0.72}(H_2O)_{2.08}]_{\Sigma 4}[K_{2.08}(H_2O)_{1.92}]_{\Sigma 4}\}[(H_2O)_{3.40}K_{0.56}Ca_{0.04}]_{\Sigma 4}(Fe_{0.95}Mn_{0.75}\square_{0.30})_{\Sigma 2}(Nb_{4.30}Ti_{3.45}Fe_{0.20}Zr_{0.05})_{\Sigma 8}(Si_{15.90}Al_{0.10})_{\Sigma 16}O_{48}[(OH)_{4.16}O_{3.84}]_{\Sigma 8} \cdot 4H_2O$  ( $Z = 1$ ). The strongest six reflections of the powder pattern [ $d_{obs}$  in Å( $hkl$ )] are: 6.92(80)(020,001), 6.42(50)(200,201), 4.94(70)(021), 3.225(100)(421,400,402), 3.114(80)(041,022), and 2.512(50)(441,401,403). The mineral is optically biaxial (+) with  $\alpha$  1.6676(2),  $\beta$  1.7001(4),  $\gamma$  1.794(1);  $2V_{meas} = 58.5(2.3)^\circ$ ,  $2V_{calc} = 63.71(1)^\circ$ . The Mohs hardness is about 5;  $D_{meas} = 2.82(2)$ ,  $D_{calc} = 2.830$  g/cm<sup>3</sup>. The pseudo-orthorhombic crystals are flattened on {001} and elongate along [010]. Five crystal forms were observed: {100}, {010} (subordinate), {001}, {201}, and {021}.

**Keywords:** gjerdingenite-Fe, new mineral species, labuntsovite group, zeolite-like structure, twinning, miarolitic cavities, ekerite, Oslo Region, Norway.

### SOMMAIRE

La gjerdingenite-Fe se présente en prismes jaunes ou en lamelles atteignant 1 mm de long dans des cavités miarolitiques d'un granite sodique ("ekerite") à Gjerdingselva, Lunner, Oppland, dans la région d'Oslo, en Norvège. La formule simplifiée de cette nouvelle espèce serait:  $K_2[(H_2O)_2(Fe,Mn)][(Nb,Ti)_4(Si_4O_{12})_2(OH,O)_4] \cdot 4H_2O$ , *i.e.*, elle est un analogue des minéraux ayant la racine kuzmenkoïte dans leur nom, et donc  $Ti > Nb$ . La gjerdingenite-Fe est monoclinique,  $C2/m$ ,  $a$  14.529(2),  $b$  13.943(2),  $c$  7.837(2) Å,  $\beta$  117.61(1)°,  $V$  1406.8(9) Å<sup>3</sup>,  $Z = 2$ . La structure cristalline en a été affinée jusqu'à un résidu  $R = 0.054$  en utilisant 1677 réflexions observées; un maillage sur {001} simule une maille orthorhombique à faces centrées. Nous évaluons la répartition des cations et des molécules de H<sub>2</sub>O sur les sites  $B$ ,  $B'$ ,  $C$ , qui occupent les canaux de cette structure, semblable à celle d'une zéolite; dans le cas du cristal qui a servi à l'affinement de la structure, voici la formule cristallographique, établie en évaluant les données sur la composition et les résultats de l'affinement:  $\{[K_{1.20}Na_{0.72}(H_2O)_{2.08}]_{\Sigma 4}[K_{2.08}(H_2O)_{1.92}]_{\Sigma 4}\}[(H_2O)_{3.40}K_{0.56}Ca_{0.04}]_{\Sigma 4}(Fe_{0.95}Mn_{0.75}\square_{0.30})_{\Sigma 2}(Nb_{4.30}Ti_{3.45}Fe_{0.20}Zr_{0.05})_{\Sigma 8}(Si_{15.90}Al_{0.10})_{\Sigma 16}O_{48}[(OH)_{4.16}O_{3.84}]_{\Sigma 8} \cdot 4H_2O$  ( $Z = 1$ ). Les six raies les plus intenses du spectre de diffraction (méthode des poudres) [ $d_{obs}$  en Å( $hkl$ )] sont: 6.92(80)(020,001), 6.42(50)(200,201), 4.94(70)(021), 3.225(100)(421,400,402), 3.114(80)(041,022), et 2.512(50)(441,401,403). Le minéral est biaxe (+), avec  $\alpha$  1.6676(2),  $\beta$  1.7001(4),  $\gamma$  1.794(1);  $2V_{mes} = 58.5(2.3)^\circ$ ,  $2V_{calc} = 63.71(1)^\circ$ . La dureté de Mohs est d'environ 5;  $D_{mes} = 2.82(2)$ ,  $D_{calc} = 2.830$  g/cm<sup>3</sup>. Les cristaux pseudo-orthorhombiques sont aplatis sur {001} et allongés selon [010]. Nous notons la présence des cinq formes suivantes: {100}, {010} (subordonné), {001}, {201}, et {021}.

(Traduit par la Rédaction)

**Mots-clés:** gjerdingenite-Fe, nouvelle espèce minérale, groupe de la labuntsovite, structure zéolitique, maillage, cavités miarolitiques, ékerite, région d'Oslo, Norvège.

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## INTRODUCTION

The history of investigation of the new mineral species gjerdingenite-Fe spans quite a few years. X-ray powder-diffraction diagrams made in 1973 gave a pattern resembling that of nenadkevichite (Kuz'menko & Kazakova 1955), albeit with an apparently larger cell. The interpretation of Weissenberg and precession patterns made in 1975 proved to be difficult, and twinning was suspected. Tentative and approximate unit-cell dimensions of 13.8, 27.6 and 14.45 Å were determined. Potassium was found to be a major element and, unfortunately, collectors distributed the mineral very early, labeled as a K-dominant analogue of nenadkevichite. New investigations with a four-circle single-crystal diffractometer in 1987 gave an orthorhombic cell with  $a$  7.287(2),  $b$  13.904(4),  $c$  6.987(2) Å, space group *Pbn*. However, the twinning problem could not be handled at that time. Only recently, new single-crystal diffraction data and the use of modern software designed to handle twinning brought a solution to the problem and showed that the mineral is monoclinic *C2/m* with twinning on {001}, simulating an orthorhombic *F*-centered lattice (see below). The numerous publications by Russian scientists on minerals related to nenadkevichite and labuntsovite and their crystal structures, culminating in the recently approved nomenclature of the labuntsovite group (Chukanov *et al.* 2002), have been a useful prerequisite for our own investigations.

The mineral and name were approved by the Commission on New Minerals and Mineral Names, IMA (2001–009). The name is derived from the type locality, Lake Gjerdingen, with the suffix -Fe to indicate the dominant cation in the *D* site (see below). The type material is deposited at the Geological Museum, University of Oslo (catalogue nos. 33712, 33713, and 33715).

## OCCURRENCE

Ekerite is a local name of a sodic granite from the Permian Oslo Region, a paleorift area in southern Norway. Its petrography was described by Barth (1945), Sæther (1962) and Dietrich *et al.* (1965). A mineralogically unique pluton of ekerite, measuring about  $2 \times 4$  km<sup>2</sup>, is situated east-southeast of Lake Gjerdingen in the forest area of Nordmarka, some 30 km north of Oslo. The locality is commonly known as Gjerdingen, but is actually close to Gjerdingenselva, a river that flows from Lake Gjerdingen. A correct locality name would be Gjerdingenselva, Lunner, Oppland, Norway. This particular pluton of ekerite contains elpidite and kupletskite as rock-forming minerals, and is rich in miarolitic cavities and pegmatitic pods. The mineralogy of the miarolitic cavities was briefly treated by Dietrich *et al.* (1965), Sæbø (1966) and Raade (1972). An interesting suite of uncommon fluorides was described by Raade & Haug (1980, 1981), and a compilation of the cavity mineral-

ogy was published by Raade & Haug (1982). The Gjerdingenselva ekerite is the type locality of janhaugite, an Na-Mn-Ti silicate of the cuspidine group (Raade & Mladeck 1983, Annehed *et al.* 1985).

The new mineral species gjerdingenite-Fe has a hydrothermal origin, as it lines miarolitic cavities, and is most closely associated with quartz, orthoclase, albite, aegirine, kupletskite, elpidite, lorenzenite, pyrochlore, monazite-(Ce), gagarinite-(Y), ralstonite, gearsutite, and molybdenite. It may form an epitaxial overgrowth on elpidite (which has  $a$  7.120,  $b$  14.665,  $c$  14.740 Å) and may have a coating of microcrystalline ralstonite. Epitaxial growth of labuntsovite on elpidite and elpidite on labuntsovite is known from Mont Saint-Hilaire, Quebec, Canada (Henderson 1979, 1994). Petersen *et al.* (1996) have described crystals of "K-dominant nenadkevichite" (probably vuoriyarvite-K, *cf.* Chukanov *et al.* 2002) epitaxially overgrown on elpidite from Narssârssuk, Greenland. Gjerdingenite-Fe is quite widespread in the miarolitic cavities but invariably in small amounts. It is one of the few K-rich minerals (besides orthoclase and kupletskite) in a paragenesis dominated by Na-rich silicates and fluorides.

## MORPHOLOGY AND PHYSICAL PROPERTIES

A color photograph and an SEM photomicrograph of the mineral now known as gjerdingenite-Fe were published by Raade & Haug (1982). A different SEM photomicrograph is reproduced here (Fig. 1). The mineral occurs as prismatic to lath-shaped crystals up to 1 mm in length. They may form subparallel or irregular aggregates to 3 mm. Five crystal forms were identified by goniometric measurements: pinacoids {100}, {010}, {001}, {20 $\bar{1}$ }; prism {021} (Fig. 2). The crystals are flattened on {001} and elongate along [010]. The form {010} is invariably subordinate or may be lacking. The crystals have a distinct pseudo-orthorhombic habit. Twinning on {001} is shown to be present on a structural basis (see below). The color varies from pale yellow to orange yellow or brownish yellow, and the streak is white to faintly yellow. The crystals are translucent or rarely transparent, with a vitreous to waxy luster. They show no fluorescence in long- or short-wave ultraviolet light. No cleavage or parting was observed. The fracture is uneven, and the mineral is very brittle. By suspension in bromoform, a density of 2.82(2) g/cm<sup>3</sup> was determined.

Spindle-stage measurements ( $\lambda = 589$  Å), using the microrefractometer equipment designed by Medenbach (1985), showed the mineral to be biaxial (+), with  $\alpha$  1.6676(2),  $\beta$  1.7001(4),  $\gamma$  1.794(1);  $2V_{\text{meas}}$  58.5(2.3)°,  $2V_{\text{calc}}$  63.71(1)°; orientation:  $Y = b$ . No axial dispersion was observed, and the mineral is non-pleochroic. Gjerdingenite-Fe has the largest  $\beta$  index among the Nb-dominant labuntsovite-group minerals (*e.g.*, for organovaitite-subgroup minerals, which are analogues of gjerdingenite with a doubled  $c$  parameter,  $1.685 < \beta <$

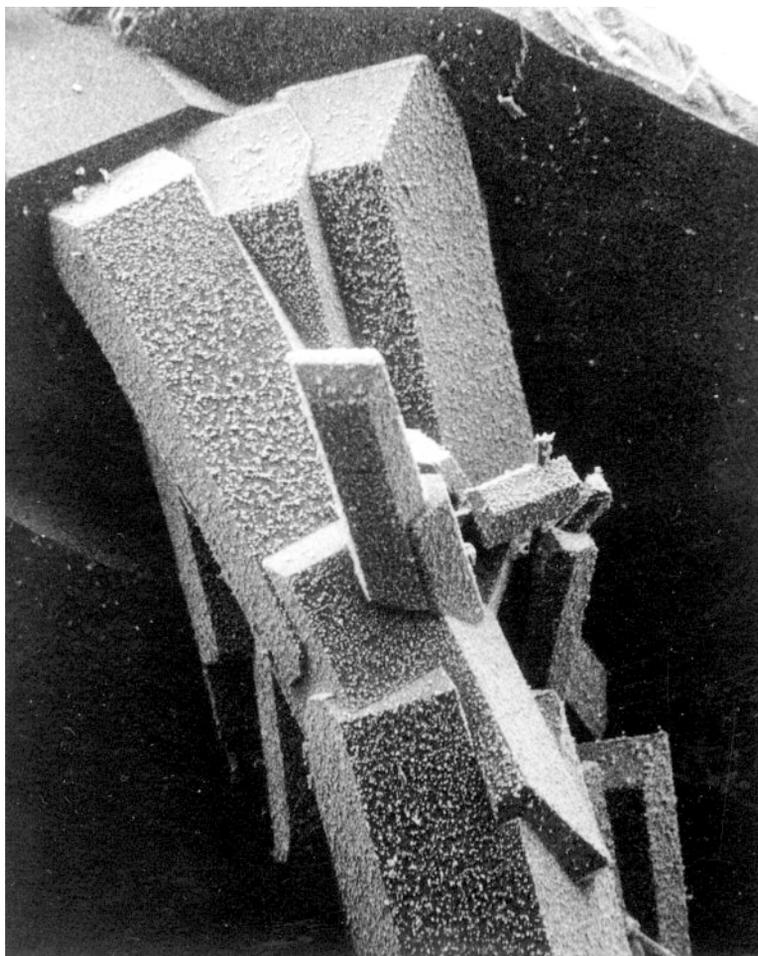


FIG. 1. SEM photomicrograph of gjerdingenite-Fe. Length of the aggregate is  $\sim 0.5$  mm. The mineral is dusted with tiny crystals of two phases. At high magnification, one of them is seen to form cubes and is probably ralstonite.

1.692). This feature could possibly be used as a diagnostic characteristic of gjerdingenite.

#### CHEMICAL DATA AND INFRARED SPECTRUM

##### *Chemical analyses*

Three crystals of gjerdingenite-Fe, including the one used for the present single-crystal study, were analyzed by two different wavelength-dispersion electron microprobes. The Cameca Camebax electron microprobe housed at the Geological Museum in Oslo was operated at an accelerating voltage of 15 kV and a sample current of 10 nA (and a fourth crystal was also analyzed there), using the following standards: albite (Na), or-

thoclase (K), wollastonite (Ca, Si),  $\text{MnTiO}_3$  (Mn, Ti),  $\text{Fe}_2\text{O}_3$  (Fe),  $\text{Al}_2\text{O}_3$  (Al), Zr metal (Zr), and Nb metal (Nb). Areas of  $50 \times 50 \mu\text{m}^2$  were scanned to minimize any loss of Na and  $\text{H}_2\text{O}$ . The ARL-SEMQ electron microprobe of the University of Modena and Reggio Emilia was operated at 15 kV and a sample current of 20 nA, using the following standards: albite (Na), microcline (K), clinopyroxene (Ca, Si), ilmenite (Fe, Ti), spessartine (Al, Mn), Zr metal (Zr), and Nb metal (Nb). A dearth of material prevented a direct determination of  $\text{H}_2\text{O}$ ; its presence is shown by the infrared spectrum and structural results (see below). Bands of carbonate groups were not observed in the infrared spectrum. All Fe is assumed to be divalent.

All the analyses show low totals and low silica contents relative to the structural results (Table 1). The following considerations could justify the low values: (i) poor contact of the crystals with the surrounding epoxy (it is known that the preparation technique used for isolated small single crystals often leads to poor conductivity of the sample); (ii) too thin a carbon coating; (iii) voids in the crystals. Actually, the three Oslo mounts, which were re-polished and analyzed in Modena, gave anhydrous results with higher totals around 88 wt.% but with poorer values of the (Nb,Ti):(Si,Al) ratio. Bearing these difficulties with the analytical results in mind, we have refrained from calculating empirical formulae from any one of the analytical datasets.

On the basis of (Si + Al) = 16 and the refinement of the structure (see below for a discussion), the following

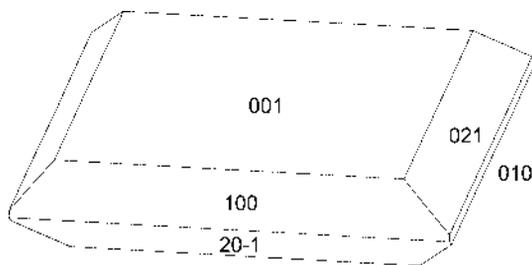


FIG. 2. Crystal drawing of gjerdingenite-Fe showing five forms (four pinacoids and one prism). The pinacoid {010} may be lacking. The most common habit of the crystals is tabular to lath-shaped. In some crystals, the form {001} is less dominant, and the crystals have a more prismatic habit. The crystals are distinctly pseudo-orthorhombic.

crystal-chemical formula is obtained:  $\{[K_{1.20}Na_{0.72}(H_2O)_{2.08}]_{\Sigma 4}[K_{2.08}(H_2O)_{1.92}]_{\Sigma 4}\}[(H_2O)_{3.40}K_{0.56}Ca_{0.04}]_{\Sigma 4}(Fe_{0.95}Mn_{0.75}\square_{0.30})_{\Sigma 2}(Nb_{4.30}Ti_{3.45}Fe_{0.20}Zr_{0.05})_{\Sigma 8}(Si_{15.90}Al_{0.10})_{\Sigma 16}O_{48}[(OH)_{4.16}O_{3.84}]_{\Sigma 8} \cdot 4H_2O$ . The chemical composition corresponding to this formula is given in Table 1 (column C). Iron substituting for (Nb,Ti) is here treated as divalent, although considering charge and ionic size,  $Fe^{3+}$  would be closer to Nb and Ti than  $Fe^{2+}$ . The amount of Fe in the *M* site being low, its valence has only a minor influence on the OH:O ratio.

The calculated density, based on the crystal-chemical formula (unit-formula weight 2397.72) and the cell volume from the single-crystal study, is  $2.830 \text{ g/cm}^3$ , in good agreement with the measured density of  $2.82(2) \text{ g/cm}^3$ . The Gladstone-Dale relationship gives a compatibility index  $1 - (K_p/K_c)$  of 0.0012 using  $D_{calc}$  and  $-0.0024$  using  $D_{meas}$ ; both are superior (Mandarino 1981).

It should be noted that some parts of crystal no. 1 have  $Mn > Fe$  (Table 1). Of the seven individual analyses made in Oslo on this crystal, all show  $Mn > Fe$  (mean wt.%: MnO 3.15, FeO 2.46), whereas three of the six individual analyses made in Modena on the same crystal have  $Mn > Fe$ . Strictly speaking, this is a different mineral species, the Mn-dominant analogue of gjerdingenite-Fe. We have based the definition of our new species on crystals where  $Fe > Mn$ ; the chemical data of crystal no. 1 are reported for completeness.

#### Infrared-absorption data

The infrared-absorption spectrum of gjerdingenite-Fe was recorded with a Perkin-Elmer spectrophotometer using a Nujol mull with *ca.* 0.03 wt.% of the mineral. Owing to this low concentration, some of the

TABLE 1. ELECTRON-MICROPROBE DATA ON GJERDINGENITE-Fe DONE IN OSLO (A) AND MODENA (B), COMPARED TO THE CHEMICAL DATA GIVEN IN THE TEXT (C)

	A				B				C					
	Crystal 1 (7)*	Crystal 2** (7)	Crystal 3 (4)	Crystal 4 (2)	Crystal 1 (6)	Crystal 2** (8)	Crystal 3 (4)							
$Na_2O$ wt.%	1.21	1.02-1.39	0.68	0.56-0.84	0.69	0.55-0.83	0.95/1.06	1.41	1.31-1.50	0.72	0.58-0.82	0.76	0.74-0.78	0.93
$K_2O$	6.37	6.19-6.51	6.76	6.45-7.26	6.03	5.39-6.58	4.69/4.84	6.30	6.00-6.56	7.13	6.90-7.77	6.50	6.46-6.53	7.54
CaO	0.02	0.00-0.07	0.08	0.04-0.10	0.05	0.02-0.08	0.05/0.08	0.03	0.02-0.04	0.09	0.04-0.12	0.07	0.06-0.08	0.09
MnO	3.15	2.92-3.38	2.97	2.66-3.22	2.90	2.64-3.11	2.18/2.40	2.99	2.91-3.09	3.10	3.03-3.21	3.09	3.02-3.13	2.22
FeO	2.46	2.16-2.75	3.44	2.90-4.57	4.31	3.33-5.01	3.07/2.87	3.14	2.78-3.47	3.59	2.65-4.07	4.63	3.65-5.17	3.45
$Al_2O_3$	0.17	0.15-0.21	0.20	0.09-0.43	0.37	0.27-0.48	0.04/0.05	0.20	0.15-0.28	0.21	0.12-0.29	0.43	0.22-0.52	0.21
$SiO_2$	37.07	36.84-37.26	36.35	36.08-36.93	36.00	35.24-37.00	37.78/37.74	37.85	37.04-38.41	37.50	36.59-38.36	36.89	36.26-37.80	39.84
$TiO_2$	9.30	9.10-9.69	10.14	9.37-11.24	9.75	8.98-10.56	9.06/8.83	11.23	10.19-12.71	10.58	9.26-11.13	10.89	10.13-11.75	11.49
ZrO <sub>2</sub>	2.13	1.42-2.61	0.71	0.52-1.01	0.32	0.19-0.48	0.20/0.06	1.01	0.40-1.85	0.65	0.43-0.91	0.33	0.17-0.50	0.26
$Nb_2O_5$	23.77	22.58-24.57	23.24	21.32-24.91	23.97	21.63-26.18	25.14/26.88	23.68	21.89-24.59	25.03	23.77-26.07	24.76	22.90-26.62	23.84
$H_2O$	n.d.		n.d.		n.d.			n.d.		n.d.		n.d.		10.13
Sum	85.65	84.57	84.39	83.16/84.81	87.84	88.60	88.35	100.00						

\* The number of analyses made is given in parentheses for each crystal. \*\* Crystal no. 2 was used for the structure determination. Barium, Sr, Zn and Mg were sought but not found. n.d.: not determined. In each case, the range of values is given.

absorption bands are not well resolved. The wavenumbers of the absorption bands are (in  $\text{cm}^{-1}$ ):  $\sim 3560$  (broad), 1640, 1595 (shoulder), 1110 (strong),  $\sim 1070$ ,  $\sim 1020$ , 950 (strong), 775, and 690 (strong).

The band at  $3560\text{ cm}^{-1}$  is due to O–H stretching, and the ones at 1640 and  $1595\text{ cm}^{-1}$ , to H–O–H bending. The splitting of the  $\sim 1600\text{ cm}^{-1}$  band indicates that  $\text{H}_2\text{O}$  is present in at least two different sites (the structure refinement shows that  $\text{H}_2\text{O}$  is located in four positions: *B*, *B'*, *C* and *W*, see below). The prominent  $690\text{ cm}^{-1}$  band, representing a (Nb,Ti)–O stretching vibration, has a similar wavenumber to that in the structurally related minerals kuzmenkoite-Mn (Chukanov *et al.* 1999), organovaita-Mn (Chukanov *et al.* 2001a), and parakuzmenkoite-Fe (Chukanov *et al.* 2001b). The other members of the labuntsovite group have wavenumbers below  $690\text{ cm}^{-1}$  for this mode. The three absorption bands in the region  $1000\text{--}1200\text{ cm}^{-1}$  are Si–O–Si stretching modes.

#### X-RAY POWDER-DIFFRACTION DATA

The X-ray powder-diffraction pattern of gjerdingenite-Fe, obtained with a Guinier – de Wolff quadruple focusing camera, is given in Table 2. Correct indexing of the 19 observed reflections was achieved by comparison with the powder-diffraction pattern calculated from the structure data. The pseudo-orthorhombic symmetry is reflected in the multiple indexing of most of the reflections. The agreement between observed and calculated intensities is reasonably good, considering the visual estimates of observed intensities and the high

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR GJERDINGENITE-Fe

$I_{\text{obs}}$	$I_{\text{calc}}$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$hkl$	$I_{\text{obs}}$	$I_{\text{calc}}$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$hkl$
80	57	6.92	6.97	0 2 0	50	25	2.512	2.516	$\bar{4}$ 4 1
100		6.95	6.95	0 0 1	11			2.513	4 0 1
50	25	6.42	6.44	2 0 0	11			2.512	$\bar{4}$ 0 3
25		6.44	6.44	$\bar{2}$ 0 1	20	21	2.461	2.461	0 4 2
70	59	4.94	4.92	0 2 1	5	7	2.038	2.038	4 4 1
10	8	3.903	3.909	2 0 1	7			2.038	$\bar{4}$ 4 3
	8		3.907	$\bar{2}$ 0 2	15	9	1.930	1.930	0 4 3
100	35	3.225	3.223	$\bar{4}$ 2 1	10	3	1.878	1.882	4 2 2
	40		3.221	4 0 0	3			1.881	$\bar{4}$ 2 4
	40		3.221	$\bar{4}$ 0 2	10	2	1.825	1.827	$\bar{6}$ 0 4
80	67	3.114	3.116	0 4 1	9			1.818	$\bar{8}$ 0 2
	39		3.111	0 2 2	5	10	1.740	1.743	0 8 0
20	17	3.069	3.066	2 4 0	7			1.738	0 0 4
	17		3.065	$\bar{2}$ 4 1	20	8	1.707	1.705	4 4 2
20	11	2.928	2.924	4 2 0	8			1.704	$\bar{4}$ 4 4
	11		2.924	$\bar{4}$ 2 2	10	7	1.575	1.570	$\bar{8}$ 4 3
20	11	2.596	2.601	2 4 1	7			1.570	$\bar{8}$ 4 1
	11		2.601	$\bar{2}$ 4 2	5	3	1.534	1.533	4 8 0
	8		2.597	2 0 2	3			1.533	$\bar{4}$ 8 2
	8		2.597	$\bar{2}$ 0 3					

Guinier – de Wolff camera,  $\text{FeK}\alpha$  radiation, Mn filter. Internal standard: lead nitrate. Intensities are visually estimated. The  $\bar{8}02$ ,  $\bar{8}43$  and  $\bar{8}41$  reflections were not used for calculation of the unit-cell parameters. The refined parameters are:  $a$  14.54(1),  $b$  13.941(7),  $c$  7.844(4) Å,  $\beta$  117.59(4)°,  $V$  1409(1) Å<sup>3</sup>.

number of overlapping reflections. Refined unit-cell parameters from powder data are:  $a$  14.54(1),  $b$  13.941(7),  $c$  7.844(4) Å,  $\beta$  117.59(4)°,  $V$  1409(1) Å<sup>3</sup>. The refinement included all multiple indices listed in Table 2, except three, as noted.

#### SINGLE-CRYSTAL DIFFRACTOMETRY AND TWINNING

A suitable single crystal was selected from several crystals tested. We used a single-crystal X-ray diffractometer (Table 3) to collect 3809 reflections on the basis of an  $F$ -centered orthorhombic lattice with cell parameters  $a_{\text{or}}$  14.529(3),  $b_{\text{or}}$  13.943(2),  $c_{\text{or}}$  27.779(6) Å, obtained by least-squares refinement of 24 reflections with  $21.2^\circ < 2\theta < 28.8^\circ$ . The occurrence of non-space-group systematic absences, besides the systematic absences required by the space group  $Fmmm$ , suggested the presence of twinning in our crystal, as already observed in other labuntsovite-group minerals by Rastsvetaeva *et al.* (1994).

The type of twinning occurring in gjerdingenite-Fe deserves a detailed analysis as an illustrative and complex example where the crystal structure can be solved by the aid of available software like the SHELX-97 package (Sheldrick 1997), which includes the treatment of twinning according to Herbst-Irmer & Sheldrick (1998).

#### Twinning in real space

Figure 3 shows that the monoclinic  $C$ -centered lattice of gjerdingenite-Fe can be split into two identical orthorhombic  $F$ -centered sublattices with a relative shift of ( $\frac{3}{4}$  0  $\frac{1}{4}$ ). The monoclinic  $C$ -centered cell is obtained from the orthorhombic  $F$ -centered supercell by the transformation  $100\ 010\ -\frac{1}{4}\ 0\ \frac{1}{4}\ 1$  and has parameters  $a_{\text{mon}} = a_{\text{or}} = 14.529(2)$ ,  $b_{\text{mon}} = b_{\text{or}} = 13.943(2)$ ,  $c_{\text{mon}} = 7.837(6)$  Å  $\approx c_{\text{or}}/3.5$  and  $\beta = 117.61(1)^\circ$ . With refer-

TABLE 3. EXPERIMENTAL CONDITIONS AND CRYSTAL DATA FOR GJERDINGENITE-Fe

Chemical formula	$\text{K}_2[(\text{H}_2\text{O})_2(\text{Fe},\text{Mn})][(\text{Nb},\text{Ti})_2(\text{Si}_4\text{O}_{12})_2(\text{OH},\text{O})_4] \cdot 4\text{H}_2\text{O}$
Radiation and wavelength	$\text{MoK}\alpha$ , 0.71069 Å
$\mu$	2.47 $\text{mm}^{-1}$
Diffractometer, monochrom.	Siemens P4, graphite
Space group, $Z$	$C2/m$ , 2
Unit-cell dimensions	$a$ 14.529(2), $b$ 13.943(2), $c$ 7.837(2) Å, $\beta$ 117.61(1)°
Unit-cell volume	1406.8(9) Å <sup>3</sup>
$D(\text{calc.})$ , $D(\text{meas.})$	2.830, 2.82(2) $\text{g}/\text{cm}^3$
Crystal size	$0.20 \times 0.10 \times 0.07\text{ mm}$
Index ranges	$-13 \leq h \leq 13$ , $0 \leq k \leq 13$ , $-7 \leq l \leq 7$
Four standard reflections	every 100 reflections
Collected reflections	3809
Indep. reflect. with $I > 2\sigma(I)$	1677; $R_{\text{int}} = 0.05(5)$
Refinement method	full-matrix least-squares on $F^2$
Weights	$1/[O(\text{Fo})^2 + (0.093\text{P})^2 + (13.7\text{P})^2]$ $P = [\text{max}(\text{Fo})^2 + 2(\text{Fc})^2]$
$R(F)$ , $R(F^2)$ , $G_{\text{oof}}$	0.054; 0.166; 1.35
Refined parameters	124
Largest residues ( $e/\text{Å}^3$ )	1.07; -0.69

ence to monoclinic indexing, the (001) and  $(\bar{4}01)$  planes correspond to the (001) and (100) mirror planes of the orthorhombic sublattice, respectively. Each of these two planes can act as a twinning element and generate the same twin by reticular merohedry (*cf.* Catti & Ferraris 1976, Nespolo & Ferraris 2000). The monoclinic lattice can be split also into pseudo-hexagonal sublattices (Fig. 3). Complex multiple twinning is in principle possible according to this higher pseudosymmetry, but it has not been observed.

#### *Twinning in reciprocal space*

Figure 3 shows the (*h*0*l*) and (*h*1*l*) planes of the reciprocal lattice, twinned according to the (001) plane. Indices referred both to the two monoclinic components of the twin and to the resulting orthorhombic twin-lattice are given; the *k* index is the same for all types of indexing. For  $k = 2n$ , each node of one component (orange axes in Fig. 3) exactly overlaps a non-equivalent node of the second component (blue axes); for  $k = 2n + 1$ , the nodes of the two components intercalate such as to halve the periodicity along *c*\*. According to the indexing in the orthorhombic reference-system (green color), besides the space-group systematic absences of an *F*-centered lattice (*h*, *k* and *l* are either all even or all odd), non-space-group systematic absences are observed for  $3h + l \neq 4n$  and  $k = 2n$ . The latter absences are due to the extra nodes occurring in the orthorhombic *F*-centered cell at  $(\frac{3}{4} 0 \frac{1}{4})$ ,  $(\frac{1}{4} 0 \frac{3}{4})$ ,  $(\frac{1}{4} \frac{1}{2} \frac{1}{4})$  and  $(\frac{3}{4} \frac{1}{2} \frac{3}{4})$  (Fig. 3).

Mathematically, the non-space-group systematic absences can be proved by splitting the formula of the structure factor into two parts: one part contributed only by the subset of atoms *j* in the positions (*x<sub>j</sub>*, *y<sub>j</sub>*, *z<sub>j</sub>*), and a second one contributed only by the subset of *j*' atoms in the positions (*x<sub>j</sub>* +  $\frac{3}{4}$ , *y<sub>j</sub>*, *z<sub>j</sub>* +  $\frac{1}{4}$ ). Each of the two subsets of atoms corresponds to one of the two orthorhombic sublattices, with the relative shift being  $(\frac{3}{4} 0 \frac{1}{4})$  as mentioned above.

#### *Refinement of the structure*

The anisotropic refinement (isotropic for the sites *B* and *W*; Table 4) of gjerdingenite-Fe in the space group *C2/m* converged to  $R(F) = 0.054$  for 1677 independent reflections with  $I > 2\sigma(I)$  obtained by merging the equivalent reflections of the measured set ( $R_{\text{int}} = 0.05$ ). The two components of the twin have the same volume, as refined by SHELX-97 (Sheldrick 1997). Taking into account the main ion occupying each crystallographic site, the following scattering curves have been used for the refinement:  $B = C = K$ ,  $B' = K + O$  (the ratio K/O was refined),  $D = \text{Fe}$ ,  $M = \text{Ti} + \text{Nb}$  (the ratio Ti/Nb was refined), and  $W = O$ . Except for the Si and O sites, the total content of electrons was refined as shown in Table 4. The site *B* can have a maximum occupancy of 50% only because it is close  $[0.90(1) \text{ \AA}]$  to the corre-

sponding position generated by the mirror plane. Attempts to solve and refine the structure in the lower-symmetry space groups *C2* and *Cm* were inconsistent. Information on data collection and refinement, atom coordinates and equivalent thermal-displacement parameters, and selected interatomic distances are reported in Tables 3, 4, and 5, respectively. Tables with  $F_0$  and  $F_c$  and the values of the anisotropic displacement parameters are deposited at the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

#### STRUCTURE AND CRYSTAL-CHEMICAL FORMULA

The nomenclature of the labuntsovite group has recently been approved by the IMA-CNMMN (Chukanov *et al.* 2002). The group includes alkali silicates of Ti and Nb represented by the general formula:  $A_4B_4 [C_{4-2x}(H_2O, OH)_{2x}]D_x[M_8(Si_4O_{12})_4(OH, O)_8] \cdot nH_2O$ . Here, *A* and *B* are mainly alkalis; in the present case, *A* is vacant. The *C* and *D* sites can contain several types of cations but exclude each other, their distance being only  $\sim 2 \text{ \AA}$  [ $C-D = 2.226(7) \text{ \AA}$  in the present case]. If the site *D* is occupied by cations, to a maximum of  $x = 2$ ,  $2x$  oxygen atoms (usually  $H_2O$  molecules or OH groups) occur in *C* to complete the octahedral coordination of the *D* cations. *M* contains mainly Ti or Nb and corresponds to two independent sites in the present case; besides the site *W* (Table 4), some of the  $nH_2O$  molecules partially occupy also the sites *B* and *B'* in the present case.

#### *The structure*

On the whole, the crystal structure of gjerdingenite-Fe (Fig. 4) shows the typical framework of minerals of the labuntsovite group. It is built up by chains of (Nb, Ti) octahedra linked by four-membered rings of  $SiO_4$  tetrahedra to form a complex anion  $[M_8(Si_4O_{12})_4(OH, O)_8]^{n-}$ . The *D* site can be considered as part of the framework (Chukanov *et al.* 2002). The extra-framework cation sites *B*, *B'*, and *C* occupy zeolite-like channels and cavities.

A bond-valence calculation (Brown & Shannon 1973; not reported), even though approximate because of the complex composition, shows that the oxygen atoms of the sites *B*, *B'*, *C* and *W* must be assigned to  $H_2O$  molecules; in fact, they are involved only in weak bonds (Table 5) that cannot neutralize the OH groups. The most underbonded oxygen atom is O1, which is the only framework oxygen atom not bonded to Si; therefore, it represents OH groups. The oxygen atom of the  $H_2O$  molecule in the site *W* is at  $2.67(2) \text{ \AA}$  from *B'* and  $3.03(1) \text{ \AA}$  from *C* (Table 5). These distances allow either coordination with cations or a hydrogen bond with  $H_2O$  occupying the sites *B'* and *C* instead of cations. Also the distances *B*-oxygen, with a minimum value of  $2.7 \text{ \AA}$ , allow the presence in this site of  $H_2O$  where a

cation vacancy occurs. The distances D–oxygen are instead too short for an O...O distance; consequently, a cation vacancy in this site cannot be filled by a molecule of H<sub>2</sub>O; this latter feature is common to all known labuntsovite-group minerals.

Except those of the site C, the H<sub>2</sub>O molecules are only weakly bonded to alkali cations and do not form strong hydrogen bonds. As shown by the range of chemical compositions, leaching of alkalis, favored by the presence of zeolite-like channels, is presumably easy

and, as a consequence of the weak bonds mentioned, H<sub>2</sub>O molecules also are lost together with cations. The amount of H<sub>2</sub>O and alkalis that can be retained by the structure presumably depends on the overall chemical composition, as shown by the different situations encountered in kuzmenkoite-Mn. The samples of this mineral, refined by Golovina *et al.* (1998) in space group *C2/m* and by Rastsvetaeva *et al.* (2000) in space group *Cm*, show a different distribution and higher content of H<sub>2</sub>O relative to gjerdingenite-Fe. The latter authors also claim the presence of (H<sub>3</sub>O)<sup>+</sup>.

### Crystal-chemical formula

According to the refined occupancy (number of electrons =  $e_{\text{ref}}$ , see Table 6), the site B' shows  $e_{\text{ref}} = 13.7(4)$ ; therefore, it contains not only H<sub>2</sub>O but also an element heavier than oxygen. The content of B' is within the coordination sphere of the site B (which is occupied by both H<sub>2</sub>O and alkalis) at a distance B'–B = 2.667(9) Å. If a cation is in B', locally the site B must bear either an oxygen atom or a vacancy. Refinement of the scattering factor of O against that of K for the site B' converges to an occupancy of 0.48O + 0.52K. A very small occurrence of K in this site has already been reported in the structure of kuzmenkoite-Mn by Rastsvetaeva *et al.* (2000).

On the basis of the values of  $e_{\text{ref}}$ , a reasonable content of the sites can be established, taking into account the results of the chemical analyses (Table 1) and that (1) the site A is empty, (2) the site B' contains 0.48O + 0.52K, (3) the site B cannot be vacant where B' carries K, otherwise its  $e_{\text{ref}}$  cannot be reasonably accounted for by the available ions (its number of electrons can be matched by putting in it an amount of oxygen equal to the amount of K in B'), and (4) the content  $x$  of the site D is limited by the related content  $2x$  of H<sub>2</sub>O in the site C.

Table 6 shows a partitioning of chemical elements in the sites, which leads to the following crystal-chemi-

TABLE 4. ATOM COORDINATES, REFINED NUMBER OF ELECTRONS PER SITE ( $e_{\text{ref}}$ ) AND EQUIVALENT DISPLACEMENT FACTOR  $U_{\text{eq}}$  IN GJERDINGENITE-Fe

Site	<i>x</i>	<i>y</i>	<i>z</i>	$e_{\text{ref}}$	$U_{\text{eq}}^*$
Si1	0.2079(2)	0.1091(1)	0.7998(3)	-	0.0143(7)
Si2	0.6852(2)	0.8897(1)	0.7542(3)	-	0.0147(7)
M1	0	0.7676(1)	½	14.9(2)	0.0191(9)
M2	¼	¼	¼	16.1(2)	0.0204(9)
B	0.4307(7)	0.0323(5)	0.731(1)	6.3(2)	0.078(3)
B'	¼	0.8312(5)	0	13.7(2)	0.084(3)
C	0.0899(6)	0	0.335(1)	10.9(2)	0.079(3)
D	0	0	½	23.6(2)	0.016(1)
O1	0.9032(5)	0.7704(3)	0.6113(8)	-	0.017(1)
O2	0.9161(4)	0.8823(3)	0.3308(7)	-	0.016(1)
O3	0.2598(3)	0.8705(3)	0.3787(7)	-	0.018(1)
O4	0.2721(3)	0.8198(3)	0.7334(7)	-	0.018(1)
O5	0.4152(4)	0.82098(4)	0.3032(7)	-	0.022(1)
O6	0.3557(5)	0	0.2710(9)	-	0.012(2)
O7	0.2331(3)	0.8721(4)	0.0260(7)	-	0.020(1)
O8	0.2422(5)	0	0.7844(9)	-	0.020(2)
W	0	0.140(1)	0	-	0.102(4)

\* Isotropic  $U(\text{Å}^2)$  for B and W.

TABLE 5. SELECTED BOND-LENGTHS (Å) FOR GJERDINGENITE-Fe

Si1 – O2	1.612(5)	Si2 – O7	1.595(5)
O4	1.603(5)	O3	1.602(5)
O8	1.625(3)	O6	1.627(3)
O7	1.656(5)	O5	1.626(6)
Average	1.624	Average	1.612
M1 – O5 × 2	1.912(5)	M2 – O3 × 2	1.967(5)
O1 × 2	1.969(6)	O4 × 2	1.963(5)
O2 × 2	2.073(5)	O1 × 2	1.999(6)
Average	1.985	Average	1.976
D – O2 × 4	2.108(5)	B–B'	2.667(9)
C × 2	2.226(7)	O8	2.99(1)
Average	2.147	O3	3.04(1)
		O4	3.098(9)
C – O3 × 2	2.947(7)	O5	3.136(9)
O2 × 2	3.000(8)	O6	3.14(1)
W × 2	3.03(1)	O6	3.278(9)
O2 × 2	3.130(8)	Average	3.050
O8	3.177(9)	B'–B	2.667(9)
O1 × 2	3.224(5)	W	2.67(2)
Average	3.076	O4 × 2	2.990(4)
		O1 × 2	3.049(6)
		O5 × 2	3.146(5)
		Average	2.963

B, B' and C contain both cations and H<sub>2</sub>O (see text).

TABLE 6. NUMBER OF REFINED ELECTRONS ( $e_{\text{ref}}$ ) AND ASSIGNED ELECTRONS ( $e_{\text{am}}$ ) FOR EACH SITE IN GJERDINGENITE-Fe

Site*	$e_{\text{ref}}^{\dagger}$	$e_{\text{am}}^{\ddagger}$	Content of the site per cell
A (8)	0	0	-
B (8) <sup>§</sup>	6.3(2)	5.9	$[\text{K}_{1.20}\text{Na}_{0.72}(\text{H}_2\text{O})_{2.08}]_{24}$
B' (4)	13.7(4)	13.7	$[\text{K}_{2.08}(\text{H}_2\text{O})_{1.92}]_{24}$
C (4)	10.9(2)	9.7	$[(\text{H}_2\text{O})_{1.40}\text{K}_{0.56}\text{Ca}_{0.04}]_{24}$
D (2)	23.6(2)	21.7	$(\text{Fe}_{0.99}\text{Mn}_{0.75}\square_{0.30})_{12}$
M1 + M2 (4 + 4)	31.0(2)	32.4	$(\text{Nb}_{1.30}\text{Ti}_{1.10}\text{Fe}_{0.20}\text{Zr}_{0.05})_{24}$
W (4)	8	8	4H <sub>2</sub> O

\* the multiplicity of the site is given in parentheses.

† estimated standard deviation in parentheses.

‡ according to the content of the site.

§ maximum occupancy 50% because of disorder.

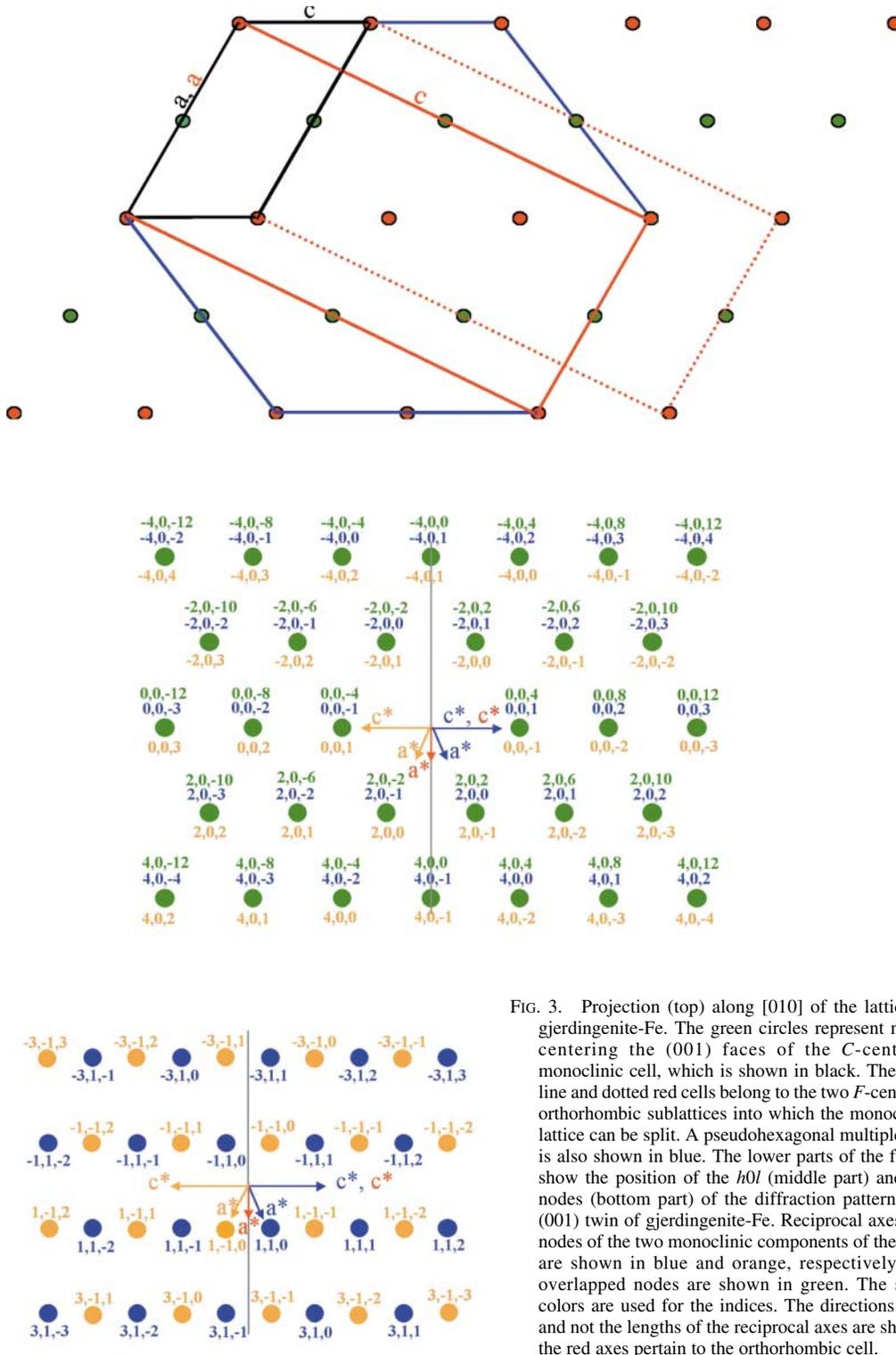


FIG. 3. Projection (top) along [010] of the lattice of gjerdingenite-Fe. The green circles represent nodes centering the  $C$ -faces of the  $C$ -centered monoclinic cell, which is shown in black. The full-line and dotted red cells belong to the two  $F$ -centered orthorhombic sublattices into which the monoclinic lattice can be split. A pseudohexagonal multiple cell is also shown in blue. The lower parts of the figure show the position of the  $h0l$  (middle part) and  $h1l$  nodes (bottom part) of the diffraction pattern of a (001) twin of gjerdingenite-Fe. Reciprocal axes and nodes of the two monoclinic components of the twin are shown in blue and orange, respectively; the overlapped nodes are shown in green. The same colors are used for the indices. The directions only and not the lengths of the reciprocal axes are shown; the red axes pertain to the orthorhombic cell.

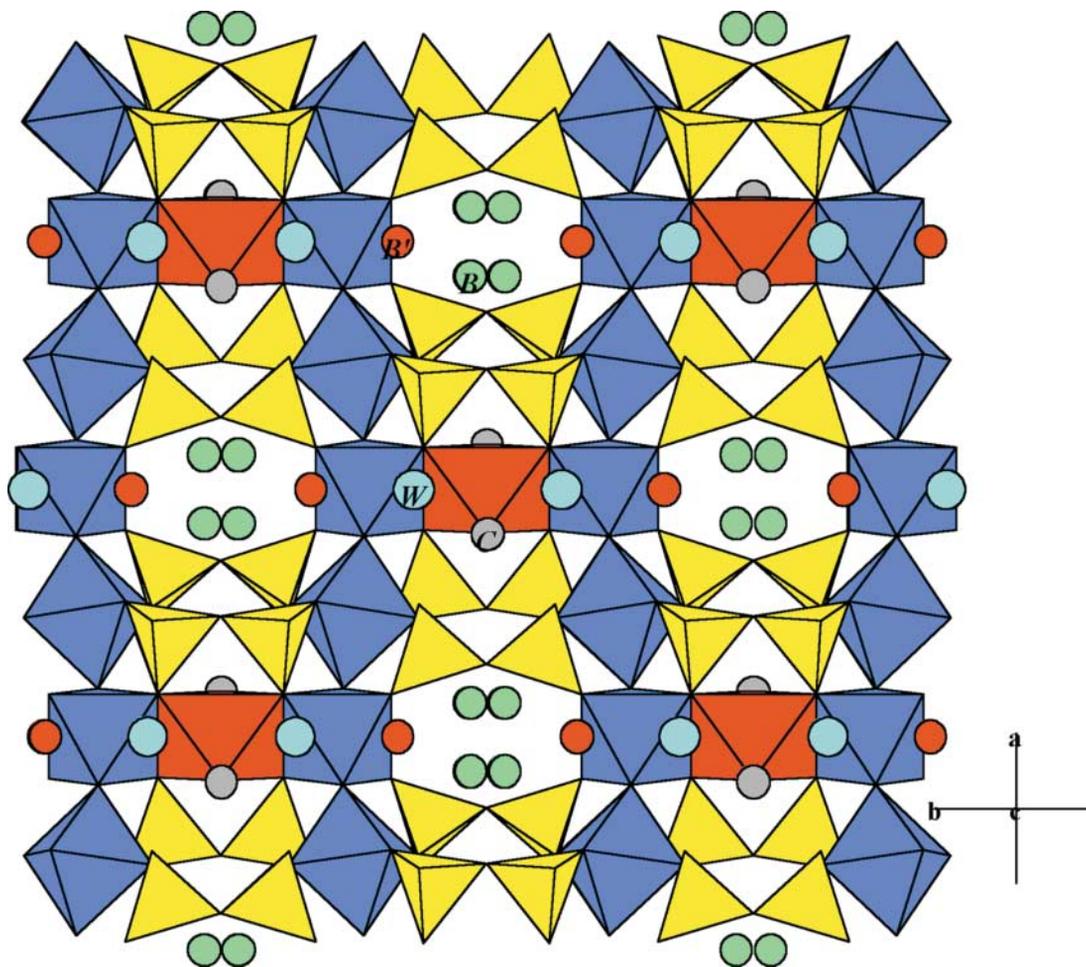


FIG. 4. Crystal structure of gjerdingenite-Fe seen along [001]. The [100] chains of (Nb,Ti) octahedra (blue) alternate with rows of four-membered silicate rings (yellow). The extra-framework sites *B*, *B'* and *C*, carrying both alkali cations and H<sub>2</sub>O, are shown as circles of different color; only H<sub>2</sub>O occurs at the bluish green circles *W*. The red octahedra are centered on the site *D*.

cal formula already mentioned above (*B* and *B'* are in braces):  $\{[K_{1.20}Na_{0.72}(H_2O)_{2.08}]_{\Sigma 4}[K_{2.08}(H_2O)_{1.92}]_{\Sigma 4}\} [(H_2O)_{3.40}K_{0.56}Ca_{0.04}]_{\Sigma 4}(Fe_{0.95}Mn_{0.75-0.30})_{\Sigma 2}(Nb_{4.30}Ti_{3.45}Fe_{0.20}Zr_{0.05})_{\Sigma 8}(Si_{15.90}Al_{0.10})_{\Sigma 16}O_{48}[(OH)_{4.16}O_{3.84}]_{\Sigma 8} \cdot 4H_2O$ .

The number of H atoms in addition to H<sub>2</sub>O is established by balancing the formula. The minor amount of Fe assigned to the *M* sites could be trivalent rather than divalent. This would require a bit less H in the formula. The total H<sub>2</sub>O content is close to the difference in some of the chemical datasets from 100%; on the whole, the wt.% calculated from the crystal-chemical formula compares well with the analytical data (Table 1). Grouping together the contents of the sites *C* and *D* and the H<sub>2</sub>O molecules coordinated by alkali atoms, the following

simplified formula is obtained for gjerdingenite-Fe, referred to two unit formulae per unit cell:  $K_2[(H_2O)_2(Fe, Mn)][(Nb, Ti)_4(Si_4O_{12})_2(OH, O)_4] \cdot 4H_2O$ .

#### GJERDINGENITE-Fe AND THE LABUNTISOVITE GROUP

Several monoclinic and two orthorhombic members of the labuntsovite group are known (Table 7). In the latter case (nenadkevichite and korobitsynite with  $a \approx 7.4$ ,  $b \approx 14.2$ ,  $c \approx 7.1$  Å), the chains of octahedra are straight, and there are only two extra-framework sites, with Na in 8- and 9-fold coordination. The monoclinic members show a doubled *a* and, in some cases, also doubled *c* (subgroups of paralabuntsovite, parakuzmenkoite, and organovaitite). In general, they contain

an *A* site (Na, □), which corresponds to the 9-fold site in the orthorhombic structure, and three sites *B*, *C*, and *D*, which correspond to the 8-fold orthorhombic site. The *D* site becomes larger in the monoclinic structures because of the deformation of the framework and, in particular, the zig-zag disposition of chains of (Ti,Nb) octahedra. The *B* site is larger than *A* and is normally filled with K; *C* may have K, Ba, Sr, □, but only oxygen atoms where *D* is occupied by cations; *D* = Fe, Mg, Mn, Zn, □.

The naming of the monoclinic minerals of the labuntsovite group is based on combinations of root names and suffix modifiers by analogy with the nomenclature of *REE* minerals, zeolites, etc. (Chukanov *et al.* 2002). Mineral species have different root names (Table 7) if at least one of the following conditions is satisfied: (1) the structure is of different type; (2) the dominant cations occupying the sites *A* (not Na), *B* (not K), and *M* (Ti,Nb) are different; (3) the total content of cations in the *C* or *D* sites is 50 to 100% of the full occupancy of these sites. If the *D* site is more than 50% occupied (*i.e.*,  $\Sigma\text{cations} > \square$ ), the cation that predominates in this sum is considered to be a species-forming cation, and a suffix modifier defining that mineral species is added.

Gjerdingenite (as a root name) has Nb > Ti in *M* and is an analogue of kuzmenkoite (root name), which has Ti > Nb (Table 7). The species name is determined by the prevailing *D* cation, *i.e.*, gjerdingenite-Fe. Organovaite-Mn is claimed to be the Nb-dominant analogue of kuzmenkoite-Mn by Chukanov *et al.* (2001a); however, with a doubling of the *c* parameter for organovaite-Mn, this conclusion cannot be correct. According to the recently approved nomenclature of the labuntsovite group (Chukanov *et al.* 2002), the prefix para- is used to indicate a cell doubling, thus the root name organovaite is not in accordance with this rule (*cf.* Table 7).

TABLE 7. ROOT NAMES OF MINERALS OF THE LABUNTSOVITE GROUP

Space group	<i>M</i> site: Nb > Ti	<i>M</i> site: Ti > Nb	Criterion for species name
<i>Pbam</i>	Nenadkevichite <sup>1</sup>	Korobitsynite <sup>2</sup>	no modifiers
<i>C2/m</i>		Labuntsovite <sup>3</sup>	<i>D</i> cation
<i>I2/m</i>		Paralabuntsovite <sup>4*</sup>	<i>D</i> cation
<i>C2/m</i>		Lemleinite <sup>5</sup>	<i>C</i> cation
<i>C2/m</i>	Gjerdingenite <sup>6</sup>	Kuzmenkoite <sup>7</sup>	<i>D</i> cation
<i>C2/m</i>	Organovaite <sup>8*</sup>	Parakuzmenkoite <sup>4,9</sup>	<i>D</i> cation
<i>Cm</i>	Vuoriyarvite <sup>10</sup>	Tsepinite <sup>11</sup>	<i>A</i> cation
<i>Cm</i>		Gutkovaite <sup>12</sup>	<i>D</i> cation

\* The prefix para- is used to indicate a doubling of the unit cell (Chukanov *et al.* 2002). The name organovaite is a violation of this rule, as it has a doubled *c* parameter compared to gjerdingenite and kuzmenkoite.

<sup>1</sup> Kuz'menko & Kazakova (1955), <sup>2</sup> Pekov *et al.* (1999), <sup>3</sup> Semenov & Burova (1955), Khomyakov *et al.* (2001), <sup>4</sup> Chukanov *et al.* (2002), <sup>5</sup> Khomyakov *et al.* (1999), <sup>6</sup> This paper, <sup>7</sup> Golovina *et al.* (1998) and Chukanov *et al.* (1999) [a recent refinement of kuzmenkoite-Mn was made in space group *Cm* (Rastsvetaeva *et al.* 2000)], <sup>8</sup> Chukanov *et al.* (2001a), <sup>9</sup> Chukanov *et al.* (2001b), <sup>10</sup> Subbotin *et al.* (1998), <sup>11</sup> Shlyukova *et al.* (2001), <sup>12</sup> Rastsvetaeva *et al.* (2001), Pekov *et al.* (2002)

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