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Stacking Variations in Cancrinite Minerals

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Abstract

TEM reveals (0001) stacking faults and periodic superstructures in cancrinite-related minerals, afghanite and franzinite, which are interpreted as aperiodic or periodic displacements of the hexagonal $[(Si,Al)_6O_{12}]$ ring units. Franzinite also shows a superstructure when the structure is projected onto the *xy* plane; satellites occur in the *hk*0 diffraction patterns.

Cancrinite is an alumosilicate mineral with a structure characterized by six-membered $[(Si,Al)_6O_{12}]$ rings which are linked to form a continuous three-dimensional framework. The ring units give rise to hexagonal nets in a projection onto the (0001) plane. The stacking pattern is analogous to close packing of spheres. The structure of cancrinite has a stacking sequence *ABAB*, resulting in a 5·11 Å *c* repeat. There is a whole family of related structures of similar chemical composition $(Na,Ca,K)_{6-8}Al_6Si_6O_{24}(CO_3,SO_4,Cl,OH)_{1-2}$, 1–5$H_2O$, with six-membered rings that can be stacked in three different ways along the *z* axis (Fig. 1), thereby giving, theoretically at least, infinitely many different framework structures. Some of the naturally occurring phases have very complicated stacking sequences (Table 1). With regard to the convention adopted in describing these frameworks (*i.e.* by stacking sequences), such structures could be classified as polytypes, even though the steric arrangement in the various structures is different. In *AB* sequences there are large open channels of the same kind as those found in zeolites, while *ABC* sequences create cages thus accommodating different cations and anions. In addition, the space-group symmetry in the various types constrains Si–Al order. In cancrinite, Al and Si alternate regularly (Brown & Cesbron, 1973). In liottite, afghanite and franzinite, there may be only short-range order (Merlino & Mellini, 1978) similar to that found in the related mineral wenkite (Wenk, 1973). X-ray diffraction experiments on cancrinite (Brown & Cesbron, 1973; Foit, Peacor & Heinrich, 1973) show diffuse reflections indicating a high density of stacking faults. Superstructure reflections which were described in the case of wenkite (Lee, 1976) were to be expected. Thus this mineral group appeared to be a good candidate for an investigation with the transmission electron microscope.

The analyzed specimens come from Pitigliano and Sacrofano (Italy). Oriented 30 μm thin sections containing the *z* axis were prepared from single crystals; they were further thinned to electron transparency by ion-beam etching. Foils were then examined

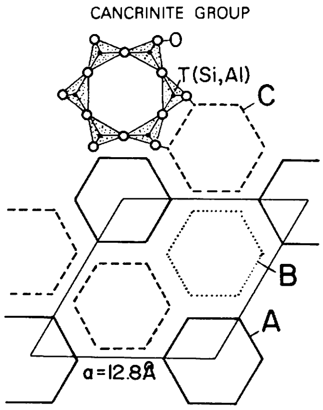

Fig. 1. Schematic sketch illustrating a *z*-projection of the tetrahedral framework of cancrinite. The six-membered rings *A* are linked with a second set of rings, either *B* or *C*, which are spaced 2·6 Å in the *z* direction.

Table 1. *Cancrinite minerals*

	a (Å)	*c* (Å)	Space group	Stacking sequence	Selected reference
Cancrinite	12·8	5·11	$P6_3$	*AB*	Jarchow (1965)
Microsommite	22·2	5·24	$P6_3$	*AB*	Klaska & Jarchow (1977)
Liottite	12·8	16·09	$P\bar{6}m2$	*ABABAC*	Merlino & Orlandi (1977*a*)
Afghanite	12·8	21·35	$P6_3mc$	*ABABACAC*	Merlino & Mellini (1976)
Franzinite	12·8	26·58	$P\bar{3}m1$	*ABCABCBACB*	Merlino & Orlandi (1977*b*)

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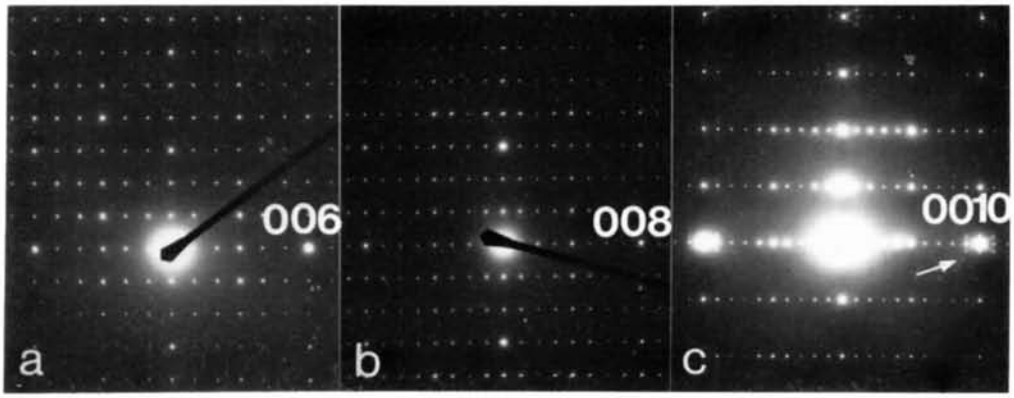

Fig. 2. Electron diffraction patterns of (*a*) liottite, (*b*) afghanite, and (*c*) franzinite. c^* is horizontal. Notice the correspondence of reflections 006 in (*a*) with 008 in (*b*) and 0,0,10 in (*c*) which denote the basic 2·6 Å stacking unit. Satellites about 0,0,10 in (*c*) (arrow) are probably due to short-range Al–Si order.

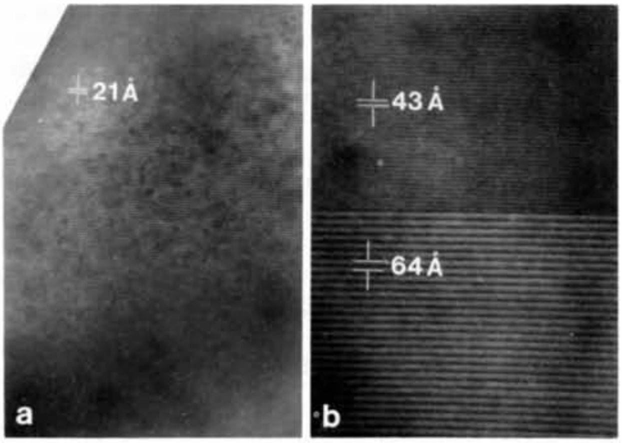

Fig. 3. 00*l* fringes in afghanite, imaged in dark-field. (*a*) Region with regular 21·3 Å fringes. (*b*) Local area with 2× and 3× 21·3 Å fringes due to periodic stacking. The two stacking sequences occur next to each other in the same crystal as (*a*).

on a JEM 100C transmission electron microscope equipped with tilt-rotation stage. Bright-field, dark-field and selected-area diffraction techniques were used to characterize the microstructure. The microscope was operated at 100 kV. Samples were reasonably stable under the electron beam during the period of observation. Radiation damage does occur though and is visible in the photomicrographs as a mottled background texture (*e.g.* Fig. 4*b*).

Liottite is very homogeneous like a perfect single crystal. No faults could be imaged. The diffraction pattern (Fig. 2*a*) shows sharp reflections with a 16.11 Å *c* repeat. Strong reflections at $l = 6n$ indicate the basic layer unit (2.685 Å).

Afghanite is on the whole structurally homogeneous with regular 21 Å fringes observable both in bright-field and dark-field, consistent with an eight-layer *c* repeat (*ABABACAC* stacking sequence) (Fig. 3*a*). In a few

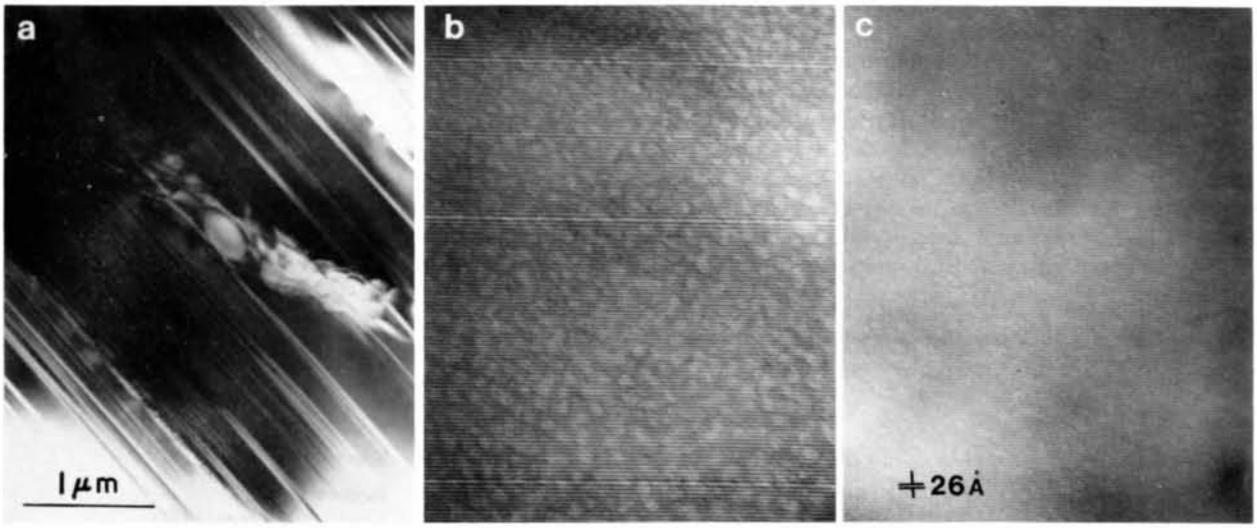

Fig. 4. Dark-field photomicrographs of franzinite: (*a*) displays stacking faults imaged at low magnification; (*b*) at higher resolution. In (*b*) we see numerous faults which interrupt the regular 26 Å stacking with insertion of smaller and larger units; (*c*) is taken at the same magnification as (*b*) but of a part of the crystal which is unfaulted.

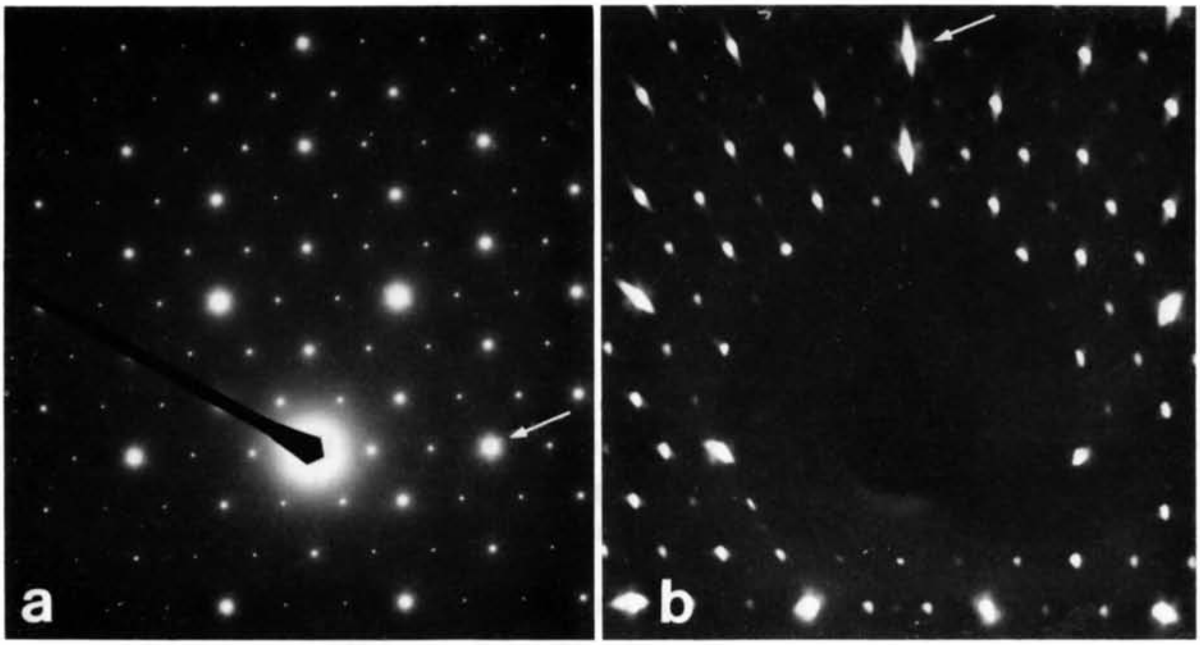

Fig. 5. *hk*0 diffractograms of franzinite illustrating the presence of weak satellites: (*a*) is an electron diffraction pattern, (*b*) a strongly exposed X-ray photograph. Only with a graphite monochromator could the background be sufficiently reduced to permit these weak and diffuse superstructure reflections to be shown by X-ray methods. Reflections with low diffraction angles in the X-ray pattern are absorbed by the beam trap.

local areas of the same crystal, Wenk (1978) found more complex structures corresponding to 42 and 64 Å repeats (Fig. 3*b*) adjacent to each other. These repeats have not so far been observed over larger regions.

Franzinite has a proposed stacking order *ABCABCBACB* (Merlino & Mellini, 1976) which extends over ten layers. Stacking faults are common and can be seen in dark-field even at low magnifications (Fig. 4*a*). They show up more clearly in lattice-fringe resolution (Fig. 4*b*), typically in the thicker areas of the foil. In other parts the structure is very regular (Fig. 4*c*).

Electron-diffraction patterns of franzinite show diffuse and weak satellites (Figs. 2*c* and 5*a*) at ~50 Å. These satellites are indicative of a noncommensurate superstructure due to distortions in the Al–Si framework caused either by ordering of large cations and anions or by long-range Al–Si order similar to a modulated superstructure found in hauyne (Sadanaga, Takéuchi & Morimoto, 1978). They were first observed by electron diffraction (Fig. 5*a*) and later confirmed by X-ray diffraction using monochromatic Mo $K\alpha$ radiation for strongly exposed precession photographs (Fig. 5*b*). This superstructure gives diffraction effects very similar to those observed in ordered $NbTe_2$ (Van Landuyt, Van Tendeloo & Amelinckx, 1975). We do not venture a structural interpretation for these irrational satellites which also show diffuse streaks (arrow in Fig. 2*c*). The satellite reflections are very weak and we were unable to resolve the modulation directly with our electron microscope.

Electron microscopy has enabled us further to characterize cancrinite minerals at a point where X-ray diffraction could no longer provide information, and the findings may help refine X-ray structure determinations, which so far converged at R values of ~16% for liottite and afghanite and ~27% for franzinite (Merlino & Mellini, 1978). It was surprising to find locally regular superstructures in afghanite which extend over several hundred unit cells.

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References

Brown, W. L. & Cesbron, F. (1973). *C. R. Acad. Sci. Ser. D*, **276**, 1–4.

Foit, F. F., Peacor, D. R. & Heinrich, E. W. (1973). *Can. Mineral.* **11**, 940–951.

Jarchow, O. (1965). *Z. Kristallogr.* **122**, 407–422.

Klaska, R. & Jarchow, O. (1977). *Naturwissenschaften*, **64**, 93.

LEE, F. (1976). In *Electron Microscopy in Mineralogy*, edited by H. R. WENK, pp. 361–370. Heidelberg: Springer.

MERLINO, S. & MELLINI, M. (1976). In *'Zeolite 76' Programs and Abstracts*, 47. Tucson, Arizona.

MERLINO, S. & MELLINI, M. (1978). Personal communication.

MERLINO, S. & ORLANDI, P. (1977*a*). *Am. Mineral.* **62**, 321–326.

MERLINO, S. & ORLANDI, P. (1977*b*). *Neues Jahrb. Mineral. Monatsh.* pp. 163–167.

SADANAGA, R., TAKÉUCHI, Y. & MORIMOTO, N. (1978). *Recent Prog. Nat. Sci. Jpn*, **3**, 141–206.

VAN LANDUYT, J., VAN TENDELOO, G. & AMELINCKX, S. (1975). *Phys. Status Solidi A*, **29**, K11–K13.

WENK, H. R. (1973). *Z. Kristallogr.* **137**, 113–126.

WENK, H. R. (1978). *Proc. 9th Int. Congr. Electron Microsc.* Toronto, Vol. 3, pp. 404–419.

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X-ray Intensity Measurements on Large Crystals by Energy-Dispersive Diffractometry. IV. Determination of Anomalous Scattering Factors near the Absorption Edges of GaAs by the One-Intensity-Ratio Method

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Abstract

The imaginary part $f''(\omega)$ of each scattering factor for Ga and As has been measured through the absorption coefficient on a nearly perfect GaAs crystal plate in the energy regions near the K absorption edges of both Ga and As atoms. The intensity ratio r_{555} between 555 Friedel-pair reflexions has been measured in the same energy regions. From these data, the real part $f'(\omega)$ has been determined in the same way as has already been published [Fukamachi & Hosoya (1975). *Acta Cryst.* A**31**, 215–220]. The $f'(\omega)$ values above the edges thus obtained show fairly good agreement in fine structure with those calculated from $f''(\omega)$ values with the dispersion relation, but some discrepancies are found in the regions below the edges.

Introduction

In the papers of the present series (I: Fukamachi, Hosoya & Okunuki, 1976*a*; II: Fukamachi, Hosoya & Okunuki, 1976*b*; III: Fukamachi, Hosoya, Kawamura & Okunuki, 1977), the energy-dispersive intensity measurement method has been developed with a solid-state detector (SSD) diffractometer and in particular a study has been made on the energy dependence of diffraction intensity including the anomalous scattering factors (III, 1977). Measurements were carried out on the integrated reflexion powers R_h from a perfect GaAs crystal in the Laue and Bragg cases. The results could be interpreted by the dynamical theory of X-ray diffraction including the absorption effect (Miyake, 1969). The agreement between the measurements and the calculations was fairly good in energy regions not very near the edges. The following relation

$$r_h = R_h/R_{\bar{h}} = |F_h|^2/|F_{\bar{h}}|^2 \qquad (1)$$

was also confirmed to hold experimentally and theoretically for both perfect and mosaic polar crystals in the symmetrical Laue and Bragg cases (II, 1976*b*). Equation (1) is very useful for determining the anomalous scattering factors (Hosoya, 1975; Fukamachi & Hosoya, 1975) using a crystal with a known simple polar structure without parameters.

In the present paper, we report on the determined f' values of the atoms in a perfect GaAs crystal in the energy regions near Ga and As K edges by the measurement of the r_h values. This was carried out earlier by Fukamachi & Hosoya (1975) for GaP, but the energy resolution is improved in the present case. The results are compared with other f' values such as those calculated by Hönl's theory (Hönl, 1933*a*,*b*) and by the dispersion relation (III, 1977). The discrepancies in f' values obtained by these methods are also discussed.

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