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High-resolution electron microscopy of dumortierite[1]

DIRK VAN DYCK, PAUL TAMBUYSER, JOSEPH VAN LANDUYT AND SEVERIN AMELINCKX[2]

Rijksuniversitair Centrum Antwerpen(RUCA)
Middelheimlaan, 1,b-2020 Antwerpen, Belgium

Abstract

High-resolution images of dumortierite, a nesosubsilicate, have been obtained, viewed down the *c* axis. The electron micrographs can be interpreted in terms of the crystal structure, projected along this axis. Slight deviations from the projected structure in the images provide more information about the two-dimensional space group.

Introduction

Recently, the power of high-resolution electron microscopy in the study of minerals with large unit cells has been demonstrated convincingly by Buseck and Iijima (1974) for a number of different silicate structure types. In this contribution we focus attention on dumortierite, another type of silicate structure, consisting of isolated SiO_4 tetrahedra. Direct lattice images showing a one-to-one relationship to the atomic arrangement could be obtained.

Usually, direct lattice images have been interpreted in terms of the projected crystal structure, *i.e.* the projected charge density (PCD) and the thin phase grating (TPG) approximations. However, in the present study, by comparing the images obtained with the dumortierite structure, it could be shown that this approximation does not strictly hold; *i.e.* small deviations are consistent with the space group of the crystal.

The structure of dumortierite

Dumortierite, $(Al, Fe)_7[O_3|BO_3|(SiO_4)_3]$, being a nesosubsilicate, consists of isolated SiO_4 tetrahedra, with BO_3 triangles as additional anions. The SiO_4 tetrahedra are held together by Al ions in sixfold coordination (Fig. 1). The mineral is orthorhombic, with space group D_{2h}^{16}-*Pcmn* and unit-cell parameters $a = 11.79$, $b = 20.21$, $c = 4.70$ Å, as first described by Claringbull and Hey (1958). The presence of one short axis makes it an especially suitable material for direct imaging. Viewing down the [001] direction (Fig. 1), the crystal can be considered as consisting of channels filled with distorted face-sharing AlO_6 octahedra (*A* channels) and channels with BO_3 triangles (*B* channels). The *A* and *B* channels are in a 6/3 coordination, every *A* channel being surrounded by 6 *B* channels, and every *B* channel by 3 neighboring *A* channels.

Experimental

The specimen, a fibrous compact mass from the Rochester mining district, Nevada, was characterized by means of X-ray powder diffractometry. An X-ray fluorescence spectrographic analysis showed Fe and Ti as minor constituents. The specimens were prepared by grinding the crystals to a fine powder in an agate mortar, making a suspension of this powder in methanol, and depositing a drop of this suspension on a perforated supporting film. Thin wedge-shaped crystal flakes, partly covering the holes of the film, were searched for at low magnification and served to obtain the best crystal-lattice images.

A JEM 100C, 100KeV electron microscope equipped with a side-entry goniometer stage was used. The ultimate point resolution is limited to 5 Å by the large spherical aberration coefficient (8.2mm) of the lens assembly with this stage. By tilting with the goniometer stage while observing the diffraction pattern, the specimens were oriented until the incident beam was exactly parallel to the *c* axis. In this orientation, the (*hk*0) systematic reflections are excited. A 120μm objective aperture has been used, which included all diffracted beams up to 3 $Å^{-1}$ (Fig. 2). Images were taken at different focus values. An underfocus of about 1500 Å provided the best con-

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[2] Also at Studiecentrum voor Kernenergie (S.C.K.), Mol (Belgium)

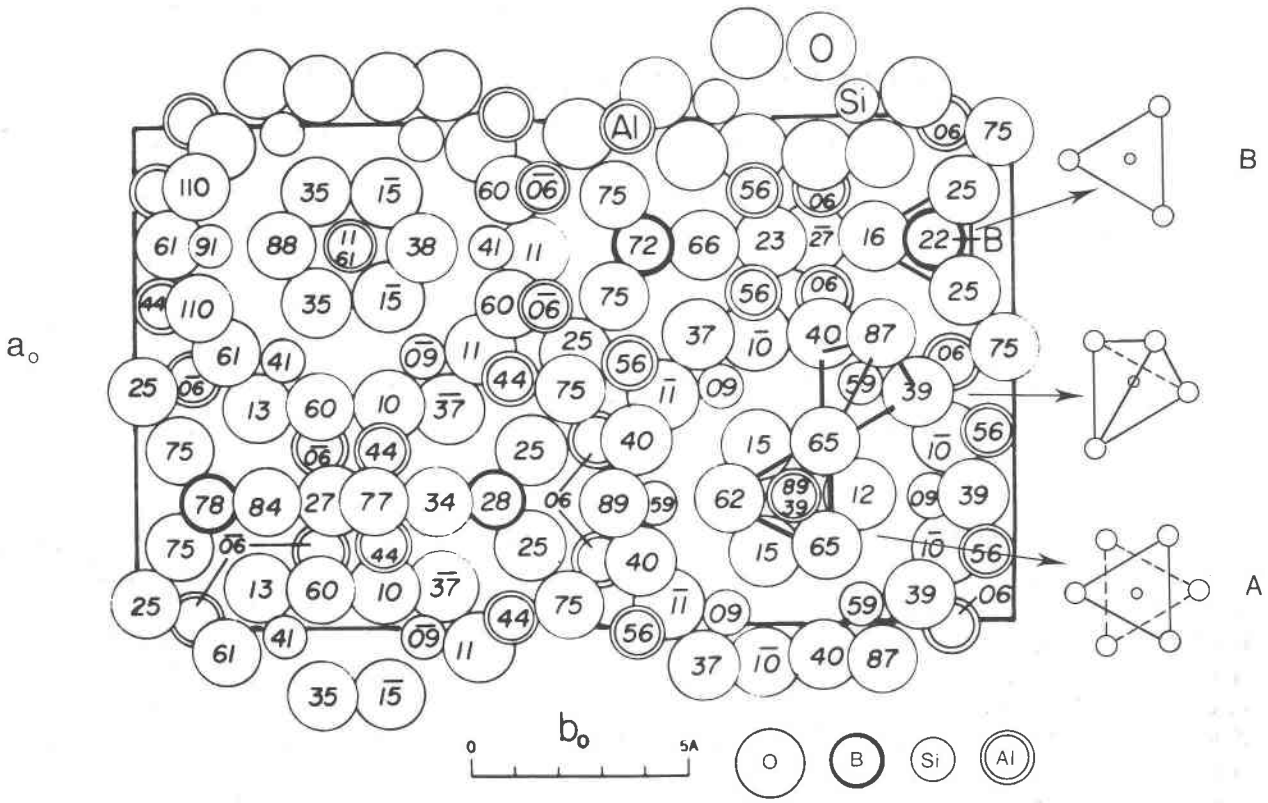

FIG. 1. The structure of dumortierite projected along the *c* axis; the relative height of the atoms is indicated (after Wyckoff, 1968). The polyhedral configurations are shown separately.

trast and structural detail. No change in the images was observed during the observation, which indicates the stability of the mineral in the electron beam.

Results

Figure 3 shows a magnification of $10^7 \times$ of the structure image, consisting of white spots on a dark background. From the intensities, two types of spots can be clearly distinguished. According to their configuration, the white spots can be identified as the *A* channels and the grey spots as the *B* channels. A one-to-one correspondence with the real crystal structure becomes obvious when comparing the lattice image with the X-ray structure as shown at the same scale in the inset. The channels are represented schematically by circles.

The projection of the crystal structure onto a plane perpendicular to a crystal axis may acquire additional symmetry elements as compared to the spatial crystal structure seen along the same zone. If the PCD or TPG approximation were correct, the image as well as the diffraction pattern should show the higher symmetry of the projected crystal structure. However, since the lattice image as well as the diffraction pattern are in fact produced by an admittedly thin but nonetheless three-dimensional crystal, deviations may be expected. According to Wyckoff (1968), the projection of the dumortierite structure along the *c*

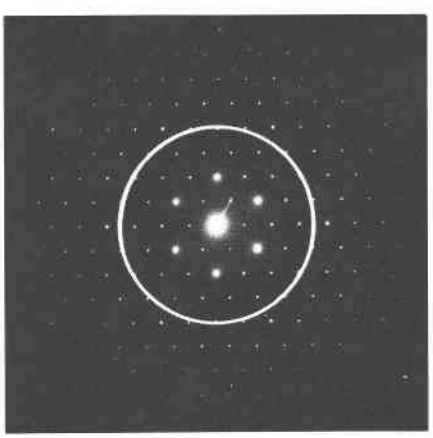

FIG. 2. The electron diffraction pattern showing the (*hk*0) reflections. The objective aperture area, including the imaging beams, is also indicated.

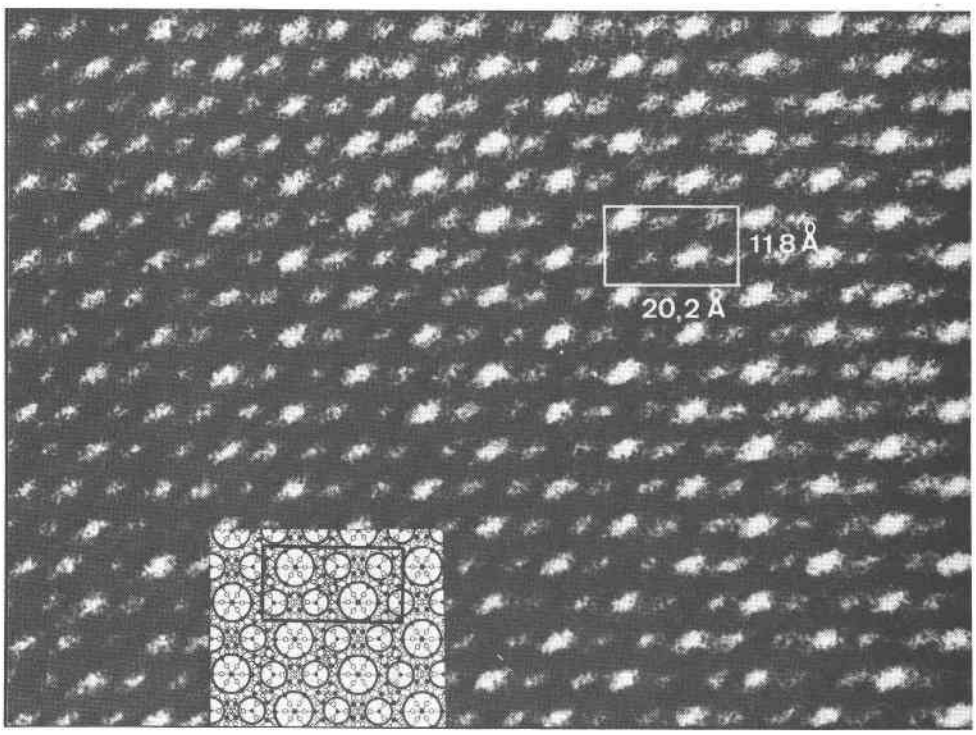

FIG. 3. High resolution electron micrograph of dumortierite seen along the c axis. The unit cell is outlined. For comparison a projection of the crystal structure is inserted.

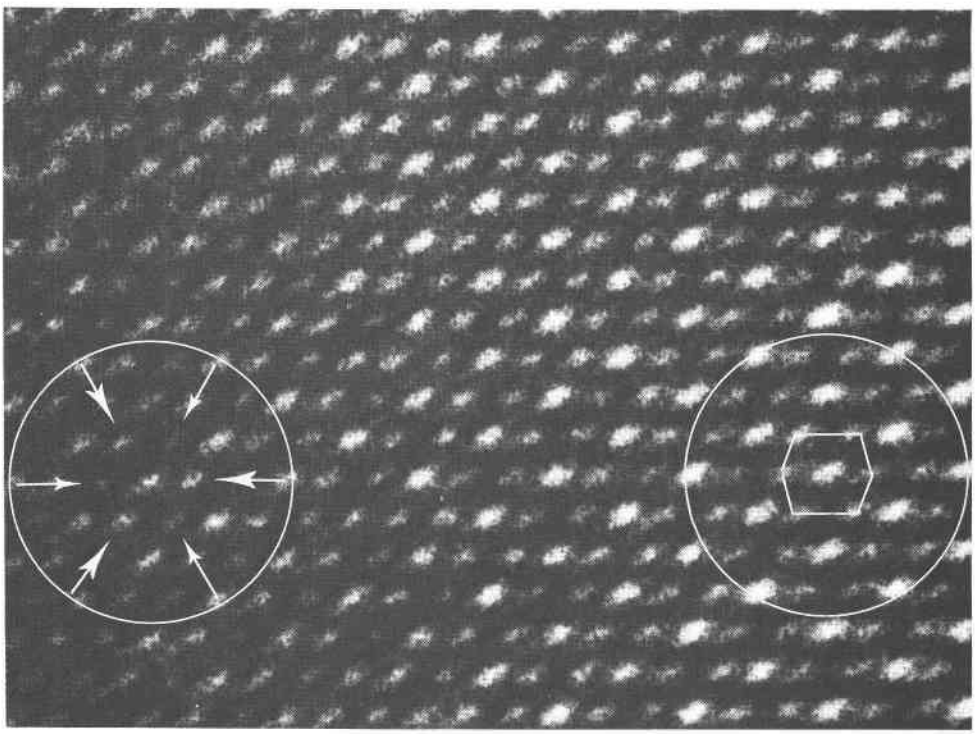

FIG. 4a. High-resolution image of a part of the dumortierite crystal showing two deviations of the projected structure. In the right (thinnest) area, a flattening of the B hexagon can be observed, whereas in the left (thicker) area, due to minor intensity differences, two types of B channels can be distinguished.

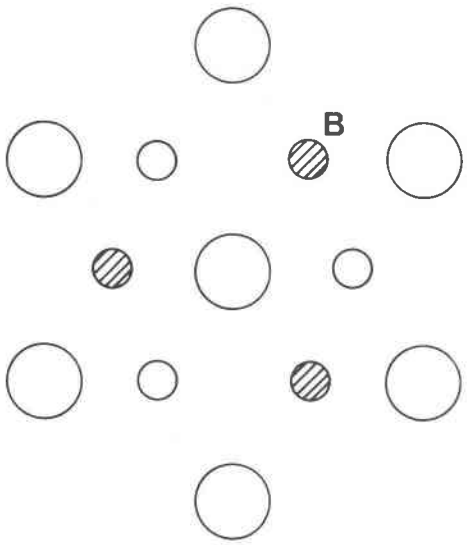

FIG. 4b. Schematic representation of the resolution image, showing two types of anomalies as observed in Fig. 4a: the flattening of the *B* hexagons and the slight intensity differences (indicated by hatching).

axis shows a pseudo-6*mm* symmetry, which at first sight was also observed in the diffraction pattern (Fig. 2) and in the direct image of the thinnest crystal parts (Fig. 3, on the right). However, a closer examination of the lattice image shows two deviations from this symmetry. First the hexagons formed by the *B* channels surrounding an *A* channel are flattened in the *b* direction as if every *B* channel tends towards its nearest *A* neighbor in the *b* direction (Fig. 3 and 4). Secondly, according to minor intensity differences, two types of *B* channels can be observed in the thicker crystal area (Fig. 3, left, and Fig. 4). This deviation of the projected crystal structure can be due to the different vertical positions and orientations of the BO_3 triangles in the *B* channels. These effects reduce the possible two-dimensional space group to *pm* or *cm*. No further distinction could be made, since no deviations of the projected structure approximation could be observed for the *A* channels.

Conclusions

The symmetry of the direct lattice images for dumortierite clearly shows some deviations from the symmetry of the projected crystal structure. These deviations permit us to restrict the possible real two-dimensional space group to *pm* or *cm*, which is consistent with the space group *pm* as determined by X-rays. It can be concluded that lattice images can be used to get more information about the two-dimensional space group.

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