Yellow apophyllite from Korsnäs, Finland

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Summary. The honey-yellow apophyllite from Korsnäs, Finland, for which chemical, optical, and X-ray data are given, shows a complex twinning. An inner penetration twin is surrounded by two outer penetration twins. The twin laws have been established. The prism faces of the complex crystal are not (100) as conventionally taken for apophyllite but (520). The space group $P4/mnc$ commonly accepted for apophyllite could not be confirmed. It is suggested that the mineral is only pseudotetragonal, the true symmetry possibly being orthorhombic with space group $Pnn2$ or $Pnnm$.

THE apophyllite to be described in this paper was found in the Korsnäs lead mine *c.* 40 km south of the town Vaasa in western Finland. The mine was opened by the Outokumpu Mining Company in 1958 and was temporarily closed in 1962. At the present time the mine is not working. No general account of the geology of the mine is available. On the —190 m level in the mine, a tunnel crossed a large cavity that was filled with water under pressure. The width of the cavity measured up to 1½ m and the total visible length some 30 m. The walls of the cavity were covered by crystals of beautifully honey-yellow apophyllite, white to greyish harmotome, yellow calcite, some pyrite cubes, and a few flesh-red prisms of apatite. Later on, smaller and less spectacular cavities were found in the mine with a mineral content similar to that of the large cavity mentioned. The mineralogy of the harmotome from Korsnäs is under study and will be given in a later paper.

Crystal form

The yellow apophyllite occurs as well-developed prismatic crystals up to 5 mm in length and 2 mm in width. Only exceptionally have prisms up to 2 cm long been collected. The crystals show the faces conventionally named (100) and (111). No basal plane (001) has been seen. The crystals usually have their *c*-axes sticking out of the calcite matrix or are sometimes lying on their (100) face. However, a closer inspection of the crystals reveals the fact that they invariably represent a penetration twin schematically illustrated in fig. 1. No untwinned crystals have been found. Both (100) and (111) faces clearly show a more or less regular line parallel to the trace of the *c*-axis that divides the face in two parts reflecting light in slightly differing directions. The angle between the two parts is not exactly 180° but, in cross-section perpendicular to the *c*-axis, the crystal shows a top view drawn in fig. 2 in a strongly exaggerated manner. This angle between the two parts of a prism face was measured on a few crystals with an optical goniometer. Individual measurements on the best crystal yielded values ranging from 179° 0′ to 178° 41′ with an average of 178° 52′±5′.

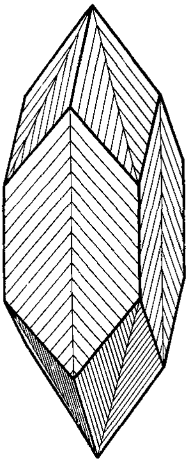

FIG. 1

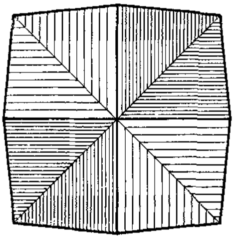

FIG. 2

FIG. 1. Shape of the penetration twin of apophyllite from Korsnäs.

FIG. 2. Top view of the penetration twin of apophyllite from Korsnäs. The angle between the two parts of the vertical planes strongly exaggerated.

Chemical composition

For chemical analysis, hand picked crystals were used that often were slightly turbid in the core. As will be mentioned below, the turbidity is caused by mica inclusions. Rb, Cs, Sr, and Ba were determined by X-ray fluorescence and the rest of the components by ordinary wet methods. The result of the analysis is as follows: SiO_2 52·19, Al_2O_3 1·65, Fe_2O_3 (total iron) 0·03, MgO 0·1, CaO 24·00, SrO 0·01, Na_2O 0·28, K_2O 4·81, Rb_2O 0·03, H_2O^+ 16·15, H_2O^- 0·20, F 1·90, −O 0·80, total 100·55. Mn, Ba, Cs, Ti, Pb, SO_4, and CO_2 were not found. After correcting the result of the analysis for the mica inclusions, the unit-cell content was found as follows, based on (O,OH,F) = 29: Si 8·04, Ca 4·14, Na 0·08, K 0·89, H 17·09, F 0·96. The correction for the mica inclusions was made assuming that all aluminium was contained in the mica. The unit-cell content agrees fairly well with the formula accepted for apophyllite, except for H. This discrepancy in H is not considered serious because the water content of the mica inclusions is difficult to estimate and, further, because the water determination with the Penfield method may not be quite accurate. As indicated by the total of the analysis, the figure for water obtained might be somewhat too high. It is remarkable that the apophyllite contains no Ba despite its occurrence in contact with harmotome.

The *specific gravity* was determined by floating an entirely clear crystal in heavy liquid and by measuring the specific gravity of the liquid with an accurately calibrated Mohr balance. The result is $d = 2{\cdot}359 \pm 0{\cdot}003$.

Optical properties

The description of the optical properties must be based on the complex twinning illustrated in figs. 3 and 4. All portions of a twin are invariably optically biaxial and positive, the optical γ direction being parallel to the crystallographic *c*-axis.

Quite a number of crystals optically studied show a remarkable constancy in the optical properties. The perfect basal cleavage characteristic of apophyllite allows an easy and quick preparation of thin plates perpendicular to the *c*-axis. Of such plates, the directions of the optic axial planes and the optic axial angles were determined. The optic axial planes are presented in fig. 4B. The optic axial angles were measured on 33 crystals from the interference figure using the relationship $\sin V = d/2\beta k$, where d is the distance between the traces of the two optic axes expressed in readings of the micrometer eyepiece, β is the refractive index, and k is the Mallard constant. The Mallard constant was separately determined for the optical system using a Leitz apertometer. The results indicate that there is a marked and constant difference in optic axial angle between portions *H–K* of fig. 4 on the one hand and portions 1–4 on the other. The averages are: $2V_{\text{H-K}} = 18° \pm 2°$ and $2V_{1-4} = 30° \pm 3°$. These results apply for sodium light. A notable dispersion of the optic axial angle with $v > r$. No crossed or inclined dispersion is observable.

The refractive index α is $1{\cdot}536 \pm 0{\cdot}001$ (immersion method). The birefringence on the basal section $(\beta - \alpha)$ is too small for accurate

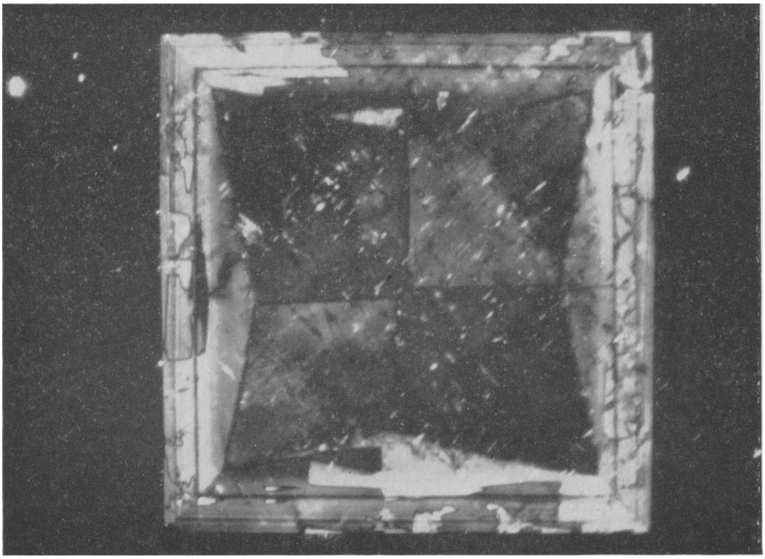

FIG. 3. Microphotograph of an apophyllite crystal from Korsnäs perpendicular to the c-axis showing the complex penetration twinning. Cross-section c. 2 × 2 mm.

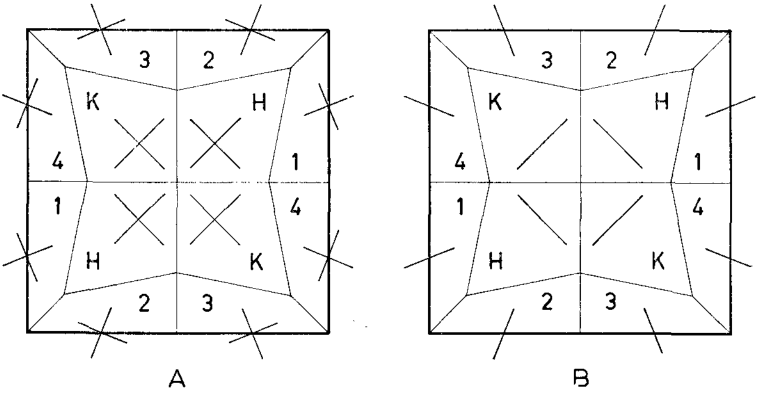

FIG. 4. Schematical cross-section of a complex penetration twin of apophyllite from Korsnäs. Perpendicular to the c-axis. In each portion of the twin are indicated (A) the directions of the two horizontal crystallographic axes and (B) the directions of the optic axial planes.

measurement with a Berek compensator. For that reason, a rotating mica compensator was used. The results show that $\beta-\alpha$ for portions 1–4 is less than 0·0002 and the ratio between $\beta-\alpha$ in *H–K* and in 1–4 is *c.* 1:3. All these data apply for sodium light. The considerably weaker birefringence in the core part of the complex crystal in relation to that of the marginal portion is clearly visible from fig. 3. For measuring $\gamma-\alpha$ in portion *H–K*, a plate was ground of the complex twin in a way illustrated in fig. 5. The retardation was measured with a Berek compensator using a monochromator. The thickness of the plate was determined under the microscope by turning the plate in a vertical position and using a screw micrometer eyepiece. The result indicates $\gamma-\alpha = 0{\cdot}0016$ for sodium light and the relative dispersion of the birefringence $\Gamma_D/(\Gamma_F-\Gamma_C) = -6{\cdot}9$, where Γ_D, Γ_F and Γ_C represent the retardations for the Fraunhofer lines *D*, *F*, and *C*, respectively. This figure for the relative dispersion of the birefringence indicates clearly abnormal interference colours that are known to be characteristic of apophyllite.

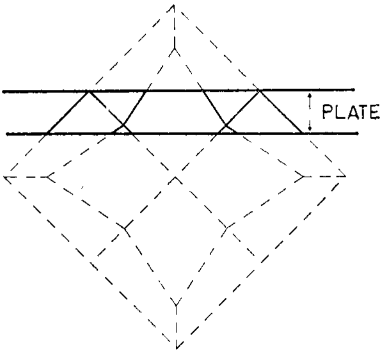

FIG. 5. Position of the plate cut out of a complex apophyllite twin for measuring $\gamma-\alpha$.

X-ray data

For determining the symmetry of the apophyllite from Korsnäs, a plate 0·2 mm thick was ground perpendicular to the *c*-axis. Of this plate, portion *H* (fig. 4) was cut out with a razor blade under the binocular microscope. The crystal fragment thus obtained showed uniform orientation and was used for single crystal work. *a*- and *c*-axis oscillation and Weissenberg photographs (Cu-radiation) and *c*-axis precession photographs (Mo-radiation) were prepared. The following conditions limiting possible reflections were found: for *hkl* no conditions; for *hhl* $l = 2n$; for $0kl$ $k+l = 2n$; for $h0l$ $h+l = 2n$; for $hk0$ no conditions; for $h00$ $h = 2n$; for $0k0$ $k = 2n$; for $00l$ $l = 2n$. These conditions would agree with the space group *P4/mnc* known for apophyllite. As the optical properties raised some doubt about the true tetragonal symmetry of the mineral, very strongly exposed 1-, 3- and 5-layer *c*-axis precession photographs were additionally prepared. In these photographs the following reflections were found: 661, 333, 555, 665, and 995. These reflections are weak, but definitely existing. Accordingly, there are no conditions limiting possible reflections of the type *hhl* and the space group mentioned above is not correct for the Korsnäs apophyllite. No deviation from strictly tetragonal axes was detected in the photographs. Of portion 2 (fig. 4) a uniformly oriented crystal fragment was cut out in a way explained above. A 0-layer *c*-Weissenberg photograph did not indicate any readily measurable difference in length between the two horizontal axes. If such a difference exists, it must be considerably smaller than 0·01 Å. No superstructure is visible. The precession photographs indicate that one of the horizontal axes coincides with the trace of the optic axial plane in section perpendicular to *c*. The directions of the horizontal crystallographic axes are as indicated in fig. 4A.

The unit-cell dimensions were determined by powder pattern. An average of three runs using silicon standard gave $a_0 = 8{\cdot}98 \pm 0{\cdot}03$ Å and $c_0 = 15{\cdot}80 \pm 0{\cdot}06$ Å. These values agree with those obtained from single crystal photographs. Separate powder patterns prepared of the core (portions *H*–*K*) and of the margin (portions 1–4) gave no measurable difference between these portions.

Twinning

The twinning (figs. 3 and 4) was studied optically on a plate cut perpendicular to the *c*-axis. Fig. 4 neglects the small angle between the prism faces 2/3 and 1/4 and, in contrast to fig. 2, the traces of the four prism faces are drawn as straight lines. The twinning may be described as follows:

An inner penetration twin *H*–*K* is surrounded by a double penetration twin 1–3 and 2–4. As was deduced from optic interference figures, the *c*-axes of all portions *H*, *K* and 1–4 are parallel to the morphological *c*-axis of fig. 1.

The boundary between portions *H* and *K* is always a perfectly sharp and straight line. The positions of the optic axial planes as deduced from the interference figures (fig. 4B) and the directions of the horizontal crystallographic axes as deduced from precession photographs (fig. 4A) indicate approximately the symmetrical orientation of portions *H* and *K* in relation to the boundary between the two portions. Accordingly, the boundary between *H* and *K* represents a true twin plane with indices 110. More accurately, this conclusion is evidenced by the following optical facts. In a position on the microscope stage in which the vibration directions of the nicols make an angle of 45° with the outer faces of the crystal, the extinction is uniform throughout the inner penetration twin *H*–*K*. The boundary between *H* and *K* disappears. The maximum difference in interference colour between *H* and *K* is seen in a position with the nicols parallel to the outer faces of the crystal. In ordinary light, the boundary between *H* and *K* becomes faintly visible only by using phase contrast optics.

The outer penetration twin 1–4 is doubled consisting of the two penetration twins 1–3 and 2–4. In both these penetration twins the twin law is the same as in the inner penetration twin *H*–*K*, i.e. the twin plane is (110). Measurements made with an optical goniometer have shown that the prism face of portion 1 is exactly perpendicular to that of portion 3 and, similarly, the prism face of portion 2 exactly perpendicular to that of portion 4.

The relationship between the two penetration twins 1–3 and 2–4 is more complicated. The boundaries 1:2 and 3:4 are sharp and straight. These boundaries make an angle of approximately 45° with the outer faces of the crystal. The boundaries 2:3 and 1:4, on the other hand, are perpendicular to the outer faces of the crystal. These boundaries are also sharp, but are mostly more or less irregular. Fig. 4 has been drawn just schematically, an example of the true boundaries being illustrated in fig. 3. In most crystals, portion 2 contains separate patches of portion 3 and vice versa or portion 1 patches of portion 4. On the other hand, portion 2 never shows patches of portion 1 nor portion 3 those of portion 4 nor vice versa. In ordinary light, all boundaries between portions 1–4 become faintly visible by using phase contrast optics. In addition, the outer margin of all portions 1–4 appears to be zoned. The 'zoning' is parallel to the outer faces of the crystal and cuts through the boundaries 2:3 and 1:4. It seems, however, that the phenomenon is not true zoning but is caused by slabs that alternately belong to the two penetration twins 1–3 and 2–4 thus causing formal resemblance of zoning. The chemical composition of the mineral is very close to that of an ideal apophyllite and, accordingly, does not give much possibility for zoned crystallization.

The low birefringence on a basal section renders it difficult to determine accurately the extinction position. For that reason, the direction of the optic axial plane was determined on the basis of interference figures. It was found that the parallel position of the biaxial interference figure could be determined with an accuracy of one degree, if averaging several readings. With the accuracy obtainable in such a way, it was found that the angle between the optic axial plane and the outer crystal face is 68°. This would mean that the boundaries 1:2, 3:4, 2:3, and 1:4 and the outer faces of the complex twin crystal all represent lattice planes 520 or 250 that in the apophyllite structure should be identical. These are the lowest possible indices that reasonably well fit the angle mentioned. However, the reservation must be made that the plane has higher indices. In this paper, the indices 520 or 250 will be adopted. Accordingly, the faces parallel to the *c*-axis shown in fig. 1 are not to be named (100) as is usually done for apophyllite but (520). This nomenclature applies for the apophyllite from Korsnäs. The twin plane between the two penetration twins 1–3 and 2–4 may, accordingly, be taken as 250. In a strictly tetragonal crystal the angle between the planes 250 and $\bar{2}50$ must be 43° 36′. Because this angle deviates 1° 24′ from 45°, the two (520) faces of portions 2 and 3 or 1 and 4 cannot be parallel to each other, but must make an angle of 178° 36′. This value agrees reasonably well with the goniometric measurements mentioned above according to which the angle was 178° 52′±5′. The double penetration twin 1–4 with approximately correct angles is illustrated in fig. 6. For clarity, this figure neglects the inner penetration twin *H–K*.

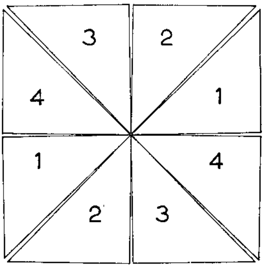

FIG. 6. Doubled penetration twin 1–4 of apophyllite in section perpendicular to the *c*-axis. Angles drawn approximately correctly. Inner penetration twin *H–K* neglected.

It is evident that the angle between the optic axial planes in the inner and in the outer penetration twin is also 68°. Accordingly, the twin plane

H:2 and *H*:1, etc., is also 250. In this case, however, the boundary *H*:2, *H*:1, etc., is not parallel to the twin plane but appears to be 320. This boundary that is mostly a fairly straight line is faintly visible in ordinary light and becomes quite clear on using phase contrast optics.

Summing up the twin laws found, the following scheme may be given:

	Twin plane	Boundary on basal section
H–*K*	110	110 Regular
1–3 and 2–4	110	—
1–2 and 3–4	250	250 Fairly regular
2–3 and 1–4	250	250 Mostly irregular
H–1 and *H*–2	250	320 Fairly regular

Mica inclusions

In a section perpendicular to the *c*-axis under the microscope a number of narrow flakes are seen that have a relatively high birefringence and much higher refractive indices than apophyllite. The flakes are too small for accurate study of their optical properties. Most probably the flakes represent micaceous material (sericite) with their *c*-axes perpendicular to the *c*-axis of the apophyllite host. In portions *H*–*K* of the apophyllite penetration twin the flakes are arranged parallel to the horizontal axes indicated in fig. 4A. The flakes sometimes extend in unchanged direction from the inner penetration twin *H*–*K* to the outer penetration twin 1–4. In the outer penetration twin 1–4 they, however, are often perpendicular to the outer faces (520) of the crystal. The amount of the micaceous inclusions is not constant. Some crystals contain more and others less inclusions. Still other crystals are virtually free from any inclusions and are entirely clear.

Discussion

As a summary the following statements may be made: The optical properties of the yellow apophyllite from Korsnäs are too regular to be explained just as 'optical anomalies' caused by strain in the structure. The optical properties are not consistent with tetragonal symmetry. A possible difference in length between the two horizontal axes is too small for detection. The space group is not $P4/mnc$. These statements suggest that the yellow apophyllite from Korsnäs is only pseudotetragonal the true symmetry possibly being orthorhombic with a space group $Pnn2$ or $Pnnm$. The deviation from a strictly tetragonal symmetry must evidently be very slight and probably does not affect notably the crystal structure given by Taylor and Náray-Szabó (1931).

The suggestion of a non-tetragonal symmetry for apophyllite is not new. The matter has been reviewed and discussed by Gossner and Kraus (1928). These authors regard the 'twinning' commonly found in apophyllite not as true twinning but as a regular intergrowth of portions with differing F to OH ratio. A change of this ratio would cause strain in the structure that affects the optical properties, thus giving the optical illusion of twinning. According to the crystal structure known for apophyllite, F and OH can, however, replace each other only to a limited extent. In addition, the mutual regularity of the three penetration twins in the Korsnäs apophyllite for which definite twin laws can be established must be considered a true twinning.

The difference in optic axial angle between the inner penetration twin *H–K* and the double outer penetration twin 1–4 cannot be interpreted at present. A possible, though not proved, explanation would be that the deviation from strictly tetragonal symmetry is slightly larger in the outer penetration twin 1–4 than in the inner penetration twin *H–K*.

Acknowledgements. The author is indebted to the following staff members of the Geological Survey of Finland: Mr. V. Hoffrén for the X-ray fluorescence work; Mr. Aulis Heikkinen for the fluorine determination; Dr. H. B. Wiik for the rest of the chemical analysis; Dr. Atso Vorma, Mrs. Toini Mikkola, and Dr. Kai Hytönen for various kinds of help and for fruitful discussions. He is also grateful to the Outokumpu Mining Company for the opportunity of collecting the material for study. The persons in that Company that kindly assisted the author in one way or another are too many to be listed here.

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