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X-ray powder data for idocrase

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SUMMARY. An X-ray powder pattern of idocrase (vesuvianite) from Canzoccoli, Italy, has been indexed by the method described by Nedoma (1968*a*, *b*). The improved X-ray data collected in the paper can be useful in identifying this mineral and in discussing the influence of diadochic substitutions on the lattice parameters of idocrase.

IDOCRASE (vesuvianite) is a rather common constituent of metamorphic rocks. Its structure had already been determined in 1931 by Warren and Modell but its general chemical formula has been, even in recent years, an object of discussion (Barth, 1963). Because of the lack of exact and commonly approved *d*-spacings, especially in the low-angle range, the identification of this mineral meets with several difficulties and the interpretation of powder diagrams leads sometimes to confusing results (Żabiński, 1966). The indexing of X-ray reflections proposed in the literature is also incomplete and sometimes ambiguous or even contradictory. It seemed therefore necessary to make an attempt to reinterpret the powder data for this mineral.

X-ray investigations were carried out on a brown-coloured coarsely crystalline variety of idocrase from Canzoccoli, Italy.[1] A camera of diameter 114·6 mm and filtered Cu-$K\alpha$ radiation were used. On the powder photograph more than 80 lines were registered. The interpretation of this pattern was carried out by a method developed by one of us, consisting in measuring the reflections in such a manner that every line is characterized by two numbers giving the upper and lower limits of an interval in which the line is certainly contained (Nedoma, 1968*b*).

We first made an attempt to verify if the lattice parameters proposed by other authors (Deer, Howie, and Zussman, 1962) are the only possible values to index the powder pattern. Using the method described by Nedoma (1968*a*) we obtained a diagram, fig. 1, containing all possible A and B values fitting the four first lines, where $A = \lambda^2/4a^2$, $B = \lambda^2/4c^2$. As can be seen from this diagram there are several fields containing points with coordinates A and B fitting the experimental data. Among the points with greatest coordinates we have found numerically that the point marked in fig. 1 with an arrow is the one permitting us to index all experimental $\sin^2\theta$ values with reasonable extinctions. The coordinates of points lying on the marked field agree approximately with those proposed by other authors and obtained by other techniques (rotation photographs) demonstrating that there is no possibility of correctly indexing the powder diagram with other (greater) A and B values.

The indexing was carried out by the following method: from the diagram we obtained approximate values for A = 0·00247 and B = 0·00428 (fig. 1). Calculating

[1] Idocrase from this locality has been analysed by J. H. Vogel, *Zeits. Kryst. Min.* **17** (1890), 215.

all possible values of $\sin^2\theta$ for the first reflections according to the well-known equation $\sin^2\theta = A.(h^2+k^2)+B.l^2$, we obtained:

hkl	100	001	110	101	111	200	210	201	211	002	220
$\sin^2 \times 10^3$	2·47	4·28	4·94	6·75	9·22	9·88	12·35	14·16	16·63	17·12	19·76

As can be seen from these data and from fig. 2 the first X-ray line must be unequivocally indexed as 110 and the second as 101. Knowing the lower and upper limits of intervals containing the true values of $\sin^2\theta$ we can write inequalities

$$0{\cdot}00463 < 2A < 0{\cdot}00511$$

and

$$0{\cdot}00639 < A+B < 0{\cdot}00700,$$

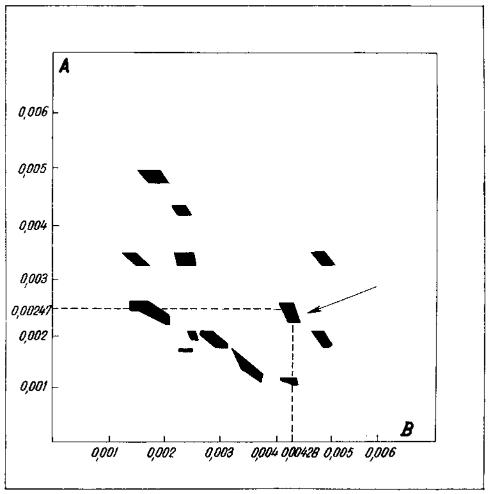

FIG. 1. Superposition of $\sin^2\theta$ diagrams for the four first lines according to the method described by Nedoma (1968*a*). The field marked by the arrow contains the point with coordinates A and B fulfilling the Bragg equation for all reflections registered on the X-ray powder photograph.

from which it follows that A and B must fulfil the conditions

$$0{\cdot}002315 < A < 0{\cdot}002555$$

and

$$0{\cdot}003835 < B < 0{\cdot}004685.$$

With the aid of these new A and B values we can calculate again all possible values for $\sin^2\theta$ and search among experimental data for lines that can be indexed unequivocally. Using these new indexed values we can write new inequalities and determine in the same manner new limits of intervals containing the A and B values. The whole powder pattern has been passed through in this manner and the last, smallest intervals determined for A and B were used for calculating all possible $\sin^2\theta$ values. In this way we could index many lines unequivocally and show that others can be indexed with two and even more sets of *hkl*-values. The method of comparing the calculated and experimentally observed data is illustrated by fig. 2 for $\sin^2\theta$ values less than 0·125. In this way we could classify the reflections into reflections that appear on the diagram and can be indexed unequivocally, reflections overlapping each other and observed on the photograph on the same place as one line, reflections not observed on our photograph because of their weakness, and reflections that do not appear because of systematic extinctions.

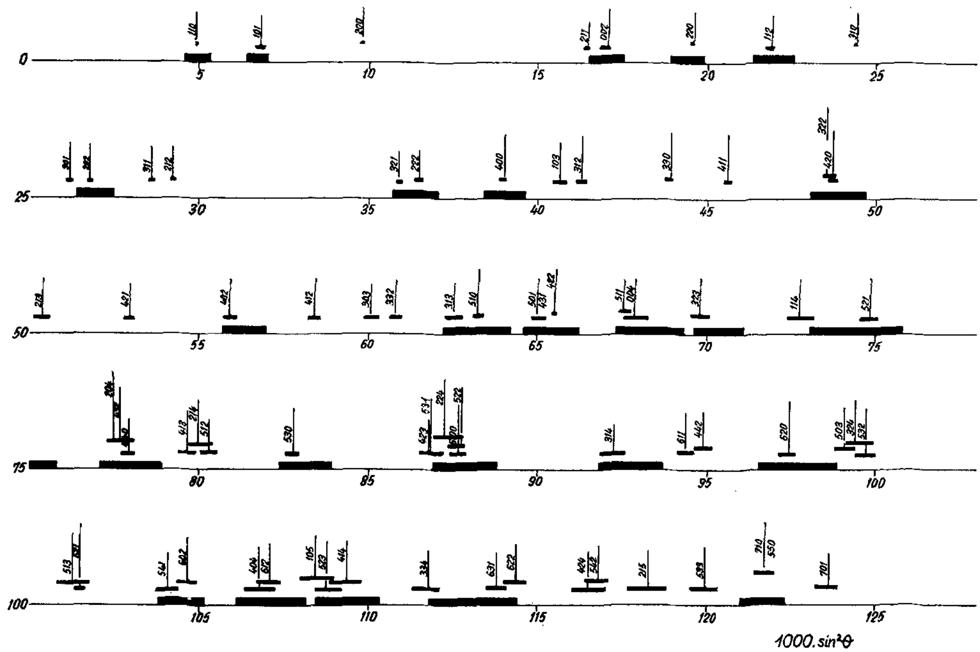

FIG. 2. Comparison of experimental and calculated $\sin^2\theta$ values for all reflections possible in the range 0–0·125. Heavy lines on the diagram illustrate the measured (deliberately broadened) intervals containing true $\sin^2\theta$ values. The calculated intervals of $\sin^2\theta$ values are drawn with thin lines and marked with corresponding *hkl* indices.

All these data are collected in fig. 3. Some of the reflections appearing on the powder photographs may really be composed of coinciding lines and must be therefore correctly indexed with several sets of *hkl*-indices. In other cases some of the calculated data may correspond to such weak reflections that these should be ignored and the observed line should be indexed only with one set of *hkl*-values. The ambiguity of indexing such reflections can be resolved on the basis of intensities calculated for the proposed structure, or by single-crystal photographs.

The interpretation of the powder pattern of idocrase from Canzoccoli leads to lattice constants: *a* 15·634±0·027, *c* 11·827±0·047 Å. The space group D_{4h}^4 ($P4/nnc$) is confirmed by the systematic extinctions. The calculated values of *d*-spacings and their accuracy limits calculated by the method of successive approximations as well as their

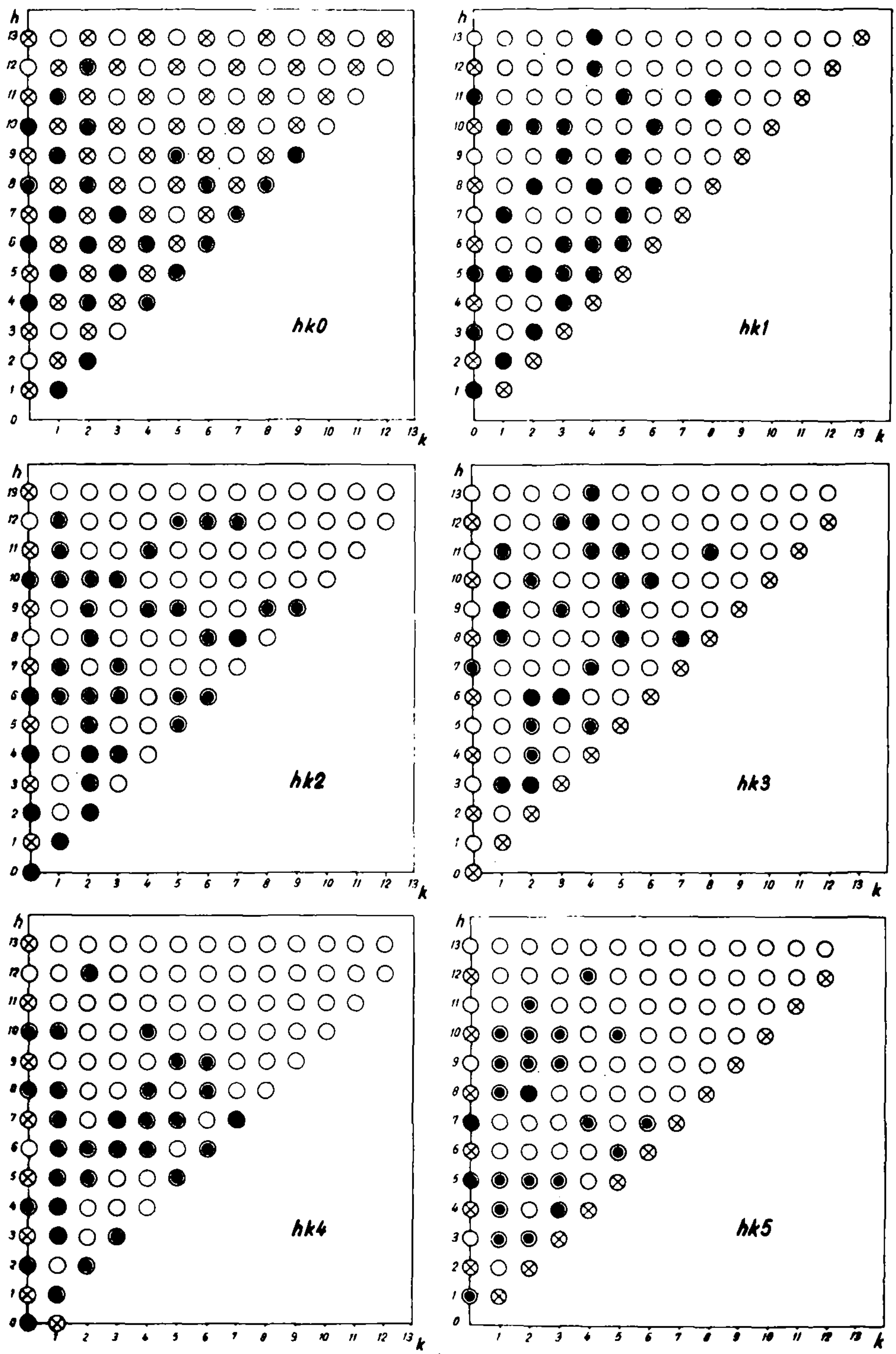

FIG. 3.

TABLE I. *Interplanar spacings and corresponding hkl-indices for idocrase (vesuvianite) from Canzoccoli. Unambiguous and most probable sets of indices in bold face type*

d	Δd	I	hkl
11·05 Å	0·30	3	**110**
9·42	0·22	1	**101**
5·91	0·09	4	211, **002**
5·53	0·07	1	**220**
5·19	0·06	1	**112**
4·697	0·05	2	301, **202**
4·038	0·04	3	321, **222**
3·899	0·03	2	**400**
3·485	0·03	4	322, 420
3·246	0·02	3	**402**
3·064	0·03	4	313, **510**
3·013	0·02	4	501, 431, **422**
2·948	0·02	6	511, 004
2·905	0·02	1	**323**
2·823	0·03	1	**521**
2·759	0·02	10	204, 432, 440
2·672	0·02	1	**530**
2·599	0·02	8	423, 224, 600, 522, 531
2·530	0·02	1	**314**
2·465	0·02	6	**620**
2·383	0·01	1	541, 602
2·354	0·01	1	404, 612
2·329	0·01	1	105, 523, **414**
2·291	0·02	1	334, 631, 622
2·208	0·02	2	710, 550
2·167	0·02	1	711, 640, 632
2·128	0·01	5	315, 641, 514
2·093	0·01	1	**623**
2·070	0·01	1	325, 543, 524, 712, 552
2·049	0·01	1	**730**
1·998	0·01	2	415, **633**
1·971	0·01	1	006, 651
1·934	0·01	1	614, 732
1·892	0·01	3	652, 820, 624, 505, 435
1·868	0·01	1	515, **821**
1·829	0·005	1	525, 316, 634
1·799	0·003	1	822, 751
1·767	0·004	5	714, 554
1·726	0·003	2	**841**, 910
1·682	0·004	3	**734**
1·666	0·003	5	**436**
1·625	0·005	8	931, 804, **705**, 922
1·576	0·005	1	913, 770, 606
1·562	0·003	4	616, 664, 10.0.0, 860
1·545	0·003	1	754, 861
1·530	0·005	1	10.2.0, 546, 942
1·517	0·005	1	933, 10.2.1, 950
1·500	0·005	3	636, 844, 815, 745, 10.1.2
1·478	0·005	1	10.2.2, **625**, 008
1·425	0·005	1	10.2.3, **872**, 736
1·413	0·005	1	953, 11.1.0, 11.0.1
1·391	0·005	3	**774**
1·376	0·005	1	10.0.4, 864, 880, 873, 925, 765, 10.1.4, 11.1.2
1·348	0·003	3	935, 954
1·329	0·003	1	11.1.3, 10.6.1
1·301	0·003	4	10.4.4, 11.4.2, 10.1.5
1·283	0·003	2	11.5.1, 12.2.0
1·267	0·003	3	856, 10.6.3, 982, 12.1.2, 10.3.6
1·226	0·002	1	11.5.3, 12.4.1, 990
1·200	0·001	1	956, 12.3.3, 992
1·175	0·002	1	12.2.4, 12.4.3, 876, 12.5.2
1·142	0·001	1	13.4.1, 11.8.1, 12.6.2
1·105	0·002	3	14.2.0, 11.4.6, 12.7.2
1·094	0·002	1	14.0.2, 12.4.5, 14.1.2
1·078	0·002	2	
1·072	0·002	2	
1·063	0·002	1	
1·043	0·002	1	
1·035	0·002	2	
1·026	0·002	1	
1·008	0·002	1	
0·968	0·003	1	
0·953	0·002	1	
0·947	0·002	1	
0·940	0·002	1	
0·928	0·002	1	
0·921	0·002	2	
0·885	0·001	2	
0·875	0·001	2	

FIG. 3. Plot of *hkl* reflections against *h* and *k* coordinates for different *l* values from 0 to 5. ●, reflections that have been detected unequivocally on the powder photograph; ⊙, reflections that probably appear on the photograph but because of coincidences cannot be identified unequivocally; ○, reflections not registered on the photograph because of their weakness; ⊗, reflections that could not appear on the photograph due to systematic extinctions.

intensities determined visually on a decimal scale are listed in table I. These data may be useful in identifying idocrase as well as in discussing the influence of diadochic substitutions on the lattice parameters of this mineral.

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