

Further Fractographic Studies of Synthetic Single Crystals*

BY C. A. ZAPFFE AND C. O. WORDEN

6410 Murray Hill Road, Baltimore 12, Md., U.S.A.

(Received 11 April 1949)

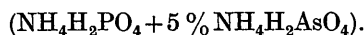
Previous fractographic studies with synthetic ammonium dihydrogen phosphate single crystals are extended to similar crystals containing 5 and 20% of ammonium arsenate, respectively, and to crystals of potassium dihydrogen phosphate. These materials are found to be distinguishable by their cleavage patterns; and the outstanding characteristic is an optical grating effect occurring in the arsenated crystals. The study proceeds to show that this optical effect is associated with a subtle physical structure having the nature of lamellar texture. The recently announced micellar theory is used to explain the phenomenon on the basis of a layer-like crystal growth of micelles in which the arsenate is unequally distributed between surface and body of the individual micelle, thereby providing an inhomogeneity sufficient in degree and in periodicity to develop the optical effect, also a condition of strain which has been noted by others.

Introduction

In the preceding communication (Zapffe & Worden, 1949*b*), the technique of fractography was applied to the fracture surfaces of an ammonium dihydrogen phosphate synthetic single crystal prepared by the Crystal Section of the Naval Research Laboratory, using conventional methods. The principal purpose of the investigation was to determine whether phenomena of texture and crystal imperfection can be detected with this technique.

Because a considerable number of observations were made whose further exploration is warranted, the study was extended to include three variations of the same type of crystal:

(A) Ammonium dihydrogen phosphate, containing 5% of ammonium dihydrogen arsenate



(B) Same, but containing 20% of the arsenate.

(C) Potassium dihydrogen phosphate (KH_2PO_4).

Details regarding the experimental procedure and the methods of interpreting fractographs can be found elsewhere (Zapffe & Worden, 1949*a*).

Observations on ADP containing arsenate (samples A and B)

Grating effect

With 5% of ammonium arsenate added to 'ADP' (Sample A), as the ammonium dihydrogen phosphate will hereafter be designated, a modification of properties is detectable in fractographs. This is further emphasized by the addition of 20% of the arsenate (Sample B). Such sensitivity of the cleavage pattern conforms with the experience with metals; and the following fractographs will illustrate certain pecu-

liarities by which this alloyed material can be distinguished from crystals of pure ADP, described in the preceding paper.

In both samples A and B, in common with materials not having pronounced directional weaknesses, excellent examples of hackle structure appear. This has been defined as a Type II cleavage pattern (Zapffe & Worden, 1949*a*), and two examples are presented in Fig. 1. The first fractograph shows several interposed cleavage areas. The second fractograph suggests a single fracture direction. Rows of both coarse hackle and fine hackle appear; and perpendicular to them is a fairly uniform mass of fine striae, probably relating to the progress of the wave front of the fracturing stress, but possibly relating also to a lamellar substructure of the crystal. These structures are similar to those found in pure ADP.

However, upon closer study, peculiarities are soon found. In Fig. 2, for example, a strong undulating effect appears on a cleavage of sample A. The tips of a number of hackle markings are seen projecting into this field; and their relationships with the undulations where they lie in the troughs and again where they cross a ridge are most interesting.

In sample B, the increased arsenate content seems to aggravate a puzzling optical peculiarity also noted in sample A. Fig. 3, for example, shows an area which is subject to some interference activity providing a marked grating in two directions. The phenomenon is common in this sample. The puzzling feature is that the effect seems to be purely optical in some cases, and physical in others. For example, in Fig. 4 an area similar to the center of the previous figure indicates a direct relationship between the optical bands and a physically terraced structure; and in Fig. 5, the phenomenon is definitely associated with lamellae which are sufficiently distinct physically to be focused upon.

Because in other cases the optical effect is definitely a subsurface phenomenon which cannot be focused

* From research conducted in the laboratory of the senior author under sponsorship of the Office of Naval Research.

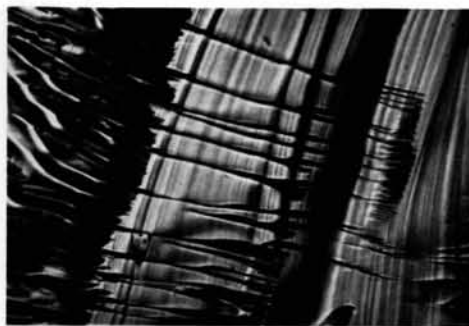


Fig. 1. Typical examples of Type II (hackle) structure in Samples *A* and *B*. 150 \times .



Fig. 2. Fractograph of an unusual undulating field in Sample *A*, showing an interesting relationship with the tip-ends of an intruding hackle structure. 80 \times .



Fig. 3. Typical optical effects observed in Sample *B*. 80 \times .



Fig. 4. Indication of an association of the special optical effects with a physical structure. 52 \times .



Fig. 5. An instance in which the optical effect is definitely associated with a lamellar substructure. 160 \times .

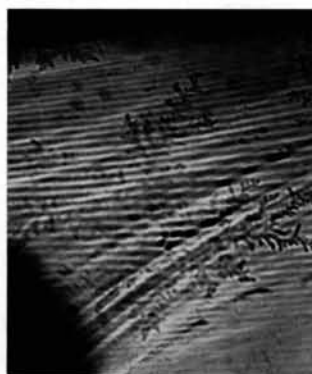


Fig. 6. Combination of the grating effect and one of the puzzling dendrite structures studied in the previous work. The field is out of focus because in this case the grating phenomenon does not concern a surfacial physical structure. $160\times$.

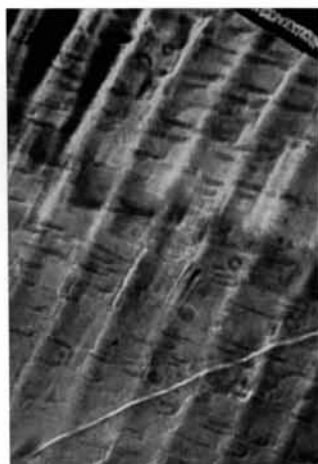


Fig. 7. Associated physical and optical effects appearing slightly beneath the transparent cleavage surface of Sample *B*. Also note the faintly visible mosaic pattern of fine-scale rectilinear form. $100\times$.



Fig. 8. Fractograph disclosing what appears to be the residua of a foreign phase (gas, liquid, or solid) which deposited during a certain period of crystal growth and later deflected the hackle cleavage traverse as shown. $160\times$.

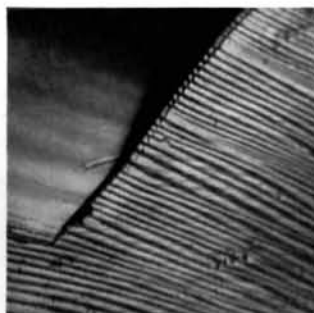


Fig. 9. Type I cleavage patterns in KDP, showing lamellar texture at low and at high magnifications. (Left: $54\times$; right: $344\times$.)



Fig. 10. Pitting phenomenon in KDP suggestive of the dendrites found in ADP. $190\times$.

upon, and cannot therefore be distinguished from a purely optical interference, these fractographs are particularly important. Fig. 5, for example, shows an area in which some unusual and unidentified action seems literally to have peeled back a cutaneous layer to reveal the underlying physical structure accounting for the optical effect; and one can perhaps observe, even in the reproduction, the submerged grating effect appearing optically from within this cutaneous layer where it is not removed. Thus in the one photograph we have an instance in which the grating effect can be focused upon as a physical structure, and another in which it cannot.

Egli (private correspondence) stated in submitting these samples that they are homogeneous solid solutions so far as can be determined by X-ray evidence, but that they exhibit a peculiar grating effect and appear highly strained.

On the basis of the fractographic evidence, it is suggested that these crystals have a fundamental micellar constitution in accord with the micellar theory for the solid state put forward from this laboratory (Zapffe, 1949), and that the arsenate is unevenly proportioned between surface and interior of the individual micelle or micelle groups. Since the crystal presumably grows by layer-like accretion of micelles, this segregation could be expected to display itself as a lamellar structure of intensified boundaries, thereby accounting for both the strain and the optical effects.

Textural imperfections

In closing this discussion of ADP crystals containing ammonium arsenate, several observations of textural imperfections also deserve mention. In Fig. 6, for example, an instance recurs of the puzzling dendrite formations which were observed in ADP, but never explained (Zapffe & Worden, 1949*b*). This fractograph is particularly interesting because it combines the dendrite structure with a strong grating pattern; and the rather poor focus follows from the fact, just explained, that the grating effect in this case is the result of a subsurface condition, requiring some unfocusing of the surficial dendrite in order to record both phenomena on the single plate.

In Fig. 7, the grating effect occurs in relation to a physical structure suggestive of the previous Fig. 4. There seems to be a subtle mosaic imperfection of tetragonal characteristics visible slightly beneath the actual cleavage surface (which again accounts for the mediocre focus). It will be tentatively suggested that this may be a plan view of the lamellar structure revealed in cross-section in the previous Fig. 5, the faint rectilinear markings denoting lateral limits of micelle groupings and therefore a type of mosaic imperfection. However, the matter is complex and must be left for subsequent special investigation.

Lastly, Fig. 8 is presented to record what appears to be a foreign phase (gas, liquid, or solid) which deposited

at some period in the history of the crystal growth, and which layer deflected the hackle pattern of cleavage as shown.

Observations on potassium dihydrogen phosphate (sample C)

'KDP', as this material shall here be referred to, shows much typically hackle cleavage traverse which, because the pattern is a function of stress rather than crystal structure, is quite uninformative so far as distinguishing crystal characteristics are concerned. Consequently, the fractographs in the previous Fig. 1 serve as well for depicting a large proportion of KDP cleavage area.

Where non-hackle, or Type I, patterns can be found, the crystal characteristics immediately make themselves visible; and once again we find marked registrations of a lamellar substructure. However, unlike samples *A* and *B*, and similar to pure ADP, no particular grating effects concur with the lamellar texture. This confirms the opinion that a special distribution of the arsenate within the ADP micelle develops special characteristics of optics and strain within the subsequent lamellar growth.

In Fig. 9, Type I patterns are shown at low and at high magnifications. These obviously represent cleavage traverses primarily influenced by directional weaknesses within the crystal. While the angularity can be ascribed to atomic or molecular factors, the fine-scale and highly periodic disturbances in the traverse seem to depict directly the micellar and lamellar constitution which has been hypothesized.

In Fig. 10 an instance of a pitting imperfection occurs in the fractograph which suggests the dendrite phenomenon of the previous Fig. 6, also the dendrites found in pure ADP. The cause of the marking is unknown; but it occurred on a fresh fracture and, together with the evidence on water-etching in the work with ADP (Zapffe & Worden, 1949*b*), suggests that the effect is intrinsic to the particular crystal.

Conclusion

This investigation extends the earlier study of pure ADP single crystals to ascertain the effect on the cleavage pattern of (a) additions of ammonium arsenate to ADP, and (b) substitution of potassium for the ammonium radical (potassium dihydrogen phosphate, or 'KDP'). The following tentative conclusions can be drawn:

(1) As with ADP, fractographic study of the present crystals discloses both Type I structural patterns and Type II stress patterns.

(2) Among the Type I markings are found imperfection textures in the forms of dendrites, pits, subtle roughnesses, and a pronounced lamellar mosaic structure on a fine scale.

(3) By far the outstanding feature of the arsenated ADP is an optical grating effect, by which crystals of this material can be immediately identified.

(4) Evidence on the cleavage patterns seems to prove that this optical effect is directly related to a physically lamellar structure.

(5) Since lamellar structure is also observed in the other crystals, the postulate is submitted: (a) that these crystals grow by accretion of micelles, in keeping with the micellar theory for the solid state recently announced from this laboratory, (b) that the arsenate distributes itself unevenly between surface and interior of the micelle, in a sense segregating, (c) that the conventional layer-like accretion of these micelles therefore provides a lamellar structure in the present case whose inhomogeneity is intensified in a manner giving rise to the observed optical effects.

Acknowledgment is due to the Office of Naval Research for its sponsorship of the basic research program from which the present manuscript stems as a special study; and to Messrs P. Egli, P. Smith, and S. Zerfoss of the Naval Research Laboratory for their contribution of samples, and for their encouraging interest in the study.

References

- EGLI, P. H. (Private correspondence). 29 January 1948.
 ZAPFFE, C. A. (1949). *Trans. Amer. Soc. Met.* (in the press).
 ZAPFFE, C. A. & WORDEN, C. O. (1949*a*). *Acta Cryst.* **2**, 377.
 ZAPFFE, C. A. & WORDEN, C. O. (1949*b*). *Acta Cryst.* **2**, 383.

Acta Cryst. (1949). **2**, 388

Crystal Chemical Studies of the 5*f*-Series of Elements. XII. New Compounds Representing known Structure Types

BY W. H. ZACHARIASEN

Argonne National Laboratory and the Department of Physics, University of Chicago, Chicago, Illinois, U.S.A.

(Received 27 June 1949)

The paper summarizes crystal-structure information for fifty-five new compounds of 4*f*- and 5*f*-elements representing thirteen known structure types.

This paper summarizes crystal-structure results for a number of new compounds (of 4*f*- and 5*f*-elements) with structures corresponding to well-known types. The information is given without the supporting experimental evidence. Detailed accounts of the various investigations including experimental data will be published in future articles of the present series. The summary of the following pages is submitted for publication because the preparation of the complete papers has been delayed by unforeseen circumstances.

1. Compounds isostructural with NaCl

The unit-cell constants for compounds with the NaCl type of structure are listed in Table 1. These compounds have predominantly metallic character.

Table 1. NaCl type

Compound	<i>a</i> (kX.)	Compound	<i>a</i> (kX.)
NpO	5.00 ± 0.01	NpN	4.887 ± 0.002
PuO*	4.948 ± 0.002	PuN	4.895 ± 0.001
AmO†	4.95 ± 0.01	PuC	4.910 ± 0.005

* Result due to R. C. L. Mooney and W. H. Zachariasen.

† Degree of purity unknown.

2. Compounds isostructural with CaF₂

Table 2 contains the unit-cell constants for substances with the fluorite type of structure.

For PaO₂ one should expect *a* = 5.51 kX. by interpolation between ThO₂ and UO₂. The largest observed value for protactinium oxide preparations is

$$a = 5.45 \pm 0.01 \text{ kX.}$$

It is therefore suggested either that the preparations were impure, or that the composition of the investigated oxide is PaO_{2.2}, i.e. that the reduction to the tetravalent state is incomplete, and that there is a deficit of metal atoms or an excess of oxygen atoms in the structure.

Table 2. CaF₂ type

Compound	<i>a</i> (kX.)	Compound	<i>a</i> (kX.)
PaO _{2.2} ?	5.45 ± 0.01	α-K ₂ ThF ₆	5.994 ± 0.004
NpO ₂	5.425 ± 0.001	α-K ₂ UF ₆	5.934 ± 0.001
PuO ₂ *	5.386 ± 0.001	α-Na ₂ ThF ₆	5.676 ± 0.005
AmO ₂ †	5.377 ± 0.003	α-Na ₂ UF ₆	5.565 ± 0.004
AcOF	5.931 ± 0.002	α-KLaF ₄	5.932 ± 0.001
PuOF	5.70 ± 0.01	α-KCeF ₄	5.894 ± 0.001

* Result due to R. C. L. Mooney and W. H. Zachariasen.

† Degree of purity unknown.

The alpha phase of the compounds A₂XF₆ and AXF₄ is formed by quenching from the melt (Na₂ThF₆, Na₂UF₆, KLaF₄, KCeF₄) or by rapid precipitation from solution (K₂ThF₆, K₂UF₆). The A atoms and the X atoms are randomly distributed over the metal sites of the fluorite structure. Thus the unit cell contains $\frac{4}{3}$ molecules A₂XF₆ and two molecules AXF₄.

The compounds A₂XF₆ as well as the compounds AXF₄ have a wide homogeneity range corresponding to unit cell contents of

$$A_{4-k}X_kF_{4+3k}, \quad 1.33 \leq k \leq 1.60 \quad \text{for } A_2XF_6,$$

$$A_{4-k}X_kF_{4+2k}, \quad 2.00 \leq k \leq 2.40 \quad \text{for } AXF_4.$$