A NEW SYNTHETIC HYDRATE OF ALUMINUM ARSENATE*

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Abstract

In an attempt to grow large crystals of aluminum orthoarsenate ($AlAsO_4$) by the hydrothermal method, a dense polycrystalline product resulted. The aggregate was in the form of fibrous crystallites in parallel arrangement which readily parted into fine, clear needles. Thermal decomposition analyses, chemical analysis, and powder and single crystal x-ray diffraction studies indicate this material to be a new hydrate of aluminum arsenate. The oxide formulation as determined by chemical analysis is:

$$Al_2O_3 \cdot 3As_2O_5 \cdot 10H_2O.$$

An orthorhombic unit cell was established from rotation and Weissenberg studies as follows:

$$a = 12.30\text{Å} \qquad b = 4.64\text{Å} \qquad c = 8.61\text{Å}.$$

The systematically absent reflections indicate a body-centered unit cell; the possible space groups are:

$$D_{2h}^{25} - I_{mmm}, \qquad C_{2v}^{20} - I_{mm2}, \qquad D_2^8 - I_{222}.$$

Two molecules per unit cell gives a calculated density $\rho = 3.27$. The pycnometric density is 3.21.

Introduction

One part of the research program of the Signal Corps Engineering Laboratories has been directed toward the synthesis of substitutes for piezoelectric quartz. In this connection, the growth and properties of aluminum orthoarsenate ($AlAsO_4$) have been studied because of its marked isomorphism with the natural piezoelectric quartz.[1] This compound has been shown to be isostructural with α-quartz with the three silicon atoms of the elementary cell of quartz statistically substituted in a 1:1 ratio by Al^{+3} and As^{+5} cations. The c-axis is doubled in order to distribute properly the Al^{+3} and the As^{+5} ions. In the course of an attempt to increase the size of aluminum orthoarsenate crystals grown by the hydrothermal method, changes were made in the normally used temperature gradient and ratio of Al_2O_3, As_2O_5, and H_2O of the feed materials. Instead of obtaining a single crystal with the usual well developed morphology, a dense polycrystalline product resulted. This aggregate was in the form of fibrous crystallites, in parallel arrangement, which readily parted into exceedingly fine, clear needles of a fibrous nature.

Figure 1 shows the gross character of the polycrystalline product. The overall height of this cross-sectional view is approximately 1.5 cm. The

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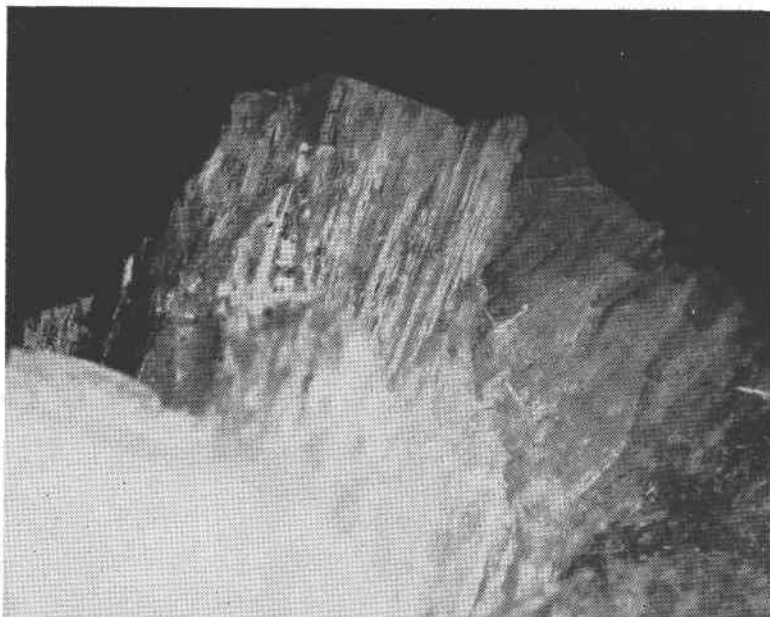
Fig. 1. Cross-sectional view of polycrystalline aggregate. Mag. 5×

electron micrograph (Fig. 2) shows the needle-like nature of the crystallites. The crystallites are generally triangular in cross-section and frequently have a characteristic cleavage at their tip, making an angle of approximately 110° with the needle axis.

Thermal Analyses

As an initial step, the x-ray diffraction powder pattern made from selected clear crystals was compared with a reference pattern of aluminum orthoarsenate. The comparison disclosed at once that the material under study was not of the α-quartz structure (see Fig. 5). Since spectrochemical analysis showed aluminum and arsenic to be the only cations present in structurally significant amount, the possibility was considered that the material might be a hydrate of aluminum arsenate. In order to check this, a decomposition study was made of this compound using the differential thermal analysis method. The sample was heated from room temperature to 1,000° C. at a rate of 13° C./min. (Fig. 3). The DTA curve showed several endothermic peaks and a very small exothermic one. Such a DTA curve is not uncommon for hydrous compounds such as the hydrous aluminum phosphates.[2] The endothermic reactions at low temperature indicate the loss of water of crystallization; those at higher temperatures are correlated with the loss of water due to hydroxyl
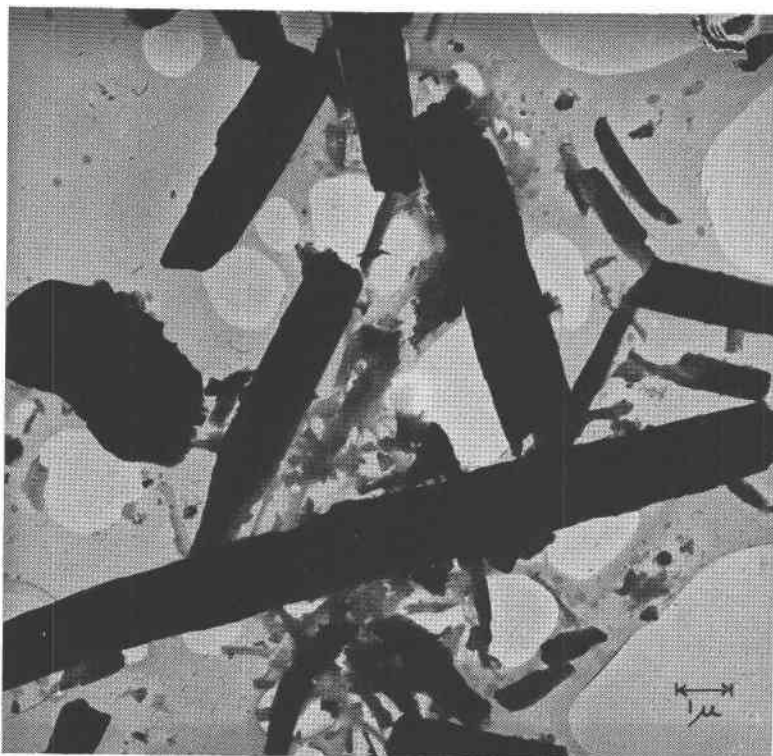
Fig. 2. Electron micrograph of crystallites showing their acicular nature and characteristic cleavage at the end of needles. Mag. 7,500×
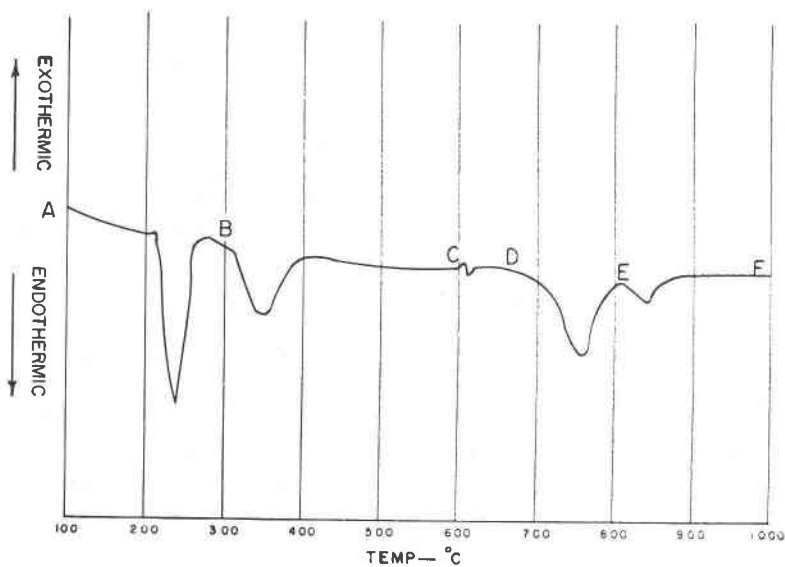

Fig. 3. Differential thermal analysis curve, heating rate—13° C./min.

groups in the structure. Recrystallization is indicated by exothermic re-action peaks.

As will be shown from the chemical analysis, this structure is believed to have a total of 10 waters per unit cell. A rough comparison was made of the area under each of the major endothermic peaks in order to explain the various steps of the conversion to the anhydrate. The first sharp peak at 240° C. appears to be the loss of all the water of crystallization. This water is bonded by van der Waals' forces and may be expected to
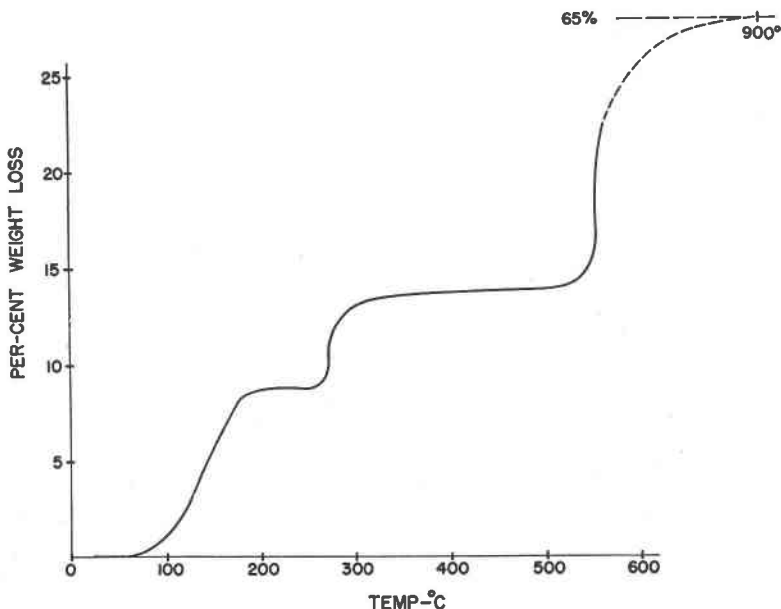

Fig. 4. Static loss-in-weight curve.

be the first to leave the structure. This would mean that all the waters of crystallization would leave at 240° C. and the remaining 6 waters, due to hydroxyl groups, would be distributed among the other three endothermic peaks according to their relative areas; namely, 3 waters at 355° C., 2 waters at 765° C., and 1 water at 835° C.

In order to check the *DTA* results concerning the water loss, a loss-in-weight study of a heated sample of this aluminum arsenic compound was made (Fig. 4). A powdered sample was heated at progressively higher temperatures; the specimen being held at each temperature for a three-hour period. The two steps in the curve below 300° C., which cor-respond to the first two endothermic peaks of the *DTA* curve, indicate
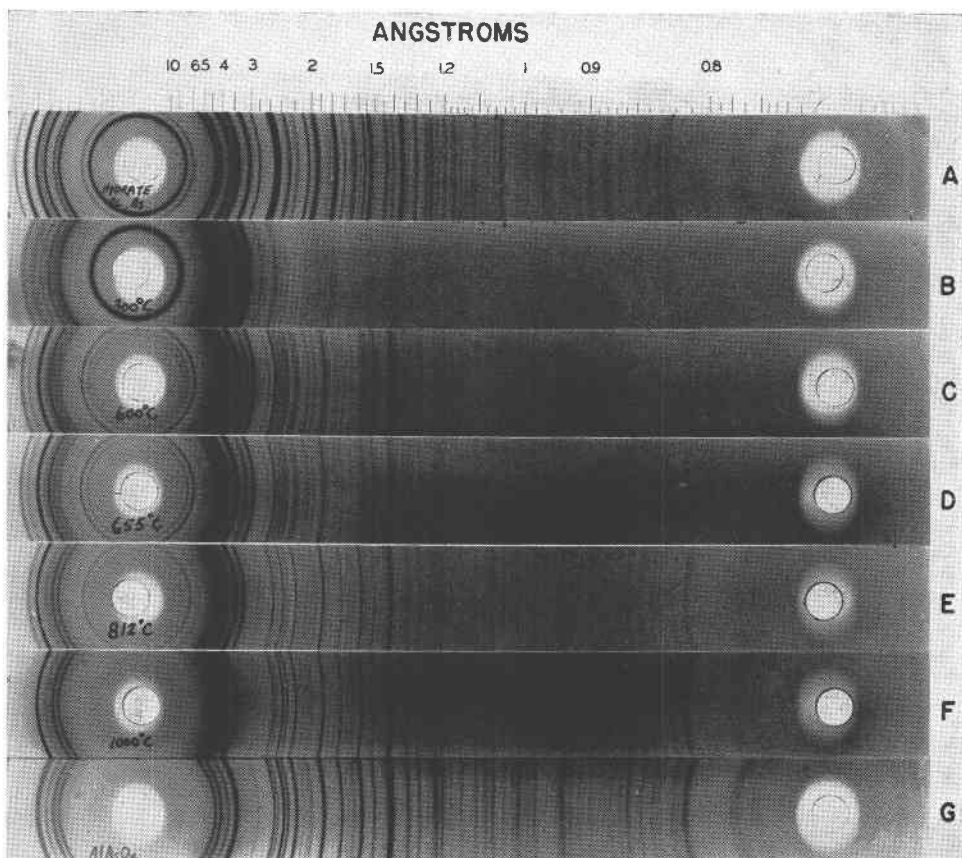
FIG. 5. *X*-ray powder patterns taken using CuK radiation λ=1.5418 Å; camera radius 57.3 mm. All patterns taken at room temperature. *A*—Hydrate of aluminum arsenate—unheated. *B*—Hydrate after air-quenching from 300° C. *C*—Hydrate after air-quenching from 600° C. *D*—Hydrate after air-quenching from 655° C. *E*—Hydrate after air-quenching from 812° C. *F*—Hydrate after air-quenching from 1000° C. *G*—Aluminum orthoarsenate—pattern made from ground single crystal.

a loss-in-weight of about 14%. This compares very well with the calculated losses of $4H_2O$ between 100°–170° C. and $3H_2O$ in the vicinity of 270° C. which give a theoretical cumulative loss of 13%, 1% difference is attributed to adsorbed water. Above 600° C. there was a marked increase in the weight-loss accompanied by the evolution of As_2O_3 and O_2 from the sample. Since no differentiation could be made between the water loss and the loss due to As_2O_3 and O_2, the loss-in-weight measurements were discontinued.

X-Ray Diffraction Powder Analysis

To further monitor the decomposition study, Debye-Scherrer powder patterns were made of samples after being heated in the *DTA* unit to temperatures bracketing each reaction peak as indicated by the lettered points in Fig. 3. Each of the samples was heated at the same rate of 13° C./min., as in the *DTA* run, to the desired temperature and then immediately air-quenched. The powder patterns in Fig. 5 were obtained from air quenched specimens corresponding to the lettered points in the *DTA* curve (Fig. 3). While the patterns of each of the quenched specimens have not been completely identified, the patterns which bracket the *DTA* peaks indicate phase transitions, some probably representing mixtures of two or more phases. It is interesting to note from the diffraction patterns that a marked change occurs in the heating interval between room temperature and 300° C.; after the evolution of the water of crystallization, the sample exhibits broader diffraction lines. Between 300° C.–600° C. there is another noticeable change reflected in the diffraction patterns. The characteristic 6 Å and 7Å lines of the original material re-appear with a reversal in their relative intensity. At the same time, the first appearance of the strongest characteristic lines of $AlAsO_4$ are detected, at 3.45 Å, 2.18 Å, 1.88 Å, 1.42 Å, 1.41 Å. It is surprising to note that before reaching the last decomposition step the final phase has already appeared. Its intensity shows that only a small amount has been converted. However, an attempt to complete the formation of $AlAsO_4$ by heating this compound for four days at 500° C. was unsuccessful. At 655° C. there is a more noticeable appearance of the final $AlAsO_4$ phase with a gradual diminution in the intensity of the intermediate phase represented by the 6 Å and 7 Å lines. A slight shift is noted in the 5 Å line changing to 5.2 Å. At 812° C. only the 6.5 Å, 5.5 Å, and 2.79 Å lines are detectable in addition to those of the $AlAsO_4$ pattern. At 1000° C. the material is completely converted to $AlAsO_4$; its pattern can be seen to be identical to that made from a pure $AlAsO_4$ single crystal (see Fig. 5, pattern G).

These results led us tentatively to designate this material as a hydrate of aluminum arsenate. A literature study of the arsenates and phosphates has indicated the existence of a number of mineral hydrates of the phosphates and arsenates. Table 1 summarizes various reported hydrates found in nature. Among these is a di-hydrate of aluminum orthoarsenate called mansfieldite, ($AlAsO_4 \cdot 2H_2O$) reported by V. T. Allen, J. J. Fahey, and J. M. Axelrod.[3] However, no crystallographic data were given other than that the powder pattern of the material, which was intimately intergrown with kaolinite and quartz, was similar to that of scorodite

($FeAsO_4 \cdot 2H_2O$). A comparison of the powder pattern made from a sample of mansfieldite supplied by the authors with the powder pattern of this material under investigation established them to be different compounds; yet mansfieldite may well be $AlAsO_4 \cdot 2H_2O$. In all the hydrates reported in Table 1, there is a 1:1 atomic ratio of the metal cations.

TABLE 1. ISOSTRUCTURAL α-QUARTZ COMPOUNDS AND MINERAL DI-HYDRATES
OF PHOSPHATES AND ARSENATES

Formula	Name	a_0	b_0	c_0	β	ρ_x	$\rho_{s\,g.}$
SiO_2	Quartz	4.90 Å	---	5.39 Å	—	2.65	—
$AlAsO_4$	Aluminum ortho-arsenate[1]	5.03 Å	—	2x 5.61 Å	—	3.34	3.30
$AlPO_4$	Aluminum ortho-phosphate	4.93 Å	—	2x 5.47 Å	—	2.56	—
$FePO_4 \cdot 2\,H_2O$	Phosphosiderite[4]	5.30 Å	9.79 Å	8.67 Å	90°36′	2.74	2.76
$FePO_4 \cdot 2\,H_2O$	Phosphosiderite[5]	5.28 Å	9.75 Å	8.71 Å	90°36′	—	2.76
$FePO_4 \cdot 2\,H_2O$	Strengite[5]	10.06 Å	9.85 Å	8.65 Å	—	2.89	2.86
$FeAsO_4 \cdot 2\,H_2O$	Scorodite[6]	8.88 Å	10.26 Å	9.98 Å	—	3.35	3.41
$FeAsO_4 \cdot 2\,H_2O$	Scorodite[7]	10.42 Å	8.96 Å	10.15 Å	—	3.24	3.27
$AlPO_4 \cdot 2\,H_2O$	Variscite[4]	9.85 Å	9.55 Å	8.50 Å	—	2.61	2.5
$AlPO_4 \cdot 2\,H_2O$	Metavariscite[4]	5.15 Å	9.45 Å	8.45 Å	$\sim$90°	2.53	2.54
$AlAsO_4 \cdot 2\,H_2O$	Mansfieldite[3]	—	—	—	—	—	3.03

CHEMICAL ANALYSIS

A chemical analysis was made in order to compare the composition of the hydrate under investigation with those shown in the table. The following result was obtained:

	Analysis *Wt. %*	*Postulated* *Formula*	*Calculated* *Wt. %*
Al_2O_3	11.7	$1 \cdot Al_2O_3$	10.5
As_2O_5	69.8	$3 \cdot As_2O_5$	71.0
H_2O	18.0	$10 \cdot H_2O$	18.5
	99.5%		100.0%

This indicates a 1:3 ratio of Al: As. The total loss-in-weight of the sample, including the loss of water and of other volatile decomposition products, when ignited at 900° C., was found to be 64.6%. From this it can be assumed that a decomposition has taken place with the liberation of As_2O_3 and O_2 as well as water. Taking 18% from the loss as the amount of liberated water the remainder of the loss would correspond to two moles of As_2O_5.

From these results the following formula for this hydrate of aluminum arsenate was proposed:

$$Al(H_2AsO_4)_3 \cdot 2H_2O.$$

Using this formula, it can be assumed that the following decomposition takes place:

$$2[Al(H_2AsO_4)_3 \cdot 2H_2O] \rightarrow 2AlAsO_4 + 2As_2O_3 \uparrow + 2O_2 \uparrow + 10H_2O \uparrow$$
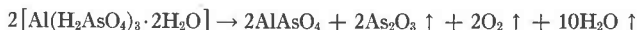
SINGLE CRYSTAL ANALYSIS

As described earlier, no difficulty was encountered in obtaining a fine, clear needle of the material suitable for single-crystal x-ray studies.
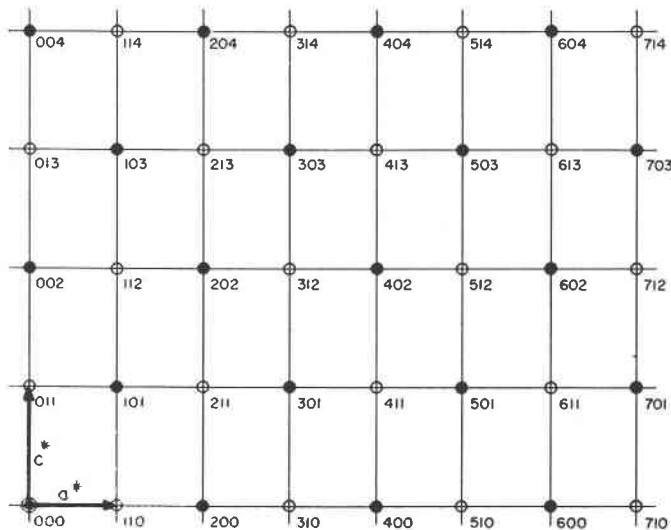

FIG. 6. Zero and 1st level of the reciprocal lattice from b-axis rotation.
●—zero level. ○—1st level.

Uniformly parallel optical extinction between crossed Nicols along the needle or fiber axis indicated this direction to be a crystallographic axis. Rotation photographs were taken of this crystal; the crystal being rotated about the fiber axis. The identity period, as determined from the rotation photograph, is 4.64 Å. In addition, Weissenberg photographs were taken for the zero, first, and second layer lines. Figure 6 represents the reciprocal lattice drawn to scale as found from the evaluation of the Weissenberg photographs. The dots represent the zero level, the circles the first layer line. The two reciprocal axes chosen lie 90° apart giving an

TABLE 2. X-RAY POWDER DATA—HYDRATE OF ALUMINUM ARSENATE—
$Al_2O_3 \cdot 3\ As_2O_5 \cdot 10\ H_2O$

Orthorhombic: $a = 12.30$ Å, $b = 4.64$ Å, $c = 8.61$ Å; $Z = 2$

Possible Space Groups: D_{2h}^{25}—I_{mmm}, C_{2v}^{20}—I_{mm2}, D_2^8—I_{222}

Radiation: Cu-Ni filter $\lambda = 1.5418$ Å

I	d(meas.)	hkl	d(calc)*	I	d(meas.)	hkl	d(calc.)*
VS	7.09	101	7.04			600	2.05
				M	2.04	022	2.04
M−	6.10	200	6.15			204	2.03
VS	4.33	110	4.34	M, B	1.963	321	1.966
		002	4.31				
M	4.08	011	4.08	M+	1.944	512	1.940
						222	1.938
VS	3.69	301	3.70	M−	1.925	114	1.929
						413	1.918
M	3.54	202	3.53				
VS	3.39	211	3.40	W	1.860	503	1.868
		400	3.08	W	1.845	420	1.852
VS	3.06	310	3.07			602	1.851
		112	3.06	W, B	1.833	611	1.832
M	2.81	103	2.80	M	1.785	123	1.785
S	2.51	312	2.50	S	1.766	404	1.763_4
		402	2.49			314	1.762_9
M+	2.44	411	2.46	M	1.708	105	1.705
		013	2.44			422	1.701
VW	2.31	501	2.37	VW, B	1.652	521	1.656
		303	2.35			323	1.651
		020	2.32	M−	1.640	710	1.643
M	2.27	213	2.27	M−	1.622	015	1.614
VW	2.20	121	2.20	M−	1.593	305	1.588
M−	2.17	510	2.17_3			024	1.578
		220	2.17_1	M	1.570	613	1.570
		004	2.15				

* Calculated d spacings taken from indices of zero, 1st, and 2nd level Weissenberg photographs, b-axis rotation CuK radiation.

TABLE 2—*continued*

I	d(meas.)	hkl	d(calc.)*	I	d(meas.)	hkl	d(calc.)*
M	1.560	424	1.567			903	1.234
		215	1.561			1000	1.230
				M, B	1.229	705	1.229
		800	1.537			822	1.228
		620	1.536			107	1.224
M+	1.534	712	1.535				
		514	1.529			525	1.205
		224	1.528	M, B	1.203	516	1.198
						226	1.197
M	1.519	604	1.515				
M	1.493	703	1.499	VVW	1.187	017	1.189
						1002	1.183
VW, B	1.470	523	1.455			1011	1.178
				M, B	1.176	307	1.177
		802	1.448			606	1.176
M	1.446	622	1.447				
				M, B	1.153	035†	1.151
		811	1.437	W+	1.139	426	1.134
W	1.437	006	1.435				
		413	1.429	W	1.122	914	1.120
M, B	1.410	505	1.411			815	1.113
				W, B	1.115	417	1.109
		125	1.374			1101	1.109
M	1.370	901	1.367				
						824	1.101
M	1.360	116	1.363	W, B	1.098	507	1.100
						1013	1.098
		910	1.311				
		325	1.310			1110	1.087
W, B	1.309	714	1.306			1020	1.086_7
		813	1.301	W, B	1.084	725	1.084
		406	1.300_3			127	1.083
		316	1.300_1			716	1.081
						905	1.071
VW	1.275	820	1.282	W, B	1.069	1004	1.068
						208	1.060
M, B	1.268	615	1.268				
						1112	1.054
		912	1.254			327	1.050
M, B	1.248	804	1.251	M, B	1.053	806	1.049
		624	1.250			626	1.048_8

† Reflection outside sphere of reflection for *b*-axis rotation. B broad diffraction line.

orthorhombic real unit cell. The unit cell dimensions were determined to be:

$$a = 12.30\text{A}$$
$$b = 4.64\text{Å}$$
$$c = 8.61\text{Å}$$

Table 2 is an evaluation of the powder pattern using the lattice parameters obtained from the rotation and Weissenberg data. The indices for the calculated d spacings were obtained from the zero, 1st, and 2nd level Weissenberg photographs. The d spacings for indices outside the sphere of reflection for b-axis rotation using Cu/Ni filtered radiation were not calculated.

Using the previously postulated chemical formula of $Al(H_2AsO_4)_3$ $\cdot 2H_2O$ together with the unit cell dimensions, the density can be calculated

$$\rho_x = \frac{M \cdot Z \cdot 1.65}{V}$$

M = Mol. weight

Z = Moles per unit cell

V = Unit cell volume in Å^3

assuming $Z = 2$, we get:

$$\rho_x = \frac{485.70 \times 2 \times 1.65}{12.30 \times 4.64 \times 8.61} = 3.27.$$

Due to the characteristic fibrous nature of the crystals, it was necessary to powder the material in order to obtain accurate density measurements. The pycnometric density determined using toluene was 3.21.

Figure 7 shows the indexing of the reciprocal lattice of the zero and 1st level directly on the Weissenberg photographs. The 2nd level was a repetition of the zero level.

The following reflections were found to be systematically absent:

hkl	with	$h + k + l = 2n + 1$
$00l$	with	$l = 2n + 1$
$h00$	with	$h = 2n + 1$
$h0l$	with	$h + l = 2n + 1$
$0kl$	with	$k + l = 2n + 1$

This indicates a body-centered unit cell. Considering the assumed chemical formula of the compound and the extinction rules found, the possible space groups are: $D_{2h}^{25} - I_{mmm}$, $C_{2v}^{20} - I_{mm2}$, $D_2^8 - I_{222}$.[8]

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[8] R. Pepinsky, private communication April 20, 1954, Penn. State University, hydrate of aluminum arsenate found to be clearly piezoelectric. This data, which is in agreement with the detection of optical activity and triboluminescence, eliminates the centrosymmetric space group $D_{2h}^{25} - I_{mmm}$.
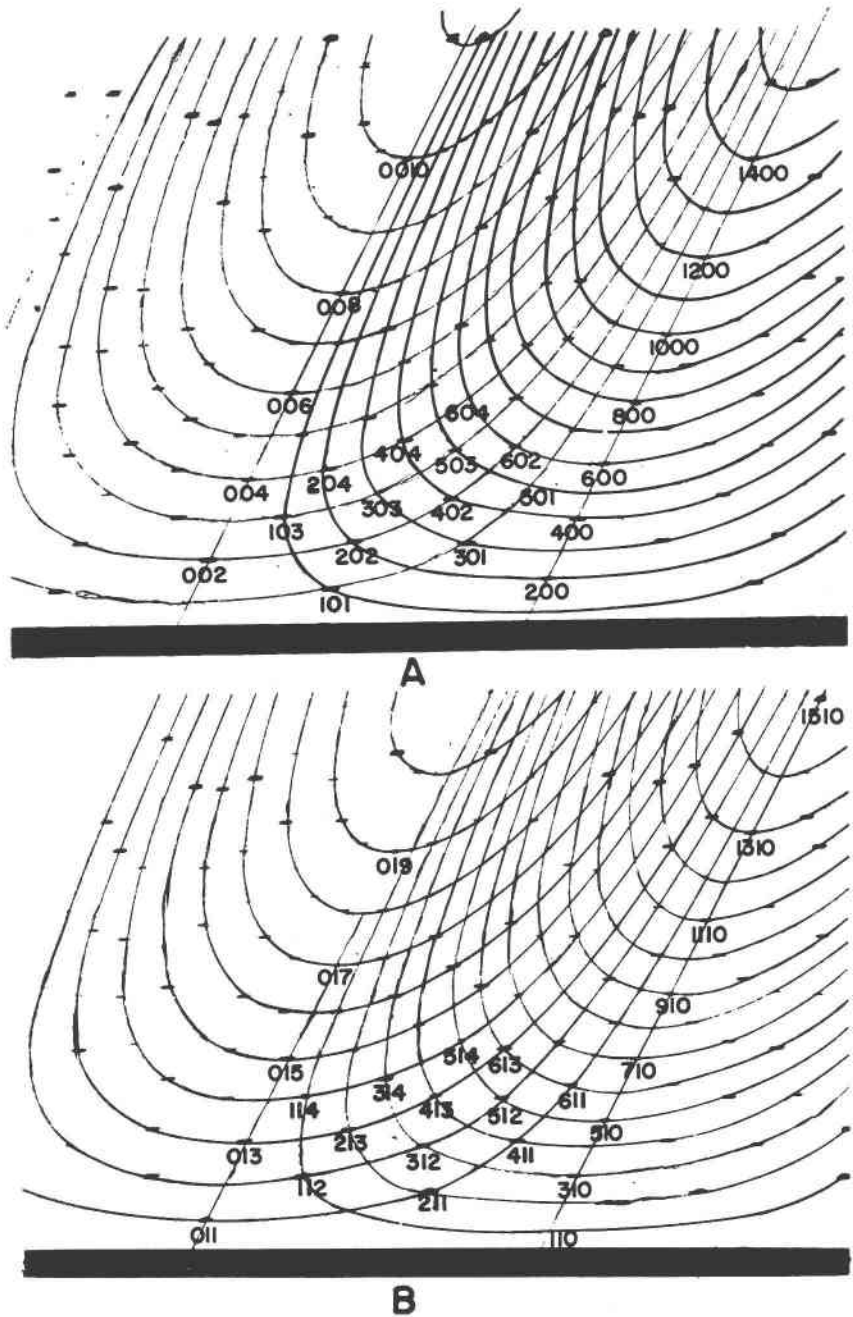
FIG. 7. Indexed Weissenberg photographs. A—zero level. B—1st level.

This paper has described the identification and characterization and preliminary structure postulation of a new synthetic hydrate of aluminum arsenate. A complete structure determination has been started.

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