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X-ray Crystallographic and Powder Data for Some Salts of Phthalic Acid

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Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
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Project No. 7360, Task No. 736005

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FOREWORD

This report was prepared by the Physics Laboratory. The work was initiated under Project No. 7360, "Materials Analysis and Evaluation Techniques," Task No. 736005, "Compositional, Atomic and Molecular Analysis." It was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, with D. W. Fischer acting as project engineer.

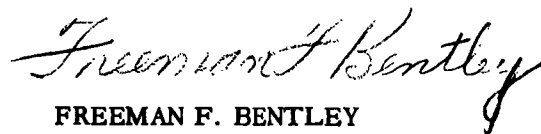
This report covers work conducted from August 1962 through February 1963.

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ABSTRACT

Results are shown for X-ray diffraction analysis and X-ray crystallographic analysis of seven salts of phthalic acid. Lattice parameters, space groups, densities and indexed powder data are given for each salt. The results show that crystals of these salts would make quite good dispersing agents for soft X rays in the .10 to 25Å region.

This report has been reviewed and is approved.



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Chief, Analytical Branch
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INTRODUCTION

One of the main problems of soft X-ray spectroscopy is the lack of a suitable dispersing crystal in the 15 to 50Å region. A crystal cannot disperse X rays which are longer in wavelength than the "2d" spacing of the crystal. Until very recently the largest "2d" available in a commercial crystal was mica at 19.9Å. Most investigators find mica unsuitable and have to settle on ADP with a 2d of 10.642Å.

This report presents X-ray crystallographic and powder data for a family of crystals of phthalic acid salts which surpass mica and ADP in both "2d" spacing and reflecting efficiency.

THE FAMILY OF PHTHALIC ACID SALTS

All compounds used in this work were prepared by the University of Dayton Chemistry Department. The seven salts made were lithium, sodium, potassium, rubidium, cesium, thallium and ammonium acid phthalate.

Phthalic acid (ref 2) and its lithium salt both crystallize in the monoclinic system. The other six salts are all orthorhombic. All members of the series appear morphologically to crystallize in isomorphic forms, although the space groups and cell volumes differ considerably in some cases. One outstanding property of these crystals is that they all cleave very nicely, in fact much like mica, along the (001) face.

It is this (001) face which is of interest in soft X-ray spectroscopy. The usable "2d" spacing along this direction is between 24 and 27 Å for the whole series.

The potassium salt is now being sold commercially as a dispersing crystal by Isomet Corporation of Palisades Park, New Jersey.

There seems to be no difficulty in growing large size crystals of any of these salts suitable for X-ray spectroscopy.

POWDER DATA

The powder data was obtained by placing 325 mesh or finer powder in thin walled 0.7 mm glass capillaries. Prepared specimens were then placed in a 2-radian Siemens camera and irradiated with CuK_α radiation.

The indexed powder patterns are presented in tables 2 - 4.

CRYSTALLOGRAPHIC DATA

Small seed crystals of about 0.5 mm in cross section were grown by slow evaporation of a saturated solution in water. These seeds were then mounted on a goniometer head and single crystal patterns taken on both the Weissenberg camera and the precession camera, using CuK_α radiation.

The Weissenberg technique was used to determine the lattice constants from both rotation photographs and layer line photographs.

Systematic absences of certain sets of X-ray reflections were found using the precession technique along with the Weissenberg.

LATTICE PARAMETER MEASUREMENT

Two methods were used to determine the C_0 lattice constant, since this is the one of most interest.

The most accurate method was measuring the K_{α_1} and K_{α_2} spots of higher reflection orders on the reciprocal lattice lines of a zero level Weissenberg photograph.

After making allowances for film shrinkage, these values were then extrapolated to

$$\frac{1}{2} \left[\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] = 0$$

With this method accurate values to five places can be obtained. In all cases at least the 16th order came through for this series of crystals.

Since crystals of the potassium salt are now sold commercially and no accurate C_0 measurement has been published, an extrapolation curve for this crystal is presented in figure 2.

A second but less accurate method of determining lattice parameters is to grow a crystal large enough for a diffraction pattern of the C_0 direction to be taken on a diffractometer. The higher order of reflections are used and their K_{α_1} and K_{α_2} values are extrapolated to $\cos^2 \theta = 0$.

Lattice constants which are listed in table 1 for the whole series resulted from the first method and were run at 27°C.

Figure 3 shows the relationship of the ionic radius to the cell volumes for the four salts of space group P2ab.

SPACE GROUP DETERMINATION

In all cases a space group could be unambiguously assigned for each salt from systematic X-ray absences alone.

The absences were determined from zero, first and second level precession photographs which were taken around each of the three axes.

In table 1, the space groups assigned by the author differ for four of the salts from those reported by Okaya and Pepinsky (ref 1).

In some cases the lattice parameters also differ, but the largest discrepancy is in the b_0 parameter for the thallium salt.

Also included in table 1 are the numbers of molecules per unit cell and the theoretical densities for each salt.

CONCLUSION

For a crystal to be a good dispersing agent in the soft X-ray region it should have the following characteristics:

1. stable to the atmosphere
2. very low vapor pressure so that it will be stable in vacuum
3. melting point greater than 50°C
4. 2d spacing from 15 to 50 Å
5. good reflectivity for soft X rays
6. good mechanical strength
7. good cleavage properties in plane perpendicular to direction of maximum 2d spacing
8. good crystal growth characteristics

Most of the phthalic acid salts mentioned in this report fulfill these conditions very well. In particular the potassium, cesium, rubidium and thallium salts have quite strong (001) reflections and should help fill the gap in the lack of soft X-ray dispersing crystals up to the 25 Å region. The sodium salt also appears to be quite good although the (002) reflection must be used in this case, due to the absence of (001) reflections when l is odd. This makes no difference, however, since the C_0 parameter is 26 Å.

For the lithium and ammonium salts, the (004) reflections are much stronger than the (001) reflections, making them much less useful than the other salts in the soft X-ray region.

LIST OF REFERENCES

1. Okaya, Y., and Pepinsky, R., Acta Cryst. (1957) 10, 324.
2. vanSchalkwyk, T. G. D., Acta Cryst. (1954) 7, 775.

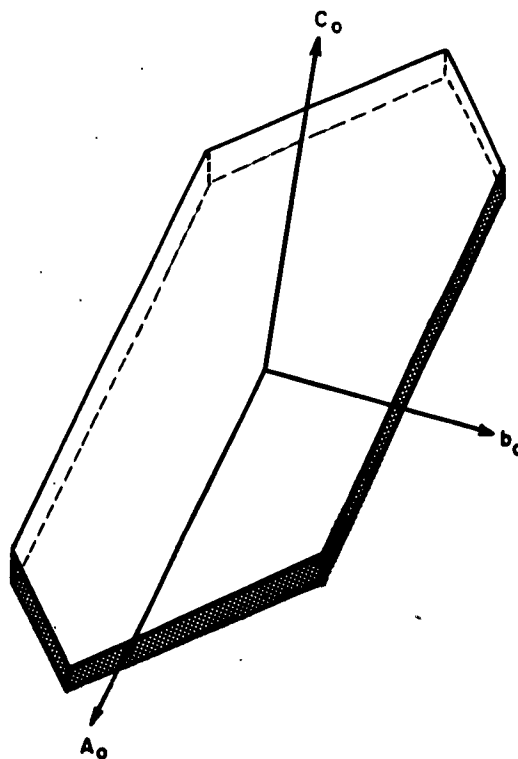


Figure 1. Crystal Habit of Phthalic Acid Salts

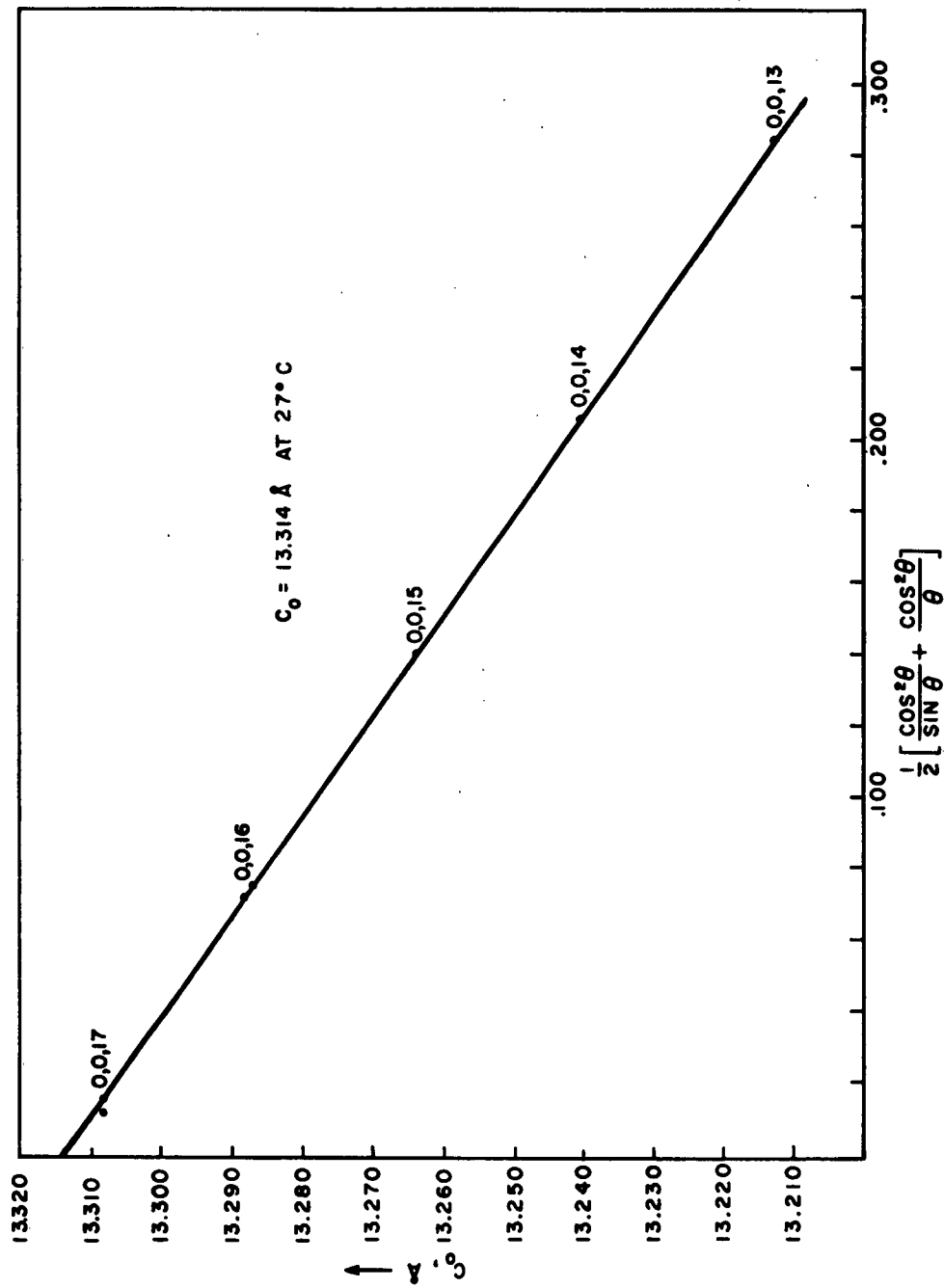


Figure 2. Extrapolation of C_0 for Potassium Acid Phthalate

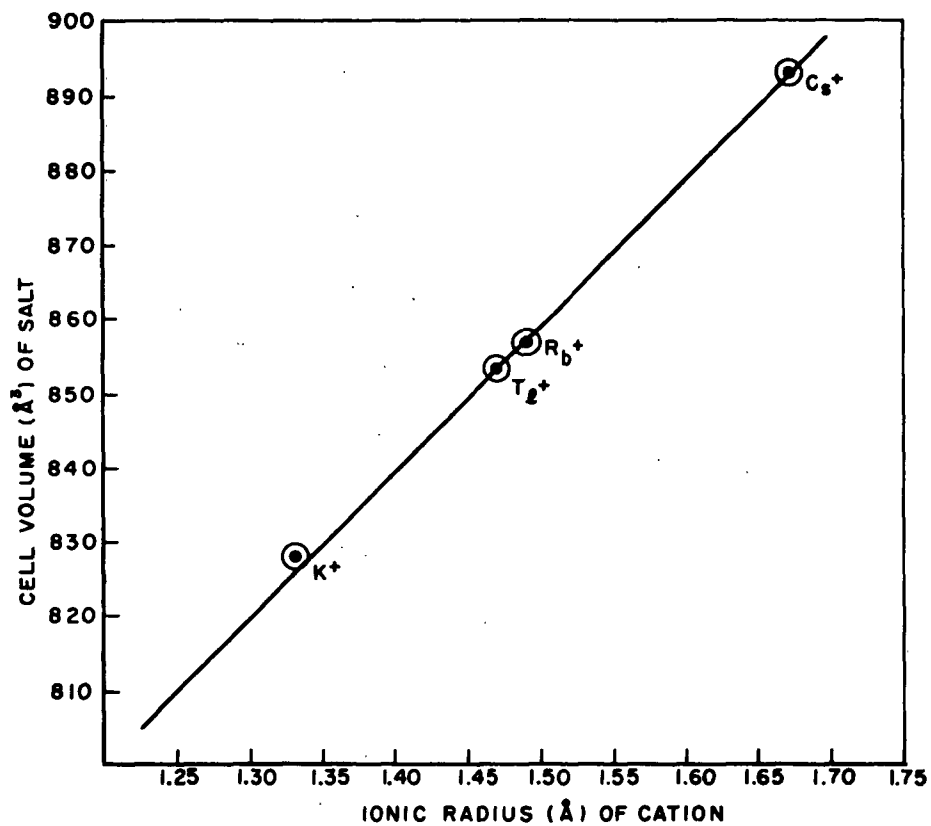


Figure 3. Relationship of Ionic Radius to Cell Volume for Salts of Space Group P2ab

TABLE 1

LATTICE PARAMETERS, SPACE GROUPS AND DENSITIES FOR
THE PHTHALIC ACID SALTS

Salt	Fischer						Okaya and Pepinsky			
	A ₀	B ₀	C ₀	S.G.	σ	Z	A ₀	B ₀	C ₀	S.G.
Na	6.76	9.29	26.39	B2ab	1.508	8	6.76	9.31	26.42	B2ab
K	6.47	9.61	13.314	P2ab	1.638	4	6.47	9.61	13.26	P2 ₁ 2 ₁ 2
Rb	6.55	10.02	13.046	P2ab	1.943	4	6.55	10.02	12.99	P2 ₁ 2 ₁ 2
Cs	6.53	10.71	12.780	P2ab	2.214	4	6.58	10.81	12.84	P2 ₁ 2 ₁ 2
Tl	6.61	10.03	12.876	P2ab	2.871	4	6.63	10.54	12.95	P2 ₁ 2 ₁ 2
NH ₄	6.40	10.23	26.14	Pcab	1.499	8	6.40	10.23	26.14	Pcab

TABLE 2

INDEXED POWDER DATA FOR SODIUM AND AMMONIUM
ACID PHTHALATES

Sodium Acid Phthalate			Ammonium Acid Phthalate		
$d_1 \text{ \AA}$	I/I_1	hkl	$d_1 \text{ \AA}$	I/I_1	hkl
13.3	100	002	13.1	30	002
7.63	3	012	8.15	5	012
6.63	5	004	6.58	100	004
5.38	10	111	5.34	10	021
4.66	15	020	4.62	25	113
4.42	1	006	4.19	15	114
3.99	22	016	4.03	25	024
3.81	10	115;024	3.77	5	115
3.53	2	123	3.41	5	124
3.39	2	200	3.21	5	200
3.20	2	026	3.12	5	202
3.10	7	117;125	3.04	8	211
2.87	1	214	2.99	10	131
2.81	3	133	2.89	5	213
2.59	3	119	2.78	5	214
2.49	2	135	2.54	3	041
2.26	6	137	2.37	5	141
2.20	2	1.1.11			
2.11	1	228			
2.04	2	139			

TABLE 3

INDEXED POWDER DATA FOR POTASSIUM AND CESIUM
ACID PHTHALATES

Potassium Acid Phthalate			Cesium Acid Phthalate		
d_1 Å	I/I ₁	hk1	d_1 Å	I/I ₁	hk1
13.3	100	001	12.8	100	001
6.67	5	002	6.41	15	002
5.00	5	111	5.49	2	012
4.20	2	112	4.27	5	003
4.05	10	013	3.97	15	013
3.73	1	121	3.48	5	122
3.44	2	113	3.39	5	113
3.35	2	122	3.16	2	211
3.16	5	014	3.06	4	014
3.00	3	211	2.97	1	123
2.92	3	123	2.91	2	202
2.84	2	114	2.78	5	114
2.67	3	005	2.53	2	124
2.53	2	124	2.48	5	140
2.39	4	115	2.38	2	034
2.22	2	006	2.32	5	115
2.06	5	205	2.08	3	035
1.90	3	007	1.99	2	116
1.87	3	017	1.671	1	127
			1.596	2	163

TABLE 4

INDEXED POWDER DATA FOR RUBIDIUM AND THALLIUM
ACID PHTHALATES

Rubidium Acid Phthalate			Thallium Acid Phthalate		
d_1 , Å	I/ I_1	hk1	d_1 , Å	I/ I_1	hk1
13.1	100	001	12.9	100	001
6.53	7	002	6.44	65	002
5.08	1	111	5.42	3	012
4.36	4	003	5.07	5	111
4.21	1	112	4.29	50	003
4.00	6	013	4.19	10	112
3.82	1	121	4.00	15	120
3.42	3	113	3.94	20	013
3.27	1	004	3.82	18	121
3.19	1	201	3.39	40	113
3.11	2	014	3.30	15	200
3.04	1	211	3.21	17	004
2.94	1	123	3.06	12	014
2.81	2	212	2.97	8	032
2.62	1	005	2.94	13	202
2.53	2	015;222	2.78	15	114
2.47	1	041	2.71	5	024
2.36	2	115	2.64	5	033
2.26	1	214	2.53	5	213
2.21	1	142	2.35	20	230
2.18	1	006	2.29	5	025

<p>Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt Nr ASD-TDR-63-356. X-RAY CRYSTALLOGRAPHIC AND POWDER DATA FOR SOME SALTS OF PHTHALIC ACID. Final report, May 63, 10p. Incl. illus., tables, 2 refs.</p> <p>Uncl. saified Report</p> <p>Results are shown for X-ray diffraction analysis and X-ray crystallographic analysis of seven salts of phthalic acid. Lattice parameters, space groups, densities and indexed powder data are given for each salt. The results show that crystals of these salts</p> <p style="text-align: right;">(over)</p>	<p>1. X-ray diffraction analysis Phthalic acid salts</p> <p>2. Crystallization AFSC Project 7360, Task 736005</p> <p>3. David W. Fischer In ASTIA collection</p> <p>4. Aval fr OTS</p>	<p>1. X-ray diffraction analysis Phthalic acid salts</p> <p>2. Crystallization AFSC Project 7360, Task 736005</p> <p>3. David W. Fischer In ASTIA collection</p> <p>4. Aval fr OTS</p>	<p>1. X-ray diffraction analysis Phthalic acid salts</p> <p>2. Crystallization AFSC Project 7360, Task 736005</p> <p>3. David W. Fischer In ASTIA collection</p> <p>4. Aval fr OTS</p>
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