

THE SPECIES DUFTTE

by

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## ABSTRACT

The poorly described mineral duftite, which had been separated into two species,  $\alpha$  and  $\beta$  duftite, is reexamined.

$\alpha$  duftite is orthorhombic: space group  $P2_12_12_1$ ,  $\underline{a} = 7.736 \pm 0.005 \text{ \AA}$ ,  $\underline{b} = 9.202 \pm 0.003 \text{ \AA}$ ,  $\underline{c} = 5.995 \pm 0.003 \text{ \AA}$ ,  $a:b:c = 0.8407:1:0.6515$ ;  $Z = 4$ . Strongest lines in the X-ray powder photographs are: 3.26 (10), 2.853 (9), 2.577 (8). Optically (-) with  $2V$  (cal) =  $71^\circ$ . The indices of refraction are  $n_X = 2.04$ ,  $n_Y = 2.08$ ,  $n_Z = 2.10$ ;  $a = X$ ,  $c = Y$ ,  $b = Z$ .

Two forms,  $\{110\}$  and  $\{031\}$ , were found on the crystals measured on the goniometer, and a third was noted on some unmeasurable crystals. Chemical analysis gives PbO 51.78, CuO 19.91, ZnO 0.398,  $As_2O_5$  25.67,  $H_2O$  1.34, corresponding to  $PbCu(AsO_4)(OH)$ .

$\beta$  duftite is orthorhombic: space group  $P2_12_12_1$ ,  $\underline{a} = 7.504 \pm 0.003 \text{ \AA}$ ,  $\underline{b} = 9.031 \pm 0.004 \text{ \AA}$ ,  $\underline{c} = 5.920 \pm 0.003 \text{ \AA}$ ,  $a:b:c = 0.8309:1:0.6555$ ;  $Z = 4$ . Strongest lines in the X-ray powder photographs are: 3.16 (10), 2.614 (9), 2.868 (8).  $2V_X$  (meas) =  $94^\circ$  (-) and  $2V_X$  (cal) =  $83^\circ$  (+). The indices of refraction are  $n_X = 1.905$ ,  $n_Y = 1.93$ ,  $n_Z = 1.95$ ;  $a = X$ ,  $b = Y$ ,  $c = Z$ . Forms recognized were  $\{011\}$  and  $\{3\bar{4}6\}$  (?).

Analysis recalculated to 100% gives PbO 21.21, CaO 11.18, CuO 23.76, ZnO 5.29,  $As_2O_5$  33.44,  $CrO_3$  0.10,  $H_2O$  5.02.  $(Pb, Ca)(Cu, Zn)(AsO_4)(OH)$  was deduced as the formula.

It is suggested that  $\alpha$  duftite remain as duftite, and  $\beta$  duftite be called calcian zincian duftite and include a range of compositions. A solid solution series between duftite and austinite is proposed.



## INTRODUCTION

Pufahl (1920) named duftite from material found at Tsumeb, South West Africa and, based on chemical analysis, assigned to it the formula  $2\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{Cu}(\text{OH})_2$ . He gave the size, density, and hardness of the crystals. Since his characterization of the mineral was limited to this information, later workers defined the species farther.

Barth and Berman (1930) gave optical data for duftite. They included three indices of refraction and stated that duftite is biaxial negative with a large  $2V$ . Based on Pufahl's (1920) chemical analysis, they placed it in the olivenite group of minerals.

Hintze (1933) attributed to duftite, with reservation, the formula  $\text{AsO}_4(\text{Pb}, \text{Cu})[\text{PbOH}]$ .

Richmond (1940) for the first time determined an axial ratio for duftite from a Weissenberg X-ray diffraction study but gave no detailed morphology. He stated that this was because crystals were poorly developed and faces lacked sufficient luster to give adequate reflections. He described the habit as prismatic, the crystals being terminated only by  $\{011\}$ . The space group was tentatively given as  $P_{\text{nan}}$ , and Richmond noted that his criteria were inconsistent. Based on Pufahl's (1920) analysis, Richmond found the formula for duftite to be  $\text{CuPb}(\text{AsO}_4)(\text{OH})$  with a unit cell content of four. He placed duftite in the adelite group.

Berman in his work of 1932 noted three morphological forms for duftite which appear in the angle table in Dana's System of Mineralogy, Vol. II (Palache, Berman, and Frondel, 1951). The axial ratio given

there is that of Richmond (1940); however, the forms are presented with the crystal reoriented. The transformation, Berman to Richmond, is 001/010/100.

Claringbull (1951) described duftite from three localities. He compared samples from Tsumeb; Mapimi, Mexico; and Brandy Gill, Cumberland, England. He gave comparative X-ray powder data for the duftites and indexed them, using the single crystal measurements of Richmond (1940), but he noted that the restrictions imposed by the somewhat doubtful space group determination were not applied.

Guillemin (1956) later proposed two species of duftite, which he called,  $\alpha$  duftite and  $\beta$  duftite. He published axial ratios, space groups, physical descriptions, specific gravities, X-ray powder data, chemical analyses, and formulas for each. He gave the optical indices and an optical description of  $\alpha$  duftite and one index of refraction for  $\beta$  duftite. Included in his paper was a short morphological description of  $\alpha$  duftite together with a figure. Guillemin synthesized  $\alpha$  duftite.

The purpose of this study is to define better the species duftite from natural crystals. Some question has arisen as to the quality of existing data. As mentioned previously, the early workers described only one mineral, and later Guillemin (1956) separated duftite into two species,  $\alpha$  duftite and  $\beta$  duftite. His nomenclature is used in this paper, but his  $\beta$  duftite is expanded to include a range of compositions rather than just the specific composition given by Guillemin.

New chemical, physical, optical, morphological, and X-ray property determinations are reported for the two species,  $\alpha$  duftite and  $\beta$  duftite.

## $\alpha$ DUFTITE

### Occurrence and Associations

The  $\alpha$  duftite used in this study is from Tsumeb, South West Africa, and was obtained from the U.S. National Museum and the Geological Museum at Harvard University. Some of the material is associated with calcite and azurite, and some  $\alpha$  duftite specimens are partially altered to a bright yellow powder. This yellow substance defied identification but was found to contain lead, iron, and arsenic.

Dana's System of Mineralogy describes duftite at Tsumeb as occurring with azurite and yellowish films of a bauxite-like material (Palache et al., 1951).

Guillemin (1956) observed his  $\alpha$  duftite in association with azurite, olivenite, mottramite, and malachite on Tsumeb material. He also cited  $\alpha$  duftite from Cap Garonne and Vosges, France.

### Physical Properties

The  $\alpha$  duftite occurs in botryoidal masses, as individual crystals, and as masses or clusters of crystals. One specimen from Tsumeb consists of bright green crystals while another contains dull gray-green crystals. The crystals vary from sub-millimeter to two millimeters in length; the majority are one millimeter or less.

No cleavage is observed, and the fracture is conchoidal. The luster of the bright green crystals is vitreous as is the luster on the fracture surfaces of the gray-green crystals. The luster on the crystal

faces of the latter is dull. The streak of all the  $\alpha$  duftite crystals tested is pale green.

The hardness is about four on the Mohs scale. The specific gravity, determined by repeated measurements of a 45-milligram sample on a Berman balance, was found to be  $6.57 \pm 0.05$ .

### Composition

Forty-five milligrams of the Tsumeb  $\alpha$  duftite were hand picked under the microscope for chemical analysis. The many crystals which contained cavities of the unidentifiable yellow powder were not used for analysis, results of which are presented in Table 1.

Table 1. Chemical Analysis of  $\alpha$  Duftite

	Weight % <sup>a</sup> (obs)	Weight % (recal)	Oxide Proportion	Mole Ratio	Weight % <sup>b</sup>
PbO <sup>c,d</sup>	51.78	52.25	0.2320	2.077	52.31
CuO	19.91	20.09	0.2503	2.241	18.65
ZnO	0.398	0.40	0.0049	0.044	---
As <sub>2</sub> O <sub>5</sub>	25.67	25.90	0.1117	1.000	26.93
H <sub>2</sub> O <sup>e</sup>	<u>1.34</u>	<u>1.35</u>	0.0744	0.666	<u>2.11</u>
Total	99.098	99.99			100.00

a. Analyst: Schwarzkopf Microanalytical Laboratory, Woodside, New York.

b.  $\text{PbCu}(\text{AsO}_4)(\text{OH})$ .

c. Pb, Cu, Zn, and As were obtained by atomic absorption.

d. Pb, Cu, and Zn are the average of two analyses.

e. Obtained by combustion under an oxygen environment and drying in nitrogen at 150°C.

From the above analysis, the empirical formula of  $\alpha$  duftite is  $\text{Pb}_{2.08}\text{Cu}_{2.24}(\text{AsO}_4)_2(\text{OH})_{1.34}$ . The ideal formula is  $\text{PbCu}(\text{AsO}_4)(\text{OH})$ . The small amount of zinc is probably substituting for copper. It will be noted that the percentage of water is low. It is felt that this is due to analytical problems attendant upon the small amount of material (ca. 45 mg) available for analysis.

### Optical Properties

In transmitted light  $\alpha$  duftite is pleochroic with X = pale green, Y = green, and Z = yellow green. The mineral is biaxial negative with a large  $2V$ .  $2V$  was calculated to be  $71^\circ (-)$ . The optical indices, determined in white light, are:  $n_X = 2.04$ ,  $n_Y = 2.08$ , and  $n_Z = 2.10$ , all  $\pm 0.005$ . The optical orientation is a = X, c = Y, and b = Z.

### Crystallography

$\alpha$  duftite is orthorhombic with class symmetry of rhombic disphenoidal, 222, as will be shown in the "Weissenberg Data" section. The crystals used in this study are elongate parallel to  $[100]$  and are terminated by  $\{110\}$ . Some of the bright green crystals from Tsumeb are doubly terminated and yield fair goniometrical signals. These crystals are simple, showing only the  $m\{110\}$  and  $l\{031\}$  forms (Figure 1).

The gray-green crystals from Tsumeb show three forms, but the faces lack sufficient luster to give reflections. Two of these forms appear to be  $m$  and  $l$ ; and the third form is a first order rhombic prism, thought to be  $\{011\}$ . An angle table is presented in Table 2.

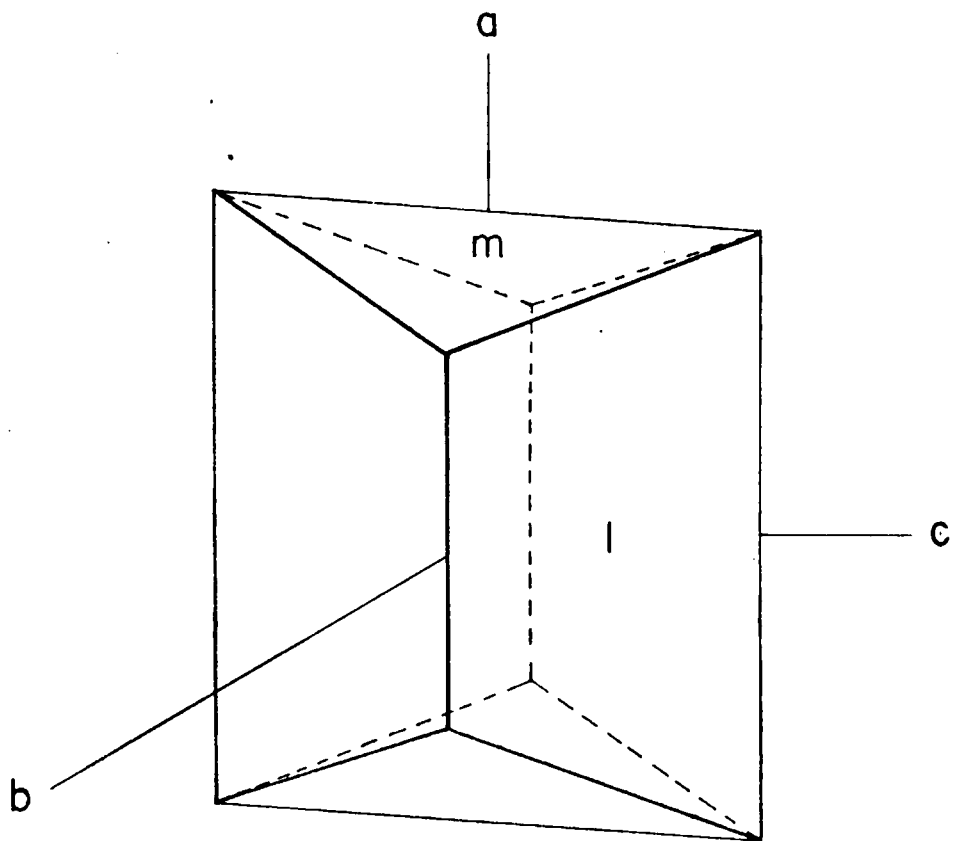


Figure 1.  $\alpha$  Duftite from Tsumeb, South West Africa

Table 2.  $\alpha$  Duftite Angle Table

Orthorhombic; disphenoidal--222.

$$a:b:c = 0.8407:1:0.6515$$

$$p_0:q_0:r_0 = 0.7749:0.6515:1$$

$$q_1:r_1:p_1 = 0.8407:1.2904:1$$

$$r_2:p_2:q_2 = 1.5349:1.1895:1$$

Form	$\phi$	$\rho = C$	$\phi_1$	$\rho_1 = A$	$\phi_2$	$\rho_2 = B$
m 110	49°57'	90°00'	90°00'	40°03'	0°00'	49°57'
1 031	0 00	62 54	62 54	90 00	90 00	27 06

Since the reflective quality of the crystals was not good enough to obtain accurate measurements on the goniometer, the axial ratio and other data of the angle table were calculated from the unit cell determined from single crystal Weissenberg photographs.

### X-ray Study

#### Weissenberg Data

A series of oscillation photographs was taken of a single  $\alpha$  Duftite crystal using copper radiation in order to orient it on the a and c crystallographic axes. Zero, first, and second level Weissenberg photographs were taken rotating on the a and c axes of the  $\alpha$  Duftite crystal.

A quartz crystal was used as a standard on each zero level photograph to compensate for systematic errors. A single quartz crystal was rotated twice for 1.5 hours each, using a layer line screen to produce a row of indexed zero level reflections along two edges of the film. The  $2\theta$  values of the quartz reflections were measured, and the actual

$2\Theta$  values at room temperature were derived from the cell dimensions (International Tables for X-ray Crystallography, Vol. III by Lonsdale, 1968, p. 122). Each  $2\Theta_{\text{cal}}$  was divided by  $2\Theta_{\text{meas}}$  giving a number close to unity which was plotted against  $2\Theta_{\text{meas}}$ .

Measurements of  $2\Theta$  for pairs of high order  $\alpha$  duftite reflections were made on the zero level photographs. Each  $2\Theta$  for  $\alpha$  duftite was corrected for systematic errors by multiplying it by an appropriate value found from the graph. Using only reflections that lie on the axes, the cell parameters could easily be calculated by hand; however, for greater accuracy more reflections were used.  $2\Theta$  values for all high order reflections, therefore, were measured and cell parameters derived by use of a computerized least squares procedure.

Thirty-seven  $K\alpha$ , six  $K\alpha_1$ , and six corresponding  $K\alpha_2$  reflections were measured on the zero level photograph taken with the a axis of the  $\alpha$  duftite crystal perpendicular to the X-ray beam. Twenty-three  $K\alpha$ , two  $K\alpha_1$ , and one  $K\alpha_2$  reflections were measured on the zero level photograph taken with the c axis perpendicular to the X-ray beam.

From these measurements, the cell parameters of  $\alpha$  duftite are  $\underline{a} = 7.736 \pm 0.005 \text{ \AA}$ ,  $\underline{b} = 9.202 \pm 0.003 \text{ \AA}$ , and  $\underline{c} = 5.995 \pm 0.003 \text{ \AA}$ , and  $a:b:c = 0.8407:1:0.6515$ .

The  $\alpha$  duftite reflections on each zero, first, and second level Weissenberg film were indexed. The only systematic absences were found to be in  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd. Thus,  $\alpha$  duftite conforms uniquely to the space group  $P2_12_12_1$ .

The unit cell content ( $Z$ ) was derived from the cell volume, composition, and the measured density.  $Z$  is calculated as 3.94 and



assumed to be 4. Using  $Z$ , composition, and the cell volume, the specific gravity is 6.64 as compared to the measured specific gravity of 6.57.

#### Powder Data

After considering formula weight, absorption, and  $d$  spacings,  $\text{Pb}(\text{NO}_3)_2$  was chosen for use as an internal standard in the  $\alpha$  duftite powder work. Separate spindles of the internal standard and  $\alpha$  duftite were made and X-rayed. A spindle of the two substances combined was made, using one part  $\text{Pb}(\text{NO}_3)_2$  to two parts  $\alpha$  duftite, and X-rayed. The X-ray diffraction photographs were taken by the Debye-Scherrer method using the Straumanis mounting (camera diameter = 114.59 mm) and copper radiation with a nickel filter.

The values of  $|\sin^2\theta_{\text{obs}} - \sin^2\theta_{\text{cal}}|$  for the  $\text{Pb}(\text{NO}_3)_2$  reflections were plotted against the Nelson-Riley function. The Nelson-Riley values for each  $\alpha$  duftite reflection on the same film were located on the curve, and  $\sin^2\theta_{\text{obs}}$  for each  $\alpha$  duftite reflection was corrected by adding to it the corresponding  $|\sin^2\theta_{\text{obs}} - \sin^2\theta_{\text{cal}}|$  value. From the resulting  $\sin^2\theta$  values, corrected  $d$  spacings for the  $\alpha$  duftite reflections were calculated using the Bragg law.

Intensity values for each line were visually estimated. The reflections were indexed as far as resolution of the pattern would allow. In a few cases, the assignments of indices are uncertain. The X-ray powder data for  $\alpha$  duftite are presented in Table 3.

The principal reflections of the pattern compare favorably with those given by Guillemin (1956) which are given in Table 7 (p. 20), but he did not index his pattern.

Table 3. X-ray Powder Data for  $\alpha$  Duftite from Tsumeb, South West Africa(CuK $\alpha$  = 1.5418 Å; Ni filter. Camera diameter = 114.59 mm)

I <sup>a</sup>	d <sub>obs</sub>	d <sub>cal</sub>	hkl <sup>b</sup>	I <sup>a</sup>	d <sub>obs</sub>	d <sub>cal</sub>	hkl <sup>b</sup>
3	5.04	5.02	011	2	1.940	1.934	400
						1.935	103
2	4.62	4.60	020	4	1.880	1.878	241
4	4.23	4.21	111	1	1.830	1.830	042
						1.833	023
3	3.94	3.95	120	2	1.790	1.790	150
2	3.58	3.57	210	1	1.776	1.776	142
						1.775	203
1	3.31	3.30	121	1	1.717	1.717	340
						1.716	151
10	3.26	3.25	201	4	1.652	1.651	242
						1.650	341
3	3.01	3.00	002	3	1.631	1.636	430
						1.636	133
9	2.853	2.851	130	1/2	1.583	1.580	303
		2.850	012			1.580	431
7	2.667	2.674	112	1/2	1.558	1.557	313
8	2.577	2.575	131	3	1.535	1.534	060
3	2.514	2.513	022	2	1.499	1.499	004
1	2.409	2.403	230	1/2	1.482	1.481	143
3	2.300	2.301	040	2	1.456	1.459	161
1	2.255	2.250	320	1	1.406	1.406	243
						1.404	333
1	2.210	2.205	140	3	1.389	1.387	261
2	2.112	2.106	222	1	1.356	1.354	053
		2.106	321				
3	2.070	2.070	141	1	1.325	1.327	134
2	1.982	1.978	240	1	1.302	1.301	451

Table 3. X-ray Powder Data for  $\alpha$  Duftite--Continued

$I^a$	$d_{obs}$	$d_{cal}$	$hkl^b$	$I^a$	$d_{obs}$	$d_{cal}$	$hkl^b$
1	1.286	1.287	262	2	0.906		
		1.287	361				
2	1.267	1.267	171	1	0.894		
2	1.259			1/2	0.888		
1	1.216	1.217	063				
1	1.199						
1	1.186	1.189	015				
2	1.164	1.162	054				
2	1.151						
2	1.139	1.138	180				
2	1.117	1.117	035				
2	1.086						
2	1.075						
1	1.059						
1/2	1.028						
1	1.000						
1	0.991						
1	0.977						
1/2	0.968						
1	0.940						
1	0.925						

a. Intensity visually estimated.

b. Indexing on basis of the Weissenberg data.

## $\beta$ DUFTITE

### Occurrence and Associations

The  $\beta$  duftite used in this study was found at the Granite Gap mining district, located 19 miles north of Rodeo, New Mexico, on U.S. Highway 80 by Dr. S. A. Williams and the author. The material was found in association with calcite and several arsenates, including beudantite, hidalgoite, mixite, scorodite, mimetite, and austinite. In places, botryoidal  $\beta$  duftite was found to coat adamite.

Guillemin (1956) notes the occurrence of  $\beta$  duftite from Tsumeb, South West Africa; Vosges, France; the Lower Congo; Brandy Gill, Cumberland, England; the Ojuela mine, Mapimi, Mexico; and Saint-Nicolas, Germany. The Mapimi sample was in association with wulfenite, and one sample from Tsumeb occurred on tennantite. The German material consisted of quartz with malachite, azurite, and mimetite, containing small radiating masses of  $\beta$  duftite.

### Physical Properties

The Granite Gap  $\beta$  duftite occurs as very fine, needlelike crystals and botryoidal masses. From another location in the same district, the  $\beta$  duftite occurs as clusters of stouter crystals up to 200 microns in length.

The color ranges from the gray green of the botryoidal masses to the light green of the distinct crystals. In comparison, a sample from Tsumeb, tentatively identified as  $\beta$  duftite from its X-ray powder

pattern, was examined and found to occur as green crystalline masses on calcite. No single crystals of this material were found.

No cleavage is observed in  $\beta$  duftite, and the fracture is conchoidal. The luster is vitreous, the streak pale green, and the hardness is about four on the Mohs scale. The specific gravity measured by Williams (Phelps Dodge Corporation, personal communication, 1968) on a Berman balance was 4.37.

### Composition

About 50 milligrams of  $\beta$  duftite were hand picked under the microscope for chemical analysis, results of which are presented in Table 4. From this analysis, the empirical formula of  $\beta$  duftite is  $(\text{Pb}, \text{Ca})_{2.02}(\text{Cu}, \text{Zn})_{2.50}(\text{AsO}_4)_{2.00}(\text{OH})_{1.91} \cdot \text{H}_2\text{O}$ . The ideal formula might be  $(\text{Pb}, \text{Ca})(\text{Cu}, \text{Zn})(\text{AsO}_4)(\text{OH}) \cdot 1/2\text{H}_2\text{O}$ . In the sample analyzed, the ratio of Ca/Pb is 2.1 and that of Cu/Zn is 4.6. If a portion of the water is considered to be nonessential, the formula may be written  $(\text{Pb}, \text{Ca})(\text{Cu}, \text{Zn})(\text{AsO}_4)(\text{OH})$ . It is interesting to note that Guillemin (1956) in his analysis of  $\beta$  duftite found a higher percentage of water present than would conveniently fit into his formula. He considered the excess to be nonessential water.

### Optical Properties

$\beta$  duftite is biaxial. The optical indices, determined in white light, are:  $n_x = 1.905$ ,  $n_y = 1.93$ , and  $n_z = 1.95$ , all  $\pm 0.005$ .  $2V_x$  (meas) =  $94^\circ (-)$ , and  $2V_x$  (cal) =  $83^\circ (+)$ . This discrepancy is accounted for by the sensitivity of the formula used in calculating  $2V_x$  to variation in the optical indices. If the indices are varied slightly

Table 4. Chemical Analysis of  $\beta$  Duftite

	Weight % <sup>a</sup> (obs)	Weight % (recal)	Oxide Proportion	Mole Ratio	Weight % <sup>b</sup>
PbO <sup>c,d</sup>	20.78	21.21	0.0931	0.653	23.74
CaO <sup>e</sup>	10.96	11.18	0.1954	1.371	11.31
CuO	23.28	23.76	0.2925	2.053	20.91
ZnO	5.18	5.29	0.0637	0.447	4.54
As <sub>2</sub> O <sub>5</sub>	32.76	33.44	0.1425	1.000	36.62
CrO <sub>3</sub>	0.096	0.10	0.0010	0.007	---
H <sub>2</sub> O <sup>f</sup>	<u>4.92</u>	<u>5.02</u>	0.2728	1.914	<u>2.87</u>
Total	97.976	100.00			99.99

a. Analyst: Schwarzkopf Microanalytical Laboratory, Woodside, New York.

b. (Pb, Ca) (Cu, Zn) (AsO<sub>4</sub>) (OH) with Ca/Pb = 2.1 and Cu/Zn = 4.6.

c. Pb, Cu, Zn, As, and Cr were obtained by atomic absorption.

d. Pb, Ca, Cu, and Zn are the average of two analyses.

e. Obtained by flame emission spectrophotometry.

f. Obtained by combustion under an oxygen environment and drying in nitrogen at 150°C.

(within the  $\pm 0.005$  margin of error), the  $2V$  (cal) ranges from positive through  $90^\circ$  to negative. The optical orientation is  $a = X$ ,  $b = Y$ ,  $c = Z$ .

### Crystallography

$\beta$  duftite is orthorhombic with class symmetry of rhombic disphenoidal, 222, as will be shown in the section on "Weissenberg Data." The crystals from Granite Gap used in this study are elongate on  $[100]$ . No doubly terminated crystals were observed. The crystals are simple, showing only the  $f\{011\}$  and  $e\{3\bar{4}6\}$  (?) forms (Figure 2). The crystals show rough and pitted faces which gave very poor to poor reflections; therefore, the indices of the disphenoid are in doubt. An angle table is presented in Table 5.

Table 5.  $\beta$  Duftite Angle Table

Orthorhombic; disphenoidal--222.

$$a:b:c = 0.8309:1:0.6555 \quad p_0:q_0:r_0 = 0.7889:0.6555:1$$

$$q_1:r_1:p_1 = 0.8309:1.2676:1 \quad r_2:p_2:q_2 = 1.5256:1.2035:1$$

Form	$\phi$	$\rho = C$	$\phi_1$	$\rho_1 = A$	$\phi_2$	$\rho_2 = B$
f 011	$0^\circ 00'$	$33^\circ 15'$	$33^\circ 15'$	$90^\circ 00'$	$90^\circ 00'$	$56^\circ 45'$
e $3\bar{4}6$ (?)	137 56	30 29	-23 24	70 08.	68 28	152 15

Because the reflective quality of the crystals was not good enough to obtain accurate measurements on the goniometer, the data of the angle table were calculated from the unit cell parameters determined from single crystal Weissenberg photographs.

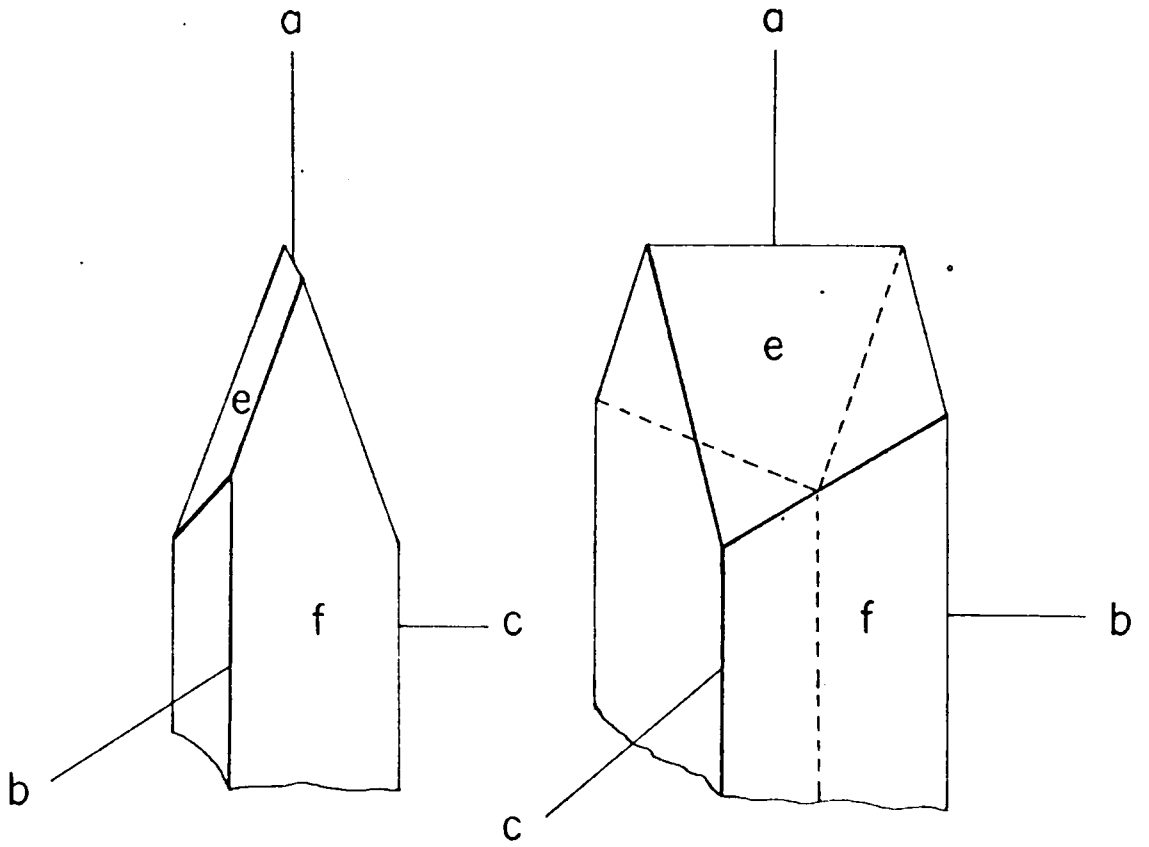


Figure 2. Two Views of  $\beta$  Duftite from Granite Gap, New Mexico



## X-ray Study

### Weissenberg Data

A series of oscillation photographs was taken of a single  $\beta$  duftite crystal using copper radiation in order to orient it on the a and b crystallographic axes. Zero, first, and second level Weissenberg photographs were taken rotating on the a and b axes of the  $\beta$  duftite crystal. A quartz crystal was used for standardization purposes employing the method described previously in the "Weissenberg Data" section under  $\alpha$  duftite.

$2\Theta$  for pairs of high order reflections on the zero level Weissenberg photographs were measured and corrected for systematic errors. The corrected  $2\Theta$  values and their corresponding indices were used to obtain the cell parameters.

Nine  $K\alpha$ , 26  $K\alpha_1$ , and 26 corresponding  $K\alpha_2$  reflections were measured on the zero level photograph taken with the a axis of the  $\beta$  duftite crystal perpendicular to the X-ray beam. Fourteen  $K\alpha$ , 7  $K\alpha_1$ , and 7 corresponding  $K\alpha_2$  reflections were measured on the zero level photograph taken with the b axis perpendicular to the X-ray beam.

From these measurements, the cell parameters of  $\beta$  duftite are  $\underline{a} = 7.504 \pm 0.003 \text{ \AA}$ ,  $\underline{b} = 9.031 \pm 0.004 \text{ \AA}$ , and  $\underline{c} = 5.920 \pm 0.003 \text{ \AA}$ , and  $a:b:c = 0.8309:1:0.6555$ .

The  $\beta$  duftite reflections on zero, first, and second level Weissenberg films were indexed. The only systematic absences were found to be in  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd, and  $00l$  with  $l$  odd. Thus,  $\beta$  duftite conforms uniquely to the space group  $P2_12_12_1$ .

The unit cell content ( $Z$ ) was derived from the cell volume, composition, and the measured density.  $Z$  is calculated as 3.36 and assumed to be 4. It is believed that due to the small amount of material available for measurement, the measured specific gravity for  $\beta$  duftite is low, and therefore the calculated value of  $Z$  is low. Using  $Z$ , composition, and the cell volume, the calculated specific gravity is 5.19 as compared to the specific gravity measured by Williams (Phelps Dodge Corporation, personal communication, 1968) of 4.37.

#### Powder Data

$\text{Pb}(\text{NO}_3)_2$  was also used as the internal standard in the  $\beta$  duftite powder work. An X-ray pattern was obtained, and the  $d$  values of its reflections were corrected by the methods previously described for  $\alpha$  duftite. Intensity values for each line on the pattern were visually estimated. The indexed X-ray powder data for  $\beta$  duftite are presented in Table 6.

The principal reflections of the pattern compare favorably with those given by Guillemin (1956) as shown on Table 7, but he did not index his pattern.

Table 6. X-ray Powder Data for  $\beta$  Duftite from Granite Gap(CuK $\alpha$  = 1.5418 Å; Ni filter. Camera diameter = 114.59 mm)

I <sup>a</sup>	d <sub>obs</sub>	d <sub>cal</sub>	hkl <sup>b</sup>	I <sup>a</sup>	d <sub>obs</sub>	d <sub>cal</sub>	hkl <sup>b</sup>
2	5.79	5.77	110	6	1.702	1.715	213
1	5.02	4.95	011	1/2	1.685	1.684	151
1	4.62	4.65	101	7	1.614	1.613	332
5	4.14	4.13	111	2	1.575	1.569	251
3	3.73	3.75	200	2	1.527	1.527	313
1	3.47	3.46	210	3	1.475	1.476	160
10	3.16	3.17	201	1/2	1.433	1.434	114
8	2.868	2.886	220	2	1.382	1.381	243
3	2.798	2.794	130	3	1.311	1.312	153
9	2.614	2.634	112	1/2	1.275	1.274	304
1	2.488	2.476	022	1/2	1.250	1.250	540
2	2.402	2.411	310	3	1.220	1.220	270
1	2.324	2.324	202	1/2	1.183	1.183	072
2	2.237	2.233	311	1	1.128	1.128	272
3	2.066	2.066	222	1	1.084	1.084	434
3	1.943	1.934	240	1/2	0.897	0.897	1·10·0
3	1.878	1.876	400	3	0.866	0.866	840
3	1.835	1.837	410	3	0.841		

a. Intensity visually estimated.

b. Indexing on basis of the Weissenberg data.

Table 7. Comparison of X-ray Powder Data Presented by Guillemin (1956) and This Study

$\alpha$ duftite author (Å)		$\alpha$ duftite Guillemin (kX)		$\beta$ duftite author (Å)		$\beta$ duftite Guillemin (kX)	
I	d	I	d	I	d	I	d
	--		--	2	5.79		--
3	5.04	mw	5.02	1	5.02	mw	4.99
2	4.62	w	4.59	1	4.62	w-ww	4.71
4	4.23	m	4.20	5	4.14	m	4.14
3	3.94	w	3.94	3	3.73	ww	3.74
2	3.58	w	3.55	1	3.47	ww	3.47
1	3.31		--		--	ww	3.32
10	3.26	S-SS	3.25	10	3.16	S-SS	3.14
3	3.01	mw	2.98		--	www	2.95
9	2.853	S	2.84	8	2.868	S	2.89
	--		--	3	2.798		--
7	2.667	S	2.64	9	2.614	S-SS	2.61
8	2.577	mS	2.56		--		--
3	2.514	ww	2.48	1	2.488	w	2.50
1	2.409	ww	2.38	2	2.402	ww	2.41
3	2.300	m	2.28	1	2.324		--
1	2.255	ww	2.23	2	2.237	mw	2.25
1	2.210	ww	2.19	3	2.066	w	2.07
2	2.112	w	2.09		--		--
3	2.070	mw	2.05		--		--

Table 7. Comparison of X-ray Powder Data--Continued

$\alpha$ duftite author (Å)		$\alpha$ duftite Guillemin (kX)		$\beta$ duftite author (Å)		$\beta$ duftite Guillemin (kX)	
I	d	I	d	I	d	I	d
2	1.982	ww	1.96		--		--
2	1.940	ww	1.93	3	1.943		--
4	1.880	m	1.87	3	1.878		--
	--	ww	1.85		--	mw	1.85
1	1.830	ww	1.82	3	1.835		--
	--	ww	1.81		--		--
2	1.790	ww	1.78		--		--
1	1.776	ww	1.77		--		--
	--	www	1.75		--	mw	1.74
1	1.717	w	1.71	6	1.702		--
4	1.652	m	1.64	1/2	1.685		--
3	1.631	m	1.62	7	1.614	m	1.62
1/2	1.583	w	1.58	2	1.575	w	1.58
1/2	1.558		--		--	ww	1.56
3	1.535	mw	1.53	2	1.527		--
2	1.499	w	1.49	3	1.475	ww	1.47
1/2	1.482		--		--		--
2	1.456	w	1.45	1/2	1.433	ww	1.41
1	1.406		--		--		--
3	1.389	w	1.38	2	1.382	ww	1.38

Table 7. Comparison of X-ray Powder Data--Continued

$\alpha$ duftite author (Å)		$\alpha$ duftite Guillemin (kX)		$\beta$ duftite author (Å)		$\beta$ duftite Guillemin (kX)	
I	d	I	d	I	d	I	d
					--	ww	1.34
				3	1.311	w	1.31

## CONCLUSIONS

Following is a tabulation (Table 8) comparing the data of Richmond (1940), Guillemin (1956), and the author.

In this study, an expanded version of Guillemin's (1956) nomenclature was used for convenience; the name  $\beta$  duftite, as here used, includes duftites with substitutions of zinc for copper as well as calcium for lead. Only one sample of  $\beta$  duftite was analyzed in this study, and therefore it necessarily had specific ratios of copper to zinc and calcium to lead. It is not intended to restrict  $\beta$  duftite to this specific composition, rather it appears reasonable that it include a range of substitutions. Although Guillemin's nomenclature was used throughout the study, it is felt that it is undesirable to give two separate species names to the duftites; rather, it would be better to use adjectival prefixes. Guillemin's  $\alpha$  duftite conforms closely to the description of the type material and should remain as duftite. His  $\beta$  duftite would better be termed calcian duftite or, with zinc substituting as well (as in the Granite Gap material), calcian zincian duftite.

On the basis of his X-ray diffraction powder photographs, Guillemin (1956) proposed for  $\beta$  duftite an isomorphous series with conichalcite ( $\text{CaCu}(\text{AsO}_4)(\text{OH})$ ). The author proposes instead a solid solution series with the type duftite ( $\alpha$  duftite) as one end member and austinite ( $\text{CaZn}(\text{AsO}_4)(\text{OH})$ ) as the other (Figure 3). The calcian zincian duftites occupy an intermediate position, which depends on the amounts of lead, calcium, copper, and zinc present. For this proposal to be

Table 8. Comparison of Data Presented by Richmond (1940), Guillemin (1956) and This Study

	$\alpha$ duftite author	$\alpha$ duftite Guillemin	duftite Richmond	$\beta$ duftite author	$\beta$ duftite Guillemin
<u>a</u>	7.736	7.81	7.50	7.504	7.49
<u>b</u>	9.202	9.19	9.12	9.031	9.36
<u>c</u>	5.995	6.08	5.90	5.920	5.91
$n_x$	2.04	2.04	2.06	1.905	---
$n_y$	2.08	2.08	2.08	1.93	1.97
$n_z$	2.10	2.10	2.09	1.95	---
space group	$P2_12_12_1$	$P_{nma}$	$P_{nan} (?)$	$P2_12_12_1$	$P2_12_12_1$



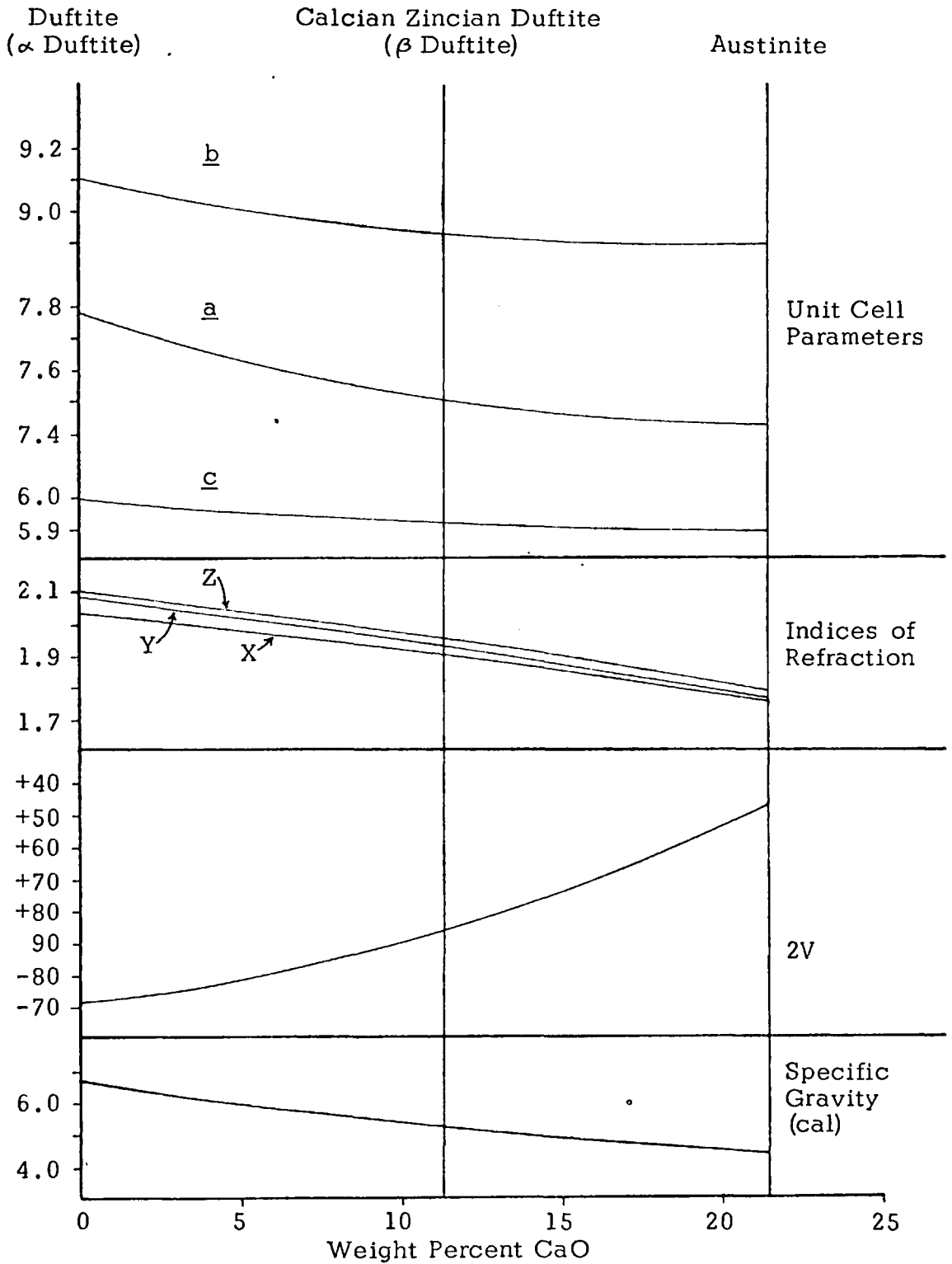


Figure 3. Properties vs. Weight Percent CaO in Proposed Duftite-austinite Solid Solution Series

further substantiated, it would be necessary to study more samples of the material between the end members. In Figure 3, the optical indices, unit cell parameters,  $2V$ , and calculated specific gravity are plotted against weight percent of CaO. The positions of austinite, Granite Gap calcian zincian duftite ( $\beta$  duftite) and duftite ( $\alpha$  duftite) are indicated on the graph. If other calcian zincian duftites are analyzed, it is thought that their properties will fall on or near the curves in Figure 3.

In Figure 4, the properties of duftite ( $\alpha$  duftite), Granite Gap calcian zincian duftite ( $\beta$  duftite), and conichalcite (Dana's System of Mineralogy, Vol. II, 1951) are plotted against weight percent of CaO. It can be seen in Figure 4 that the curves for  $2V$  and  $b$  show a reversal that is not seen in any of the curves in Figure 3. Because of this and the fact that a duftite-conichalcite-solid solution series would not account for the substitution of zinc for copper, the duftite-austinite solid solution series is proposed. It is recognized, however, that the possibility of a three end membered series of duftite-austinite-conichalcite, with  $\beta$  duftite occupying intermediate positions, cannot be ruled out at this time. More data would be needed to prove or disprove this possibility.

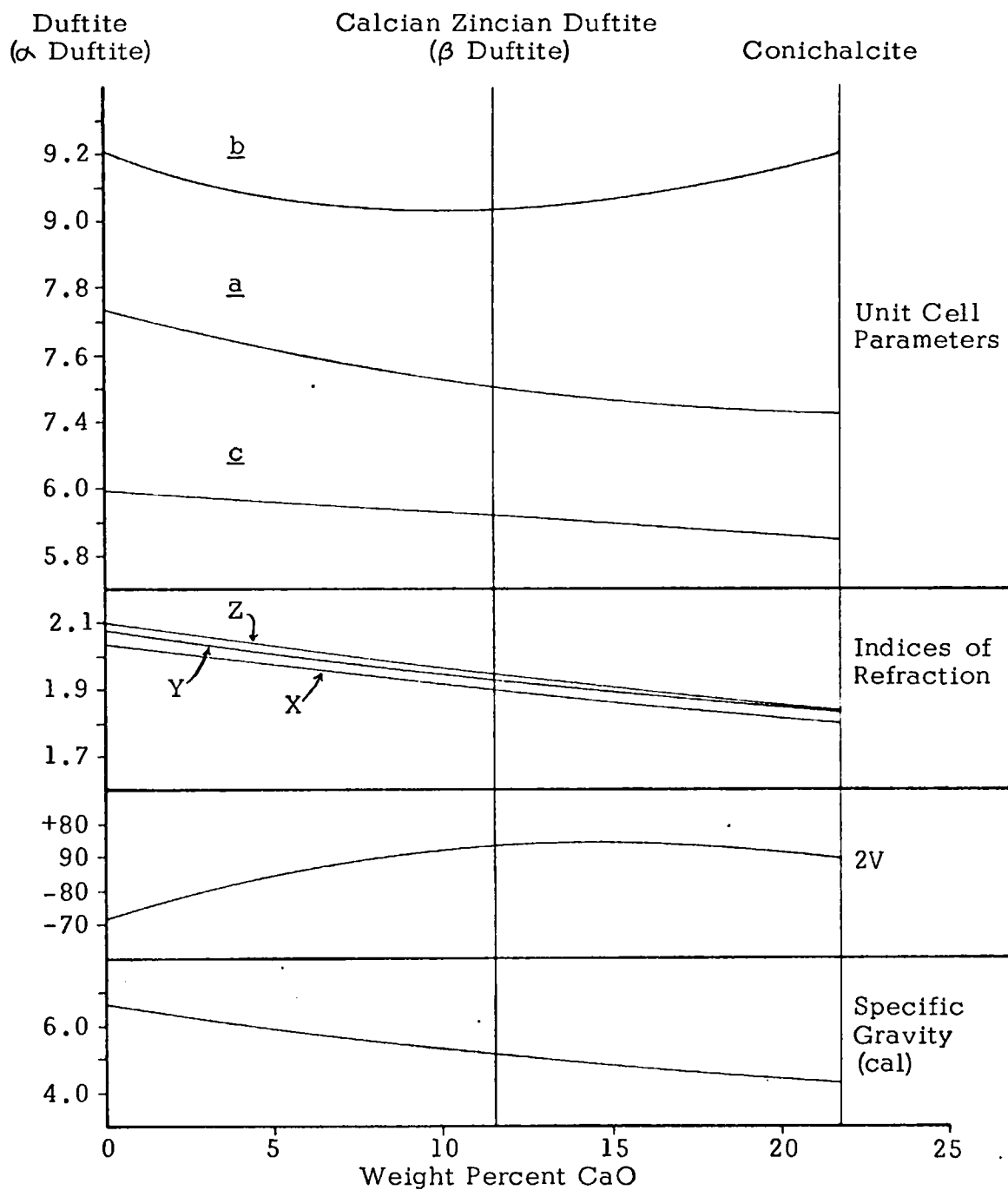


Figure 4. Properties vs. Weight Percent CaO in Hypothetical Duftite-conicalcrite Solid Solution Series

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