

## The Crystal Structure of Metal Diethyldithiophosphates. II. Lead Diethyldithiophosphate

By TETSUZO ITO

The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wako-Shi, Saitama, 351, Japan

(Received 31 August 1971)

The crystal structure of lead diethyldithiophosphate,  $\text{Pb}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_2$  has been determined. The final  $R$  value was 8.6%. The crystal is triclinic, space group  $P\bar{1}$ , with  $a=10.102$  (2),  $b=10.366$  (3),  $c=9.702$  (2) Å,  $\alpha=99.82$  (4),  $\beta=109.91$  (2),  $\gamma=86.17$  (3)°,  $Z=2$ . The formula units exist as monomers in the crystal. The monomers are packed three-dimensionally with van der Waals contacts. The two diethyldithiophosphate groups are coordinated to the lead atom with the four sulphur ends in a distorted tetragonal pyramidal environment. The Pb-S distances are 2.754, 2.790, 2.990 and 3.022 (0.006) Å. The molecule has an approximate twofold symmetry axis passing through the lead atom.

### Introduction

The main interest of this series of crystal structure analyses is the nature of heavy metal-sulphur bonds in relation to the flotation of sulphide minerals. The first paper dealt with the structure of zinc diethyldithiophosphate,  $\text{Zn}(\text{EP})_2$  (Ito, Igarashi & Hagihara, 1969). It was found that the coordination of sulphur atoms about a zinc atom in  $\text{Zn}(\text{EP})_2$  was similar to those in zinc salts of other dithioacids (xanthates and dithiocarbamates).

The second compound investigated was lead diethyldithiophosphate,  $\text{Pb}(\text{EP})_2$ . The structure determination of this compound will be useful for the understanding of the stereochemistry of the lead atom, because a new type of six-sulphur coordination about a lead atom was reported by Lawton & Kokotailo (1969) in lead diisopropylidithiophosphate,  $\text{Pb}(\text{isoPP})_2$ , a higher homologue of  $\text{Pb}(\text{EP})_2$ .

### Experimental

#### Crystal data

Lead(II) bis-(*O,O'*-diethyldithiophosphate),

$\text{Pb}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_2$ ; F.W. 577.4.

Triclinic prismatic along the  $b$  axis (twinned),

$a=10.102$ (2),  $b=10.366$ (3),  $c=9.702$ (2) Å,

$\alpha=99.82$ (4),  $\beta=109.91$ (2),  $\gamma=86.17$ (3)°,

$V=941.3$ (4) Å<sup>3</sup> (at 25°C).

$D_m=2.0$  g.cm<sup>-3</sup> (by flotation),  $Z=2$ ,  $D_x=2.04$  g.cm<sup>-3</sup>.

Space group  $P\bar{1}$  or  $P1$ ;  $P\bar{1}$  was assumed.

Powder of  $\text{Pb}(\text{EP})_2$  was precipitated by combining aqueous solutions of lead acetate and sodium diethyldithiophosphate, NaEP. The NaEP used was synthesized from  $\text{P}_2\text{S}_5$ ,  $\text{C}_2\text{H}_5\text{OH}$  and NaOH (Bode & Arnswald, 1962). Colourless prismatic crystals elongated along the  $b$  axis were obtained by recrystallization of the powder from an ethyl ether solution. All the crystals examined showed twinning in various ratios of the twin components. The twin plane was (10 $\bar{1}$ ) with a rotation of 180°.

The cell parameters were determined from eighteen high-angle reflexions recorded by the Straumanis meth-

od around the  $a$ ,  $b$  and  $c$  axes. The wavelength used was 1.54051 Å for Cu  $K\alpha_1$  radiation. The space group was assumed to be the centric  $P\bar{1}$ , which was subsequently confirmed by the solution of the structure.

#### Intensity measurements

Sets of multiple-film equi-inclination Weissenberg photographs were taken by the use of an integrating cassette around the  $a$  (0 to 1st layers),  $b$  (0 to 9th layers) and  $c$  (0 to 1st layers) axes with Ni-filtered Cu  $K\alpha$  radiation. Crystals almost free from twinning were selected for the measurements. Since the ratios of the twin components, as estimated from the intensities of common reflexions, were less than 0.02, the effects of twinning on the intensities were neglected. The specimens mounted about the  $a$  and  $c$  axes were cut out from the prisms elongated along the  $b$  axis. The dimensions of the specimens were 0.13 × 0.13 × 0.16, 0.05 × 0.05 × 0.25 and 0.11 × 0.18 × 0.09 mm for the  $a$ ,  $b$  and  $c$  axes respectively (the length is the third dimension indicated).

The peak intensities of the integrated spots were measured with a microphotometer and altogether 3114 independent reflexions, about 72% of those possible with Cu  $K\alpha$  radiation, were collected. The intensities were

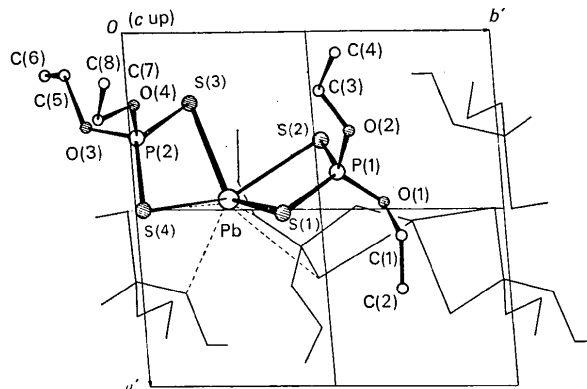


Fig. 1. Structure of lead diethyldithiophosphate, viewed along the  $c$  axis. The broken lines indicate the intermolecular  $\text{Pb}\cdots\text{S}$  and  $\text{Pb}\cdots\text{O}$  contacts.

corrected for Lorentz and polarization factors and for spot extensions. Absorption effects were corrected with spherical ( $a$  and  $c$  axes) and cylindrical ( $b$  axis) approximations. No extinction corrections were applied.

### Determination of the structure

From a three-dimensional Patterson map, approximate coordinates of the lead atom were readily found. All the nineteen non-hydrogen atoms were located by usual procedures of the heavy-atom method.

The structure was then refined by a block-diagonal least-squares method. Unit weights were given to all reflexions. The hydrogen atoms were neglected. After five cycles of isotropic refinement the  $R$  value was 12.1%. An additional five cycles of anisotropic refinement reduced  $R$  to a final value of 8.6%, based on the observed reflexions only.

The final atomic coordinates and thermal parameters are given in Tables 1 and 2. The observed and calculated structure factors are compared in Table 3. A correction for anomalous dispersion was applied to the lead, sulphur and phosphorus atoms (imaginary parts ignored). The atomic scattering factors and the dispersion and absorption correction factors were taken from *International Tables for X-ray Crystallography* (1962).

### Results and discussion

#### Crystal structure

The atomic arrangements in the unit cell of  $\text{Pb}(\text{EP})_2$ , as seen along the  $c$  and  $b$  axes are shown in Figs. 1 and 2. Two diethyldithiophosphate groups coordinate to a lead atom with the sulphur end atoms; the sulphur coordination about the lead atom is a distorted tetragonal pyramid. Thus, the  $\text{Pb}(\text{EP})_2$  molecule exists as a monomeric unit in the crystal. These molecules are

packed three-dimensionally with van der Waals contacts.

Table 1. Atomic coordinates with standard deviations ( $\times 10^4$ )

	$x/a$	$y/b$	$z/c$
Pb	4707 (1)	2546 (1)	5268 (1)
S(1)	5088 (7)	3999 (5)	8027 (6)
S(2)	3112 (6)	5077 (5)	4890 (6)
S(3)	2046 (6)	1678 (6)	4944 (8)
S(4)	5017 (5)	346 (5)	7040 (6)
P(1)	3953 (6)	5455 (5)	7067 (6)
P(2)	2961 (5)	243 (5)	6080 (6)
O(1)	4875 (15)	6739 (14)	7468 (16)
O(2)	2797 (17)	5968 (14)	7852 (18)
O(3)	2684 (14)	-1168 (13)	5052 (18)
O(4)	2115 (18)	239 (14)	7198 (19)
C(1)	5774 (29)	7173 (26)	8977 (29)
C(2)	7290 (31)	7140 (31)	8949 (34)
C(3)	1697 (36)	5057 (33)	7679 (47)
C(4)	749 (44)	5751 (38)	8464 (54)
C(5)	1254 (25)	-1577 (27)	4157 (36)
C(6)	1241 (38)	-2092 (33)	2592 (37)
C(7)	2495 (40)	-760 (31)	8196 (45)
C(8)	1466 (41)	-669 (31)	8982 (37)

The monomeric structure of  $\text{Pb}(\text{EP})_2$  is definitely different from the linear chain structure in  $\text{Zn}(\text{EP})_2$  (Ito *et al.*, 1969); instead, it is similar to those found in lead diethyldithiocarbamate,  $\text{Pb}(\text{EC})_2$  (Iwasaki & Hagihara, 1972) and lead xanthates (Hagihara & Yamashita, 1966; Hagihara, Watanabe & Yamashita, 1968; Hagihara, Yoshida & Watanabe, 1969).

It should be noted that the structure of  $\text{Pb}(\text{EP})_2$  is significantly different from that in lead diisopropylthiophosphate,  $\text{Pb}(\text{isoPP})_2$  (Lawton & Kokotailo, 1969). In  $\text{Pb}(\text{isoPP})_2$  each lead atom is coordinated with six sulphur atoms; *i.e.*, in addition to the four within the molecule, two other sulphur atoms from dif-

Table 2. Thermal parameters with standard deviations

The thermal parameters refer to the expression

$$T = \exp \{ -10^{-3} \cdot 2\pi^2 (U_{11}h^2a^*2 + \dots + 2U_{12}hk a^*b^* \dots) \}.$$

The  $B_{\text{eq}}$  values are the equivalent isotropic temperature factors proposed by Hamilton (1959).

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$B_{\text{eq}}$
Pb	44 (1)	37 (1)	54 (1)	1 (1)	22 (1)	13 (1)	3.4
S(1)	94 (4)	52 (3)	60 (3)	14 (3)	32 (3)	24 (3)	5.2
S(2)	60 (3)	46 (3)	59 (3)	4 (2)	17 (2)	16 (2)	4.3
S(3)	49 (3)	62 (4)	100 (5)	9 (2)	27 (3)	37 (3)	5.3
S(4)	52 (3)	50 (3)	70 (3)	2 (2)	18 (2)	20 (3)	4.5
P(1)	58 (3)	45 (3)	57 (3)	0 (2)	26 (3)	16 (2)	4.0
P(2)	46 (3)	46 (3)	71 (3)	2 (2)	28 (2)	20 (3)	4.0
O(1)	57 (8)	57 (9)	60 (9)	-12 (7)	16 (7)	20 (7)	4.5
O(2)	79 (11)	53 (9)	83 (11)	2 (8)	48 (9)	7 (8)	5.3
O(3)	41 (7)	49 (8)	89 (11)	-2 (6)	21 (7)	-2 (8)	4.8
O(4)	92 (12)	48 (9)	108 (13)	9 (8)	72 (11)	29 (8)	5.6
C(1)	89 (18)	76 (17)	75 (16)	-34 (14)	25 (14)	8 (13)	6.3
C(2)	84 (19)	102 (23)	96 (21)	-13 (17)	27 (17)	2 (18)	7.6
C(3)	117 (25)	102 (24)	210 (40)	-17 (20)	122 (28)	27 (25)	9.8
C(4)	150 (34)	119 (29)	232 (47)	7 (25)	149 (36)	10 (29)	11.6
C(5)	48 (13)	80 (18)	136 (67)	-15 (12)	32 (15)	-3 (17)	7.0
C(6)	122 (28)	98 (24)	96 (64)	1 (21)	16 (21)	1 (19)	8.9
C(7)	160 (32)	88 (22)	194 (78)	49 (22)	111 (30)	99 (25)	10.0
C(8)	176 (34)	93 (22)	116 (66)	-12 (22)	102 (26)	24 (19)	8.9

Table 3. Observed and calculated structure factors

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC																																																																																																																																																																																																																																																																																							
0	0	0	1	10	10	2	20	20	3	30	30	4	40	40	5	50	50	6	60	60	7	70	70	8	80	80	9	90	90	10	100	100	11	110	110	12	120	120	13	130	130	14	140	140	15	150	150	16	160	160	17	170	170	18	180	180	19	190	190	20	200	200	21	210	210	22	220	220	23	230	230	24	240	240	25	250	250	26	260	260	27	270	270	28	280	280	29	290	290	30	300	300	31	310	310	32	320	320	33	330	330	34	340	340	35	350	350	36	360	360	37	370	370	38	380	380	39	390	390	40	400	400	41	410	410	42	420	420	43	430	430	44	440	440	45	450	450	46	460	460	47	470	470	48	480	480	49	490	490	50	500	500	51	510	510	52	520	520	53	530	530	54	540	540	55	550	550	56	560	560	57	570	570	58	580	580	59	590	590	60	600	600	61	610	610	62	620	620	63	630	630	64	640	640	65	650	650	66	660	660	67	670	670	68	680	680	69	690	690	70	700	700	71	710	710	72	720	720	73	730	730	74	740	740	75	750	750	76	760	760	77	770	770	78	780	780	79	790	790	80	800	800	81	810	810	82	820	820	83	830	830	84	840	840	85	850	850	86	860	860	87	870	870	88	880	880	89	890	890	90	900	900	91	910	910	92	920	920	93	930	930	94	940	940	95	950	950	96	960	960	97	970	970	98	980	980	99	990	990	100	1000	1000





Table 4. Bond distances and angles with standard deviations ( $\sigma$ )

Dithiophosphate (I)		Dithiophosphate (II)		Average	Difference ( $d$ )	$d/\sigma$
Pb—S(1)	2.754 (6) Å	Pb—S(3)	2.790 (6) Å	2.772 Å	0.036 Å	6.0
Pb—S(2)	2.996 (5)	Pb—S(4)	3.022 (6)	3.009	0.026	4.3
S(1)—P(1)	1.995 (8)	S(3)—P(2)	1.991 (9)	1.993	0.004	0.4
S(2)—P(1)	1.969 (7)	S(4)—P(2)	1.968 (7)	1.969	0.001	0.1
P(1)—O(1)	1.59 (2)	P(2)—O(3)	1.61 (1)	1.60	0.02	1.0
P(1)—O(2)	1.62 (2)	P(2)—O(4)	1.59 (2)	1.61	0.03	1.5
O(1)—C(1)	1.45 (3)	O(3)—C(5)	1.46 (3)	1.46	0.01	0.3
O(2)—C(3)	1.45 (4)	O(4)—C(7)	1.48 (4)	1.47	0.03	0.8
C(1)—C(2)	1.54 (5)	C(5)—C(6)	1.52 (5)	1.53	0.02	0.4
C(3)—C(4)	1.49 (7)	C(7)—C(8)	1.48 (7)	1.49	0.01	0.1
S(1)—Pb—S(3)	94.1 (0.2)°	S(2)—Pb—S(4)	138.2 (0.2)°			
S(1)—Pb—S(2)	71.1 (0.2)	S(3)—Pb—S(4)	70.6 (0.2)	70.9°	0.5°	2.5
S(1)—Pb—S(4)	80.7 (0.2)	S(3)—Pb—S(2)	81.1 (0.2)	80.9	0.4	2.0
Pb—S(1)—P(1)	89.8 (0.3)	Pb—S(3)—P(2)	89.1 (0.3)	89.5	0.7	2.3
Pb—S(2)—P(1)	83.5 (0.2)	Pb—S(4)—P(2)	83.1 (0.3)	83.3	0.4	1.3
S(1)—P(1)—S(2)	115.4 (0.3)	S(3)—P(2)—S(4)	116.2 (0.4)	115.8	0.8	2.0
S(1)—P(1)—O(1)	110.8 (0.6)	S(3)—P(2)—O(3)	112.0 (0.6)	111.4	1.2	2.0
S(1)—P(1)—O(2)	109.7 (0.7)	S(3)—P(2)—O(4)	103.7 (0.6)	106.7	6.0	9.0
S(2)—P(1)—O(1)	107.6 (0.7)	S(4)—P(2)—O(3)	105.2 (0.6)	106.4	2.4	3.4
S(2)—P(1)—O(2)	112.2 (0.6)	S(4)—P(2)—O(4)	114.2 (0.6)	113.2	2.0	3.3
O(1)—P(1)—O(2)	100.1 (0.8)	O(3)—P(2)—O(4)	105.2 (0.9)	102.7	5.1	5.7
P(1)—O(1)—C(1)	120.7 (1.7)	P(2)—O(3)—C(5)	120.2 (1.4)	120.5	0.5	0.3
P(1)—O(2)—C(3)	116.9 (1.8)	P(2)—O(4)—C(7)	118.2 (2.0)	117.6	1.3	0.7
O(1)—C(1)—C(2)	106.5 (2.3)	O(3)—C(5)—C(6)	107.8 (2.6)	107.2	1.3	0.5
O(2)—C(3)—C(4)	107.2 (2.7)	O(4)—C(7)—C(8)	108.0 (2.7)	107.6	0.8	0.3

ecule rotated by 180° about the bisector of the angle, S(1)—Pb—S(3), coincides with the original one within the discrepancies of 0.35 Å, except for the pair of the ethyl ends, C(3)—C(4) and C(7)—C(8), which deviate by about 2.0 Å; in particular, the discrepancies of the central part of the molecule (the Pb, S and P atoms) are less than 0.07 Å.

It is interesting to note that this approximate symmetry axis coincides with the twin axis of the crystal, a normal to (10 $\bar{1}$ ); the angle between the two axes is only 2.0°. Therefore, the persistent twinning found in all the crystals examined was probably caused by molecular reorientation in the course of crystal growth.

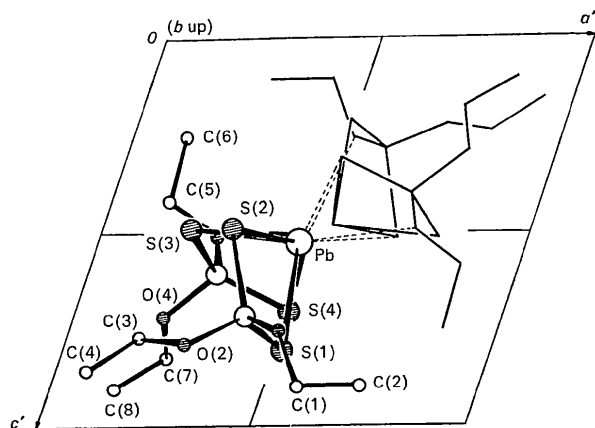


Fig. 2. Structure of lead diethyldithiophosphate, viewed along the  $b$  axis. The broken lines indicate the intermolecular Pb...S and Pb...O contacts.

Furthermore, the relatively large temperature factors observed for C(3), C(4), C(7) and C(8) might be attributed to some disorders associated with the twinning.

#### Intermolecular van der Waals contacts

The closest intermolecular contacts are summarized in Table 5. All the distances are normal compared with the expected values (Pauling, 1960). It should be noted that no intramolecular van der Waals contact with the lead atom is found above the top of the PbS<sub>4</sub> pyramid. Instead, S(2) and S(4) of different molecules are relatively close to it; the Pb...S distances are 3.469(6) and 3.478(6) Å. This situation is common among related lead salts of dithioacids (Iwasaki & Hagihara, 1972), except for Pb(isoPP)<sub>2</sub> mentioned before (Lawton &

Table 5. Intermolecular van der Waals contacts

The primes denote inversion at ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ).

Pb...S(2')	3.469 (6) Å
Pb...S(4', -b)	3.478 (6)
Pb...O(3', -b)	3.00 (1)
Pb...O(1')	3.04 (2)
S(2)...S(2')	3.74 (1)
S(4)...S(4', -b)	3.89 (1)
S(1)...C(1', +c)	3.71 (3)
S(3)...C(5', -a-b)	3.73 (3)
O(2)...C(7, +b)	3.35 (3)
O(4)...C(5', -a-b)	3.49 (2)
O(1)...C(7, +b)	3.56 (4)
C(1)...C(7, +b)	3.75 (4)
C(4)...C(8, +b)	3.75 (5)
C(2)...C(4, +a)	3.84 (6)
C(2)...C(8', +c)	3.92 (4)
C(8)...C(6', -a-b)	3.95 (5)

& Kokotailo, 1969). In  $\text{Pb}(\text{EP})_2$ , two oxygen atoms of different molecules are also relatively close to the lead atom; the  $\text{Pb}\cdots\text{O}$  distances are 3.00(1) and 3.04(2) Å. The  $\text{Pb}\cdots\text{S}$  and  $\text{Pb}\cdots\text{O}$  contacts mentioned above are indicated in Figs. 1 and 2.

The numerical calculations were performed on the HITAC5020E computer of the computer center of the

University of Tokyo and on the FACOM270-30 computer of this Institute, with a universal crystallographic computation program system, UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

The author is grateful to Dr H. Hagihara for his encouragement and valuable discussions throughout the work.

#### References

- BODE, H. & ARNSWALD W. (1962). *Z. anal. Chem.* **185**, 99.  
 HAGIHARA, H. & YAMASHITA, S. (1966). *Acta Cryst.* **21**, 350.  
 HAGIHARA, H., YOSHIDA, N. & WATANABE, Y. (1969). *Acta Cryst.* **B25**, 1775.  
 HAGIHARA, H., WATANABE, Y. & YAMASHITA, S. (1968). *Acta Cryst.* **B24**, 960.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 ITO, T., IGARASHI, T. & HAGIHARA, H. (1969). *Acta Cryst.* **B25**, 2303.  
 IWASAKI, H. & HAGIHARA, H. (1972). *Acta Cryst.* **B28**, 507.  
 LAWTON, S. L. & KOKOTAILO, G. T. (1969). *Nature, Lond.* **221**, 550.  
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.  
 SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* **43**, 62.

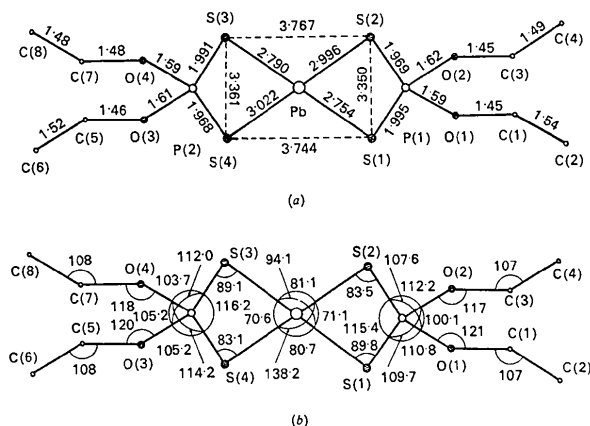


Fig. 3. (a) Interatomic distances (in Å) and (b) bond angles (in degrees) in lead diethyldithiophosphate.

*Acta Cryst.* (1972), **B28**, 1040

## Structure Studies on $\text{Al}_2\text{TiO}_5$ at Room Temperature and at 600°C\*

BY B. MOROSIN AND R. W. LYNCH

*Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.*

(Received 3 June 1971)

The room-temperature structure of  $\text{Al}_2\text{TiO}_5$  has been re-examined and is compared with the 600°C structure. This material is isomorphous with pseudobrookite, crystallizing in space group *Bbmm* with cell dimensions  $a_0=9.429$ ,  $b_0=9.636$ , and  $c_0=3.591$  Å at room temperature and  $a_0=9.481$ ,  $b_0=9.738$ , and  $c_0=3.583$  Å at 600°C. Our results, as well as refinement of previously published data, indicate that there is complete disorder in the metal sites for this compound. Provided that allowances are made concerning electrostatic interactions, the differences in the structure at the two temperatures appear to support the suggestion that the coordination polyhedra about the metal ions tend towards more regular configurations with increasing temperatures. The importance of cleavage planes, resulting from edge-shared octahedra in the hysteresis of the thermal expansion of the ceramic, is pointed out.

### Introduction

As part of a program in which the relationship between the degree of anisotropy of crystal structures and their thermal expansion behavior is being studied, several oxide materials have been examined (Morosin & Lynch, 1971). Of particular interest are materials which, when heated, contract along at least one crystal-

lographic direction. Cartz (1968) and Li & Peacor (1969) suggested that the critical feature of crystalline anisotropy, leading to thermal expansion anisotropy, is the degree of distortion of the atomic coordination polyhedra. By 'distortion' it is implied that the bond lengths and angles vary markedly about the cations.

Aluminum titanate (tielite),  $\text{Al}_2\text{TiO}_5$ , is such a material. As a ceramic body, it exhibits a very low bulk thermal expansion coefficient, primarily because of a complex system of internal stresses and fractures. These stresses and fractures are developed upon

\* This work was supported by the U.S. Atomic Energy Commission.