Recently, Edwards and Pearson[17] have discussed important factors which contribute to nucleophilicity. Basicity and polarizability of the nucleophile play an important role. In the $(CH_3)_2SOH_2^{2+}$ substrate, nucleophilic attack at either sulfur or oxygen should be correlated by a combination of basicity and polarizability in the nucleophile, because each center bears a positive charge and possesses an unshared pair of electrons. Since polarizability increases and basicity decreases in the series Cl^-, Br^-, I^-, the two factors cannot be separated unambiguously in this system. It is likely that the solvent–solute interactions control the nucleophilicities observed. For example, thiocyanate ion, which is more basic and more polarizable than the halide ions, should be an effective nucleophile. The lack of reactivity of thiocyanate must be due to its considerable stability in both protic and aprotic solvents. Thus, the nature of the solvent is critical in understanding reactivity in the system investigated in this paper and, in general, should be taken into account whenever comparisons of nucleophilicity are made among solvents of different types.

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[17] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

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Substoichiometry of Tungsten Trioxide; the Crystal Systems of $WO_{3.00}$, $WO_{2.98}$, and $WO_{2.96}$[1]

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From the results of powder and single crystal X-ray measurements together with measured densities and chemical analyses it has been demonstrated that substoichiometric tungsten trioxides possess structures which are significantly different from that of the stoichiometric trioxide. For the composition $WO_{2.98}$ the space group is $P2_1/m$ and the unit cell contains four tungsten atoms and has the dimensions $a = 7.354 \pm 0.005$ Å., $b = 7.569 \pm 0.005$ Å., $c = 3.854 \pm 0.005$ Å., and $\beta = 90.6°$. The tungsten subcell is of the same type but slightly larger than that of the stoichiometric oxide. The results for the composition $WO_{2.96}(\alpha)$ indicate the space group P2/c and a unit cell containing the formula $W_{50}O_{148}$ and having the cell constants $a = 11.90 \pm 0.02$ Å., $b = 3.826 \pm 0.012$ Å., $c = 59.64 \pm 0.06$ Å., and $\beta = 98.4°$. The proposed structure is uniquely solved for the x and z coordinates but not for the y coordinates, which appear to be located in a number of planes staggered about $y = {}^1/_2$. Each unit cell contains two hexagonally-shaped ordered defects that are bisected by recurrent dislocation planes. A higher temperature polymorph, $WO_{2.96}(\beta)$, with a unit cell tentatively containing the formula $W_{25}O_{74}$ becomes stable at approximately 1250°.

Introduction

The basic chemical and physical properties of binary compounds of the group VI transition metals Cr, Mo, and W are generally complex. In recent years, a number of investigations dealing with the crystallographic and thermodynamic behavior, particularly of Mo and W oxides, have elucidated the complex chemical bonding that occurs both in the solid and vapor phases. Furthermore, in the case of a number of transition metal oxides, carbides, sulfides, and phosphides, gross deviations from ideal stoichiometry are readily obtained and must be acknowledged in physicochemical descriptions of these systems. In a recent thermodynamic investigation of the tungsten–oxygen system[2] it was observed at temperatures of 1300–1550°K. that tungsten trioxide becomes substoichiometric and evaporates congruently at a composition near $WO_{2.96}$ under the influence of the particular vacuum conditions (10^{-6}–10^{-7} mm. pressure) employed. The X-ray diffraction patterns of powders of this material at room temperature are significantly different from those of the stoichiometric trioxide and cannot be explained on the basis of only an oxygen-deficient trioxide structure. Actually, the existence of a substoichiometric region of WO_3 was first suggested by Glemser and Sauer,[3] who reported that the basic structure of the WO_3 phase extends to the composition $WO_{2.95}$. However, Hägg and Magneli[4] refer to a paper given by Westgren[5] in which is proposed the existence of a new oxide phase corresponding to approximately $WO_{2.97}$. Gado[6] has recently reported the existence of a phase between $W_{20}O_{58}$ and WO_3. The structure at room temperature of the unit cell of the stoichiometric trioxide as reported by Andersson[7] and by previous investigators contains four WO_3 units and has the space group $P2_1/a$; however, the direct observations by

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] R. J. Ackermann and E. G. Rauh, *J. Phys. Chem.*, **67**, 2596 (1963).

[3] O. Glemser and H. Sauer, *Z. anorg. Chem.*, **252**, 144 (1943).

[4] G. Hägg and A. Magneli, *Arkiv Kemi, Mineral. Geol.*, **19A**, No. 2 (1944).

[5] A. Westgren, *Nord. Naturforskarmötet Helsingfors*, 89 (1936).

[6] P. Gado, *Acta Cryst.*, **16**, Part 13, A182 (1963).

[7] G. Andersson, *Acta Chem. Scand.*, **7**, 154 (1953).

Tanisaki[8] of weak first- and third-order layer lines on rotation photographs, taken with the c axis rotating, indicate a unit cell containing eight WO_3 units with a $P2_1/n$ space group and a c axis which is twice that of Andersson's. Since there appear to be a number of divergent conclusions dealing with the trioxide and its region of substoichiometry the present investigation was undertaken in an attempt to contribute to a greater understanding by means of a further analysis of this rather complicated system. In the present investigation the conclusions are to be drawn from both powder and single crystal diffraction data and measured densities obtained at room temperature and chemical analyses.

Experimental Section

The samples of tungsten oxides corresponding to the range of composition WO_3–$WO_{2.96}$ used in this investigation were prepared *via* two methods. In the first, the composition $WO_{2.96}$ resulted from the reduction of stoichiometric trioxide in the interval of 1050–1225° under vacuum and in the second the reaction of the appropriate amounts of trioxide and metal powders at 1250–1300° under a purified argon atmosphere produced apparently homogeneous products of the desired composition. In the former method the samples employed were the actual residues ($O/W = 2.963$) of the effusion measurements described by Ackermann and Rauh.[2] The samples produced after several hours of heating *in vacuo* ($\sim 10^{-7}$ mm.) possessed a deep, dark blue color and contained fine, dark needles which appeared to be well-defined single crystals. However, the degree of crystalline size and homogeneity of these residues appeared to be somewhat unsatisfactory because of the relatively poor definition of high angle reflections in the powder patterns. Additional heating for about 1 hr. under vacuum at approximately 1050° generally enhanced the definition of these reflections. It was impractical to heat for longer periods of time in order to obtain larger crystals because of the great extent of free evaporation of the samples *in vacuo* at the temperatures involved. In order to prepare samples at higher temperatures, it was necessary to employ an argon atmosphere or sealed platinum capsules to reduce the rate of evaporation of the sample and thereby allow considerably longer periods of heating. Samples ($\sim$10 g.) of desired composition were synthesized by intimately mixing appropriate weights of tungsten and tungsten trioxide powders and allowing these to react at 1250–1300° in a platinum tube containing an argon atmosphere that was initially purified of water vapor and oxygen by means of columns of magnesium perchlorate and hot copper chips, respectively. The use of platinum as an inert container has been previously demonstrated.[2] Before the introduction of the sample, the platinum tube was outgassed *in vacuo* at 1300°. In spite of these precautions, oxidation of the top portion of some of the sample occurred. The lower portions of the samples were subsequently analyzed by the combustion of a weighed sample (2 to 3 g.) in air at 800° until constant weight was achieved and the light yellow-green color of the stoichiometric trioxide was obtained. The reproducibility of this method of preparation and analysis was generally sufficient to establish the atom ratio within ± 0.005. Samples having the composition $O/W = 2.960 \pm 0.005$ that were heated for periods of 2 days, 2 weeks, and 6 weeks yielded identical powder patterns that showed excellent definition at high diffraction angles. Progressively larger crystals resulted with the increase in time of heating and the crystals obtained in this manner were in general twinned about the axis of rotation. However, distinct differences in the powder patterns were noted when a comparison was made with the patterns of the fine needles obtained in the residues of the vacuum reduction of WO_3. The samples resulting from both methods of preparation had the typical slippery "graphite-like" quality upon grinding which is usually characteristic of a layer-type structure. In the course of the syntheses of samples, $O/W = 2.99$, 2.98, 2.97, and 2.96, it was apparent that as the atom ratio is decreased from 3.00 the color of the sample evolved through blue-green to a deep blue at $O/W = 2.96$.

The densities of samples of various compositions were measured by a pycnometric method. In order to minimize the effect of trapped gases in isolated voids in the finely powdered samples which causes the incomplete filling of the pycnometer by the immersing fluid and, hence, leads to low values of the density, the following precautions were taken. The samples (approximately 2 g.) were loaded into the pycnometer (2 ml.) which was then evacuated slowly in a modified vacuum desiccator. The immersing fluid, namely water to which was added a small amount of aerosol to decrease its surface tension but not affecting its density, was then added to the sample under vacuum by means of a separatory funnel attached to the desiccator through a rubber stopper. After the sample was completely immersed, it was gently boiled under vacuum by means of a heat lamp, then removed from the desiccator and centrifuged in order to precipitate any small particles suspended in the meniscus. The remaining operations including the weighings were done in the conventional manner. All weighings were performed after the pycnometer and contents had been equilibrated to 24–25°.

Determination of Lattice Parameters and Structures

Powder Measurements.—A comparison of the low angle diffraction lines of samples of stoichiometric and substoichiometric tungsten trioxide obtained with copper $K\alpha$ radiation is made in Table I. A close correspondence in both d values and intensities for the reduction of WO_3 to $WO_{2.98}$ indicates that the tungsten atoms retain essentially the same relative positions, although for the latter composition the d values are considerably larger, indicating an enlargement of the unit cell with respect to the subcell of WO_3 based on the structure by Tanisaki.[8] Similar measurements of a sample $WO_{2.99}$ yielded d spacings that were between those of WO_3 and $WO_{2.98}$. Hence, the tungsten subcell is of the same type in the WO_3–$WO_{2.98}$ region. One immediately sees that the diffraction patterns for materials of composition $WO_{2.96}$ are vastly more detailed than those of WO_3 and $WO_{2.98}$. Since the films of $WO_{2.96}$ showed more clearly the greater complexity of the powder patterns, film measurements of this composition are reported in Table I. The sample of $WO_{2.96}(\alpha)$ is one of the actual residues of the vapor pressures measurements of Ackermann and Rauh, which was produced by heating initially stoichiometric trioxide *in vacuo* at 1050–1225°. The material $WO_{2.96}(\beta)$ resulted from direct synthesis of tungsten and tungsten trioxide powders at 1250–1300° under an argon atmosphere followed by rapid quenching. The $WO_{2.96}(\beta)$ pattern can be readily distinguished from that of $WO_{2.96}(\alpha)$ by the prominent line which is located between two strong lines at $d = 3.760$ in the former compared with the faint line at $d = 3.71$ in the latter, by the closer packing of the two prominent lines in the region of $d = 2.65$, and by the intensity differences and the lesser number of lines in the region of $d = 1.94$–1.80. In general the powder patterns of $WO_{2.96}(\beta)$ had fewer and better defined reflections.

The conversion of the β to the α phase was accomplished by heating *in vacuo* at about 1100° for several

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[8] S. Tanisaki, *J. Phys. Soc. Japan*, **15**, 573 (1960).

TABLE I

COMPARISON OF INTENSITIES AND INTERPLANAR SPACINGS FOR SAMPLES OF WO_{3-x} ($0 \leq x \leq 0.04$)

WO_3		$WO_{2.98}$		$WO_{2.96}(\alpha)$				$WO_{2.96}(\beta)$			
I[a]	d(Å.)[b]	I[a]	d(Å.)[b]	I[a]	d(Å.)[a]	I	d(Å.)	I[a]	d(Å.)[a]	I	d(Å.)
S	3.835	S	3.872	VVVW	6.00	VVVW	2.01	VVVW	4.47	VVW	1.833
				VVVW	5.61	VVVW	1.97	VVW	3.857	W	1.802
MS	3.757	MS	3.795	VVVW	5.48	W	1.942	S	3.824	VW	1.719
				VVVW	4.73	W	1.908	VW	3.760	VW	1.714
S	3.646	S	3.678	VVVW	4.37	MW	1.867	S	3.654	W	1.700
				W	4.122	VW	1.827	VVVW	3.49	VVW	1.679
VVW	3.363	VVW	3.388	VVW	3.890	VW	1.801	VVVW	3.33	M	1.671
				MS	3.784	VVVW	1.76	VVVW	3.20	VW	1.649
W	3.345	W	3.368	VVVW	3.71	VW	1.733	W	3.104	VVVW	1.62
				S	3.632	W	1.693	W	3.078	VW	1.560
W	3.123	W	3.136	VVVW	3.50	M	1.676	VVVW	2.91	W	1.540
				VVVW	3.26	W	1.650	VVVW	2.85	W	1.532
W	3.082	W	3.117	VW	3.109	VW	1.560	VVVW	2.77	VW	1.514
				VVVW	3.07	VW	1.545	VVW	2.722	VVW	1.505
M	2.690	M	2.706	VVVW	2.97	W	1.535	M	2.671	VW	1.488
				VVVW	2.80	VW	1.516	M	2.640	VVW	1.477
W	2.666	W	2.667	VVVW	2.73	VVVW	1.49	VVVW	2.58	VVVW	1.38
				M	2.693	VVVW	1.47	VVVW	2.50	VVVW	1.36
M	2.624	M	2.635	MW	2.636	VVVW	1.45	VVVW	2.43	W	1.336
				VVVW	2.58	VVVW	1.41	VVVW	2.29	VVVW	1.33
VW	2.531	VW	2.537	VW	2.477	VVVW	1.38	VVVW	2.22	VVVW	1.31
				VVVW	2.33	VVW	1.365	MW	2.188	VVVW	1.30
				VVVW	2.24	VVW	1.349	VVVW	2.14	VVVW	1.28
				MW	2.198	VVW	1.338	VVVW	2.10	VW	1.265
				VVVW	2.15	VVVW	1.32	VVVW	2.01	VW	1.262
				VVVW	2.11	VVVW	1.29	VVVW	1.98		
				VVVW	2.08			MW	1.916		
				VVVW	2.06			MW	1.857		

[a] Evaluated from photographic films. [b] Evaluated from diffractometer tracings.

days a sample of the β phase which had been sealed in a platinum capsule under an inert atmosphere. The powder pattern of the sample which had been quenched to room temperature proved to be the same as that resulting from the residue of the effusion studies, *i.e.*, only the $WO_{2.96}(\alpha)$ phase was observed. The reversal of this transformation was accomplished by heating a sample of the α phase at 1290° for several hours followed by the rapid withdrawal of the capsule from the hot zone of the furnace, which permitted the successful quenching of the β phase as evidenced by the powder pattern subsequently taken. Although these experiments were of an exploratory nature in that the transition temperature has not been precisely established, it is apparent that the β phase is a high temperature form of the α phase. The polymorphic relation of the two phases is also supported by the reduction in the number of faint low-angle lines in the β phase which suggests a smaller and/or more symmetrical unit cell. Powder studies of the material $WO_{2.97}$ indicated a two-phase mixture of the $WO_{2.96}$ and the WO_{3-x} structural types. The powder studies therefore suggest some interesting structural changes, in particular in the positions of the tungsten atoms, that occur in the relatively narrow composition range between WO_3 and $WO_{2.96}$.

Single Crystal Measurements. (1) **$WO_{3.00}$.**—Single crystal photographs taken of stoichiometric trioxide confirmed the necessity of doubling Andersson's value[7] of the *c* axis as recently reported by Tanisaki.[8] The values of the monoclinic parameters agree (see Table IV) within experimental error with those reported by Tanisaki, from which parameters one calculates a theoretical density of 7.29₄ g./cm.³. The density measured pycnometrically in this investigation is 7.28₆ g./cm.³.

(2) **$WO_{2.98}$.**—The substoichiometric trioxide having the composition $WO_{2.98}$ was composed of dark blue-green crystals that were semitransparent plates or short cylinders. These crystals did not have the graphite-like quality when ground that was very noticeable in the case of the $WO_{2.96}$ materials. Single crystal photographs showed a monoclinic cell belonging to the space group $P2_1/m$. The Weissenberg photographs of the various layers were quite similar to those obtained for $WO_{3.00}$ although there was no indication of the doubling of the *c* axis as observed for the stoichiometric trioxide. By assigning equal weight to each reflection in a least-squares treatment of diffractometer measurements of a powder sample, one obtains the cell parameters: $a = 7.35_4 \pm 0.005$ Å., $b = 7.56_9 \pm 0.005$ Å., $c = 3.85_4 \pm 0.005$ Å., and $\beta \cong 90.6°$. These parameters correspond to a unit cell containing four tungsten atoms and a calculated density of 7.17₄ g./cm.³, which compares favorably with a measured density of 7.16₂ g./cm.³. In two samples having over-all compositions $WO_{2.981}$ and $WO_{2.983}$ there were a number of black needle crystals that proved to be the $WO_{2.96}$ structural type although the powder patterns taken of these samples failed to show the presence of this additional phase because of its low concentration.

(3) **$WO_{2.96}(\alpha)$.**—The preliminary study of powder samples had shown significant differences in both intensities and diffraction angles from the WO_3-type subcell which are indicative of a basic change in structure. The further elucidation of these structural differences was accomplished by measurements of single crystals obtained from the evaporation residues of a previous investigation.[2] Some of these crystals were unsatisfactory because they gave rise to streaking of the reciprocal lattice points. Equi-inclination Weissenberg photographs were taken of a needle having the dimensions 0.005 × 0.017 × 0.404 mm., with Cu Kα radiation using the multiple film technique. Using the lines of copper powder as an internal standard the following cell dimensions were obtained from rotation and Weissenberg films: $a = 11.90 \pm 0.02$ Å., $b = 3.826 \pm 0.012$ Å., $c = 59.64 \pm 0.06$ Å., $\beta = 98.4°$, $\alpha = \gamma = 90°$. The measured density of 7.12₆ g./cm.³ and the determination of the chemical composition O/W = 2.96 indicates the presence of 50 tungsten and 148 oxygen atoms in the unit cell. The theoretical density is 7.14₄ g./cm.³.

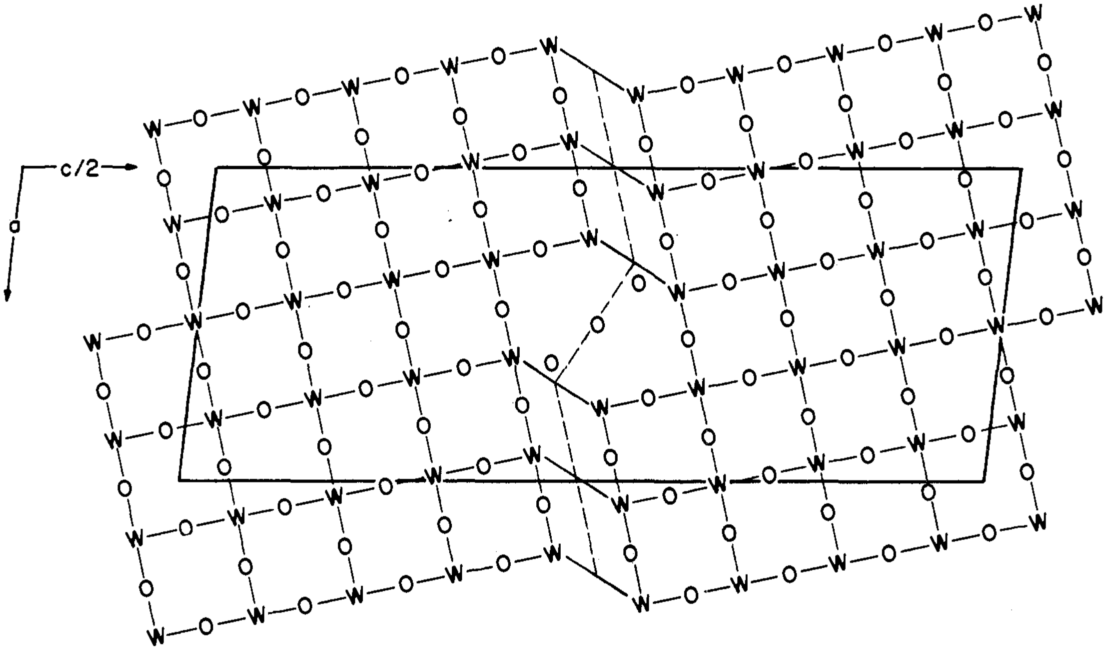

Figure 1.—010 projection of the proposed structure of $WO_{2.96}(\alpha)$.

Weak reflections on the $h1l$ and $h2l$ layers were observed when $l = 2n + 1$, which requires that the y coordinate cannot be 0 or $^1/_2$. The systematic absence of $h0l$ reflections when $l = 2n + 1$ indicated the space groups P2/c-C_{2h}^4 and Pc-C_s^2. The mean value of the experimentally-derived normalized structure factor, $E = 0.75$, compared with theoretical values of 0.798 and 0.886 for centric and acentric space groups, respectively, indicates that the centric P2/c is the preferred one. When a single crystal was rotated about the b axis, the layer-line films showed sequences of reflections lying on the reciprocal net centering about the locations of reflections for a corresponding layer-line film of $WO_{3.00}$. There was a gradual loss of intensity as the distance from the location of the corresponding $WO_{3.00}$ reflection increased. The intensity relationships on the $h1l$ and $h2l$ layers generally paralleled those of the $h0l$'s.

The intensities were measured by visual comparison with an intensity strip. The intensities were corrected for Lorentz polarization and scaled by the data reduction program of Norment.[9] A Patterson projection of $h0l$ was made using the Sly–Shoemaker Fourier program.[10] Placing the tungsten atoms in locations suggested by the Patterson projection corresponding to 2(b) and 4(g) of P2/c, calculation of the structure factor was made with the Busing–Levy least-squares program.[11,12] Arbitrary weights of 5, 4.5, and 4 for strong, weak, and unobserved reflections, respectively, were assigned to the values of F_o. The reliability factor

$$R = \frac{\Sigma \big| |F_c| - |F_o| \big|}{\Sigma |F_o|} = 0.19$$

was obtained for the $h0l$ layer.

A three-dimensional Patterson synthesis indicated that $y = 0$ or $^1/_2$ which is impossible since hkl reflections occurred when $l \neq 2n$. A Patterson projection of $0kl$ data, badly affected by absorption and limited in number, indicated that all the y coordinates are not in equivalent positions, *i.e.*, do not form two planes of tungsten atoms. When the y's were inserted at various sets of locations in either 4(g) of P2/c or 2(a) of Pc an over-all minimum value of $R \simeq 0.28$ was obtained for all observed reflections from a least-squares treatment. However, the final y coordinates were not unique. The $h2l$ layer often had an R factor approximately twice that obtained for the $h1l$ layer. Difference Fouriers of observed reflections and difference Fouriers containing unobserved reflections which had been calculated as $I_{\min}/3$ as suggested by Hamilton[13] were of no aid in uniquely locating the y coordinates. Although it was impossible to establish the y coordinates, it is suggested that they could be located in a number of planes staggered about $y = {}^1/_2$. An alternative is the existence of microphases or regions within the crystal having different types of alignment of the staggered tungsten layers. Weak satellite reflections surrounding the most intense reflections in the Weissenberg photographs and the high R factor for the $h0l$ layer indicate that there also may be significant misalignments among the domains within the single crystal even in the x–z plane. The 010 projection of one-half the unit cell of the proposed ordered-defect structure is shown in

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(9) H. G. Norment, "An X-Ray Diffraction Data Reduction Program for the IBM 704 and 7090," Naval Research Laboratory Report 5739, Feb. 16, 1962.

(10) W. G. Sly and D. P. Shoemaker, "MIFRI, Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM-704 Computer," Massachusetts Institute of Technology, Department of Chemistry Technical Report, July 1, 1960.

(11) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory, Central Files No. 59-4-37, April 14, 1960.

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FLS, A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory Report, ORNL-TM-305, Nov. 21, 1962.

(13) W. C. Hamilton, *Acta Cryst.*, **8**, 185 (1955).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $W_{50}O_{148}$

H	L	FOBS	|FCAL|	FOBS	FOBS
0	2				175
0	4				167
0	6			56	148
0	8			92	195
0	10			90	170
0	12			69	156
0	14				75
0	16				141
0	18	206	283	127	97
0	20	98	161		154
0	22			221	364
0	24			557	1007
0	26				188
0	28				172
0	30	127	76		
0	32	298	498	274	192
0	38	151	139		
0	40	222	305	188	180
0	42	281	280	212	212
0	43				186
0	44	375	274	360	214
0	45				214
0	46	526	522	451	403
0	47				214
0	48	467	556		370
0	49				212
0	50	1577	1572	1678	1584
0	51				256
0	52	314	145		206
0	54	129	81		
0	66	108	238		
1	2				127
1	4				108
1	6				114
1	8			749	1178
1	10			356	516
1	12				133
1	18				159
1	20				165
1	22				149
1	24				308
1	26				184
1	28				190
1	30				169
1	32			315	173
1	34	2098	2431	2100	1892
1	64	274	41		
1	66	1574	594	947	653
1	69				155
2	0	177	183	160	170
2	1			80	171
2	2	168	231	102	244
2	3			147	214
2	4	174	61	129	177
2	5			151	
2	6	184	210	154	129
2	8	209	205	161	133
2	10	259	247	207	196
2	12	338	297	279	287
2	14	449	429	467	334
2	16			675	596
2	18	2006	2707	1793	1720
2	19				283
2	20	835	939	870	733
2	21				169
2	22	255	220	268	172
2	23				175
2	24				178
2	25				181
2	26				184
2	27				187
2	29				192
2	31				197
2	44			443	
2	46			224	849
2	48				446
2	64				218
2	65				163
2	66				144
2	67				117
3	0	991	747	884	620
3	1			207	309
3	2	2320	1974	1275	1667
3	3			321	448
3	4	2456	2193	2619	1525
3	5			215	444
3	6	728	582	620	1933
3	7			127	410
3	8	372	282	289	645
3	9				260
3	10	255	202		263
3	11				154
3	12	173	111		156
3	14	180	59		
3	16	187	29		
3	18	160	267	486	754
3	30			465	630
3	48	257	250	159	
3	50	634	609	769	702
3	52	1604	1511	1492	1449
3	54	595	511	575	472
3	64	203	227		
3	66	263	136	208	155
4	0	219	67	160	107
4	1			56	155
4	2	222	226	161	156
4	3			139	157
4	4	202	63	140	158
4	5			100	159
4	6	179	85	142	196
4	8	183	286	145	200
4	10	109	191	149	204
4	12	251	59	458	716
4	14	116	68	710	1088
4	18	88	211		
4	19			70	
4	20	222	476		
4	24	97	396		
4	26	143	249	137	
4	27			81	
4	28	295	337	282	207
4	30	341	415	355	210
4	32	472	477	470	368
4	34	707	730	713	644
4	36	1423	1302	1359	1376
4	37				214
4	38	1202	1344	1278	1184
4	40	123	162	93	
4	58				464
4	60				436
4	68			139	
5	0			132	288
5	2				130
5	6	117	19		
5	8	169	323	114	178
5	9				180
5	10	274	216	233	181
5	11				182
5	12	307	241	291	226
5	13				263
5	14	341	282	299	325
5	15			123	268
5	16	388	344	353	331
5	17			126	272
5	18	421	387	405	337
5	19			130	278
5	20	609	561	569	443
5	21			133	347
5	22	2230	2284	2162	1469
5	24	105	162		205
5	46				324
5	48				680
5	52			207	
5	60	199	105		
5	62	223	282		
5	64	430	422		
5	66	456	264		
6	0				212
6	2	182	172		267
6	4	368	269	352	426
6	6	2805	2688	3366	1196
6	8	328	276	363	225
6	34			497	759
6	44	128	173		
6	46	179	316		171
6	48	214	364	285	160
6	50	240	250	271	256
6	52	283	377	313	281
6	54	110	295	291	145
6	56	1282	1211	1043	742
7	14				817
7	16			462	521
7	18			363	
7	38	182	259	374	
7	40	1671	1710	1797	1364
7	42	126	282	143	
8	0			498	1029
8	2			523	760
8	4				736
8	8	281	307		
8	16	242	205	156	
8	18	274	271	222	
8	20	350	442	388	
8	22	634	638	552	299
8	24	1398	1722	1355	1187
8	26	830	873	873	745
8	50				418
8	51				175
8	52			249	
8	54			126	
9	0	382	297	332	214
9	2	455	334	420	214
9	4	574	512	444	303
9	6	623	561	547	587
9	8	1362	1130	1146	957
9	10	1783	1610	1693	1371
9	25			93	
9	40				411
9	42				363
9	52	71	275		
9	54	219	245		
10	20			383	329
10	22				632
10	32	117	218		
10	34	160	287		
10	36	267	381		183
10	38	417	415	293	200
10	40	543	507	274	314
10	42	881	736	310	203
10	44	1037	1022	425	450
11	4			450	
11	6				816
11	8			382	
11	16	125	229		
11	18	123	241		
11	20	122	258		
11	22	119	311		
11	24	117	215		
11	28	1520	1518	1264	848
12	10	292	308	272	256
12	12	1749	1672	1751	1130
12	14	283	421	465	234
13	24			199	
13	26			211	
14	7			53	
14	8			179	
14	10			254	
1	-2			48	
1	-3			71	
1	-4			98	
1	-5			85	
1	-6	209	173	96	
1	-7				58
1	-8	274	190	194	161
1	-9			169	
1	-10	394	308	168	221
1	-11				282
1	-12	567	528	479	453
1	-13			185	315
1	-14	1140	1025	813	864
1	-15			204	414
1	-16			2359	1590
1	-17				130
1	-18			403	467
1	-20	343	326	249	281
1	-22	274	312	206	230
1	-24	218	139	179	124
1	-26	199	127	95	
1	-28	171	124	101	
1	-30	126	279	106	
1	-34	195	328		
1	-36	144	226	172	
1	-38				174
1	-40			456	570
1	-42			273	914
1	-48			295	
1	-56	129	313		
1	-58	180	338		
1	-60	395	269	417	268
1	-62	860	656	845	585
1	-64	1335	969	1145	975
1	-66	843	690	790	515
2	-1			80	93
2	-2	163	59	160	95
2	-3			589	110
2	-4	203	251	95	739
2	-5			734	
2	-6	185	85	123	924
2	-7				143
2	-8	164	103	107	
2	-10	172	181	116	99
2	-12	182	13	234	136
2	-13				82
2	-14	315	276		230
2	-15				91
2	-16	158	54		
2	-18	166	239		
2	-20	226	179	116	146
2	-21				174
2	-22	238	299	213	
2	-24	273	276	291	301
2	-25				138
2	-26	462	396	412	376
2	-27				145
2	-28	920	797	787	725
2	-29				216
2	-30	2129	1791	1933	1559
2	-31			155	391
2	-32	1462	1464	1452	1064
2	-33				166
2	-34	420	335	372	338
2	-35			70	172
2	-36	251	157	173	174
2	-37				172
2	-38	151	277		
2	-48	176	277	296	520
2	-64	165	374		
2	-68			68	
2	-73			267	
3	-1			118	258
3	-2	665	514	548	403
3	-3			64	181
3	-4	482	378	408	315
3	-5				142
3	-6	388	279	244	265
3	-7				85
3	-8	320	252	212	194
3	-10	251	205	171	129
3	-12	225	200		96
3	-13				99
3	-14				102
3	-15				105
3	-16	140	295		
3	-17				111
3	-18	73	55		
3	-20			608	468
3	-21			90	
3	-22	194	265	442	425
3	-30	323	311	314	
3	-44	622	584	635	693
3	-46	1835	1897	1792	1565
3	-48	353	401	470	528
3	-60	176	83		
3	-62	171	107		
3	-73			249	
4	-1				106
4	-2	218	94		
4	-4	195	162	111	
4	-6	241	124	111	
4	-8	244	195	159	
4	-10	595	503	522	
4	-12	2513	2854	2633	500
4	-13			117	
4	-14	677	672	598	
4	-15			120	402
4	-16	267	222	274	537
4	-17			125	308
4	-18	112	150	127	256
4	-19			129	
4	-20	82	162		298
4	-21			133	
4	-22	120	79		240
4	-24	88	54		289
4	-26				260
4	-28	188	145		
4	-30	138	226		
4	-38			500	970
4	-40				261
4	-58	253	220		
4	-62	1798	1430	816	992
5	-1			97	128
5	-2	158	248	841	1198
5	-3			63	
5	-4			254	385
5	-12	164	23		
5	-14	205	46		136
5	-16				140
5	-18	87	42		143
5	-20				255
5	-22				152
5	-24	189	188		156
5	-26	97	79		
5	-28	2383	2502	2274	1845
5	-30	292	169		240
5	-32	260	186		
5	-34	189	217		
5	-38				185
5	-44	175	78		
5	-54			450	712
5	-70	176	185		
5	-72	317	143		
5	-74	427	469		
6	-2	263	8		
6	-14			274	185
6	-16			663	505
6	-18				926
6	-24			244	
6	-26	330	235		
6	-38	240	215		
6	-40	458	536	462	404
6	-42	574	747	469	536
6	-44	1638	1573	1302	1334
6	-46	313	333	302	267
6	-48	182	209	152	186
6	-50	129	330		183
6	-72			160	
7	-3				165
7	-4	100	163		
7	-5				165
7	-6	515	408	447	369
7	-7				165
7	-8	1216	1056	1232	921
7	-9				332
7	-10	2320	2158	2201	1888
7	-12	741	608	669	578
7	-14	522	454	453	337
7	-16	387	303	300	241
7	-18	297	234	175	172
7	-20	213	215	177	
7	-22	153	173		
7	-24	110	159		
7	-32			347	609
7	-34			352	680
7	-42	403	309		268
7	-54	248	172		
7	-56	768	610	312	556
7	-58	1473	1109	760	1105
7	-60	702	631	342	438
8	-20	115	168		
8	-22	629	545	515	607
8	-23				185
8	-24	1892	1678	1818	1787
8	-25				229
8	-26	1155	1102	1106	1082
8	-28	502	394	350	327
8	-30	300	299	204	
8	-32	248	264	206	
8	-34	178	193	148	
8	-36	127	147		
8	-50				611
8	-52				274
9	-2	294	290	203	267
9	-4	240	278	143	
9	-6	169	59		
9	-16			544	1050
9	-18			293	559
9	-38	316	349		
9	-40	1857	1769	1778	1488
9	-58			65	
10	-6	1506	2040	2034	1642
10	-8	310	284		
10	-22	75	67		
10	-30			428	753
10	-50				128
10	-52	299	273		
10	-54	201	60		213
10	-56	1569	1341	1427	
10	-58	263	216		
10	-60	138	148		
10	-62	140	267		
11	-18	129	246		
11	-20	315	295		
11	-22	1898	1859	2040	1533
11	-24	314	299		
11	-26	221	233		
11	-46				207
11	-48				443
11	-58			248	
12	-6			432	
12	-10				498
12	-12				750
12	-34	357	420	384	285
12	-36	707	763	656	576
12	-38	1066	1194	1049	749
12	-40	416	401	349	274
12	-42	246	294	250	158
12	-44	235	235	212	
12	-46	158	214	172	
12	-48	86	140	130	
13	-2	978	910	432	693
13	-4	1350	1316	290	927
13	-6	599	505	257	466
13	-8	454	445		288
13	-10	278	190		235
13	-12	253	231		191
13	-28			287	407
13	-30			280	346
13	-36			308	
14	-16	281	267		
14	-18	1306	1294	1282	
14	-20	599	645	639	
14	-22	270	331	388	
14	-24	265	363	294	
14	-26	259	177	234	
14	-28	205	234	227	
14	-30	198	217	218	
14	-32	232	163	208	
14	-34			194	

[a] The first and second columns of structure factor values contain F_o and $|F_c|$ for $h0l$; the third and fourth columns contain F_o for $h1l$ and $h2l$, respectively.

TABLE III

TUNGSTEN POSITIONS IN THE UNIT CELL $W_{50}O_{148}$

Positions[a]	X	Y	Z
2 in 2(b)	0.5	0.5	0.0
4 in 4(g)	0.127	y_1	0.037
4 in 4(g)	0.374	y_2	0.299
4 in 4(g)	0.060	y_3	0.101
4 in 4(g)	0.371	y_4	0.118
4 in 4(g)	0.429	y_5	0.061
4 in 4(g)	0.064	y_6	0.276
4 in 4(g)	0.003	y_7	0.341
4 in 4(g)	0.186	y_8	0.476
4 in 4(g)	0.268	y_9	0.245
4 in 4(g)	0.310	y_{10}	0.184
4 in 4(g)	0.239	y_{11}	0.420
4 in 4(g)	0.309	y_{12}	0.356

[a] If the true space group is Pc, then the y coordinate in 2(b) is undetermined and 4(g) becomes 2(a) with another set of 12 positions at $\bar{x}\ \bar{y}\ \bar{z}$ corresponding to those given for 4(g).

Figure 1. Observed and calculated values of the structure factor for $h0l$ reflections and observed values for the $h1l$ and $h2l$ are given in Table II. A value of 0.12 was used for an over-all, isotropic temperature factor. The x and z coordinates of the 50 tungsten atoms in the unit cell are given in Table III.

(4) **$WO_{2\cdot96}(\beta)$.**—The single crystal measurements and structure determination of this phase are not complete at the present time; however, a discussion of some of the preliminary findings seems quite pertinent. Microscopic examination of this polycrystalline material showed that many of the smaller needles were bent and the crystallite size was generally larger than previously obtained for $WO_{2\cdot96}(\alpha)$. The larger crystals were due to the longer period of heating at a relatively higher temperature. Initially all of the crystals selected for single crystal measurements were twinned. Ultimately a single crystal was selected from a sample that had been heated 6 weeks at approximately 1250° under an argon atmosphere. A powder photograph of a sample of this material proved to be that of the $WO_{2\cdot96}$ (β) phase shown in Table I. The b axis rotation photographs of the crystal appeared to be similar to that of $WO_{2\cdot96}(\alpha)$. The Weissenberg photographs were very similar to those of $WO_{2\cdot96}(\alpha)$ although visual inspection revealed a more rapid decrease in intensity for hkl reflections when $l = 2n$. When $l \neq 2n$ the reflections were absent, indicating $y = {}^1/_2$ which is contrary to the findings for the $WO_{2\cdot96}(\alpha)$ crystals. This observation would appear to confirm the previous observation that the $WO_{2\cdot96}(\beta)$ is a more symmetrical version of $WO_{2\cdot96}(\alpha)$ because the former was found to be a higher temperature polymorph of the latter. These preliminary findings suggest that the c axis is half the length of the c axis in $WO_{2\cdot96}(\alpha)$ and the space group is P2/m. The xz projection of the unit cell containing the formula $W_{25}O_{74}$ is very likely that in Figure 1 with the tungsten atoms lying in a plane with the origin at $x = {}^1/_2$.

As was previously mentioned crystals of the $WO_{2\cdot96}$ structural type were present in samples of $WO_{2\cdot981}$

TABLE IV

COMPARISON OF CRYSTALLOGRAPHIC PARAMETERS OF TUNGSTEN OXIDES

Chemical compn.	Formula of unit cell	a, Å.	b, Å.	c, Å.	β	ρ_{calcd}, g. cm.$^{-3}$	ρ_{measd}, g. cm.$^{-3}$	Ref.
WO_3	W_8O_{24}	7.30	7.53	7.68	90.9°	7.294	7.286	8
$WO_{2.98}$	W_4O_{12-x}	7.354	7.569	3.854	90.6°	7.169	7.162	This study
$WO_{2.96}(\alpha)$	$W_{50}O_{148}$	11.90	3.826	59.64	98.4°	7.144	7.126	This study
$WO_{2.96}(\beta)$	$W_{25}O_{74}$	~11.90	~3.826	~29.82	~98.4°			This study
$WO_{2.90}$	$W_{20}O_{58}$	12.05	3.767	23.59	95.72°	7.163	7.15	b
$WO_{2.72}$	$W_{18}O_{49}$	18.28	3.775	13.98	115.14°	7.781	7.958[a]	c
WO_2	W_4O_8	5.650	4.892	5.550	120.42	10.82	...	d

[a] Measured in this investigation for a sample having the composition $WO_{2.727}$. [b] A. Magneli, *Arkiv. Kemi*, **1**, 513 (1949). [c] A. Magneli, *ibid.*, **1**, 223 (1949). [d] A. Magneli, *Arkiv Kemi, Mineral. Geol.*, **24A**, No. 2 (1946).

and $WO_{2.983}$ which were prepared at approximately 1250°. Weissenberg photographs of several of these crystals indicated intensities for *hkl* reflections for $l = 2n$ that were only slightly different from $WO_{2.96}(\alpha)$ and cell dimensions that appeared to be the same within the precision of measurement. The intensities were noticeably much weaker for *hkl* reflections when $l \neq 2n$, which indicates a greater ordering of the tungsten planes with the y coordinate nearer $^1/_2$ than in $WO_{2.96}(\alpha)$. Hence, the degree of staggering of the tungsten atoms about $y = {}^1/_2$ for these crystals appears to be between that of $WO_{2.96}(\alpha)$ and $WO_{2.96}(\beta)$ and suggests that the mechanism of the α–β phase transition may involve successive stages of unpuckering of the tungsten planes.

Discussion

There are several interesting features of the proposed structure of $WO_{2.96}(\alpha)$ which can be seen by reference to Figure 1. Each unit cell in the projected plane contains two ordered defects having the shape of a distorted hexagon. These defects are bisected by a recurrent dislocation plane shown by the dotted line. The W–W distance across this plane is considerably shorter than those elsewhere in the structure and, hence, there are probably no oxygen atoms interleaved between the tungsten atoms in this plane. It is assumed that the tungsten atoms not in this plane are surrounded by a distorted octahedron of oxygen atoms. In these aspects the structure is similar to those of other tungsten and molybdenum oxides.[14] However, based on the number of tungsten atoms found in the unit cell and the number of oxygen atoms required by the composition $WO_{2.96}$, it is necessary to insert oxygen atoms at $x \simeq {}^1/_2$, $y \simeq 0$, $z \simeq {}^1/_4, {}^3/_4$. The presence of these atoms requires that two of the tungsten atoms in the region of the defect be coordinated with seven oxygen atoms, probably forming pentagonal bipyramids as pointed out by Kihlborg[15] for other molybdenum and tungsten oxides. The three-dimensional defect channels, therefore, cannot be open holes as in the case of $W_{20}O_{58}$ and other known structures.[15]

The Weissenberg films were extremely difficult to measure not only because of the inherent difficulties in a large unit cell but also because of the large areas of no reflections on the reciprocal lattice. Of a possible 4080 reflections only 903 were observed. Furthermore, surrounding the most intense reflections were weak satellite reflections which are indications of crystal imperfection and disorder. The presence of this disorder is an additional factor which permits only a two- rather than three-dimensional solution of the crystal structure. A method of preparation of more perfect crystals at somewhat lower temperatures is believed necessary for any future study.

The results of the diffractometer measurements indicate that the trioxide phase can become substoichiometric down to $WO_{2.98}$. The single crystal measurements, however, indicate some subtle variations with composition change. The unit cell of $WO_{2.98}$ at room temperature is slightly larger than the corresponding tungsten subcell of stoichiometric WO_3. In the latter case the results of Tanisaki[8] confirmed in this study indicate two kinds of WO_6 octahedra. When oxygen is randomly removed from this structure to form $WO_{2.98}$ these two octahedra appear to become indistinguishable. Certain features of the high-temperature phase diagram based on vaporization phenomena proposed by Ackermann and Rauh[2] can now be further clarified. Since there exist quite pronounced differences in the structures of $WO_{2.96}$ and $WO_{2.98}$, and since powder patterns of the composition $WO_{2.97}$ quenched from 1200° appear to be a two-phase mixture, a miscibility gap probably extends up to at least this temperature. There also appears to be a correlation between the incongruent evaporation of the composition $WO_{2.96}$ at temperatures above approximately 1250° and the α to β phase transformation which occurs in the same region of temperature. The higher symmetry of the tungsten planes in the β phase is very likely a manifestation of a decrease in the strength of the W–O bond which permits the preferential loss of oxygen and the formation of the $W_{20}O_{58}$ phase in which the tungsten planes are completely unpuckered.[14]

A comparison of the crystallographic parameters of presently known tungsten oxides is presented in Table IV. Close agreement between the calculated and measured values of the density is seen in all cases except those for $W_{18}O_{49}$. The crystal density passes through a distinct minimum for the $W_{50}O_{148}$ phase in disagreement with earlier work reported by Glemser and Sauer[3] which shows a gradual increase from WO_3 to WO_2. The earlier work, however, must be viewed with some reservation because the value reported for a mix-

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(14) A. Magneli, *Acta Cryst.*, **6**, 495 (1953).

(15) L. Kihlborg, *Arkiv Kemi*, **21**, 471 (1963).

ture of $W_{20}O_{58}$ and $W_{18}O_{49}$ (over-all composition $WO_{2.82}$) is significantly greater than the values reported for each of the nearly pure phases.

The existence of additional defect structures prepared under different conditions and having compositions differing only slightly from that of $WO_{2.96}$ remains a distinct possibility. The recent observations by Gado[6,16] indicate a structure which is quite different from that proposed here, and the observations by Kellett and Rogers[17] may indicate a new phase which is different from those previously observed.

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(16) P. Gado, Research Institute for Telecomm. Techn., Budapest, Hungary, private communication.

(17) E. A. Kellett and S. E. Rogers, *J. Electrochem. Soc.*, **110**, 502 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,
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The Crystal Structure of Lanthanum Telluride and Tellurium-Deficient Neodymium Telluride[1]

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Single crystal X-ray diffraction studies of $LaTe_2$ and $NdTe_2$ and of the related tellurium-deficient compositions have confirmed the isomorphism with Fe_2As (C 38). Two different types of tellurium atoms exist in the structure. The atoms in the basal plane are essentially metallic in nature and give rise to the observed electrical properties. These are the atoms which can be removed from the structure to produce the tellurium-deficient compositions. This explains the increased electrical resistivity as well as the decrease in the length of the a axis and the increase in the length of the c axis observed for these compounds.

Introduction

The crystal structure of $LaTe_2$ was reported as isostructural with $CeTe_2$ by Pardo, Flahaut, and Domange,[2,3] and both compounds appear to be isostructural with the Fe_2As structure, C 38.[4] Since lanthanum and cerium have atomic numbers which are close to the atomic number of tellurium, the differences in atomic scattering factors, especially after applying a dispersion correction, are small enough to prevent the unequivocal assignment of locations for these atoms. The previous structure investigations were based on data derived from powder patterns. Investigation of the structures of the two isomorphs $NdTe_2$ and $LaTe_2$ by means of single crystal techniques promises to locate definitely the atomic species. The neodymium compound, with the greater scattering factor difference, was also deficient in tellurium. It afforded a firm distribution of the atomic species among alternative equivalent position sets, which could then be applied to the $LaTe_2$.

Experimental Section

Lanthanum and neodymium were treated with tellurium by a vapor–solid reaction in sealed Vycor tubing at 600° to yield compounds having formulas $LaTe_{2.0}$ and $NdTe_{1.8}$. The space group for these compounds is $P^4/_nmm$, and the unit cell constants obtained from powder data are $a = 4.507 \pm 0.005$ Å., $c = 9.128 \pm 0.010$ Å. for $LaTe_{2.0}$ and $a = 4.377 \pm 0.005$ Å., $c = 9.060 \pm 0.010$ Å. for $NdTe_{1.8}$; there are 2 formula weights per unit cell. The room temperature variation of lattice constants c, a, and c/a as a function of composition for the $NdTe_{2-x}$ solid solution range has been reported by Lin, Steinfink, and Weiss.[5]

Single crystals of $LaTe_{2.0}$ of dimensions $0.07 \times 0.06 \times 0.007$ mm. and of the approximate composition $NdTe_{1.8}$ of dimensions $0.05 \times 0.04 \times 0.01$ mm. were mounted along the c axis. The three-dimensional intensity data from both crystals were collected with a G.E. XRD-5 single crystal orienter using Cu Kα radiation and a scintillation counter with pulse height discrimination. Absorption corrections were necessary because of the high linear absorption coefficients of $LaTe_2$ and $NdTe_2$, 2126.7 and 2370.5 cm.$^{-1}$, respectively. The shapes of the somewhat irregular fragments were approximated by a small number of boundary planes, and the absorption corrections were computed by the Busing and Levy method.[6] This shape approximation of the fragment was rather idealized for the two large dimensions, making the $hk0$ reflections subject to large absorption errors. In this structure the x and y parameters are fixed by symmetry so the $hk0$ reflections were omitted from the refinement calculations.

The scattering factors of La, Nd, and Te were corrected for dispersion, isotropic as well as anisotropic temperature factors were used, and a full-matrix, least-squares refinement with unit weights was carried out based on the Fe_2As model.

Structure Determination

Table I shows the final positional parameters and the anisotropic temperature factors together with their

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[1] Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 806-65.

[2] M. P. Pardo, J. Flahaut, and L. Domange, *Compt. rend.*, **256**, 953 (1963).

[3] M. P. Pardo, J. Flahaut, and L. Domange, *Bull. soc. chim. France*, 3267 (1964).

[4] A. F. Wells, Structural Inorganic Chemistry, 3rd Ed., Oxford University Press, London, 1961, p. 520.

[5] W. Lin, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 877 (1965).

[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, **10**, 180 (1957).