The Crystal Structure of Ti$_5$Te$_4$

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One of the phases in the titanium–tellurium system is identified as Ti$_5$Te$_4$. This compound is tetragonal with 10 Ti and 8 Te in the body-centered cell with dimensions

$$a = 10 \cdot 164, \quad c = 3 \cdot 7720 \text{ Å}.$$

The space group is $I4/m - C_{4h}^5$ and the atomic positions are:

$$(0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + ; \quad 2 \text{ Ti in } (a) \; 0, 0, 0;$$
$$8 \text{ Ti in } (h) \; x, y, 0; \; \bar{x}, \bar{y}, 0; \; \bar{y}, x, 0; \; y, \bar{x}, 0,$$
$$\text{with } x_1 = 0 \cdot 3144, \; y_1 = 0 \cdot 3752 \text{ and } 8 \text{ Te in } (h)$$
$$\text{with } x_2 = 0 \cdot 0589, \; y_2 = 0 \cdot 2797.$$

The relationships between the Ti$_5$Te$_4$-structure and the NiAs-like structure of the Ti$_{2-x}$Te$_2$-phase are discussed.

Introduction

In a recent study of the titanium tellurides (Raaum, 1959) the existence of a phase with composition Ti$_5$Te$_4$ was established. The composition was determined by means of X-ray and density measurements. Samples were prepared by melting weighed quantities of titanium and tellurium in the stoichiometric proportions at $1400 - 1500$ °C. in crucibles of pure alumina, placed inside silica tubes which were evacuated and sealed. Single crystals were found in samples quenched from about 1200 °C. Guinier powder photographs could be indexed as tetragonal with the following cell dimensions:

$$a = 10 \cdot 164, \; c = 3 \cdot 7720 \text{ Å}; \; c/a = 0 \cdot 3711.$$

On the basis of the observed density, 6·343 g.cm.$^{-3}$, the unit cell contains ten titanium and eight tellurium atoms.

The titanium tellurides have also been studied by Hahn & Ness (1957, 1959). They report *inter alia* the existence of a Ti$_2$Te-phase with composition in the range TiTe$_{0.25}$ to TiTe$_{0.7}$. The tetragonal unit cell was found to have dimensions:

$$a = 14 \cdot 37 \pm 0 \cdot 01, \; c = 3 \cdot 590 \pm 0 \cdot 005 \text{ Å}; \; c/a = 0 \cdot 250$$

and the space group assumed to be $P4/mmm - D_{4h}^1$. The powder photograph data of Hahn & Ness leave little doubt that their Ti$_2$Te-phase is identical with the present Ti$_5$Te$_4$-phase. According to Raaum no extended range of homogeneity for this phase exists, and the composition is unequivocally determined to be TiTe$_{0.80}$ or Ti$_5$Te$_4$.

The atomic arrangement in this structure is of

considerable interest; especially its resemblance to the NiAs-like structure of the Ti$_{2-x}$Te$_2$-phase which also exists in the titanium tellurium system, and for which Raaum (1959) found $0 \cdot 39 \leq x \leq 1 \cdot 00$.

Unit cell and space group

Well formed, needle-like, single crystals with almost quadratic cross-sections were investigated on the Weissenberg goniometer with Cu K radiation ($\lambda_{\alpha_1} = 1 \cdot 5405$ Å). Weissenberg photographs were taken both along the needle axis and perpendicular to it.

The only systematic missing reflexions were of the type

$$hkl \quad \text{when} \quad h + k + l = 2n + 1.$$

The marked differences between $I(hkl)$ and $I(khl)$ show that the Laue symmetry is $4/m$. The highest symmetric space group is thus $I4/m - C_{4h}^5$.

Determination of the structure

Intensity measurements of the $hk0$ and $hk1$-reflexions were carried out visually on the Weissenberg photographs, using the multiple-film technique. Corrections for the combined Lorentz and polarization factor were made. For the calculation of the structure amplitudes the Thomas–Fermi-model values of f were taken from the *Internationale Tabellen*. Corrections for absorption and extinction were not applied. A temperature correction was attempted for the $hk0$-material, using individual temperature factors B.

The agreement between F_o and F_c is expressed by the reliability index $R = \Sigma(|F_o| - |F_c|)/\Sigma |F_o|$. F_c-values corresponding to undetected reflexions have been added with their half values.

Since the space group has the symmetry $p4$ in the

Table 1. *Observed and calculated structure factors for* Ti5Te4

hkl	F_o	¼F_c	hkl	F_o	¼F_c	hkl	F_o	¼F_c	hkl	F_o	¼F_c
200	18·8	−27·1	950	69·7	+67·7	1,13,0	48·4	−52·1	651	153·5	+158·0
400	42·7	+51·0	11,5,0	40·0	+40·8	101	28·5	+46·0	851	29·5	−24·8
600	42·8	−42·3	260	82·7	+85·9	301	138·8	+149·3	10,5,1	62·3	+59·3
800	48·8	−45·0	460	33·0	+33·0	501	78·8	−71·5	161	64·5	−61·5
10,0,0	0	−8·0	660	39·7	+41·7	701	16·5	+10·0	361	17·0	−20·3
12,0,0	59·0	−49·3	860	101·6	+98·1	901	104·3	−106·3	561	37·0	−41·0
110	8·0	+11·2	10,6,0	51·1	−45·7	11,0,1	13·5	+18·5	761	21·0	−18·0
310	35·4	−52·3	170	142·3	+154·0	211	20·5	+29·5	961	56·8	+59·0
510	70·3	−93·5	370	0	−4·0	411	146·3	+150·5	271	123·8	+148·8
710	11·3	+11·8	570	59·5	+65·6	611	27·0	+21·0	471	69·0	−77·8
910	0	+0·2	770	82·4	−88·0	811	13·5	+19·5	671	0	−7·3
11,1,0	133·2	+121·6	970	15·0	−10·8	10,1,1	40·0	+41·8	871	58·0	−53·8
220	85·0	−106·0	11,7,0	27·3	−25·3	12,1,1	72·5	−82·5	10,7,1	10·0	−13·0
420	111·0	+167·4	280	18·8	+14·0	121	106·8	−135·3	181	50·0	+44·8
620	17·3	−26·0	480	61·2	−62·4	321	39·5	+41·3	381	44·8	+48·3
820	95·6	+96·4	680	0	−8·5	521	84·7	−79·0	581	73·3	+66·0
10,2,0	44·9	+46·9	880	34·4	−36·5	721	87·8	+82·8	781	0	+0·7
12,2,0	0	+1·6	10,8,0	19·5	+18·4	921	65·0	+63·3	981	60·0	+64·0
130	66·8	+95·4	190	68·7	−67·7	11,2,1	69·0	+65·0	291	0	−2·2
330	89·1	+87·1	390	47·3	−44·0	231	38·0	−46·3	491	32·3	−29·0
530	86·6	+88·7	590	97·3	+101·7	431	69·5	−71·2	691	43·5	+46·3
730	8·0	+3·5	790	0	−1·1	631	0	−3·5	891	74·3	+77·7
930	60·4	−57·7	990	94·0	+88·8	831	79·8	−69·8	1,10,1	0	+6·8
11,3,0	13·0	−8·6	2,10,0	80·9	+79·9	10,3,1	85·5	+72·8	3,10,1	71·5	−71·5
240	15·0	−23·5	4,10,0	8·0	15·8	12,3,1	30·5	−31·0	5,10,1	30·3	+32·7
440	21·2	+25·0	6,10,0	80·9	+82·5	141	0	−2·5	7,10,1	69·3	−86·5
640	106·4	−107·1	8,10,0	18·9	−23·3	341	77·5	+101·5	2,11,1	56·7	+57·7
840	36·2	+38·9	1,11,0	0	+7·7	541	34·5	+34·5	4,11,1	76·8	+66·8
10,4,0	77·7	−82·2	3,11,0	38·4	+33·2	741	25·3	+23·8	6,11,1	23·0	−25·0
12,4,0	70·2	+61·9	5,11,0	48·4	−44·7	941	60·5	−71·0	1,12,1	51·0	+57·0
150	30·5	+36·5	7,11,0	51·7	−55·1	11,4,1	58·0	−55·0	3,12,1	17·0	−19·5
350	129·5	−133·8	2,12,0	13·9	+17·6	251	25·5	+28·0			
550	9·8	+11·3	4,12,0	76·9	−72·7	451	0	−7·0			
750	33·1	+39·9									

001-projection, with $a = \frac{1}{3}\sqrt{(2a)} = 7\cdot1871$ Å, it was decided to start with a Patterson projection on the basis of the corrected $F^2(hk0)$-values. The 001-direction is also specially suitable because of the short c-axis and because the crystal has a section not far from circular along the c-axis.

The primitive projection contains five titanium and four tellurium atoms; one titanium atom must thus be located either in 0, 0 or $\frac{1}{2}$, $\frac{1}{2}$.

The Patterson map showed the highest peak at $u = 0\cdot444$ and $v = 0\cdot117$. This peak, and a peak at $u = 0\cdot444$, $v = 0\cdot336$ with about 40% of the value for the highest peak, are probably due to vectors between the tellurium atoms. Two peaks at $u = 0\cdot056$, $v = 0\cdot278$ and $u = 0\cdot338$, $v = 0\cdot224$ with about 40% and one peak at $u = 0\cdot168$, $v = 0\cdot348$ with about 28% of the value of the highest peak are also present in the Patterson map. They are probably due to vectors between titanium and tellurium atoms.

A set of signs was calculated on the basis of the preliminary parameters for the tellurium atom and the titanium atom in the (0, 0) position. An electron-density projection was evaluated, and this clearly showed all atoms well resolved with a distinctly higher electron density in the assumed tellurium position than in the other atomic positions.

The atomic parameters were refined further by means of two Fourier and two difference syntheses. R decreased to 0·18 after the third Fourier synthesis and to 0·112 after the second difference synthesis. The observed and calculated $F(hk0)$-values are listed in Table 1, and the final Fourier map is shown in Fig. 1. The final parameters, referred to the body-centered axes, are:

2 Ti I in 0, 0, etc.
8 Ti II in $x_1 = 0\cdot3144$, $y_1 = 0\cdot3752$, etc.
8 Te in $x_2 = 0\cdot0589$, $y_2 = 0\cdot2797$, etc.

In order to determine the effect of the thermal vibrations on the final parameters of the atoms, as derived from the difference synthesis, individual B-values were computed by the method of least-squares on the Ferranti Mercury computer ('Frederic') at the Norwegian Defence Research Establishment. The refinement was terminated after five cycles. The shifts in atomic coordinates, and the B-values were:
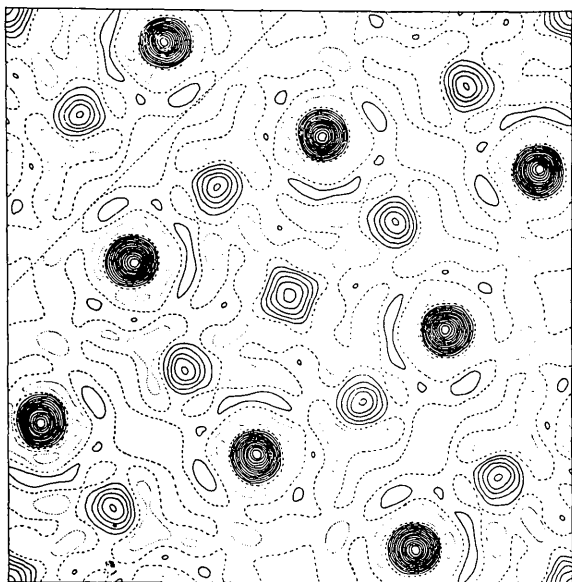
Fig. 1. Fourier projection of Ti$_5$Te$_4$ on (001). Contours are at intervals of 10 e.Å^{-2}. The zero contours are broken and the negative contours dotted.

Ti I $\Delta x = $ 0, $\Delta y = $ 0, $B = -1 \cdot 019$
Ti II $\Delta x_1 = -0 \cdot 0001$, $\Delta y_1 = +0 \cdot 0005$, $B = -0 \cdot 892$
Te $\Delta x_2 = -0 \cdot 0005$, $\Delta y_2 = +0 \cdot 0001$, $B = -0 \cdot 799$

and at this stage R was $0 \cdot 092$. The apparently negative B-values most probably represent absorption; they became $0 \cdot 7$–$0 \cdot 9$ after correction for absorption ($\mu R = 2 \cdot 5$).

The short c-axis indicates that the z-parameter for all atoms are either 0 or $\frac{1}{2}$. However, the crystals were needle-shaped in the direction of the c-axis, and the intensities for other projections than (001) were therefore subject to absorption errors which are very difficult to correct for; for this reason, no success was obtained with these projections. The only possibility left was to evaluate intensities of higher layer lines with the c-axis as rotation axis. The assumed z-coordinates were tested by comparing $|F(hk1)|_o$ with $|F(hk1)|_c$. The agreement was so good, $R = 0 \cdot 114$, that the z-coordinates selected must be correct (see Table 1).
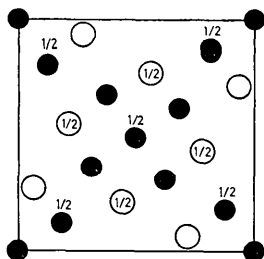

Fig. 2. The structure of Ti$_5$Te$_4$ viewed along the c-axis. Filled circles represent titanium atoms and open circles represent tellurium atoms. The z-parameters of the atoms are either 0 or $\frac{1}{2}$ as indicated.

The deduced atomic arrangement (see Fig. 2) is thus

$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$
   2 Ti I in (a) 0, 0, 0.
   8 Ti II in (h) $x, y, 0$; $\bar{x}, \bar{y}, 0$; $\bar{y}, x, 0$; $y, \bar{x}, 0$,
                with $x_1 = 0 \cdot 3144$, $y_1 = 0 \cdot 3752$.
   8 Te   in (h) with $x_2 = 0 \cdot 0589$, $y_2 = 0 \cdot 2797$.

The interatomic distances between nearest neighbours calculated using these parameters are listed in Table 2.

Table 2. Interatomic distances in Ti$_5$Te$_4$

Ti I–2 Ti I	:	$3 \cdot 772$ Å
–8 Ti II	:	$2 \cdot 954 \pm 0 \cdot 009$ Å
–4 Te	:	$2 \cdot 905 \pm 0 \cdot 002$
Ti II–2 Ti I	:	$2 \cdot 954 \pm 0 \cdot 009$ Å
–2 Ti II	:	$3 \cdot 215 \pm 0 \cdot 019$
–2 Ti II	:	$3 \cdot 428 \pm 0 \cdot 019$
–2 Ti II	:	$3 \cdot 772$
–1 Te	:	$2 \cdot 773 \pm 0 \cdot 010$
–2 Te	:	$2 \cdot 774 \pm 0 \cdot 010$
–2 Te	:	$2 \cdot 821 \pm 0 \cdot 010$
Te–1 Ti I	:	$2 \cdot 905 \pm 0 \cdot 002$ Å
–1 Ti II	:	$2 \cdot 773 \pm 0 \cdot 010$
–2 Ti II	:	$2 \cdot 774 \pm 0 \cdot 010$
–2 Ti II	:	$2 \cdot 821 \pm 0 \cdot 010$
–2 Te	:	$3 \cdot 772$
–4 Te	:	$3 \cdot 782 \pm 0 \cdot 003$
–2 Te	:	$4 \cdot 110 \pm 0 \cdot 003$
–2 Te	:	$4 \cdot 359 \pm 0 \cdot 003$

The limits indicated for the interatomic distances are standard deviations calculated according to the method of Cruickshank (1949).

Discussion of the structure

The coordination around the titanium and tellurium atoms can be seen from Fig. 3, where two unit cells of the Ti$_5$Te$_4$ structure are shown in projection on (001). The structure might be looked upon as built of quadratic columns of titanium and tellurium atoms in the direction of the c-axis. Each of the two titanium atoms (Ti I) in position (a) is surrounded by four tellurium atoms in a planar quadratic arrangement, and by eight titanium atoms (Ti II) in a prismatic, approximately cubic, arrangement. Each Ti II atom is surrounded by five tellurium atoms, four of them forming a rectangular arrangement. It is furthermore surrounded by two Ti I atoms and by six Ti II atoms, of which two are on one side and four on the other side of the plane formed by the four tellurium atoms. Each tellurium atom is located at one apex of a rectangular double pyramid formed by a rectangle of four Ti II atoms and one Ti I atom at the other apex. A sixth titanium neighbour (Ti II) is found in an adjacent column. Each tellurium atom is furthermore surrounded by ten tellurium atoms at distances shorter than $4 \cdot 36$ Å.

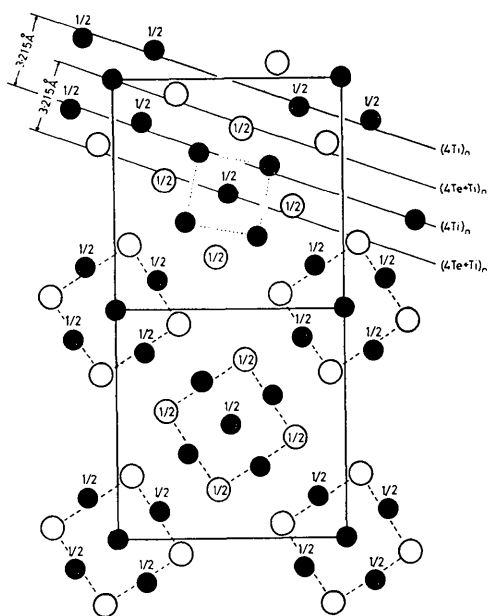The phase Ti$_5$Te$_4$ has an arrangement of atoms typical of the metallic state and correspondingly short

Fig. 3. Two unit cells of Ti_5Te_4 viewed along the c-axis. The configuration of tellurium atoms around the titanium atoms is indicated by broken lines. Dotted lines indicate the relationships to the β-Ti structure. As can be seen from the upper part of the figure, the atoms are arranged in layers approximately parallel to (310).

20% of the metal sites are unoccupied, probably in an ordered way as indicated by the crosses, by analogy with what has been found for the structurally related compounds $Ni_{0.80}Se$ (Grønvold, 1955), Fe_3Se_4 (Okazaki & Hirakawa, 1956) and Cr_3S_4 (Jellinek, 1957).
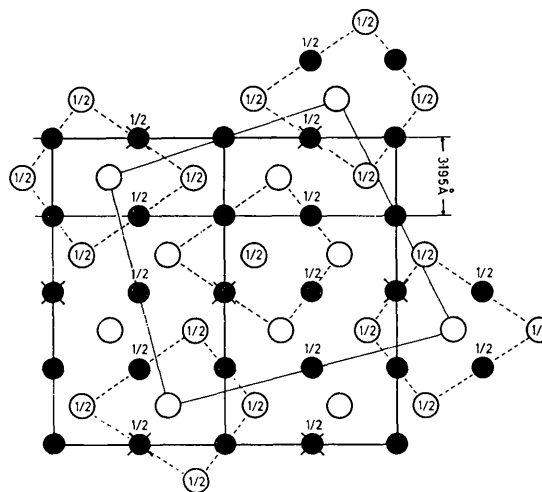

Fig. 4. Two unit cells of a NiAs-type structure with the dimensions of the $Ti_{1.61}Te_2$-structure. Probable locations of the vacancies are indicated by crosses.

metal–metal and metal–non-metal distances. The titanium–tellurium distances are even shorter than the sum of the metallic radii given by Pauling (1947): $1·467+1·51=2·977$ Å for the twelve-coordinated titanium I and six-coordinated tellurium atoms, and $1·397+1·51=2·907$ Å for the seven-coordinated titanium II and six-coordinated tellurium atoms, respectively. The titanium coordination around the Ti I atoms is the same as in the cubic body-centered β-titanium structure. According to Levinger (1953) the cube edge of β-titanium is $3·283$ Å and the shortest interatomic distances $2·843$ Å. In Ti_5Te_4 the edges in the direction of the a- and c-axis are $3·215$ and $3·772$ Å, respectively, with the shortest interatomic distances being $2·954$ Å. The titanium coordination around the Ti II atoms is more irregular, and the distances to the eight nearest neighbours range from $2·954$ to $3·772$ Å.

The structure of the Ti_5Te_4-phase shows characteristic relationships to that of the neighbouring $Ti_{2-x}Te_2$ phase with NiAs-like structure in the two-component system. According to Raaum (1959) the titanium-rich limit of the phase lies at $Ti_{1.61}Te_2$, and the structure is not hexagonal as assumed by Ehrlich (1949), but monoclinic with unit cell dimensions:

$$a=6·954, \quad b=3·836, \quad c=12·716 \text{ Å}; \quad \beta=90·63°.$$

In Fig. 4 two unit cells of $Ti_{1.61}Te_2$ are projected into the ac-plane, assuming the parameters of an ideal NiAs-like structure since the actual parameters are not yet known. It should also be remarked that about

By comparing Figs. 3 and 4 it is seen that the irregular quadrangle outlined in Fig. 4, with edge-lengths of $9·9$, $10·6$, $9·8$ and $12·0$ Å for the $Ti_{2-x}Te_2$-phase, has its characteristic counterpart in the square plane cell with $a=10·164$ Å for the Ti_5Te_4-phase. The small dotted quadrilaterals in Fig. 4 resemble those in Fig. 3 except for the fact that the central atoms are tellurium in Fig. 4 and titanium atoms in Fig. 3, and that although the four titanium atoms in both cases show a quadratic arrangement, two of them are at different heights in the $Ti_{2-x}Te_2$-structure. Inside the unit formed by the large quadrilateral in Fig. 4 there are ten tellurium atoms and eight titanium atoms when the composition of the phase is $Ti_{1.60}Te_2$. In order to obtain the Ti_5Te_4-structure from that of $Ti_{1.61}Te_2$ it is thus only necessary to substitute the tellurium atoms at the centers of the dashed quadrilaterals by titanium atoms and rearrange the vacancies so that they are now on the sides of the large quadrilateral. Evidently, these two possibilities are energetically favoured over one resulting in a compound with composition TiTe and NiAs-type structure.

Compounds structurally related to Ti_5Te_4 seem to exist in the vanadium-sulfur system (Pedersen, 1958) and in the vanadium–tellurium system (Grønvold et al., 1958). V_5S_4 is probably isostructural with Ti_5Te_4, while V_5Te_4 has a monoclinic structure of similar dimensions.

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Experimental Atomic Scattering Factors and Anomalous Dispersion Corrections for Th, U, and Pu*†

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Experimental atomic scattering factors have been determined for Th, U, and Pu with Mo $K\alpha$, Cu $K\alpha$, Fe $K\alpha$, and Cr $K\alpha$ X-radiations. The Thomas–Fermi-Dirac scattering curves were used as a theoretical basis, and the difference between the experimental and TFD curves was taken as a measure of the anomalous dispersion correction.

As a result of determining the scattering factors for Th, U, and Pu from experimental samples of ThO_2, UO_2, and PuO_2, the scattering factor for oxygen was also determined. The experimentally derived scattering curve for oxygen is in good agreement with the theoretical scattering curve for oxygen according to McWeeney.

Calculated values for $\Delta f'$ and $\Delta f''$, the real and imaginary portions of the anomalous dispersion correction are compared with experimental values for these quantities. Agreement can be described as semi-quantitative since the experimental terms are of the same order of magnitude and have the same signs as those indicated by theory.

Introduction

Accurate atomic scattering factors are essential for any careful study of interatomic distances and thermal vibration parameters by diffraction methods. Because of the interest in this laboratory in precise studies of the structures of intermetallic and other compounds of various heavy metals, the atomic scattering factors of Th, U, and Pu have been determined experimentally for Mo, Cu, Fe, and Cr $K\alpha$ X-radiations.

The Thomas–Fermi–Dirac scattering curves are used as a theoretical basis, and the difference between the experimental curves and the TFD curves is taken as a measure of the anomalous dispersion correction. The L_{III} absorption edges of Th, U, and Pu lie very close to Mo $K\alpha$ radiation, and the M_I, M_{II} absorption edges of these elements are close to Fe $K\alpha$ and Cr $K\alpha$

radiation respectively. Since no really sound theoretical treatment of anomalous dispersion for the L and M electrons has been developed, the agreement between the experimental and calculated values for anomalous dispersion in this region must be described as qualitative or at best semi-quantitative. Furthermore, any theoretical treatment is complicated because the L and M absorption edges themselves are quite complex.

Experimental theory

The atomic scattering factors of Th, U, and Pu were experimentally determined by utilizing techniques first proposed by the author (Roof, 1959a), corrected by Chipman and Paskin (1960), and subsequently revised by the author (Roof, 1960a). A brief description of these experimental techniques is given in the following paragraphs.

The experimental samples consisted of a powdered material having the geometrical shape of a slab. The equation relating the atomic scattering factor of a material having the shape of a slab to experimental

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