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The phase C16 type in the thorium-palladium alloy system.

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During researches on thorium–palladium alloys, the formation was observed, in the thorium-rich part of the system, of a phase corresponding to the structural C16 type (Pearson, 1958) or $CuAl_2$ type (Bradley & Jones, 1933).

The thorium used (Ferro, 1958), was of a purity about 99·7% (the impurities were represented by oxygen in the form of ThO_2); the palladium was of a purity not less than 99·9%. The alloys were prepared by heating the metals up to ca. 1800 °C. in argon (although the melting points for the alloys seem lower); then the samples, still in argon atmosphere, were annealed for one day at 900 °C., 7 days at 750 °C. and 15 days at 500 °C. The filings used for the X-ray examination were further annealed at 500 °C. for ca. 2 days.

The alloys were analyzed by dissolving in a mixture of HCl and H_2O_2 followed by treatment with aqua regia, precipitation of Pd with H_2S, re-solution of palladium sulphide and determination of palladium with dimethylglyoxime. In the filtrate, thorium was determined as ThO_2 via the oxalate.

The powder photographs of alloys with compositions around 18% Pd show the existence of a tetragonal phase with constants:

$$a = 7{\cdot}33_0,\ c = 5{\cdot}93_0\ \text{Å},\ c/a = 0{\cdot}80_9\ .$$

(The powder photographs were obtained with the Straumanis arrangement using Fe $K\alpha$ radiation: $K\alpha_1$, $\lambda = 1{\cdot}93597$ Å.)

The structure corresponds to the C16 type with the following atomic positions:

Space group D_{4h}^{18}

4 Pd in (a): $0, 0, \frac{1}{4};\ 0, 0, \frac{3}{4};\ \frac{1}{2}, \frac{1}{2}, \frac{3}{4};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{4}\ .$

8 Th in (h): $x, \frac{1}{2}+x, 0;\ \bar{x}, \frac{1}{2}-x, 0;\ \frac{1}{2}+x, \bar{x}, 0;$
$\frac{1}{2}-x, x, 0;\ \frac{1}{2}+x, x, \frac{1}{2};\ \frac{1}{2}-x, \bar{x}, \frac{1}{2};$
$x, \frac{1}{2}-x, \frac{1}{2};\ \bar{x}, \frac{1}{2}+x, \frac{1}{2}\ .$

The micrographic appearance agrees with the hypothesis of the existence of only one phase for a composition near the theoretical one for Th_2Pd (18·69% Pd); also the density (11·5 g.cm.$^{-3}$, for an alloy containing $19{\cdot}4_0$% Pd and $80{\cdot}6_7$% Th) appears in fair agreement with the value calculated on the basis of above structure (11·9 g.cm.$^{-3}$).

The intensities observed on the film were compared with those calculated for different values of x between 0·150 and 0·175. Although, unfortunately, the c/a value results in many coincidences which prevent the exact estimation of the separate contribution of the reflections, the best agreement between observed and calculated intensities seems to be obtained for $x = 0{\cdot}16_0$.

In Table 1 are reported the unit-cell dimensions (Å) and the molar volumes (cm.^{3}), obtained both from crystallographic data (V_M) and by adding the atomic volumes (ΣV_A), for the thorium compounds with this structure. Even considering the fact that many of these phases have probably a small composition range, it can be seen that there are no remarkable volume variations.

Table 1. *Structural data for* Th_2Me *compounds*

Th_2Me	a	c	c/a	V_M	ΣV_A	References
Th_2Al	7·614	5·857	0·769	51·1	49·7	Braun & van Vucht, 1955; Murray, 1955
Th_2Zn	7·60	5·64	0·74	49·1	48·8	Baenziger *et al.*, 1956
Th_2Cu	7·29	5·75	0·79	46·0	46·8	Murray, 1955; Baenziger *et al.*, 1956
Th_2Ag	7·56	5·84	0·77	50·3	50·0	Murray, 1955
Th_2Pd	7·33	5·93	0·81	48·0	48·6	
Th_2Au	7·42	5·95	0·80	49·3	49·9	Murray, 1955

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The anomalous temperature behavior of the 200 reflection of fluorite.*

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On a diffractometer recording of the powder pattern of CaF_2, the area of a peak is expressed in terms of the structure factor squared, the multiplicity, and the Lorentz-polarization factor, by the relation

$$A = K^2(F/4)^2 m(L.P)\ .$$

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For the three kinds of reflections in fluorite:

$$h+k+l=\text{odd}\ (A/mL.P)^{1/2}$$
$$=Kf_{\text{Ca}}\exp\left[-B_{\text{Ca}}\,(\sin\theta/\lambda)^2\right]$$
$$h+k+l=2(2n+1)\ (A/mL.P)^{1/2}$$
$$=K\{f_{\text{Ca}}\exp[-B_{\text{Ca}}(\sin\theta/\lambda)^2]-2f_{\text{F}}\exp[-B_{\text{F}}(\sin\theta/\lambda)^2]\}$$
$$h+k+l=4n\ (A/mL.P)^{1/2}$$
$$=K\{f_{\text{Ca}}\exp[-B_{\text{Ca}}(\sin\theta/\lambda)^2]+2f_{\text{F}}\exp[-B_{\text{F}}(\sin\theta/\lambda)^2]\}\,.$$

Smooth curves representing $(A/mL.P)^{1/2}$ as a function of $(\sin\theta/\lambda)$ can be made for each of the three kinds of reflections. Combinations of these three curves with the known values of f_{Ca} and $2f_{\text{F}}$ give the two quantities

$$y(\text{Ca})=K\exp\left[-B_{\text{Ca}}\,(\sin\theta/\lambda)^2\right]$$

and

$$y(\text{F})=K\exp\left[-B_{\text{F}}\,(\sin\theta/\lambda)^2\right]$$

as functions of $(\sin\theta/\lambda)$. Plots of $\ln y(\text{Ca})$ and $\ln y(\text{F})$ against $(\sin\theta/\lambda)^2$ give straight lines whose negative slopes are B_{Ca} and B_{F}. From a powder pattern of CaF_2 made at room temperature with Cu $K\alpha$ radiation, the values obtained were $B_{\text{Ca}}=0{\cdot}50$ Å^2 and $B_{\text{F}}=0{\cdot}61$ Å^2, for a temperature of 20 °C. Since the temperature effect in CaF_2 is rather small, these values are not very accurate. However the accuracy is high enough to establish that B_{F} is approximately 22% higher than B_{Ca}.

For the 200 reflection from CaF_2,

$$(\text{F}/4)^2=(f_{\text{Ca}}\exp[-M_{\text{Ca}}]-2f_{\text{F}}\exp[-M_{\text{F}}])^2,$$

where $M=B\,(\sin\theta/\lambda)^2$. Since $f_{\text{Ca}}=14{\cdot}90$ and $2f_{\text{F}}=14{\cdot}50$, the more rapid decrease of $2f_{\text{F}}\exp[-M_{\text{F}}]$ suggests that an increase in temperature could perhaps produce an increase in the integrated intensity of the 200 reflection. Including the real and imaginary parts of the dispersion correction for f_{Ca}, and assuming the dispersion correction to be negligible for f_{F}, we obtain for the 200 reflection

$$(\text{F}/4)^2=\{(f_{\text{Ca}}+\Delta f'+i\Delta f'')\exp[-M_{\text{Ca}}]-2f_{\text{F}}\exp[-M_{\text{F}}]\}$$
$$\{(f_{\text{Ca}}+\Delta f'-i\Delta f'')\exp[-M_{\text{Ca}}]-2f_{\text{F}}\exp[-M_{\text{F}}]\}\,.$$

Using the approximation

$$\exp[-(M_{\text{F}}-M_{\text{Ca}})]=1-(M_{\text{F}}-M_{\text{Ca}})\,,$$

this expression can be reduced to the simpler form

$$(\text{F}/4)^2=\{[f_{\text{Ca}}+\Delta f'-2f_{\text{F}}+2f_{\text{F}}(M_{\text{F}}-M_{\text{Ca}})]^2+[\Delta f'']^2\}$$
$$\times\exp[-2M_{\text{Ca}}]\,.$$

For numerical evaluation, we use the values $f_{\text{Ca}}=14{\cdot}90$, $2f_{\text{F}}=14{\cdot}50$; $2M_{\text{Ca}}=0{\cdot}034$, $(M_{\text{F}}-M_{\text{Ca}})=0{\cdot}004$ at 20 °C.; and $2M_{\text{Ca}}=0{\cdot}068$, $(M_{\text{F}}-M_{\text{Ca}})=0{\cdot}008$ at 310 °C. The Dauben & Templeton (1955) dispersion corrections for Ca are listed in Table 1 together with the computed values of $(\text{F}/4)^2$ for 20 °C. and 310 °C.

Table 1. *Computed values of* $(\text{F}/4)^2$ *for* 200 *fluorite*

	$\Delta f'$ (Ca)	$\Delta f''$ (Ca)	$(\text{F}/4)^2$ 20 °C.	$(F/4)^2$ 310 °C.
Cr $K\alpha$	−0·2	2·7	7·2	7·0
Cu $K\alpha$	0·2	1·4	2·46	2·46
Mo $K\alpha$	0·2	0·2	0·60	0·66

Raising the temperature from 20 to 310 °C. should produce a normal decrease of 3% using Cr $K\alpha$. With Cu $K\alpha$ there should be practically no change. Using Mo $K\alpha$ we should expect a completely abnormal behavior, an increase in intensity of about 10%. To test these predictions, diffractometer runs were made using a CaF_2 crystal obtained from the Harshaw Chemical Company. The crystal was cut to a 100 face, and then hammered and ground on emergy paper to ensure an imperfect crystal. By using a long time constant, the peak height is closely a measure of the integrated intensity. Tracings of the 200 peak were made with the crystal at 20 and at 310 °C. With Cu $K\alpha$ there was no measurable difference for the two temperatures. The results for Mo $K\alpha$ are shown by the curves of Fig. 1. The peak was traced twice at 20 °C., then twice at 310 °C., and finally twice at 20 °C. There is an increase in intensity of approximately 12% on raising the temperature.

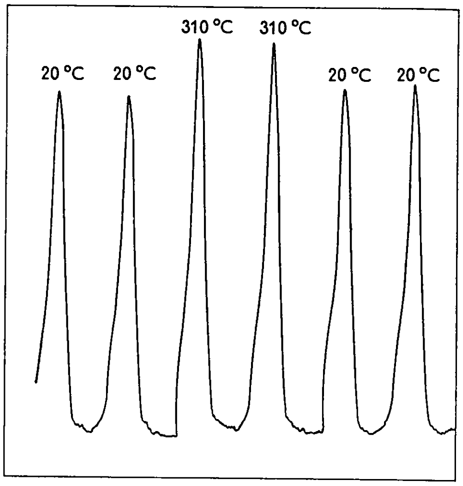

Fig. 1. Diffractometer tracings of the 200 peak of CaF_2 at 20 and 310 °C. using Mo $K\alpha$ radiation.

For general structures where the atomic parameters can change continuously with temperature, both increases and decreases in intensity are, of course, to be expected. In fluorite the atomic positions are rigidly fixed by the symmetry, and the intensity increase results from rather special conditions. The scattering factor f_A is nearly balanced by $2f_B$, and since this allows the mass of B to be only half that of A, the temperature factor of B is enough greater than that of A to produce the increase in intensity. Among structures in which the atomic positions are rigidly fixed by symmetry, there are probably not many examples where these special conditions are satisfied.

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