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The solid solution of mercury in palladium.

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During the course of a study of the system Pd–Hg, the randomly substituted solid solution of mercury in palladium was examined. The early observation of Berzelius (1813) that the last traces of mercury are quite difficult to expel from palladium amalgam suggests a solid solution. In the range from zero to 13·8 at.%, mercury dissolves in palladium, with an expansion of the palladium lattice. Values of the lattice parameter were calculated from backreflection lines showing resolved Cu $K\alpha$ doublets ($\lambda_{\alpha_1}=1{\cdot}5405$ Å, $\lambda_{\alpha_2}=1{\cdot}5443$ Å) using a North American Phillips camera with a nominal radius of 5·73 cm. The film was mounted in the unsymmetrical or Straumanis position so that the effective radius could be determined for each pattern. The values of the unit cell parameter, a_0, are given in Table 1.

Table 1. *Cell edge versus atomic percentage of palladium in palladium amalgam*

Index	100·0 at.% Pd	93·8 at.% Pd	87·6 at.% Pd
hkl	a_0	a_0	a_0
400	3·884 Å	3·907 Å	3·942 Å
331	3·888	3·909	3·943
420	3·888	3·909	3·945
Average	3·887 Å	3·908 Å	3·943 Å

Standard deviation 0·001 Å

Carefully purified palladium (Terada, 1961; Terada & Cagle, 1960) and triply-distilled mercury were heated in sealed, evacuated, Pyrex tubes to prepare the samples. The value of a_0 observed for the purified palladium, 3·887 Å, is in agreement with the value 3·8898 Å reported by Swanson & Tatge (1953). The data of Table 1 may be represented analytically by the equation

$$\Delta d = 2{\cdot}16\times10^{-3}m + 1{\cdot}93\times10^{-4}m^2(\pm 0{\cdot}002\ \text{Å})$$

in which Δd is the increase in lattice parameter in Å over that for pure palladium and m is the atomic percentage of mercury in the sample.

At concentrations above 13·8 at.% of mercury a phase PdHg which is body-centered tetragonal (AuCu type, $L1_0$) with cell parameters $a_0=3{\cdot}026$ Å, $c_0=3{\cdot}702$ Å for stoichiometric composition was obtained. This was first observed by Bittner & Nowotny (1952). It is, however, identical with the mineral potarite, discussed in detail elsewhere (Terada, 1960; Terada & Cagle, 1960), which had been previously described as apparently isometric (Palache, Berman & Frondel, 1944).

References

Berzelius, J. J. (1813). *J. Chem. u. Phys.* (*Schweigger*), **7**, 43–8.

Bittner, H. & Nowotny, H. (1952). *Monatsh. Chem.* **83**, 287–9.

Palache, C., Berman, H. & Frondel, C. (1944). *The System of Mineralogy* of J. D. Dana & E. Salisbury Dana, Yale University 1837–1892, 7th ed., p. 105. New York: Wiley.

Swanson, H. E. & Tatge, E. (1953). Standard X-ray Diffraction Powder Patterns (NBS Circular 539), Washington, D.C., U.S. Government Printing Office, Vol. 1, pp. 21–22.

Terada, K. (1961). The Crystal Structure of Some Palladium Amalgams and of the Mineral Potarite, Ph.D. Thesis, University of Utah, U.S.A.

Terada, K. & Cagle, F. W. (1960). *Amer. Min.* **45**, 1093–7.

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Structure-factor calculations with anisotropic thermal parameters.

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In a recent paper Kartha & Ahmed (1960) have shown that in structure-factor calculations an atom with anisotropic thermal movement may be represented by four atoms of $\frac{1}{4}$ weight each if the anisotropy is not too large. For two dimensions, or when the vibration ellipsoid is an ellipsoid of revolution about the major axis, the anisotropically vibrating atom need only be split into two atoms of $\frac{1}{2}$ weight each. For the two-dimensional case with $\Delta B \leq 1$ Å^2 the discrepancy between the 'correct' exponential representation of the temperature factor and the suggested approximation was stated to be less than 2% within the limiting sphere for Cu $K\alpha$ radiation. This discrepancy, however, increases for increasing values of ΔB, and soon becomes quite appreciable.

During a recent three-dimensional refinement of the crystal structure of $(PNCl_2)_4$ (Ketelaar & De Vries, 1939), it appeared that for some atoms ΔB values considerably larger than 1 Å^2 had to be applied. As only a machine programme for structure-factor calculations with isotropic thermal parameters was available, we investigated in which way K. & A.'s method could be extended. We found that for atoms with $\Delta B \leq 1{\cdot}3$ Å^2 it could be used satisfactorily in a slightly modified form. The anisotropically vibrating atoms with larger values of ΔB had, however, each to be split into more than four fractional parts.

This latter extension of K. & A.'s method, by which many 'atoms' become involved in the structure-factor calculation, is rather laborious. In general it is advantageous only if no structure-factor programme is available which can deal in the conventional way with anisotropically vibrating atoms; or for a crystal structure for which an anisotropic calculation is required for one or two atoms only.

In the following discussion of the modification and the extension of K. & A.'s method, the symbols from their paper are used. This discussion is given for two-dimensions first.

In the case of two fractional atoms, the distance Δx of the fractional atoms from the atomic centre, for which the best fit to the exponential form of the temperature factor could be obtained, was determined by trial. With

$$\Delta x = 0{\cdot}1130(\Delta B_x)^{1/2} - 0{\cdot}0069(\Delta B_x)^{3/2}\ \text{Å} \qquad (1)$$

the agreement between the temperature factor and its approximated form was better than 2% for $\Delta B_x \leq 1{\cdot}3$ Å^2 and $\xi \leq 1{\cdot}3$ Å^{-1} (cut-off for Cu $K\alpha$ radiation). As already stated above in K. & A.'s approximation with

$$\Delta x = 0{\cdot}108(\Delta B_x)^{1/2}\ \text{Å}$$

deviations of 2% occur for $\Delta B_x = 1{\cdot}0$ Å^2.

If three fractional atoms are used, two parameters must be chosen. Let the fractions be $(1-2p)$ at $(0, 0)$ and p at $(\pm\Delta x, 0)$. In the 'correct' form for the scattering in the ξ direction in reciprocal space,

$$f(\xi) = f_0(\xi)\exp(-B\xi^2/4)\exp(-\Delta B_x\xi^2/4)\ ,$$

the factor

$$f_t(\xi) = \exp(-\Delta B_x\xi^2/4)$$

is thus substituted by a factor

$$f_s(\xi) = 1 - 2p + 2p\cos 2\pi\xi\Delta x\ .$$

For $1{\cdot}4 \leq \Delta B_x \leq 5{\cdot}0$ Å^2 the best agreement between these two factors was obtained if Δx and p obeyed the following expressions:

$$\Delta x = 0{\cdot}0153 + 0{\cdot}1744(\Delta B_x)^{1/2}\ \text{Å} \qquad (2)$$

and

$$p = [0{\cdot}1923(\Delta B_x)^{-1/2} + 2{\cdot}1916]^{-2}. \qquad (3)$$

The values for Δx and p calculated from (2) and (3) are listed in Table 1 for $\Delta B_x = 1{\cdot}4\ (0{\cdot}2)\ 5{\cdot}0$ Å^2.

Table 1. *Values of Δx and p for $\Delta B = 1{\cdot}4(0{\cdot}2)5{\cdot}0$ Å^2*

ΔB_x	Δx	p
1·4 Å^2	0·2217 Å	0·1804
1·6	0·2359	0·1821
1·8	0·2493	0·1834
2·0	0·2619	0·1846
2·2	0·2740	0·1856
2·4	0·2855	0·1865
2·6	0·2965	0·1873
2·8	0·3071	0·1880
3·0	0·3174	0·1886
3·2 Å^2	0·3273 Å	0·1892
3·4	0·3369	0·1897
3·6	0·3462	0·1902
3·8	0·3553	0·1906
4·0	0·3641	0·1911
4·2	0·3727	0·1915
4·4	0·3811	0·1918
4·6	0·3894	0·1921
4·8	0·3974	0·1925
5·0	0·4053	0·1928

By using these values, the approximation of $f_t(\xi)$, within the limiting sphere for Cu $K\alpha$ radiation, is better than 2% for values of ΔB_x up to 2·4 Å^2. For ΔB_x values between 2·5 and 5·0 Å^2, the discrepancy between $f_t(\xi)$ and $f_s(\xi)$ remains smaller than 2% for the ξ values below

$$\xi_{\text{max.}} = 1{\cdot}48 - 0{\cdot}30(\Delta B_x - 2{\cdot}0)^{1/2}\ \text{Å}^{-1}, \quad \text{i.e.}$$

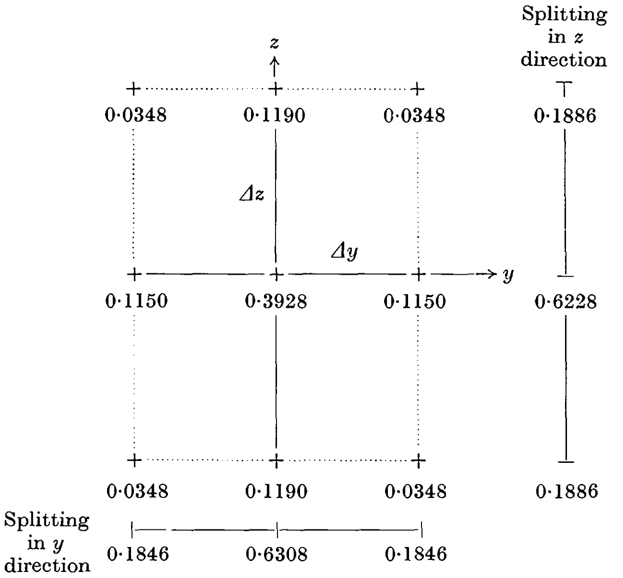
$\xi_{\text{max.}} = 1{\cdot}27$ Å^{-1} for $\Delta B_x = 2{\cdot}5$ Å^2 and $\xi_{\text{max.}} = 0{\cdot}96$ Å^{-1} for $\Delta B_x = 5{\cdot}0$ Å^2. For $\xi > \xi_{\text{max.}}$ the discrepancy between $f_t(\xi)$ and $f_s(\xi)$ increases very rapidly and $f_s(\xi)$ should no longer be used as an approximation for $f_t(\xi)$.

The general trend of $f_s(\xi)$ in comparison with $f_t(\xi)$ is shown in Table 2, in which these functions are compared for $\Delta B_x = 3{\cdot}0$ Å^2.

Table 2. *Comparison of $f_t(\xi)$ and $f_s(\xi)$ for $\Delta B_x = 3{\cdot}0$ Å^2*

ξ	$f_t(\xi)$	$f_s(\xi)$
0·0 Å^{-1}	1·000	1·000
0·1	0·993	0·993
0·2	0·970	0·970
0·3	0·935	0·935
0·4	0·887	0·886
0·5	0·829	0·828
0·6	0·763	0·761
0·7 Å^{-1}	0·693	0·689
0·8	0·619	0·614
0·9	0·545	0·539
1·0	0·472	0·468
1·1	0·404	0·403
1·2	0·340	0·346
1·3	0·282	0·301

For general anisotropy, K. & A. suggested that the smallest of B_x, B_y, B_z, say B_x, be taken as isotropic temperature factor B, and that the anisotropically vibrating atom be replaced by four atoms of $\frac{1}{4}$ weight each at $(0, \pm\Delta y, \pm\Delta z)$. As for two dimensions, this approximation is good as long as ΔB_y and ΔB_z do not exceed a value of 1·3 Å^2 when the separations of the fractional atoms are again calculated according to (1). For higher anisotropies, however, the atom should be split into more than four parts. If e.g. $B_z > B_y$, the atom should first be replaced by three fractional atoms in the z direction, in the same way as for two dimensions. Then each of these parts in its turn should be split into two or three parts dependent on the value of ΔB_y. A practical example for $\Delta B_z = 3{\cdot}0$ Å^2, $\Delta B_y = 2{\cdot}0$ Å^2, is shown in the scheme below, in which $\Delta z = 0{\cdot}3174$ Å and $\Delta y = 0{\cdot}2619$ Å.



References

Kartha, G. & Ahmed, F. R. (1960). *Acta Cryst.* **13**, 532.
Ketelaar, J. A. A. & De Vries, T. A. (1939). *Rec. Trav. chim. Pays-Bas*, **58**, 1081.