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The solid solution of mercury in palladium. By K. TERADA, *Dow Chemical Company, Midland, Michigan, U.S.A.*, and F. W. CAGLE, Jr., *Department of Chemistry, University of Utah, Salt Lake City, Utah, U.S.A.*

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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 ($\lambda_{\alpha_1} = 1.5405 \text{ \AA}$, $\lambda_{\alpha_2} = 1.5443 \text{ \AA}$) 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

$$\Delta d = 2.16 \times 10^{-3}m + 1.93 \times 10^{-4}m^2 (\pm 0.002 \text{ \AA})$$

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 $a_0 = 3.026 \text{ \AA}$, $c_0 = 3.702 \text{ \AA}$ 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).

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Structure-factor calculations with anisotropic thermal parameters. By AAFJE VOS, *Laboratorium voor Kristalchemie*, and D. W. SMITS, *Mathematisch Instituut, University of Groningen, Groningen, The Netherlands*

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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 $\Delta B \leq 1 \text{ \AA}^2$ 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 $(\text{PNCl}_2)_4$ (Ketelaar & De Vries, 1939), it appeared that for some atoms ΔB values considerably larger than 1 \AA^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 $\Delta B \leq 1.3 \text{ \AA}^2$ 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