$$\underline{{}_{9}R'_{3,0}}=\frac{\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_5\,, \tag{6·26}$$

$$\underline{{}_{10}R'_{3,0}}=\frac{7\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_6\,, \tag{6·27}$$

$$\underline{{}_{11}R'_{3,0}}=\frac{\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_7\,, \tag{6·28}$$

$$\underline{{}_{12}R'_{3,0}}=\frac{7\sigma_4^{1/2}}{8C_1\sigma_2}(2C_1-C_2)(\mathscr{E}'^2_{\mathbf{h}_1}+\mathscr{E}'^2_{\mathbf{h}_2}+\mathscr{E}'^2_{\mathbf{h}_1+\mathbf{h}_2})+\varrho_8\,, \tag{6·29}$$

and

$$\underline{{}_{13}R'_{3,0}}={}_{11}R'_{3,0}\,. \tag{6·30}$$

In order to summarize the relations among the correction terms for the various space groups in type $3P_2$, it is convenient to make the identification,

$$R\equiv R^{(0)}\,, \tag{6·31}$$

$$R'\equiv R^{(1)}\,. \tag{6·32}$$

Thus, for space groups, $R\bar{3}$, $R\bar{3}m$ and $R\bar{3}c$,

$$R^{(j)}_{i,0}={}_{1}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·33}$$

For space groups, *Pm*3, *Pn*3 and *Pa*3,

$$R^{(j)}_{i,0}={}_{1}R^{(j)}_{i,0}+{}_{9}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·34}$$

For space groups, *Pm*3*m*, *Pn*3*n*, *Pm*3*n* and *Pn*3*m*,

$$R^{(j)}_{i,0}={}_{1}R^{(j)}_{i,0}+{}_{10}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·35}$$

For space groups, *Fm*3 and *Fd*3,

$$R^{(j)}_{i,0}={}_{1}R^{(j)}_{i,0}+{}_{11}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·36}$$

For space groups, *Fm*3*m*, *Fm*3*c*, *Fd*3*m* and *Fd*3*c*,

$$R^{(j)}_{i,0}={}_{1}R^{(j)}_{i,0}+{}_{12}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·37}$$

Finally, for space groups *Fmmm* and *Fddd*,

$$R^{(j)}_{i,0}={}_{1}R^{(j)}_{i,0}+{}_{13}R^{(j)}_{i,0};\quad j=0,1;\quad i=2,3\,. \tag{6·38}$$

Note that $\underline{{}_{1}R_{2,0}}$, $\underline{{}_{1}R_{3,0}}$, $\underline{{}_{1}R'_{2,0}}$ and $\underline{{}_{1}R'_{3,0}}$ are defined in $1P$ (1959).

The remainder terms in the basic formulas are especially simple for the special case $p=q=r=2$. For this case, the formulas reduce to those obtainable by the algebraic methods proposed by us (1957).

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The Crystal Structure of K_5Hg_7

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K_5Hg_7 has an orthorhombic unit cell with $a=10·06$, $b=19·45$, $c=8·34$ Å, $Z=4$, space group, *Pbcm*. The intensity data were obtained from Weissenberg and precession photographs of single crystals. The structure was determined by Patterson and electron-density methods and refined by the least-squares method. The K_5Hg_7 structure results from that of KHg_2 (a distorted AlB_2 structure) by replacing one-eighth of the Hg atoms by potassium atoms.

Introduction

The crystal structure of K_5Hg_7 is the fourth of a series of potassium amalgams whose structures have been determined. KHg_{11} is isotructural with $BaHg_{11}$, whose structure was reported by Peyronel (1952). The structures of KHg_2 and KHg were reported by Duwell & Baenziger (1955).

Due to the stoichiometry of KHg_{11} the mercury atoms form a three-dimensional net which encompasses the potassium atoms. In the KHg and KHg_2 structures, although not required by stoichiometry, the Hg atoms tend to group together. In KHg, the Hg atoms form nearly planar square groups of four which are strung together in chains by bonds between corners of the square groups. In KHg_2 the mercury atoms form puckered hexagonal layer nets—a distortion of the $NaHg_2(AlB_2)$ ideal structure type. The K_5Hg_7 structure reported below results from the KHg_2 structure by replacing every eighth mercury atom by a potassium atom in a regular way.

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X-ray diffraction methods and data

Single crystals of K_5Hg_7 were made and isolated by the method described in the previous paper (Duwell & Baenziger, 1955). Zero through third layer Weissenberg diagrams were made of the ($hk0$) zone with Cu K radiation and zero and first level precession camera photographs were made of the ($0kl$) zone with Mo K radiation. The intensities were estimated by the visual comparison method. The Weissenberg data were affected by absorption errors to a greater extent than the precession camera data, but absorption corrections were not made because of the irregular shape of the crystal.

The unit cell is orthorhombic with

$$a = 10{\cdot}06,\ b = 19{\cdot}45,\ c = 8{\cdot}34\ \text{Å}\ ,$$
$$V = 1632\ \text{Å}^3,\ D_x = 6{\cdot}51\ \text{g.cm.}^{-3},\ Z = 4\ ,$$
$$D_m = 6{\cdot}61\ \text{g.cm.}^{-3}\ \text{(Mäey, 1899), F.W.} = 1599{\cdot}77\ .$$

From the characteristic absences, the space group could be $Pbcm$ or $Pbc2_1$. Statistical tests of the ($0kl$) data indicate the space group $Pbcm$ is more probable. At any rate, this space group was chosen for beginning the structure determination, and a satisfactory structure has been found consistent with this space group.

Structure determination

Patterson projections on (001) and (100) were made. Applying the Patterson superposition technique a plausible structure was found which quickly refined to a discrepancy factor of 0·24 based on mercury atom contributions alone—the contribution of the potassium atoms was not included in the structure factor calculations.

Two-dimensional difference electron-density projections onto (001) and (100) showed peaks which could be interpreted as potassium atoms. The maps also contained additional spurious peaks of about the same magnitude. Inclusion of the potassium atoms in the structure factor calculation based on positions obtained from the difference plots reduced the discrepancy factor to 0·23 for the ($hk0$) data. Some of the K–K and K–Hg interatomic distances seemed abnormally small, so the potassium atom positions were adjusted to make the K–K and K–Hg distances as near normal as possible within the restrictions imposed by the mercury atom positions. Using these positions the structure factors were calculated for all reflections giving an R factor of 0·23 based on observed reflections only.

At this point a least-squares refinement was carried out, partially using an IBM 650 computer (least-squares program of Templeton & Senko modified by Williams & Fitzwater of the Ames Laboratory), and partially with an LGP–30 computer and a program developed in our laboratory. In all, the refinement was carried out through six cycles with observed reflections only. An additional cycle was calculated with both observed and unobserved reflections, the unobserved reflections being given a lesser weight if the calculated F values were less than the minimum F observable. The observed intensity data estimated from each layer line of the Weissenberg or precession camera were treated independently, and a scale factor was refined for each independent set of data.

Table 1. *Atomic positions*

8 Hg_1 in (e): $\pm(x, y, z;\ \bar{x}, \bar{y}, \tfrac{1}{2}+z;\ x, \tfrac{1}{2}-y, \bar{z};\ \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z;)$ with $x = 0{\cdot}1994 \pm 5$, $y = 0{\cdot}0274 \pm 5$, $z = 0{\cdot}0646 \pm 16$, $B = 2{\cdot}70 \pm 20$.
8 Hg_2 in (e): with $x = 0{\cdot}6790 \pm 4$, $y = 0{\cdot}1194 \pm 4$, $z = 0{\cdot}5708 \pm 15$, $B = 2{\cdot}29 \pm 18$.
8 Hg_3 in (e): with $x = 0{\cdot}3737 \pm 4$, $y = 0{\cdot}1399 \pm 5$, $z = 0{\cdot}5708 \pm 16$, $B = 2{\cdot}56 \pm 19$.
4 Hg_4 in (c): $\pm(x, \tfrac{1}{4}, 0;\ x, \tfrac{1}{4}, \tfrac{1}{2};)$ with $x = 0{\cdot}8701 \pm 8$, $B = 4{\cdot}60 \pm 43$.
4 K_1 in (d): $\pm(x, y, \tfrac{1}{4};\ \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{4};)$ with $x = 0{\cdot}559 \pm 4$, $y = 0{\cdot}220 \pm 4$, $B = 3{\cdot}64 \pm 1{\cdot}96$.
4 K_2 in (d): with $x = 0{\cdot}538 \pm 3$, $y = 0{\cdot}017 \pm 4$, $B = 1{\cdot}44 \pm 1{\cdot}82$.
4 K_3 in (d): with $x = 0{\cdot}174 \pm 3$, $y = 0{\cdot}210 \pm 3$, $B = 0{\cdot}37 \pm 1{\cdot}08$.
4 K_4 in (d): with $x = 0{\cdot}009 \pm 4$, $y = 0{\cdot}398 \pm 4$, $B = 3{\cdot}65 \pm 2{\cdot}08$.
4 K_5 in (d): with $x = 0{\cdot}896 \pm 3$, $y = 0{\cdot}083 \pm 3$, $B = 1{\cdot}48 \pm 1{\cdot}43$.

	R_1°	R_1'
$0kl$	0·139	0·139
$1kl$	0·122	0·131
$hk0$	0·179	0·188
$hk1$	0·087	0·207
$hk2$	0·177	0·185
$hk3$	0·206	0·213
Total	0·163	0·174

Table 2. *Interatomic distances*

Atom	Neighbor	Distance	Atom	Neighbor	Distance
Hg_1	Hg_2	3·022 Å	Hg_2	Hg_2	2·989 Å
	Hg_1	3·092		Hg_1	3·022
	Hg_3	3·106		Hg_3	3·097
	K_5	3·52		K_2	3·52
	K_4	3·56		K_3	3·61
	K_5	3·59		K_1	3·61
	K_4	3·62		K_1	3·63
	K_2	3·74		K_2	3·95
	K_3	3·88		K_4	4·02
	K_2	3·89			
Hg_3	Hg_3	3·092	Hg_4	2 Hg_3	3·239
	Hg_2	3·097		2 K_1	3·80
	Hg_1	3·106		2 K_4	3·82
	Hg_4	3·239		2 K_5	3·86
	K_1	3·52			
	K_5	3·52			
	K_2	3·62			
	K_4	3·66			
	K_1	3·67			
	K_2	3·74			
K_1	2 Hg_3	3·52	K_2	2 Hg_3	3·62
	2 Hg_2	3·62		2 Hg_2	3·62
	2 Hg_2	3·63		2 Hg_1	3·74
	2 Hg_3	3·67		2 Hg_3	3·74
	2 Hg_4	3·80		K_5	3·83
	K_3	3·88		2 Hg_1	3·89
	K_2	3·95		K_1	3·95
	2 K_1	4·33		2 K_2	4·29

Table 2 (*cont.*)

Atom	Neighbor	Distance
K_3	2 Hg_2	3·61
	2 Hg_4	3·78
	2 Hg_2	3·85
	2 Hg_1	3·88
	K_1	3·88
	K_4	4·02
	2 K_3	4·39
K_5	2 Hg_3	3·52
	2 Hg_1	3·52
	2 Hg_1	3·59
	K_3	3·73
	K_4	3·73
	K_2	3·83
	2 Hg_4	3·86
K_4	2 Hg_1	3·56
	2 Hg_1	3·62
	2 Hg_3	3·66
	K_5	3·73
	2 Hg_4	3·82
	2 Hg_2	4·02

The final positions of the atoms together with the standard errors in the coordinates are listed in Table 1. In the refinement step including the absent reflection data, contributions to the discrepancy factor R_1' are made only if F_c is greater than the minimum F_o. For the $(hk1)$ data the minimum F_o value was set apparently too low. The total number of absent reflections in this group was larger than the number of present reflections. The R_1' value is much greater than the R_1° value, based on observed reflections only, because of the large number of absent reflections which made small contributions to the numerator, but none to the denominator.

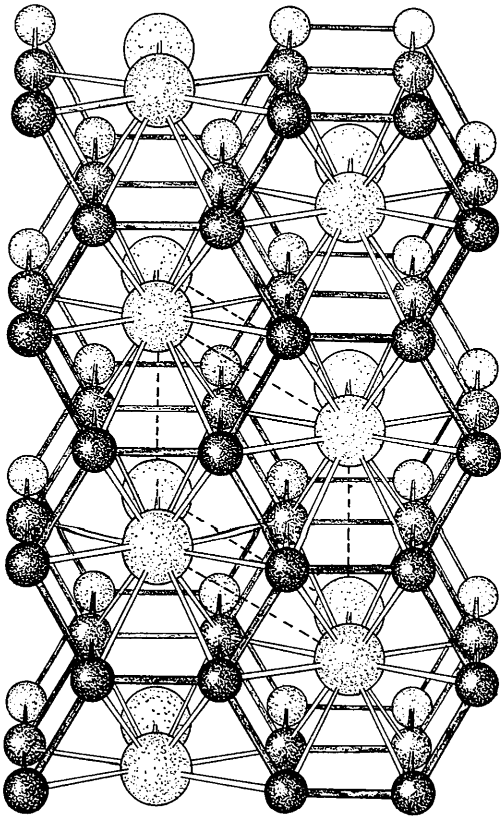

Fig. 1. The $NaHg_2$ structure—small atoms are Hg.

Discussion of the structure

In the $NaHg_2$, $LaHg_2$ and UHg_2 structures (Fig. 1), Hg atoms form regular hexagonal nets with a Hg–Hg distance in the net of about 2·9 Å, and a Hg–Hg distance between nets of 3·2 Å. This is in contrast to the metal borides (see Laves (1956) or Pearson (1958) for a listing of AlB_2 phases) which have the same structure with a larger axial ratio so that the interlayer *B–B* distances are about double the intralayer *B–B* distances. In the distorted KHg_2 structure (Fig. 2) the intralayer distances have increased to about 3·0 Å and the interlayer distances decreased to 3·1 Å. In K_5Hg_7 (Fig. 3), the vestiges of the layers have Hg–Hg distances of 3·03, 3·11, 3·19, 3·23 whereas the interlayer distances are as low as 2·99 Å. In all cases, the alkali–alkali distances are considerably shorter than in the pure alkali metal, although since the error in these distances is large, a detailed discussion of these distances would not be significant.

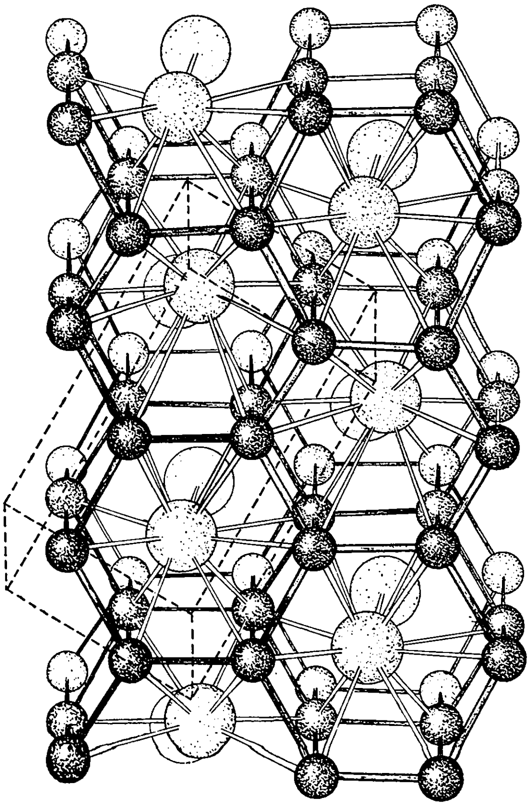

Fig. 2. The KHg_2 structure.

Of the substances known to crystallize in the AlB_2 type, the c/a ratio is 1·00 or greater when the B element is trivalent such as B or Ga (exception $ThAl_2$ with $c/a=0·95$). The compounds with much smaller c/a ratios, all have B elements which have *d* orbitals available for use in bonding. The sp^2 type of hybridization which is a natural description for the borides and

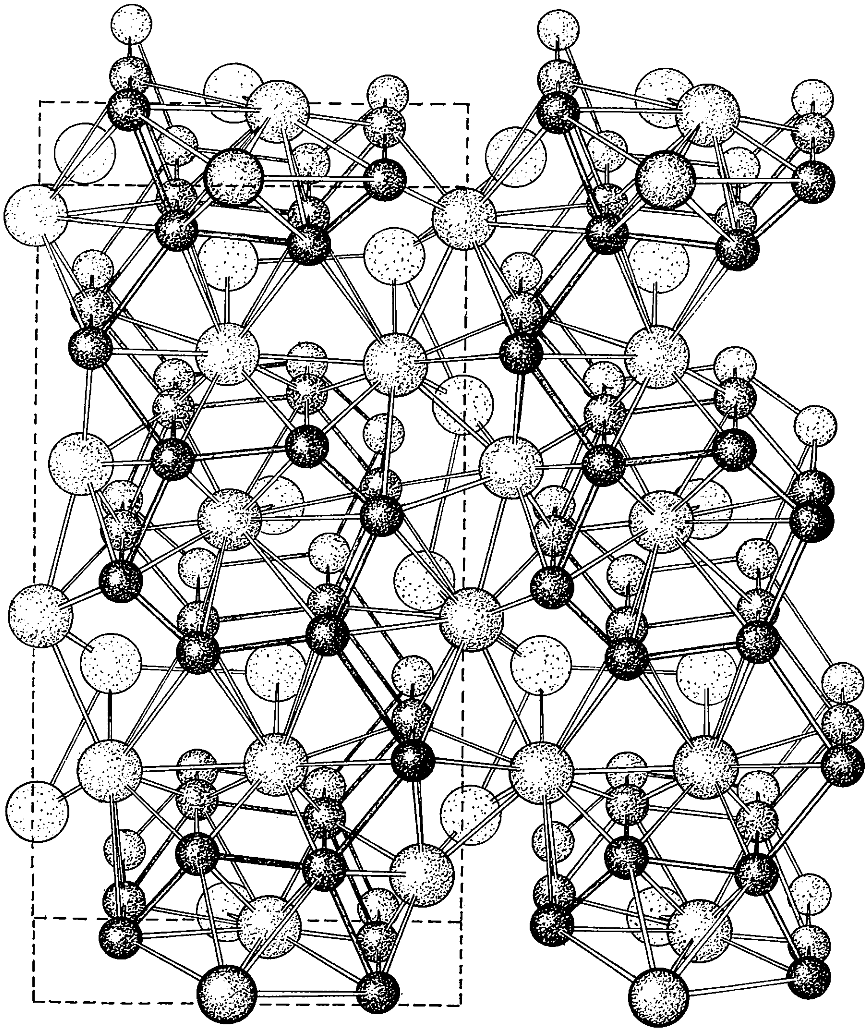

Fig. 3. The K_5Hg_7 structure.

gallides can be supplemented by ds^2 hybridization possible for the Hg, Cu, and U cases. Utilization of d orbitals in bonding would permit interlayer bonding as well as intralayer bonding—this type of directed bonding is apparently so favored in the Hg compounds that it persists in KHg_2 in spite of distortion and in K_5Hg_7 in spite of a considerable composition change.

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