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Crystal structure of $Hg_4As_2I_3$

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Abstract. The crystal structure of $Hg_4As_2I_3$ ($Pa\bar{3}$) has been solved and refined to $R = 0.030$ ($Rw = 0.038$) for 565 unique observed reflections. The framework, isostructural to that of $Cd_4As_2I_3$, is described either as a pseudo-cubic close packing of Hg atoms with As and I in the interstices or as a complex arrangement of two sorts of polyhedra surrounding Hg, sharing corners or edges. The cohesion of the structure is assumed to be due to As atoms with strong bonds As–Hg and As–As. A discussion about Hg–I distances is proposed, involving a iono-covalent character to the corresponding bond.

Introduction

Semiconducting crystals $M_4A_2X_3$ of $II_4V_2VII_3$ type are, according to Pearson (1964), polyanionic compounds because of the ratio *ne/na* of the number of valence electrons to the number of anions less than 8, since it is equal to 7.8. Several studies with Cd (as M) have been made developing electrical features (Rebbah, 1980) and structural properties of the synthesized crystals which crystallize either in the cubic system as for $Cd_4As_2I_3$ (Gallay, Allais and Deschanvres, 1975) or in the orthorhombic one as for $Cd_4P_2I_3$ (Rebbah, Yazbeck and Deschanvres, 1980). On the other hand, few studies have been made with single crystals involving Hg (as M), probably because of the very high X-ray absorption coefficient of such compounds. However, X-ray powder investigations are known: $Hg_4As_2Br_3$, $Hg_4As_2I_3$ (Puff and Gotta, 1965) and $Hg_4Sb_2I_3$ (Puff and Gotta, 1964).

The present paper deals with $Hg_4As_2I_3$ to verify its space group, its polyanionic character and to get precise interatomic distances of such compounds.

Experimental

$Hg_4As_2I_3$ is prepared from the elements Hg, I and As, placed in stoichiometric amounts in sealed, evacuated ampoules at 453 K for 24 h. I and As were previously sublimated. Then the sample, intimately and finely ground, is heated in an sealed evacuated silica ampoule at 493 K. Crystals grow into the cold area of the tube, after chemical transport reaction.

Black crystals, found in the preparation tube are large intertwinned samples forming hexahedra and octahedra or individual small plates. A powder X-ray test, performed with the first crystals, showed a pure phase, easily indexed in a cubic lattice; no splitting of the lines were observed. A Laue pattern with the incident beam normal to an octahedral face indicated clearly the existence of a threefold axis. Finally, precession patterns (111) and (001) were registered, from which the space group was unequivocally deduced to be $Pa\bar{3}$. A radiocrystallographic study of the small plates showed that they belong to the same phase as above. To minimize the absorption phenomenon, a thin, well shaped plate (001), was choosen for the collection of the diffracted intensities. $Hg_4As_2I_3$ stands indeed for the materials we studied in our laboratory, among those with the highest absorption coefficient: $\mu_1(\mathrm{Cu}K\alpha) = 1800\ \mathrm{cm}^{-1}$, $\mu_1(\mathrm{Ag}K\alpha) = 391\ \mathrm{cm}^{-1}$. The experimental data are summarized in Table 1. The cell parameters were determined based on a least-squares refinement of 25 reflections. The 1605 observed reflections were corrected for Lorentz and polarisation effects. The intensities $I(hkl)$ of equivalent reflections were then compared to their mean value $\bar{I}$: $R_{eq} = \Sigma_{hkl}\ (I(hkl) - \bar{I})/\bar{I} = 0.292$. After a correction for absorption this value was reduced to 0.036. The corresponding interatomic distances e.s.d.'s (Table 3) are less than $2 \cdot 10^{-3}$ Å. The three equivalent octants lead to the same results in the atomic coordinates (Table 2), within the limits of the experimental errors.

Description of the structure and discussion

$Hg_4As_2I_3$ is isostructural to $Cd_4As_2I_3$ (Gallay et al., 1975) which has the same space group $Pa\bar{3}$. The structure of $Hg_4As_2I_3$ can be considered in three different ways: as a pseudo-cubic close packing of Hg atoms in the interstices of which As and I atoms take place; as a set of independent atoms described with their atomic neighbourhood; as a building of atomic polyedra surrounding Hg, sharing corners and edges. We consider now each of them.

Table 1. Experimental data and structure refinement parameters.

Crystal shape and size	plate (001) bounded by (110), $(1\bar{1}0)$, $(\bar{1}\bar{1}0)$ and $(\bar{1}10)$. $192 \times 150 \times 8\ \mu m$.
Lattice parameters ($T = 294$ K)	$a = 12.999(3)$ Å $V = 2196$ Å^3
Space group	$Pa\bar{3}$ ($0kl: k = 2n$, $h0l: l = 2n$, $hk0: h = 2n$)
Dc [$g \cdot cm^{-3}$]; Z	8.06; 8
Data collection technique	diffractometer CAD 4 Enraf-Nonius, Mo$K\alpha$, ω-2θ scan, $h > 0$, $k > 0$, $l > 0$
$[(\sin\theta)/\lambda]_{max.}$	0.96
Standard reflections	3 reflections with $\Delta I/I < 0.03$
Number of measured reflections	5913
Number of reflections with $I > 3\sigma(I)$	1605
Number of reflections used in the refinement	565
Absorption correction	based on the crystal morphology
Absorption coefficient	μ_1 (Mo$K\alpha$) = 716 cm^{-1}
Transmission factors	$T_{max} = 0.563$; $T_{min} = 0.035$
Atomic scattering factors, f' and f''	Source: International Tables for X-ray Cristallography (1974), Vol. IV
Weighting scheme	linear $w\ \lvert F \rvert$ in terms of $(\sin\theta)/\lambda$
Secondary extinction coefficient	$g = 1.06(9)$
R, Rw, S	0.030, 0.038, 1.0059*

* Additional material to this paper (Table of F_o, Fc) can be ordered referring to the no. CSD 53020, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 2. Positional and thermal parameters with e.s.d.'s $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}a_ia_j$(Å^2) $U_{ij} = 1/2\pi^2\ \beta_{ij}a_ia_j$(Å^2).

Atom	x	y	z	B (Å^2)
Hg(1)	0.22092(7)	–	–	3.28(1)
Hg(2)	0.04322(7)	0.01333(7)	0.26386(6)	2.45(1)
As(1)	0.10819(14)	–	–	1.27(2)
As(2)	0.44637(12)	–	–	1.10(1)
I	0.18518(8)	0.43990(8)	0.25788(9)	1.58(2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	0.0415(4)	U_{11}	U_{11}	−0.0093(3)	U_{12}	U_{12}
Hg(2)	0.0355(4)	0.0344(4)	0.0231(4)	−0.0006(3)	0.0076(3)	0.0115(3)
As(1)	0.0161(5)	U_{11}	U_{11}	0.0046(6)	U_{12}	U_{12}
As(2)	0.0139(4)	U_{11}	U_{11}	0.0004(5)	U_{12}	U_{12}
I	0.0161(4)	0.0174(4)	0.0266(5)	−0.0004(3)	−0.0012(4)	0.0008(4)

Table 3. Interatomic distances (Å) and angles (˚)-e.s.d.'s are given in parentheses.

Hg(1)–As(1)	2.538(2)	Hg(2)–As(1)	2.516(2)
(3×) Hg(1)–I	2.924(2)	Hg(2)–As(2^{I})	2.531(2)
(3×) Hg(1)–I^{I}	3.881(2)	Hg(2)–$\mathrm{I}^{\mathrm{III}}$	3.131(2)
(3×) Hg(1)–Hg(2)	3.596(1)	Hg(2)–I^{IV}	3.481(2)
(3×) As(1)–I^{I}	3.973(2)	Hg(2)–I^{V}	3.514(2)
As(2)–As(2^{II})	2.415(2)	Hg(2)–I^{I}	3.658(2)
As(1)–Hg(2)–As(2^{I})	154.78(7)	I^{I}–Hg(2)–I^{IV}	71.58(3)
I^{I}–Hg(2)–$\mathrm{I}^{\mathrm{III}}$	146.47(4)	I^{I}–Hg(2)–I^{V}	127.51(4)
I^{IV}–Hg(2)–I^{V}	160.44(4)	$\mathrm{I}^{\mathrm{III}}$–Hg(2)–$\mathrm{I}^{\mathrm{IV}}$	75.08(3)
As(1)–Hg(2)–I^{I}	77.69(5)	$\mathrm{I}^{\mathrm{III}}$–Hg(2)–$\mathrm{I}^{\mathrm{V}}$	86.01(3)
As(1)–Hg(2)–$\mathrm{I}^{\mathrm{III}}$	113.27(5)	As(1)–Hg(1)–I^{I}	124.41(6)
As(1)–Hg(2)–I^{IV}	102.13(5)	I–Hg(1)–I^{VI}	91.20(4)
As(1)–Hg(2)–I^{V}	80.59(5)	Hg(2)–As(1)–Hg(2^{VI})	119.98(7)
As(2^{I})–Hg(2)–I^{I}	83.02(5)	Hg(2)–As(1)–Hg(1)	90.71(7)
As(2^{I})–Hg(2)–$\mathrm{I}^{\mathrm{III}}$	91.75(5)	Hg(2^{VII})–As(2)–Hg(2^{VIII})	110.74(6)
As(2^{I})–Hg(2)–I^{IV}	86.79(5)	Hg(2^{VII})–As(2)–As(2^{II})	108.17(7)
As(2^{I})–Hg(2)–I^{V}	98.91(4)		

Symmetry code:

I: $1/2-x, y-1/2, z$
II: $1-x, 1-y, 1-z$
III: $-x, y-1/2, 1/2-z$
IV: $1/2-y, z-1/2, x$
V: $y-1/2, z, 1/2-x$
VI: z, x, y
VII: $1/2-x, 1/2+y, z$
VIII: $z, 1/2-x, 1/2+y$

The location of the Hg atoms, 8 Hg(1) and 24 Hg(2), in the actual cubic cell with parameter $a \sim 13$ Å, shows that they build a pseudo-face-centered cube with parameter $a/2$. In the stacking of Hg atoms parallel to (111), two different slices of octahedra are observed which alternate in the [111] direction. The Hg–Hg distances in such slices range from 3.596 to 5.428 Å, so that the octahedra, with Hg apices, are considerably distorted. The first slice, of NaCl type (Fig. 1), shows that the octahedral insterstices are fully occupied: 3 sites out of 4 are filled with I, the fourth site is concerned with a doublet, constituted by two As(2), whose interatomic distance (Table 3) points out the strongly covalent character of the As–As bond: $r_{\mathrm{cov}}(\mathrm{As}) = 1.20$ Å. This feature involves an important off-centering of each of As(2) atoms with regard to the Hg octahedron. In the second slice, 3 octahedral sites out of 4 are once more occupied with I, but the fourth is now empty. Then, this slice is not of NaCl type. Moreover in the whole structure, some of the tetrahedral interstices, one out of eight, are occupied by As(1) atoms exclusively, which are considerably off-centered inside the site.

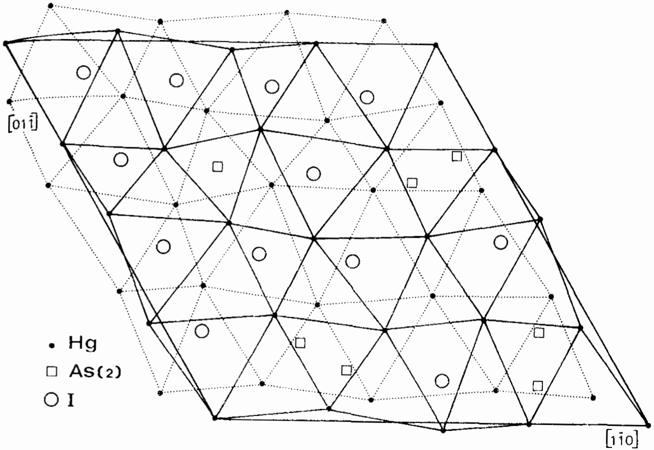

Fig. 1. Projection of the structure onto (111) showing its pseudo-compact character. Slice of NaCl type: octahedral interstices fully occupied with I or As–As doublet.

As a consequence of what is mentioned above, the coordination of the two sorts of As atoms is not of the same tetrahedral kind: As(1) is only surrounded with Hg atoms (Table 3), 3 Hg(2) and 1 Hg(1), at the apices of an irregular tetrahedron whose As(1)–Hg(1) direction is one of the threefold axis. On the other hand, As(2) which is also on a threefold axis is surrounded by 3 Hg(2) and another As(2) with which it constitutes a doublet. As the concerned distance As(2)–As(2) is slightly shorter than those of As(2)–Hg(2), so the As(2) atom is approximately situated close to the center of the related tetrahedron, as shown by the 6 similar values of the angles whose vertex is As(2). Consequently, two such approximately regular tetrahedra are overlapped and held with a As(2)–As(2) covalent bond. It must be pointed out that in $Hg_4As_2I_3$, the As(2)–As(2) distance (Table 3) is similar but slightly longer (0.02 Å) than the one found in $Cd_4As_2I_3$: 2.397 Å (Gallay et al., 1975) while on the contrary As–Hg distances are slightly shorter (0.04 Å) than the corresponding As–Cd (2.550 to 2.574 Å). Note that Hg–As is 2.60 Å in HgAs hexagonal (Vogel and Schuster, 1980). Each I atom has 6 Hg neighbours and the corresponding Hg–I distances range from 2.924(2) to 3.881(2) Å related to a very distorted octahedron. The shortest Hg–I distance is the same as Cd–I: 2.922(4) Å) in $Cd_4As_2I_3$ (Gallay et al., 1975) but several examples are found in the literature for which Hg in tetrahedral surrounding offers clearly shorter Hg–I distances: 2.68 and 2.78 Å in the red and orange varieties of HgI_2 (Wells, 1975); 2.680 Å in $Cs_2Hg_3I_8 \cdot H_2O$, 2.729 Å in Cs_3HgI_5, 2.738 Å in Cs_2HgI_4 (Sjövall and Svensson, 1988); 2.705 Å in $KHgI_3$, H_2O (Nyqvist and Johansson, 1971). All these distances indicate a strong covalent bond character, since the sum of covalent radii for I

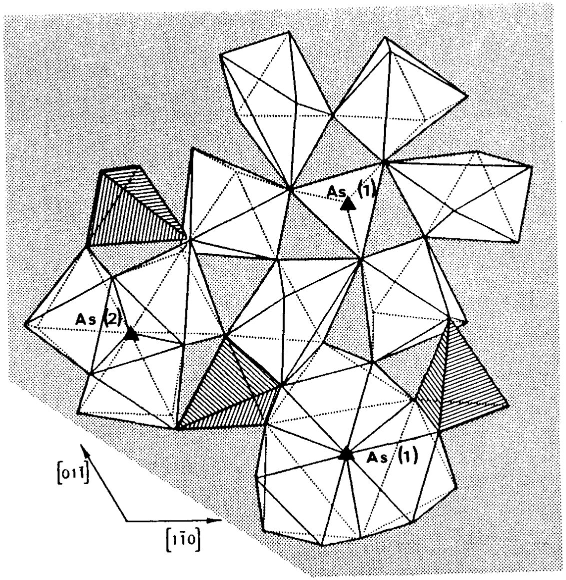

Fig. 2. $Hg_4As_2I_3$-Projection of a slab along [111]. Organisation of octahedra and tetrahedra around threefold-axes.

and Hg is equal to 2.82 Å. On the contrary, Hg when it is in octahedral coordination often forms longer Hg – I distances: for example, 3.301 and 3.341 Å in $Hg_2PbI_2S_2$ (Blachnik, Buchmeier and Dreisbach, 1986), rather indicating a ionic character of the corresponding bond since the sum of ionic radii for I^- and Hg^{2+} is 3.22 Å (Shannon, 1976). All these values reveal that in $Hg_4As_2I_3$ the chemical bond Hg – I has probably a iono-covalent character.

An attractive manner of describing the structure of $Hg_4As_2I_3$ is to consider a framework built only from 2 anionic polyhedra around Hg atoms: tetrahedral for Hg(1) and octahedral for Hg(2). Hg(1) has 3 I atoms and one As(1) as nearest neighbours; 3 other I atoms stand further away (Table 3). Consequently, one can consider that Hg(1) is located at the centre of a tetrahedron whose apices are 3 I and one As(1). In the same way, Hg(2) can be viewed at the centre of a flattened octahedron whose apices are 4 I and 2 As. The 4 I atoms build a plane trapezium, one As(1) and one As(2) being located on both sides. The organisation of these polyhedra, where Hg occupy the central part, in a plane parallel to (111) leads to a single slab, shown in Figure 2. Around each threefold axis, 3 units of polyhedra (U_1, U_2, U_3) can be seen: one block (U_1) of 3 octahedra sharing edges around As(1), a second block (U_2) of 3 octahedra sharing edges around As(2), and a set (U_3) of 6 octahedra sharing corners around a tetrahedron $Hg(1)As(1)I_3$. These 3 units are linked through 3 tetrahedra (hatched area). Thus, along each threefold axis ⟨111⟩, takes place a sequence of these 3 units, the set U_3 linking the two blocks U_1 and U_2. This sequence, repeated by means of symmetry centres, forms a column along the axis. Finally, the structure of $Hg_4As_2I_3$ can be viewed as an overlapping of such columns, in the 4 diagonal directions of a cube. One must point out the role of As whose strong bonds As – As and As – Hg ensure the cohesion of the whole structure.

The succint studies (Rebbah 1980) of the electrical properties of the phases of the system Cd – As – I and especially of the semiconductor $Cd_4As_2I_3$ suggest that $Hg_4As_2I_3$ could be strongly compensated, if one takes into account the analogy between mercury and cadmium. However the electrical behaviour of those materials is by far not understood and a careful study of their properties should allow to determine the role played by the short As – As bounds which may induce the appearance of bound donor states.

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