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Peter A. Beckmann
Bryn Mawr College, pbeckman@brynmawr.edu

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Department of Physics, Bryn Mawr College, 101 North Merion Avenue, Bryn Mawr,
Pennsylvania 19010-2899, USA

Lead Iodide (PbI_2) is an important inorganic solid for both basic scientific research and possible technological applications and in this brief review we discuss the structure of PbI_2. Although the basic structure is a simple I-Pb-I layered structure with a $[PbI_6]^{4-}$ near-octahedron being the basic building block, there are many ways of stacking the layers which results in many polytypes. We present 20 of the 23 entries for the structure of PbI_2 from the Inorganic Structural Database and order them by polytype. This represents more than 80 years of crystallographic research in the structure of this compound. We present a simple way to view the 2H, 4H, 6H, and 6R polytypes and extend the procedure to higher-order polytypes. We note a relationship, not generally appreciated, between the distortion of the near $[PbI_6]^{4-}$ octahedrons and the polytype. We suggest that the significance of vacancies has only recently been appreciated. We suggest that small discrepancies in structure determination are probably due to different distributions of vacancies and that there are, in practice, very many structures for macroscopic or even mesoscopic samples of a given polytype when vacancies are considered.

1 Introduction

Lead iodide (PbI_2) is a fascinating and much-studied solid. It has emerged as an important basis for quasi two-dimensional anisotropic semiconductors. It exists in many crystal structures or polytypes, all of which involve I-Pb-I sandwiches stacked in a variety of ways. This short review has three purposes. First, we review basic properties of the structure of PbI_2 and discuss the basic differences between the polytypes. (The same comments will apply to CdI_2.) In doing so we present a simple and convenient procedure for seeing the differences between the polytypes. Second, we review and bring together some aspects of the structure possibly known by many, but not generally appreciated or, at least, not discussed in the considerable literature concerning the structure of PbI_2. Here, we also suggest that if vacancies in the structure are considered, then one might want to think of PbI_2 as having an infinite continuum of structures. Third, 21st century computer software and the use of color in online viewing allow for a very visual presentation which makes subtle differences in structure clearer.

2 The Importance of PbI₂

As a quasi two-dimensional ionic semiconductor, PbI_2 has become both a model system for theorists and experimentalists and a practical and technologically important system for experimentalists and engineers. I call PbI_2 a quasi two-dimensional system because the I-Pb-I sandwich really is a three-dimensional system. The direction perpendicular to the I-Pb-I sandwich contains three planes of atoms and charge carrier dynamics can have several quantum states whose labels refer to dynamics in this direction. This is to be contrasted with true two-dimensional graphene where charge carrier dynamics involving the plane parallel to the covalently bonded carbon atoms can be pinned to the ground state, thus effectively eliminating that dimension in a meaningful quantum description. The references in this review are not meant to be exhaustive but contain enough recent studies to allow the reader to follow any research paper trail.

PbI_2 is used to study cluster formation [1, 2] and to study thin films of various molecules that can be placed between the layers (intercalation) [3-5]. It is a candidate for use in image recording [6]. It has potential applications such as room-temperature photocells, X-ray detectors, and low-energy gamma ray detectors [7]. It is used as a colloidal nanoparticle suspension [8,9], it is used for making nanobelt bundles [10], it is used for constructing quantum wells of different sizes using thermal annealing as a control [11], it is used for making quantum dots in solution [1], and it is used in semiconductor applications [12].

As a semiconductor, trapping centers (vacancies), impurities [13], and intercalated molecules [4, 5] can be inserted between the I-Pb-I sandwiches in a controlled manner to induce energy levels in the pure material band gap and thus control the effective band gap which is in the ideal range of 1-3 eV [6]. Very thorough band structure calculations have been made [14] and phonon dispersion calculations have been presented [7, 15]. A very helpful classical spring analogy of vibrational modes in the *z*-direction (perpendicular to the I-Pb-I plane) is available [16]. Raman spectroscopy is used to study PbI_2 particles [5, 17] and differentiate between the polytypes of PbI_2 [16, 18-20]. Acoustic modes and Raman modes in several polytypes have been calculated [21]. The effective electron mass can be very different from the effective hole mass and this is of fundamental theoretical importance [8]. PbI_2 can be embedded in porous silica to study nanoparticles [13]. Indeed, it is a model system for general inquiries involving nanotechnology research [13]. Finally, the synthesis and characterization of solid nanoparticles of PbI_2 has been reported [22].

3   The Basic Structure of PbI_2

The basic structure of PbI_2 involves a layer of Pb atoms sandwiched between two layers of I atoms with this I-Pb-I sandwich being the repeating unit (Fig. 1). Each Pb atom is surrounded by 6 I atoms forming a *near*-octahedral $[PbI_6]^{4-}$ unit (Fig. 2).
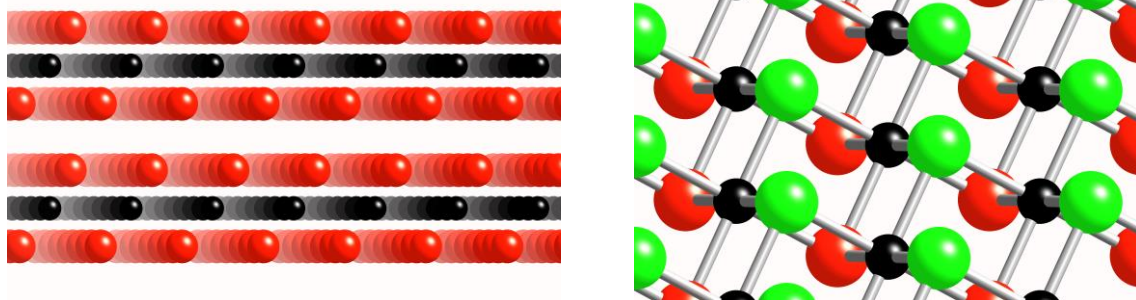

Fig. 1 The basic structure of lead iodide (PbI_2). The smaller black spheres are Pb atoms and the larger red spheres are I atoms. This view results from a rotation of 6° about an axis in the xy plane (perpendicular to the Pb and I planes) from the 110 plane. Coordinates from ICSD 068819 which are from [23].

Fig. 2 A single I-Pb-I layer of PbI_2 with the I atoms in one plane colored red and those in the other plane colored green. Pb atoms are colored black. The "bonds" in this picture are to guide the eye and indicate the near-octahedral $[PbI_6]^{4-}$ units. Coordinates from ICSD 068819 which are from [23].

Most presentations of the PbI_2 structure refer to PbI^{2+} and I^- ions rather than atoms. However, the interactions within the I-Pb-I sandwiches are not primarily ionic. There is considerable electron density between the atomic cores within the sandwich and using somewhat older procedures to define "ionicity" and "covalency," the intralayer interactions are more covalent than ionic [24]. The electron density between the layers is very low resulting in very weak interactions between the sandwiches [25]. This results in the many polytypes and complicated phase changes among the different polytypes [23]. Using traditional terminology, the interlayer interactions might be best described as Van der Waals interactions.

All figures in this review were made with CrystalMaker [26], some using depth fading for clarity. All structures are from the Inorganic Crystallographic Structure Database (ICSD) [27] and are listed in Table 1. We include the entries beginning with the important 1959 work of Richard Mitchell [28] who seems to be the first person to unambiguous identify the particular polytypes. We do not include three earlier works; ICSD #030347 [29] from 1926, #052370 [30] from 1929, and

#077324 and #0077325 [31] from 1943. We acknowledge these early pioneers and can only imagine the effort it took to get a structure in those days. But they were unable to identify particular polytypes (which had not yet been defined anyway!) and, understandably, some of the structures may not be as accurate as later works.

Table 1: X-ray diffraction studies of PbI₂

ICSD #	ref	year	Pb-I (nm)	ϕ (deg)	Z	poly-type	a & b (nm)	c/Z (nm)
024262	28	1959	0.322	0.22	1	2H	0.4557	0.6979
042013	38	1975	0.323	0.21	1	2H	0.4557	0.6979
068819	23	1990	0.323	0.16	1	2H	0.45580(5)	0.6986(3)
024263	28	1959	0.322	0.20	2	4H	0.4557	0.6979
024265	28	1959	0.322	0.20	3	6H	0.4557	0.6979
024264	28	1959	0.321	0.40	3	6R	0.4557	0.6979
060327	35	1985	0.316	2.4	4	8H	0.4557	0.69790
023762	42	1970	0.323	0.23	5	10H	0.4557	0.6979
108927	33	1973	0.316	2.4	6	12H	0.456	0.6978
108914	43	1976	0.315	4.5	6	12R	0.456	0.6978
024266	28	1959	0.321	0.08/0.66	6	12R	0.4557	0.6979
042014	38	1975	0.325	-1.1	6	12R	0.4557	0.6978
060186	40	1976	0.316	2.4	6	12R	0.456	0.6979
023763	42	1970	0.322	0.08	7	14H	0.4557	0.6979
108906	43	1976	0.316	2.4	9	18R1	0.456	0.699
108913	43	1976	0.306	6.5	9	18R2	0.456	0.620
023764	42	1970	0.323	-	10	20H	0.4557	0.6979
042510	35	1985	0.316	2.4	12	24R	0.4557	0.6979
060328	35	1985	0.316	2.4	15	30H	0.4557	0.6979
042511	35	1985	0.316	2.5	18	36R	0.4557	0.6979

There are many polytypes of PbI₂, each having different departures from the near octahedral $[PbI_6]^{4-}$ arrangement [32] (which seems not generally well known) and differences in the manner in which the I-Pb-I sandwiches are stacked, these differences being the origin of the names of the polytypes. As of 1975, 40 polytypes had been reported [33] and by the mid 1980's, the structure of 17 had been determined [34, 35]. PbI₂ has the same general structure as CdI₂. By the mid 1980's 152 polytypes of CdI₂ were known [34].

Some interesting general features emerge from Table 1. First, to two significant figures, the Pb-I distance is 0.32 nm and independent of polytype. There is a slight tendency for this distance to increase with the number of sandwiches in the unit cell but perhaps saying this really is overanalyzing the X-ray diffraction data. The angle ϕ in Table 1 is defined and discussed below. It characterizes the departure from the ideal octahedral structure of the $[PbI_6]^{4-}$ unit. We define the number of I-Pb-I layers in the unit cell as Z. The size of the *reduced* unit cell; a, b, and c/Z is remarkably independent of polytype. This says that regardless of the differences in the structures among the various polytypes, the *average* atom-atom distances, plane-plane distances, etc. do not change. The I-Pb-I layer is approximately 0.7 nm think, the distance between I atoms in neighboring sandwiches is 0.42 nm and distance between I-I planes in different sandwiches is 0.35 nm. As a reference, the I-I distance in gaseous I_2 is 0.27 nm [36].
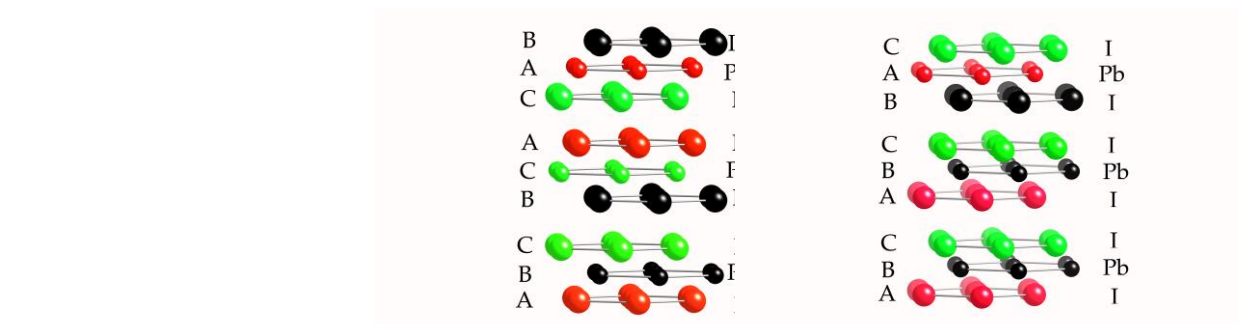
4   The 2H, 4H, 6H, and 6R Polytypes of PbI_2

We choose four polytypes of PbI_2 as examples of the differences between polytypes. Table 1 goes up to 30H and 36R. The nomenclature is due to Ramsdell [37]. The number can be taken as the number of I-Pb-I sandwiches, which is Z in Table 1, or twice the number of I layers. The letter (H for hexagonal and R for rhombohedral) refers to the Bravais lattice related to the stacking arrangement, not to the unit cell. All the unit cells are of the hexagonal lattice type.

The simplest polytype is the 2H structure shown in Fig. 3 in a manner that will be helpful is portraying more complex polytypes. This is the ABC stacking found in elementary textbooks. (If all the atoms were the same type and the CA inter-sandwich layer distance were the same as the AB and BC intra-sandwich layer distances, it would be a face-centered cubic structure.) Every plane of I and Pb atoms is an identical series of triangles or overlapping hexagons (whichever you prefer). In the 2H polytype these planes of Pb and I atoms are displaced with respect to each other as indicated in Fig. 3.

Fig. 3 The ABC structure of the 2H polytype of PbI_2. For convenience, one layer of I atoms is red and the other layer is green, as in Fig. 2. The hexagons and triangles in the plane and the lines in the *z*-direction are guides for the eye. Coordinates from ICSD 068819 which are from [23]. (a) Two identical sandwiches explicitly showing the ABC structure. (b) One sandwich using just hexagons to represent the structure. This is identical to the bottom sandwich in all three parts of Fig. 4.
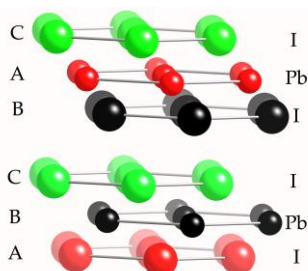
Fig. 4 The structures of the (a) 4H, (b) 6H, and (c) 6R polytypes of PbI₂. The bottom sandwich is taken to be the same in each case and is the same as the 2H polytype in Figure 3. The colors refer to atom *positions*, not atom *types*.

Figure 4 uses the hexagon representations to show how the sandwiches stack for the 4H, 6H, and 6R polytypes. Note that the colors in this figure refer to *position*, not to *atom* type. The two-sandwich 4H ABC BAC structure in Figure 4a is unique. If the top sandwich were taken to be ACB instead of BAC then the new structure is the same as the old structure turned upside down. From a purely geometric perspective, there are ten unique three-sandwich possibilities but only the two presented are found in nature (so far). For 4 or more sandwiches, those whose structure has been determined are indicated in Table 1. Polytype 2H is the stable form when crystals are grown at room temperature and polytype 12R is the stable form when crystals are grown at higher temperatures [38]. Crystal growth conditions are very important [18]. The great variety of ways of preparing PbI₂ can be found elsewhere [19, 22, 39, 40, and references therein].

5 The Geometry of the Near-octahedral Structure of the [PbI₆]⁴⁻ Groups

The [PbI₆]⁴⁻ groups are not exact octahedrons and the relationship between the departure from exact octahedral structure and polytype is an important part of the structure but has not been discussed in the crystal structure literature. Figure 5 shows the near-octahedron. It is convenient to characterize the departure from a perfect octahedral arrangement by the angles ϕ where the I-Pb-I angles are $90^O + \phi$ [32]. All values of ϕ are 0 for a perfect octahedron. The 180° angles are exact (to within the uncertainties determined by X-ray diffraction) in all structures but one in Table 1 so, excluding this entry, which has no ϕ value indicated, this leaves six potentially independent values of ϕ.
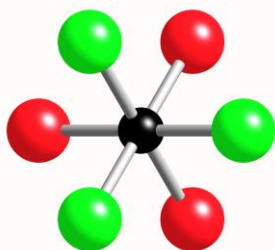

Fig. 5 The near octahedral [PbI₆]⁴⁻. The green I's are in one plane (towards the viewer) of the I-Pb-I sandwich and the red I's are in the other plane (away from the viewer).

The 1990 2H structure [23] shows two values; $\phi = 0.167^O$ for two opposite [red I-Pb-green I] angles in figure 5 and $\phi = 0.161^O$ for the other four [red I-Pb-green I] angles. ([red I-Pb-green I] means the I's are in different planes in the same sandwich.) Preserving the 180° angles means that $\phi = -0.167^O$ for one [red I-Pb-red I] and one [green I-Pb-green] angle and $\phi = -0.161^O$ for two [red I-Pb-red I] angles and two [green I-Pb-green I] angles. The same is true for the 1975 2H [38] structure where the angles are 0.203^O and 0.209^O and the 1959 2H structure [28] where the angles are 0.227^O and 0.221^O. One can quibble over the number of appropriate significant figures but the point to be made is that the three independent studies separated by 31 years show the octahedron as being stretched along the axis perpendicular to the planes and they find it has the same type of distortion (the two slightly different angles) in the plane. And, the angles determined in the three studies do not differ to three significant figures; all [red I-Pb-green I] angles are 90.2^O and all [red I-Pb-red I] and [green I-Pb-green I] angles are 89.8^O. We can find no discussion of this phenomenon in the literature but it makes sense if there is very little electron density between the sandwiches [25] and the sandwich-sandwich interaction is of the Van der Waals attractive type. One wonders if *ab initio* electronic structure calculations are able to use enough atoms in the calculation to show this distortion.

The 1959 4H structure [28] shows the two sandwiches stretched very slightly with three distinct angles in the vicinity of $\phi = 0.08^O$. The 1959 6H and 6R structures [28] both show the sandwiches stretched by approximately $\phi = 0.2^O$ There are four determinations of the 12R structure in Table 1 and the departures from octahedral structure are somewhat different. Two show the sandwiches stretched, one shows the sandwiches squashed and one shows two alternating layers with different stretching angles. These polytypes are extremely difficult to make and the most reasonable explanation for the slight differences in structure is that the structures really *are* very slightly different. The most likely candidate for this is the different concentration of vacancies.

6   The Importance of Vacancies

We draw attention to the beautiful 1990 study by Palosz, Steurer, and Schulz [23]. The authors tell us that vacancies in the 2H and 4H structures take up 15-20% of the sites and can change the structure. One can only imagine the role of vacancies in higher Z polytypes. It seems reasonable that this has very important consequences for semiconductor properties. The results of any experimental technique that measures "hopping" motions like nuclear magnetic resonance relaxation [41] and luminescence studies [6] will depend greatly on not only the overall density of vacancies, but their distribution. It seems logical that this could result in a wide distribution of local structures. An X-ray diffraction study involves a very large ensemble of electron-photon interactions in a small single crystal and will not be sensitive to vacancies unless they happen to have a significant effect on the overall structure, as opposed to just the local structure. But this could explain the differences among structures determined by X-ray diffraction in the cases where the differences between geometric parameters are deemed greater than experimental uncertainties.

7   Summary

PbI_2 is a theoretically interesting and practically important pseudo two-dimensional solid. In addition, the layered structure makes it an ideal candidate for students of the physical sciences to investigate a larger class of materials; those that always have the identical very small (one atom!) repeating unit in the plane and a large variety of arrangements (polytypes) in the way in which the planes can stack. We have reviewed the simplest few polytypes of PbI_2 in a manner that hopefully makes it clear how to more easily understand the more complicated polytypes. We have tried to bring to the forefront the fact, not generally appreciated, that the $[PbI_6]^{4-}$ units are not perfect octahedrons and their departure from a perfect octahedral arrangement is a clue for the theorist who wants to understand (and explain to the rest of us) the origins of the various stacking arrangements found in nature.

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