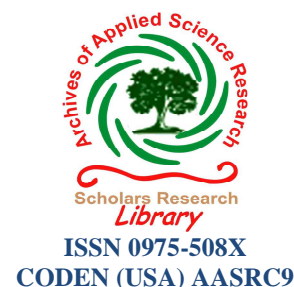




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## Growth and formation of polytypes in crystals of cadmium iodide

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### ABSTRACT

Lot of experimental work has been done on the polytypism of  $CdI_2$  and a vast structural data is now available, It is a theoretical fact that all polytypes consist of basic structures 2H and 4H. In this paper, it has been established that how the impurities present in the starting material are responsible for “why some of the structures have not been observed experimentally”. Further, it is suggested that vacancies also play a role in the formation of polytypes.

**Key words:** cadmium iodide, polytypes, impurities, phase transformations, Inorganic crystal structure.

### INTRODUCTION

Cadmium iodide crystals can be grown from solution, vapor and gel. Lot of work has been done on the growth and structure determination in the above compound and enough data is available that can help in understanding the phenomenon of polytypism. More than 250 polytypes have been observed so far and crystal structure of nearly 190 polytypes have been worked out [1]

The cadmium iodide crystals in which a large number of higher polytypes have been reported and structures worked out have been mainly grown from solution (In the melt-grown crystals only 4H structure has been reported. Similarly very few polytypes have been observed in vapor grown crystals). In the case of solution growth, there are a large number of molecules available in solution, that contribute to formation of the crystal. Initially when the supersaturation is high, rate of growth being fast, statistically, any polytypic structure can be formed and there is every possibility of formation of higher polytypes.

### 2. Theoretical Models

Wahab and Kant [2] have proposed that 2H and 4H are the most stable polytypes of  $CdI_2$  and they act as the basic structural units for the formation of higher polytypes. The details of these structures are given in the Table 1.

Table 1. Dimensions of basic units of  $CdI_2$

Polytype	Zhadnov sequence	a (nm)	b (nm)	c (nm)
2H	11	0.424	0.424	0.683
4H	22	0.424	0.424	1.366

Further a statistical thermodynamic and growth restriction (STGR) model [3] suggests that all the higher polytype can be formed by the combination of 2H and 4H units as

$$NH = n_1(2H) + n_2(4H)$$

Where  $n_1$  and  $n_2$  are numbers of 2H and 4H units.

All the structures that have been experimentally observed and *many of those not observed yet*, can be worked out theoretically by the above mathematical relation.

Till today, a large number of polytypes have been observed experimentally and more than 2000 polytypes might be explored by various workers. It is surprising that in spite of such a large number of experimental observations, so many possible structures are yet to be observed.

### 3. Explanation

One of the basic reason behind it is the presence of impurities in the starting material. During the period 1965 to 1985, over a period of 20 years, a lot of work has been done on the polytypism of  $\text{CdI}_2$  but nobody has discussed about the content of impurities present in the starting material.

The  $\text{CdI}_2$  structure consists of different stackings of  $\text{CdI}_2$  sandwiches in each of which a layer of Cd ions is sandwiched between two close packed layers of iodine ions.

The binding within a sandwich is quite strong and the two sandwiches are bounded together with weak van der Waals forces.

Each Cd atom is surrounded by 6 I atoms forming a near octahedral  $[\text{CdI}_6]^+$ . One such distorted octahedron is shown in Fig 1. Ideally  $\theta$  should be zero for a perfect octahedron but in the structure determined by various researchers the reported value of  $\theta$  ranges from  $0.51^\circ$  to  $0.61^\circ$ [4] The variation in  $\theta$  must be due to the presence of impurities sitting in the voids. The impurities present in the voids disturb the cadmium atoms and if the cadmium does not lie at the centre of symmetry of the octahedron, it may create static dipoles arising from anisotropic polarization of iodine atoms which in turn distort the octahedron. The distortion of octahedron, in turn, will disturb the iodine planes and all the atoms of iodine layers may not be in the same plane in a sandwich.

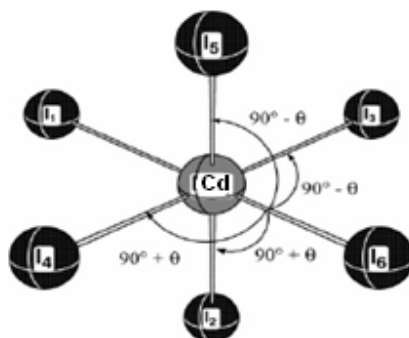


Fig. 1 The near octahedral  $[\text{CdI}_6]^+$ . The angle  $\theta$  is a measure of deviation from octahedral symmetry

Thus due to presence of impurities, the iodine layers of adjacent sandwiches are not as close packed as it should be in the absence of impurities (ideal case of close packing). Wahab and Trigunayat [5] have reported that these sandwiches are prone to translation and rotation due to weak binding and are responsible for the formation of polytypes. But in the presence of impurities the planes of iodine are uneven. If the degree of impurity is high, that may cause excessive distortion of octahedron which may make the iodine planes more uneven, that may lead to interlocking and blockade of iodine planes which in turn hamper the movement of sandwiches and in turn formation of polytypes. Thus formation of polytypes depends upon the degree of impurities present in the starting material.

Further theoretically, under ideal condition of close packing the energy of crystal does not depend upon stacking disorder and any arrangement is equally probable. We know that  $F = U - TS$ , for  $F$  to be minimum  $S$  should be maximum i.e. maximum disordered state of the system. But it is not so, all higher polytypes are not disordered, as many higher polytypes observed experimentally are well ordered. Thus impurities present in the starting material are supporting the formation of polytypes.

From the above, it is clear that impurities play a dual role. Depending upon its degree, it hinders the formation of polytypes and supports as well.

### DISCUSSION

A number of studies are of the opinion that thermodynamic considerations also do hold for the formation of polytypes. For example, till now an attempt to convert a polytypic 4H structure of CdI<sub>2</sub> into any other structure has completely failed. (4H being stable structure when grown at room temperature or at high temperature) whereas for polytypic lead iodide crystals grown at room temperature (from gel), structure 2H is formed and when grown at high temperature (from melt) structure 12R dominates even though both CdI<sub>2</sub> and PbI<sub>2</sub> are isostructural in nature [6].

In addition to thermodynamic considerations, polytype formation and phase transitions can be substantially aided by other factors in polytypic materials. The interesting 4H→2H transformation observed in the crystals of PbI<sub>2</sub> upon irradiation to Ruby Laser pulse is noteworthy [7]. It is believed to result from weakening of interlayer bonds by excitation of electronic sub systems in the structure. In this case, the governing factor has been the external pulsed laser radiation.

The crystals, in general, owe the regularity of their internal structure to the existence of atomic forces of attraction and repulsion, which exercise their influence over a short range ~ 20 Å. The observed cell heights up to thousands of angstrom units implies certain external agencies like (dust particles, lattice vibrations, vibration entropy, electron density) are also operational in their creation.

In most of the earlier studies made on CdI<sub>2</sub> crystals, the role played by the vacancies was being ignored. The degree and the distribution of vacancies is also an important parameter to be looked for the study of polytypism in the CdI<sub>2</sub> crystals. It is expected that atoms surrounded by a large number of vacancies should be considered to be more mobile than others along the layers as well as in the direction perpendicular to them. In a recent theoretical investigation, Ito et. al. [8] using ab initio pseudo potential approach have calculated that in the case of polytypic SiC with Si vacancy, crystals prefer 6H structure and 4H structure is favored in C vacancy condition. Thus concluding that vacancy formation in SiC plays an important role in stabilizing a certain structure amongst various metastable structures. Similar calculations have also been made on ZnS polytypic crystals [9]. Some experimental work is being done on similar looking polytypic crystals PbI<sub>2</sub> [10].

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