Polytypism in Melt-Grown Crystals of CdI_2, PbI_2 and $CdBr_2$

By S. K. Chaudhary

Department of Physics, University College, MD University, Rohtak, India

and G. C. Trigunayat

Department of Physics and Astrophysics, University of Delhi, Delhi-7, India

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Abstract

Single crystals of polytypic materials CdI_2, PbI_2 and $CdBr_2$ have been purified and grown using zone-refining and Bridgman–Stockbarger techniques. The crystals have been investigated by X-ray diffraction to find out how the impurities influence the growth and polytypism of the crystals. Only small-period polytypes have been found to exist in the three materials. The CdI_2 and $CdBr_2$ crystals consist only of their common room-temperature modification, but the PbI_2 crystals consist of more than one other small-period modification. Further, significant structural transformations have been observed in the PbI_2 crystals stored for long periods at room temperature. The X-ray photographs of CdI_2 and PbI_2 crystals are free from streaking and arcing. The results have been discussed in terms of creation and expansion of stacking faults.

Introduction

There are many physical factors associated with the growth of polytypes and a large number of explanations have been put forward from time to time to account for the phenomenon (Trigunayat & Verma, 1976). These have been based on diverse considerations like temperature, rate of crystallization, presence of impurities, creation of dislocations during growth, thermodynamical factors, internal rotations, electron energy *etc.* Of these the presence of impurities is a prominent one.

In the past three decades a considerable amount of work has been carried out on the polytypism of CdI_2, PbI_2 and $CdBr_2$ crystals grown from solution, vapour or gel, but little attention has been paid to the study of melt-grown crystals. Since the zone-refining technique of melt growth permits both material purification and crystal growth, it was employed for growing single crystals of these compounds for investigation by X-ray diffraction of how the impurities influence the growth and polytypism of the crystals.

Experimental

The zone-refining system, employing two separate heat zones, is schematically shown in Fig. 1. The final crystal ingot measured nearly 10 cm in length and nearly 6 mm in thickness. The details of the growth process of CdI_2 and PbI_2 crystals have been described earlier (Chaudhary & Trigunayat, 1982, 1983). With increasing purification of the crystal ingot, its transparency gradually increased and its sticking to the walls of the boat decreased. Indeed, the extents of transparency and sticking could be taken as reliable indices of the degree of purification and the single-crystal formation of the material.

On account of the high vapour pressure of $CdBr_2$ at its melting point, which is about seven times the corresponding values for CdI_2 and PbI_2, this material tended to evaporate. Therefore, for growing the single crystals of this compound, the Bridgman–Stockbarger technique was employed. The purification of the material was achieved by repeated recrystallizations. The final crystal ingot measured nearly 8 cm in length and nearly 3 cm in diameter. The details of the growth process have been given elsewhere (Chaudhary & Trigunayat, 1986).

To facilitate mounting and adjustment on the X-ray diffraction camera, long pieces of thickness 0·6–0·8 mm were first cleaved from a crystal ingot and then cut into small pieces of length 5–8 mm. The optically perfect crystals were subjected to X-ray diffraction for determining their structure and perfection. For this purpose, *a*-axis oscillation photographs of the crystals were obtained. The range of oscillation in the case of CdI_2 and PbI_2 was kept as 25–40° (*i.e.* the angle between the direction of incident X-ray beam and the *c* axis varied between 25 and 40°) and in the case of $CdBr_2$ as 19–34°. The purpose of choosing these ranges of oscillation was to record a large succession of 01.*l* reflections, which are ideally suited for obtaining the necessary structural information.

The crystals of CdI_2, PbI_2 and $CdBr_2$ are known to exhibit syntactic coalescence of polytypes. Therefore, diffraction photographs of the two basal faces of each crystal were separately obtained. Further,

because of the large size of the crystals and the fact that these crystals also sometimes exhibit parallel growth of two or more polytypes on the same face, photographs were taken from at least four different parts of the same face in the region of back reflection.

Results

CdI_2

The formation of single crystals necessitated nearly eight zone passes (Chaudhary & Trigunayat, 1982). Six crystals, which involved more than 50 X-ray diffraction photographs, were investigated. All the photographs exclusively showed the diffraction spots of the common polytype $4H$. One such photograph is reproduced in Fig. 2.

The crystals did not show any features of streaking or arcing on their X-ray photographs.

PbI_2

For X-ray diffraction work, the crystals were categorized as follows: (a) somewhat impure crystals (6–8 zone passes); (b) pure crystals (12–14 zone passes); (c) very pure crystals (20 zone passes).

Nine crystals were examined from category (a), involving 75 X-ray diffraction photographs. Of these 51 photographs (i.e. 68%) showed the presence of $12R_0/12R_R/(12R_0+12R_R)$ (Fig. 3). The same polytypes appeared in the remaining cases, but in coalescence with the polytype $4H$ (Fig. 4).

Another six crystals from category (b), involving 46 X-ray diffraction photographs were investigated. 36 photographs (i.e. 78%) showed the occurrence of polytypes $12R_0/12R_R/(12R_0+12R_R)$ and eight photographs (i.e. 18%) showed the coalescence of
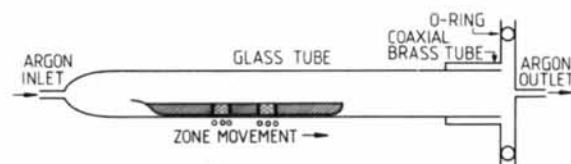
these polytypes with $4H$. Two photographs (i.e. 4%) showed the coalescence of $12R$ and $2H$.

Five crystals from category (c) involved 39 photographs, all but one of which exclusively showed polytypes $12R_0/12R_R$. The one exceptional case showed syntactic coalescence with $4H$.

After crystals had been stored at room temperature for periods extending over 7 months or more, they were again subjected to examination by X-ray diffraction. The information obtained was that (i) the structure of the crystals of category (a), stored for nearly 12 months, did not change; (ii) all but one of the crystals of category (b), stored for nearly 9 months, transformed into $2H$, the most common polytype of lead iodide at room temperature; and (iii) the structures of crystals of category (c), stored for nearly 7 months, also did not change.

Like CdI_2, the PbI_2 crystals too did not show any streaking or arcing on their X-ray photographs.

$CdBr_2$

Eight crystals, involving 58 X-ray photographs, exclusively showed the diffraction spots of $6R$ (obverse and/or reverse; Fig. 5), which is the common polytype of $CdBr_2$ at room temperature. Streaking and arcing were observed in these crystals, but only in a few cases.

Fig. 3. An a-axis 15°-oscillation photograph of a PbI_2 crystal, showing reflections of $12R_R$ and $12R_0$. Other conditions as for Fig. 2. The positions of one reflection each of $12R_R$ and $12R_0$ are indicated by arrows pointing upwards and downwards, respectively.

Fig. 1. Line sketch of the experimental set up for zone refining.

Fig. 4. An a-axis 15°-oscillation photograph of a PbI_2 crystal showing reflections of $4H$, $12R_0$ and $12R_R$. Other conditions as for Fig. 2. The positions of one reflection each of $12R_R$ and $12R_0$ are indicated by arrows pointing upwards and downwards, respectively, and one of the $4H$ positions is shown by a vertical line.
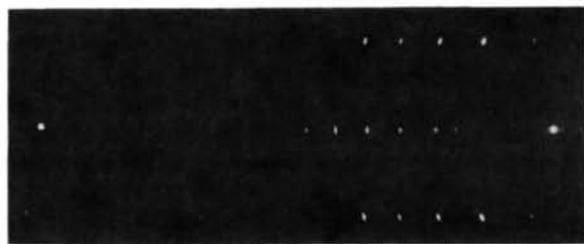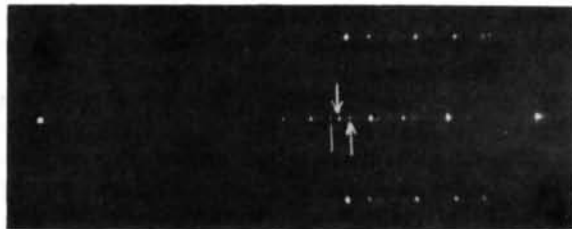

Fig. 2. An a-axis 15°-oscillation photograph of a CdI_2 crystal, showing the reflections of the most common polytype $4H$. Cu $K\alpha$ radiation; 3 cm camera.

Discussion

Every polytypic substance is characterized by the existence of a most common polytype whose frequency of occurrence at room temperature is predominantly higher than that of any other polytype. This polytype is invariably a small-period structure, as may be expected on considering the range of influence of interatomic forces. Thus the most common polytypes of the isostructural compounds CdI_2, PbI_2 and $CdBr_2$ are known to be the types $4H$, $2H$ and $6R$, respectively. Since all these compounds have close-packed layer structures, all other polytypes of either of these compounds may be regarded as metastable modifications, having stacking faults in their structures with respect to the stable most common polytype. The metastable character arises from the fact that the close packing of atomic layers leads to negligible differences in the internal energies of the various modifications.

The CdI_2 and PbI_2 polytypes are known to transform into their most common polytypes on prolonged storage of a few months at room temperature (Trigunayat, 1971; Minagawa, 1975). The transformations are believed to be brought about by the movement of edge dislocations, which in turn brings about the elimination of the stacking faults.

CdI_2 crystals

The solid-state structural transformation of all CdI_2 polytypes into the common type $4H$ has been reported in the solution-grown crystals heated for just a few hours around 530 K (Lal & Trigunayat, 1971, 1974) and has been explained as above in terms of the movement of edge dislocations. Thus $4H$ can be regarded as the thermodynamically stable polytype of CdI_2 at high temperature as well, which agrees with the present observation of the sole occurrence of this polytype in the melt-grown CdI_2 crystals. In melt growth, the temperature of the growing crystal is high, *viz* just below the melting point of the material. So enough energy is available for the move-

ment and arrangement of stacking faults to bring about the transformation of a metastable polytype structure into a common structure, which has the minimum energy configuration at that temperature.

PbI_2 crystals

However, in PbI_2, of which the most common polytype is $2H$, the stable polytypic modification at high temperatures has emerged as a different one, *viz* $12R$, in the present investigation. This agrees with the earlier observations made on structural transformations at high temperatures in gel- and vapour-grown PbI_2 crystals (Prasad & Srivastava, 1974; Minagawa, 1975). The following conclusions regarding the growth of PbI_2 polytypes can be drawn from the present work:

(1) The melt-grown PbI_2 crystals only contain small-period polytypes.

(2) $12R$ may be regarded as the thermodynamically stable high-temperature modification and $2H$ as the stable room-temperature modification of PbI_2.

(3) Impurities are responsible for the formation of the small-period polytype $4H$ of PbI_2. The more pure the material, the smaller is the chance of formation of $4H$.

(4) The presence of impurities also influences solid-state structural transformation of the polytypes at room temperature.

(5) Allowing for the observed effect of impurities on polytype growth, the occurrence of $12R$ polytypes in coalescence with $4H$ may be regarded as a common feature of melt-grown PbI_2 crystals. This may be usefully compared with the observations made in the earlier voluminous work on a very large number of gel-grown PbI_2 crystals, in which the syntactic coalescence $(nH + 3nR)$ was found to occur very frequently (Hanoka & Vand, 1968; Chand & Trigunayat, 1975).

Prasad & Srivastava (1974) have reported that the gel-grown $2H$ polytype of PbI_2 transforms into $12R$ at high temperatures. In a study of ten PbI_2 crystals grown from the vapour phase, Minagawa (1975) found that they all consisted of polytype $12R$, with three of them containing a small proportion of $4H$. These findings support our conclusion that $12R$ is to be regarded as the stable form of lead iodide at high temperatures. Interestingly, this result is at variance with the richly polytypic isostructural compound cadmium iodide, in which $4H$ has been found to be the stable form both at room temperature and at high temperatures (Trigunayat & Verma, 1976).

Some results have been reported on the effect of impurities on the polytypism of SiC, ZnS, CdI_2 and PbI_2. Lundqvist (1948), employing spectrochemical and X-ray powder analysis and Hayashi (1960), employing chemical and X-ray powder analysis, concluded that the formation of small-period polytypes $6H$, $15R$ and $4H$ was related to their aluminium

Fig. 5. An a-axis 15°-oscillation photograph of a $CdBr_2$ crystal showing reflections of $6R_R$ and $6R_0$. Other conditions as for Fig. 2. The positions of one reflection each of $6R_R$ and $6R_0$ are indicated by arrows pointing upwards and downwards, respectively.

content. However, in a subsequent extensive study, Knippenberg (1963) failed to observe such a correlation for SiC crystals grown with different proportions of aluminium at a constant temperature, which led him to conclude that the suspected impurity-structure correlation might really be a temperature-structure relationship. Later, Bootsma, Knippenberg & Verspui (1971) inferred that the nature and amount of impurity content, temperature and pressure had a combined influence on the formation of the common SiC types $6H$, $15R$ and $4H$; for higher polytypes, defects in the initial nuclei were also held responsible. Kozielski (1976) has stated that under doping with Al at a concentration of 0·01% the structure of ZnS crystals is transformed from $3C$ through intermediate polytype structures into $2H$. The transformation broadly follows the scheme $3C \rightarrow 10H \rightarrow 6H \rightarrow$ disordered structures $\rightarrow 2H$. Jain & Trigunayat (1980) have reported that in solution-grown CdI$_2$ crystals the presence of dust particles promotes the incidence of polytypism. Similarly, Chand & Trigunayat (1977) have found that the addition of AgI as impurity in the growth of PbI$_2$ crystals from gel promotes the incidence of polytypism.*

In melt growth, when the starting material is impure, the impurities may lead to constitutional supercooling (Lawson & Nielson, 1958). The impurities rejected by the growing surface form a layer immediately in front of the surface. Because of the impurity content the freezing point of the layer is lower than the rest of the melt. At the freezing point of this layer, therefore, part of the melt may be supercooled, leading to irregular crystal growth and subsequent production of dislocations.

The most likely slip plane in a crystal is always that in which the atoms are maximum close packed. The direction of the slip also follows the direction of close packing of the atoms. In the close-packed PbI$_2$ structures the most probable slip planes and slip directions are (0001) and $\langle 11\bar{2}0 \rangle$, respectively. Consequently, the edge dislocations created due to the presence of impurities and lying in the basal plane will most probably have Burgers vectors of the type $a/3\langle 11\bar{2}0 \rangle$. Such a dislocation can further dissociate into two half dislocations,

$$a/3\langle 11\bar{2}0 \rangle = a/3\langle 10\bar{1}0 \rangle + a/3\langle 01\bar{1}0 \rangle,$$
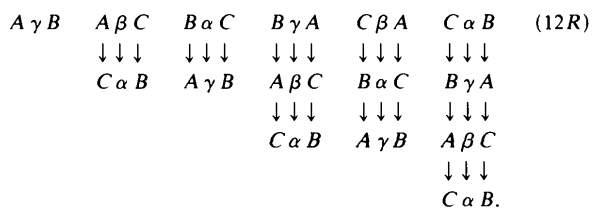
i.e. a dislocation on a (0001) plane is transformed into what is called an extended dislocation, which

consists of two partials connected by a strip of fault. Partial dislocations of the above type can also be created independently. The glide motion of these partials extends the region of faulting along the basal plane, so much so that the entire plane can become faulted, giving rise to a stacking fault at the position of the plane. In this manner, stacking faults can be created at random positions inside the structure. The faults do not involve any distortion of the nearest-neighbour bonds, such as in a grain boundary, and they possess extremely low surface energies. Consequently, a polytype can be derived from another given polytype structure by introduction of suitable stacking faults into the latter, without causing an appreciable change in the free energy of the structure.

However, for sustaining the periodicity of the structure of the polytype, it is necessary that a mechanism exists for regular repetition of the faults that are created. The existence of large screw dislocations has been visualized for this purpose in ZnS crystals (Alexander, Kalman, Mardix & Steinberger, 1970) and in PbI$_2$ crystals (Chand & Trigunayat, 1977). But unlike the ZnS crystals in which the polytypes are formed during the cooling-down period of the furnace (Mardix & Steinberger, 1970) and PbI$_2$ crystals grown at room temperature (Chand & Trigunayat, 1977), the present crystals have been grown at a high temperature, around 670 K, thus rendering enough thermal energy available for a large screw dislocation to dissociate into smaller ones. Such screw dislocations of small Burgers vector would lead to the creation of polytypes of small periods.

From empirical considerations, the polytype $12R$, which essentially has just a four-layer periodicity on account of its rhombohedral structure, thermodynamically appears to be the most stable structure at the prevalent high temperature. However, under favourable conditions, it may sometimes transform into the closely allied four-layer periodicity structure, $4H$. The scheme of introduction of stacking faults involved in the conversion of polytype $12R$ into $4H$ is probably as follows:

$$
\begin{array}{cccccc}
A\,\gamma\,B & A\,\beta\,C & B\,\alpha\,C & B\,\gamma\,A & C\,\beta\,A & C\,\alpha\,B \quad (12R) \\
& \downarrow\downarrow\downarrow & \downarrow\downarrow\downarrow & \downarrow\downarrow\downarrow & \downarrow\downarrow\downarrow & \downarrow\downarrow\downarrow \\
& C\,\alpha\,B & A\,\gamma\,B & A\,\beta\,C & B\,\alpha\,C & B\,\gamma\,A \\
& & & \downarrow\downarrow\downarrow & \downarrow\downarrow\downarrow & \downarrow\downarrow\downarrow \\
& & & C\,\alpha\,B & A\,\gamma\,B & A\,\beta\,C \\
& & & & & \downarrow\downarrow\downarrow \\
& & & & & C\,\alpha\,B.
\end{array}
$$

The arrows denote the layers where the faulting occurs. Thus, one finally arrives at the structure

$$A\,\gamma\,B \quad C\,\alpha\,B \quad A\,\gamma\,B \quad C\,\alpha\,B \quad A\,\gamma\,B \quad C\,\alpha\,B \quad (4H).$$
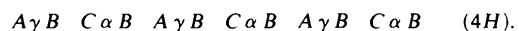
This transformation only involves displacement between I-I layers which, owing to the sandwich structure of PbI$_2$, have bond strength ~ 100 times weaker than the I-Pb bond and hence they are far

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* In the present work, the manufacturers (E. Merck, Germany) of CdI$_2$ had indicated the presence of Fe, Ag, Na and K in the raw material. Atomic absorption spectroscopy tests revealed total absence of Fe and Ag and only a nominal presence ($\ll 1$ in 10^6) of Na and K in the well purified CdI$_2$ crystals. (The proportions of Na and K were found to reduce drastically as the material purification progressed.) Unfortunately, on account of insurmountable experimental difficulties, no similar detection of impurities could be carried out for PbI$_2$ and CdBr$_2$ crystals.

more prone to interlayer displacements than the adjacent I–Pb layers (Wahab & Trigunayat, 1981).

As outlined earlier, the presence of impurities causes localized supercooling in the melt, leading to the consequential production of stacking faults and intrapolytypic conversion of $12R$ into $4H$. It follows that the more pure the material, the less should be the chance of transformation from $12R$ to $4H$, which agrees with our experimental findings. In highly purified crystals obtained after 20 zone passes, the transformation has been observed in just one case out of the 39 cases that were studied.

Minagawa (1975) has reported that seven out of ten crystals of polytype $12R$ examined by him after storage for nearly a month at room temperature transformed into $2H$, which is the well established stable modification of lead iodide at room temperature. Six of the $12R$ crystals had been obtained by annealing gel-grown $2H$ crystals at 420 K and four had been grown from vapour. Minagawa concluded that the $2H$–$12R$ transformation was reversible. He did not investigate the effect of impurities on the transformation. The present finding that both highly pure (batch c) and relatively highly impure crystals (batch a) of $12R/(12R+4H)$ do not transform into $2H$ even after prolonged storage at room temperature is significant, since it clearly outlines the role of impurities in the growth and transformation of polytypes. As mentioned earlier, an intrapolytypic conversion needs nucleation of stacking faults at appropriate positions and their subsequent regular expansion through screw dislocations present in the structure. The necessary energy for this purpose during melt growth is made available through the heating of the material. When the crystals are brought down to room temperature, the stacking faults (with respect to the stable room-temperature phase $2H$) will have negative free energy, which will provide the necessary stimulus for the nucleation and subsequent expansion of the faults for bringing about the observed transformation to $2H$. However, as already described the nucleation of faults needs the presence of impurities. Therefore, in highly pure crystals which are almost devoid of such impurities, no room-tempeature transformations may be expected. On the other hand, in relatively highly impure crystals, the presence of too many impurities will cause excessive production and consequential interlocking and blockage of dislocations, which will hamper both nucleation and expansion of the faults. Thus, only in crystals of 'intermediate' purity may the expected $12R \rightarrow 2H$ transformation at room temperature take place, as actually observed in the present work. This also explains the observed admixture of polytype $2H$ in two cases in the crystals of batch (b). Since the examination of these crystals necessitated taking as many as 46 X-ray photographs, the work was spread over a period of few weeks. Most probably, this time of storage was sufficient for partial intrapolytypic conversion to take place in the two cases. Thus, in these two cases one should not be misled into thinking that the $2H$ phase was formed during melt growth.

CdBr₂ crystals

Mitchell (1962) and recently Mehrotra (1978) have reported the growth of $CdBr_2$ crystals from vapour phase. They have reported that all the crystals were of type $6R$.

Experiments on heating of solution-grown $CdBr_2$ crystals have been conducted by Sharma (1980). It has been reported that when higher unidentified crystals were heated at about 470 K for one hour, they converted to $6R$ (obverse and/or reverse), without any features of disorder on the X-ray photographs. This observation agrees with our results, since a metastable structure formed during melt growth is expected to transform into the stable common polytype $6R$.

Streaking and arcing of reflections

The observed total absence of any features of streaking or arcing in the X-ray photographs of CdI_2 and PbI_2 crystals and their near absence in $CdBr_2$ crystals can be understood as follows. The phenomenon of streaking arises from the existence of random stacking faults in the structure and that of arcing from the movement of edge dislocations into small-angle tilt boundaries (Agrawal & Trigunayat, 1969). In melt growth, a steady supply of thermal energy is available for the necessary movement of dislocations and rearrangement of stacking faults for bringing about the transformation of all metastable polytypic modifications into a perfect polytype structure, having minimum-energy configuration at the prevalent temperature. Complete transformation is achieved in the CdI_2 and PbI_2 crystals, but not so in the $CdBr_2$ crystals, which may be partly attributed to the fact that the latter crystals, having been grown by the Bridgman–Stockbarger method, are not as pure as the former, and partly to the structural characteristic of the $CdBr_2$ crystals that in addition to the close-packed basal planes (0001) there also exist equivalent non-basal close-packed planes $(10\bar{1}2)$ along which slip can occur with equal ease and thus increase the chance of creation of edge dislocations and stacking faults (Agrawal & Trigunayat, 1970). The residual impurities in the crystals act as obstacles to the movement of dislocations and thus hinder the elimination of stacking faults.

To sum up, the growth of polytypes in the melt-grown crystals of CdI_2, PbI_2 and $CdBr_2$ has been found to be governed by both thermodynamical considerations and the degree of impurity content.

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Atom Distributions in Tau-Carbide Phases: Fe and Cr Distributions in (Cr₂₃₋ₓFeₓ)C₆ with x = 0, 0·7₄, 1·7₀, 4·1₃ and 7·3₆*

BY H. L. YAKEL

Metals and Ceramics Division, Oak Ridge National Laboratory, PO Box X, Oak Ridge, Tennessee 37831, USA

Abstract

Mo $K\alpha$ Bragg diffraction data collected from single crystals of the title phases were used in least-squares refinements of structural models that (for $x \neq 0$) included *a priori* distribution parameters for iron on three of the four metal-atom sites of the known $M_{23}C_6$ τ-carbide structure. Conventional data for the crystal with $x = 0.7_4$ were supplemented by synchrotron-radiation (SR) diffraction data collected at energies near Cr K and Fe K absorption edges. Results show that distribution parameters whose differences from chemical-average values have statistical and physical significance can be derived from extensive, precise conventional diffraction data. They demonstrate that iron atoms preferentially substitute for chromium at sites not bonded to carbon atoms; when 30-35% of the sites that are bonded to carbon are occupied by iron, the τ solid solution becomes thermodynamically unstable relative to other phases. Calculations with the SR data sets collected near the Cr K-edge energy suggest a $(\sin \theta)/\lambda$ dependence of the real part of the dispersion correction to the atomic scattering factor for chromium as well as significant departures from the theoretical free-atom calculations for these corrections at $(\sin \theta)/\lambda = 0$.

Introduction

Tau- (τ-) carbide phases formed during heat treatment of many iron- and chromium-based alloys that contain carbon can adversely affect the mechanical properties of such technologically important materials as ferritic and austenitic stainless steels (Shaw & Quarrell, 1957; Lai & Meshkat, 1978). Possible control of such effects will follow only from detailed studies of various properties of τ-carbide phases, among which crystal structure must be deemed especially relevant.

Basic features of the crystal structure of all τ carbides were first determined by Westgren (1933). Working with a phase whose composition was thought to be Cr₄C, Westgren found that X-ray diffraction and density measurements were more consistent with the formula Cr₂₃C₆. The carbide crystallized in the cubic system with a face-centered lattice ($a_0 \simeq 10.66$ Å) in which 92 metal atoms were located at the 4(a), 8(c), 32(f) and 48(h) symmetry sites of space group $Fm\bar{3}m$ (see Fig. 1). Carbon atoms were most reasonably placed on 24(e) sites (E), a result later confirmed by neutron diffraction studies (Meinhardt & Krisement, 1962). Though described