ARDITO, G., CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1985). *Z. Kristallogr.* **172**, 25-34.
BEURSKENS, P. T., PRICK, A. J., DOESBURG, H. M. & GOULD, R. O. (1979). *Acta Cryst.* **A35**, 765-772.
BROSIUS, J. (1985). *Acta Cryst.* **A41**, 613-617.
BURLA, M. C., CASCARANO, G., FARES, V., GIACOVAZZO, C., POLIDORI, G. & SPAGNA, R. (1989). *Acta Cryst.* **A45**, 781-786.
CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1985). *Acta Cryst.* **A41**, 544-551.
CASCARANO, G., GIACOVAZZO, C. & LUIĆ, M. (1987). *Acta Cryst.* **A43**, 14-22.
CASCARANO, G., GIACOVAZZO, C., LUIĆ, M., PIFFERI, A. & SPAGNA, R. (1987). *Z. Kristallogr.* **179**, 113-125.
COCHRAN, W. (1952). *Acta Cryst.* **5**, 65-67.
COCHRAN, W. (1955). *Acta Cryst.* **8**, 473-478.
ELLER, G. VON (1973). *Acta Cryst.* **A29**, 63-67.
GIACOVAZZO, C. (1980). *Direct Methods in Crystallography.* London: Academic Press.
HAUPTMAN, H. & KARLE, J. (1962). *Acta Cryst.* **15**, 547-550.
HEINERMAN, J. J. L., KRABBENDAM, H. & KROON, J. (1975). *Acta Cryst.* **A31**, 731-736.
HEINERMAN, J. J. L., KRABBENDAM, H., KROON, J. & SPEK, A. L. (1978). *Acta Cryst.* **A34**, 447-450.
HOPPE, W. (1957). *Acta Cryst.* **10**, 751.
HOPPE, W. (1963). *Acta Cryst.* **16**, 1056-1057.
KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635-651.
KRABBENDAM, H. & KROON, J. (1971). *Acta Cryst.* **A27**, 362-367.
KROON, J. & KRABBENDAM, H. (1970). *Acta Cryst.* **B26**, 312-314.
MAIN, P. & WOOLFSON, M. M. (1963). *Acta Cryst.* **16**, 1046-1051.
PONTENAGEL, W. M. G. F., KRABBENDAM, H. & KROON, J. (1987). *Acta Cryst.* **A43**, 55-60.
RIUS, J. & MIRAVITLLES (1989). *Acta Cryst.* **A45**, 490-494.
STANLEY, E. (1979). *Acta Cryst.* **A35**, 966-970.
VAUGHAN, P. A. (1958). *Acta Cryst.* **11**, 111-115.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318-321.

Acta Cryst. (1991). **A47**, 263-267

Polytypism in PbI_2-Doped Dendritic Crystals of Cadmium Iodide

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Abstract

Cadmium iodide and lead iodide have been highly purified by a horizontal zone refining technique. Dendritic single crystals of PbI_2-doped cadmium iodide have been grown from vapour phase in vacuum. The effect of doping on polytype formation and other structural characteristics has been studied by X-ray diffraction. The crystals have shown the formation of rhombohedral polytype $12R$ in about 50% of cases, along with the common polytype $4H$ of cadmium iodide. This is in sharp contrast to earlier findings for undoped dendritic crystals which exclusively contained the polytype $4H$. Further, unlike the undoped crystals, some of the doped crystals also show streaking and arcing on their X-ray photographs. The observed structural changes may be governed by both thermodynamical considerations and the kinetics of crystal growth and the observed streaking and arcing result from internal stresses built up around the relatively large Pb^{2+} ions in the host CdI_2 structure.

Introduction

A vast amount of experimental and theoretical work has been carried out on the polytypism of crystals, particularly in the last three decades. The crystals studied have had several different habits, *viz* plates, needles, prisms, pyramids *etc.*; the crystals of strongly polytypic materials like CdI_2, SiC and ZnS are usually plate shaped. No work has been done on the polytypism of dendritic crystals. In fact, no attempts have previously been made to grow dendritic crystals of a polytypic material. However, it is now realized that the formation of polytypes is also related to crystal habit. For instance, GaSe crystals have been grown in many habits like plates, needles, thin ribbons, prisms, truncated pyramids *etc.*, but polytypism has been observed only in the needle-shaped crystals grown by sublimation (Terhell, 1983). Similarly, only needle-shaped AgI crystals show polytypism, although these crystals have been grown in other shapes, *viz* hexagonal plates, pyramids, prisms *etc.* (Prager, 1983; Cochrane, 1967).

We have successfully grown large dendritic single crystals of the richly polytypic material CdI_2 from the vapour phase, measuring up to nearly 10 mm long and nearly 5 mm wide. A preliminary report has been published (Kumar & Trigunayat, 1990). Besides the crystal habit, the polytypism of crystals is known to be affected by several other factors, of which an important one is the presence of impurities (Trigunayat, 1989). A study of the effect of the introduction of some selected impurities in highly pure melt-grown crystals of cadmium iodide has been made recently (Tyagi, 1988; Tyagi & Trigunayat, 1988, 1989). It was proposed to carry out a similar study on the role played by impurities in the formation of polytypes in the dendritic crystals grown by us. Accordingly, it was planned to dope CdI_2 crystals

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with lead iodide. The selection of lead iodide as the dopant was based on the following considerations.

(*a*) PbI$_2$ crystals are isostructural with CdI$_2$ crystals.

(*b*) The ionic radius of Pb^{2+} ions (1·20 Å) is relatively large but not very different from that of Cd^{2+} ions (0·97 Å).

(*c*) The melting point of PbI$_2$ (675 K) is close to that of CdI$_2$ (661 K).

(*d*) Lead is more electropositive than cadmium.

(*e*) Both lead and cadmium are bivalent ions.

The above factors are conducive to producing a substitutional solid solution in the host material by the dopant material, as earlier achieved for a variety of impurities, *viz* Pb, Sn, In, Ga and Br in the melt-grown CdI$_2$ crystals (Tyagi, 1988; Trigunayat, 1990). The doped crystals have been characterized by X-ray diffraction, to assess the effect of doping on the polytypism of the crystals. The results have been discussed in the light of current theoretical developments regarding polytypism.

Experimental

Analar grade CdI$_2$ and PbI$_2$ were highly purified by a horizontal zone refining technique. The apparatus used for this purpose was similar to that used earlier (Chaudhary & Trigunayat, 1982), except for some modifications in the shapes of the heater and the boat. The boat was provided with four legs, so that its central section was raised to coincide with the axis of the enclosing tube and the bottom of the boat did not touch the bottom of the tube as it did in the earlier set-up. A circular heater was used instead of the earlier semicircular heater to obtain uniform heating of the charge placed in the boat. The diameter of the helical coil used in the heater was also reduced. These modifications helped to minimize the unwanted temperature gradient between the bottom and top layers of the molten zone and also led to a smaller melt zone width and a flatter solid–melt interface. The speed of the zone was maintained at 1·8 cm h^{-1}. 20 zone passes were given for the purification of both cadmium iodide and lead iodide. The relatively impure material towards the far end of the ingot was discarded; only the highly pure material from the initial and middle portions of the ingot was used for crystal growth.

The furnace used for growing dendritic single crystals of the PbI$_2$-doped cadmium iodide is shown in Fig. 1. Fig. 2 shows the temperature profile of the furnace. The purified ingots of both CdI$_2$ and PbI$_2$ were cut into small pieces. Then CdI$_2$ was mixed with 3% (wt/wt) of lead iodide and placed in a small glass cup. The cup was inserted in a glass tube of which only one end was open. This tube was placed symmetrically inside the furnace. The open end of the tube was made vacuum tight with the help of a metal flange fitted with an *O* ring. The tube was evacuated to a pressure of the order of 1–0·1 Pa. In 8–10 h, dendritic single crystals were seen to have grown nearly 10 cm away from the charge. After the growth process was over, dendrites were collected on soft tissue paper. They exhibited a light yellow colour and their surface area was approximately between 6×3 and 2×1 mm. Their thickness was of the order of 100 μm. Fig. 3 shows a full dendritic crystal.

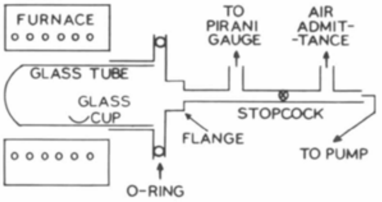

Fig. 1. Experimental set-up for growing dendritic single crystals of cadmium iodide.

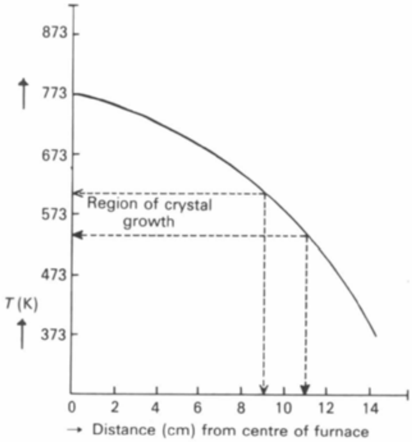

Fig. 2. Temperature profile of the furnace employed for crystal growth.

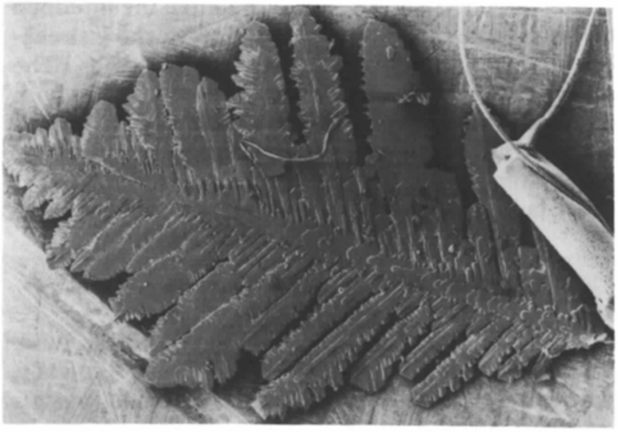

Fig. 3. Scanning electron micrograph of a PbI$_2$-doped CdI$_2$ dendrite; 5 kV; ×50.

For X-ray diffraction studies of the doped dendrites, oscillation photographs were taken about the *a* axis of the crystals. The range of oscillation was so chosen that the angle made by the *c* axis of the crystal with the incident X-ray beam varied between 25 and 40°. This range was selected to get a long sequence of consecutive $10.l$ reflections which are particularly useful in providing the required structural information. The X-ray photographs were taken from four to five different portions of both the faces of each dendrite, because CdI_2 crystals are known to exhibit parallel growth of two or more different polytypes on the same crystal face. All the photographs were recorded on a cylindrical camera of radius 3 cm, employing Cu $K\alpha$ radiation.

Experimental results

Most of the dendritic crystals looked fairly transparent, like the undoped dendritic crystals of cadmium iodide grown earlier (Kumar & Trigunayat, 1990). Their light-yellow tinge indicated partial formation of lead iodide as a result of doping because PbI_2 crystals are yellow in colour. The presence of PbI_2 within the crystals was confirmed by chemical analysis.

In all, 20 crystals were investigated by X-ray diffraction. By exposing different portions of the crystals to the X-ray beam, 89 oscillation photographs were obtained from all the crystals. The information gathered from them is summarized below.

Number of crystals studied	20
Number of photographs taken	89.

Break-up of X-ray photographs of various polytypes (or mixture of polytypes):

$4H$	41 (46%)
$4H+12R$	16 (18%)
$4H+12R_R+12R_O$	28 (31%)
$4H$ + unidentified	4 (5%)
Number of X-ray photographs showing streaking	10 (11%)
Number of X-ray photographs showing arcing	6 (7%).

The intensity of the $12R$ reflections was generally found to be weaker than the $4H$ reflections. Further, no structural changes were observed in the crystals stored at room temperature even up to 6 months.

Fig. 4 shows an X-ray oscillation photograph of a common $4H$ polytype. Figs. 5 and 6 depict the same for $4H+12R$ and $4H+12R_R+12R_O$, respectively. Figs. 7 and 8 illustrate the phenomena of streaking and arcing, respectively.

Discussion

A striking feature of the experimental data is that 50% of the oscillation photographs show the occurrence of the higher polytype $12R$, in addition to the common CdI_2 polytype $4H$. This is in sharp contrast with the earlier data on highly purified undoped CdI_2 dendritic single crystals, similarly grown in vacuum, which show exclusive occurrence of the common polytype $4H$ (Kumar & Trigunayat, 1990). Evidently, the formation of $12R$ has resulted from the doping of PbI_2 in CdI_2. In the CdI_2 crystals the stable room-temperature modification and the stable high-temperature modification are the same, *viz* the polytype $4H$. But in the PbI_2 crystals they are known to be different, *viz* the polytype $2H$ at room temperature and the polytype $12R$ at high temperatures (Salje, Palosz & Wruck, 1987). Since in the present method of crystal growth the crystallization occurs at fairly high temperatures, *viz* around 570 K, the PbI_2 crystals formed in the host structure will naturally tend to occur as $12R$. It is obvious that, in spite of their small concentration (as only 3% PbI_2 was doped into CdI_2), they are surprisingly able to 'induce' the host structure to do the same in about 50% of the crystals. It is noteworthy that in the absence of PbI_2 all the CdI_2 crystals have been found to grow exclusively as $4H$ (Kumar & Trigunayat, 1990).

The formation of $12R$ in nearly half of the cases implies that the probability of formation of PbI_2-$12R$ nuclei at the prevalent high temperature of growth was high, as could be expected on the basis of thermodynamic considerations. Although only 3% of PbI_2 has been doped into the host material, it should be remembered that an accumulation of just a few hundred atoms is enough to produce a viable nucleus for crystal growth. The CdI_2 crystals growing around these PbI_2 nuclei acquire the same structure, *viz* $12R$. However, since the high-temperature modification of CdI_2 is $4H$, in all the cases the formation of CdI_2-$4H$ nuclei will be favoured thermodynamically. Subsequent growth around these nuclei will produce the $4H$ structure, which accounts for the observed occurrence of $4H$ in all the crystals. On account of the preponderance of CdI_2 in the material (leading to the formation of a far larger number of CdI_2 nuclei as compared to the PbI_2 nuclei) and because of the natural preference of CdI_2 to grow as $4H$ at high

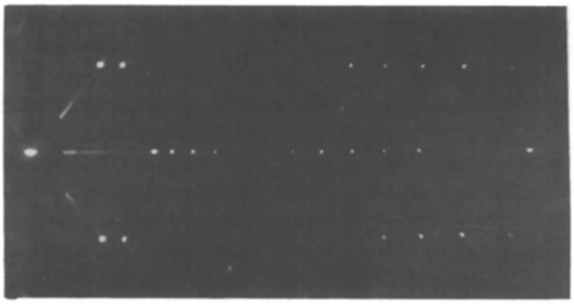

Fig. 4. *a*-axis 15° oscillation photograph of a dendritic single crystal showing reflections of the $4H$ polytype; camera radius 3 cm; Cu $K\alpha$ radiation; ×1.

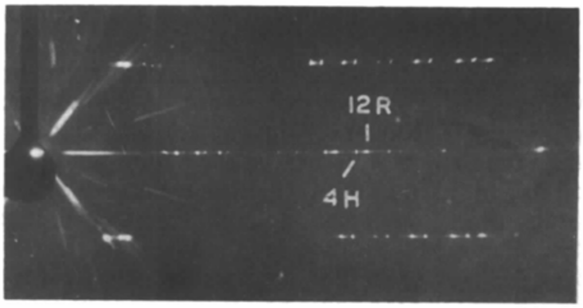

Fig. 5. *a*-axis 15° oscillation photograph of a dendrite showing reflections of $4H+12R$; other conditions are the same as in Fig. 4; relative positions of one $4H$ and one $12R$ reflections are marked by arrows.

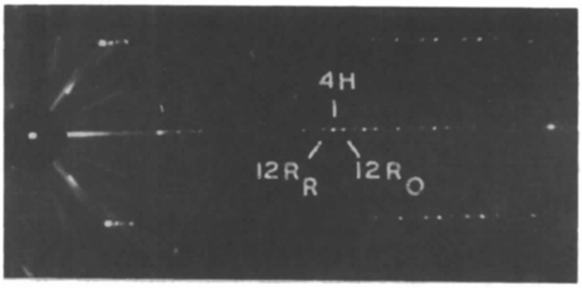

Fig. 6. *a*-axis 15° oscillation photograph of a dendrite showing reflections of $4H+12R_O+12R_R$; other conditions are the same as in Fig. 4; relative positions of one $4H$, one $12R_O$ and one $12R_R$ reflections are marked by arrows.

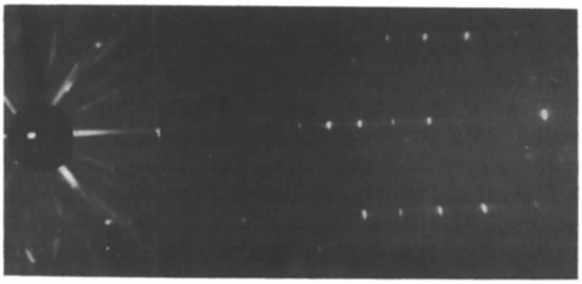

Fig. 7. *a*-axis 15° oscillation photograph of a dendrite showing streaking; polytype $4H$; other conditions are the same as in Fig. 4.

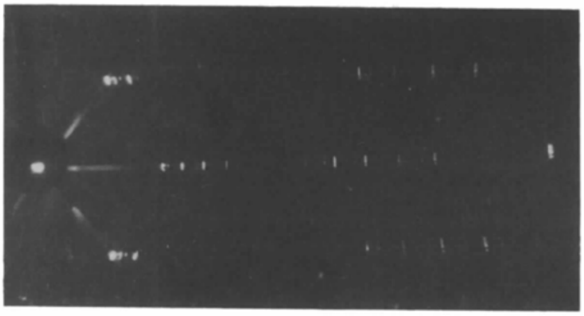

Fig. 8. *a*-axis 15° oscillation photograph of a dendrite showing arcing; polytype $4H$; other conditions are the same as in Fig. 4.

temperatures the crystals may grow either entirely as $4H$ (in spite of the existence of some $12R$ nuclei) or preponderantly as $4H$ which agrees with the observation that mixed crystals of $4H$ and $12R$ have much higher intensity for the $4H$ reflections compared with the $12R$ reflections.

These considerations of crystal growth are obviously not applicable to any possible phase transformations resulting from prolonged storage of the crystals at room temperature, such as those observed earlier for solution-grown CdI_2 crystals and melt-grown PbI_2 crystals (Trigunayat, 1990). In the PbI_2 crystals the solid-state phase transformation $2H$-$12R$ is known to be reversible in nature. The phase $2H$ changes into $12R$ upon heating up to nearly 533 K and the phase $12R$ reverts back to $2H$ after storage of a couple of weeks or a few months at room temperature. In our crystals any structural change in the $4H$ crystals is ruled out by the fact that the structure $4H$ happens to be the stable phase of CdI_2 both at room temperature and at high temperatures. The $12R$ phase, which has resulted from the growth of CdI_2 around PbI_2 nuclei and thus almost wholly consists of cadmium iodide, may be expected to transform into $4H$ upon storage at room temperature on the basis of thermodynamic considerations. The fact that no such transformation has been observed to occur implies that the barrier energy for the transformation $12R$-$4H$ is high.

The streaking has been observed in 11% of cases. In contrast, the dendrites of undoped CdI_2 do not show streaking at all (Kumar & Trigunayat, 1990). The streaking originates from the presence of randomly distributed stacking faults in the structure. As pointed out in the *Introduction*, if PbI_2 is doped into CdI_2 there is a good chance of the substitution of Cd^{2+} ions by Pb^{2+} ions, leading to the formation of a substitutional solid solution. The introduction of the relatively large-sized Pb^{2+} ions (ionic radius = 1·20 Å *cf.* ionic radius of $Cd^{2+} = 0{\cdot}97$ Å) in the CdI_2 structure produces local distortions, which build up strong local internal stresses in the structure. The stresses may be relieved by mutual slippage of the molecular layers I-Cd-I, which are bound together by weak van der Waals forces and so are easily amenable to slip with respect to one another. The most probable slip planes and slip directions in a crystal are those having closest packing of atoms. In CdI_2 crystals they are the $\{0001\}$ basal planes and the $\langle 11\bar{2}0\rangle$ directions, respectively. A slip thus originated creates a unit edge dislocation lying in the basal plane and having Burgers vector $\mathbf{a}/3\langle 11\bar{2}0\rangle$. The dislocation can easily dissociate into two partials as

$$\mathbf{a}/3\langle 11\bar{2}0\rangle = \mathbf{a}/3\langle 10\bar{1}0\rangle + \mathbf{a}/3\langle 01\bar{1}0\rangle.$$

The partials may also be created independently. The movement of the partials leads to generation of stacking faults in the crystals. Normally, the faults so produced will be randomly distributed inside the crystal. When the faults are able to arrange themselves in a regular fashion, a well ordered polytype is produced; otherwise they are retained as faults in the structure and manifest themselves as streaks between reflections on the X-ray photographs.

In the dendrites grown in an argon atmosphere using analar grade CdI_2, some higher polytypes were observed and the streaking, too, was observed in 9% of cases (Kumar & Trigunayat, 1990). Both higher polytypes and streaking were eliminated when the charge material was well purified by zone refining and the argon atmosphere was replaced by vacuum. Now, when Pb ions are introduced in the CdI_2 structure as impurities, both polytype formation and streaking are again observed. This clearly establishes the role of impurities, including lead, in the formation of polytypes in CdI_2 crystals.

Arcing of the reflections arises from the arrangement of edge dislocations into small-angle tilt boundaries. Like streaking, it has been observed in just 7% of cases in the present work which means that the density of the dislocations produced in the structure was low.

In the earlier work it was found that the melt-grown CdI_2 crystals doped with PbI_2 unusually required long exposure time (~8-10 h) to produce well exposed X-ray photographs compared with the usual exposure time of nearly 1 h for the undoped CdI_2 crystals (Tyagi & Trigunayat, 1988). It was argued that when the large-sized Pb^{2+} and I^- ions (ionic radii 1·20 and 2·16 Å, respectively) occupy the vacant octahedral voids present in the CdI_2 structure, local displacements are produced which lead to weakening of the X-ray reflections (Vainshtein, Fridkin & Indembom, 1982). However, in the present case of PbI_2-doped dendritic crystals, the time required for producing well exposed X-ray photographs was the same as for the undoped CdI_2 dendritic crystals, *viz* about 1 h. It follows that no such local displacements are produced in the present vapour-grown dendritic crystals, the reason for which may be the following. In the melt growth, when the melt solidifies in the growth chamber, the substituted Cd^{2+} ions and the liberated I^- ions cannot escape and are therefore compelled to accommodate themselves at suitable positions in the host structure. This enfored entry of the large I^- ions (ionic radius = 2·16 Å) causes excessive local distortions and hence large local displacements in the structure. No such constraints exist in vapour growth, so the I^- ions are free to escape into the surroundings. They may also combine with the substituted Cd^{2+} ions to form CdI_2 molecules, which may deposit elsewhere in the growth chamber.

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References

CHAUDHARY, S. K. & TRIGUNAYAT, G. C. (1982). *J. Cryst. Growth*, **57**, 558-562.

COCHRANE, G. (1967). *Br. J. Appl. Phys.* **18**, 687.

KUMAR, B. & TRIGUNAYAT, G. C. (1990). *Proc. Indian Natl Sci. Acad. Part A*. In the press.

PRAGER, P. R. (1983). In *Crystal Growth and Characterization of Polytypic Structure*, edited by P. KRISHNA, p. 451. Oxford: Pergamon.

SALJE, E., PALOSZ, B. & WRUCK, B. (1987). *J. Phys. C*, **20**, 4077-4096.

TERHELL, J. C. J. M. (1983). In *Crystal Growth and Characterization of Polytypic Structure*, edited by P. KRISHNA, p. 55. Oxford: Pergamon.

TRIGUNAYAT, G. C. (1989). *Phase Transitions*, **16/17**, 509-527.

TRIGUNAYAT, G. C. (1990). *Solid State Ion.* In the press.

TYAGI, U. P. (1988). PhD thesis, Univ. of Delhi, India.

TYAGI, U. P. & TRIGUNAYAT, G. C. (1988). *Acta Cryst.* **C44**, 1157-1162.

TYAGI, U. P. & TRIGUNAYAT, G. C. (1989). *Phase Transitions*, **16/17**, 537-541.

VAINSHTEIN, B. K., FRIDKIN, V. N. & INDENBOM, L. V. (1982). *Modern Crystallography* II: *Structure of Crystals*. New York: Springer-Verlag.

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Thermal Vibrations in Convergent-Beam Electron Diffraction

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Abstract

The frozen phonon technique is introduced as a means of including the effects of thermal vibrations in multislice calculations of CBED patterns. This technique produces a thermal diffuse background, Kikuchi bands and a Debye-Waller factor, all of which are neglected in the standard multislice calculation. The frozen phonon calculations match experimental silicon (100) CBED patterns for specimen