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# Phase transition in a tetragonal $\text{In}_{90}\text{Pb}_{10}$ alloy under high pressure: a switch from $c/a > 1$ to $c/a < 1$

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## Abstract

The effect of pressure on tetragonal In–Pb alloys with 10, 15, and 22 at.% Pb has been studied up to pressure 30 GPa with diamond anvil cells using synchrotron radiation. The In-type face-centred tetragonal phase of the In alloy with 10 at.% Pb undergoes under pressure a phase transition with a discontinuous jump of the axial ratio from  $c/a > 1$  to  $c/a < 1$  via a two-phase region from 7 to 20 GPa. The tetragonal phases of the In alloys with 15 and 22 at.% Pb with  $c/a < 1$  at ambient pressure show only a slight decrease in  $c/a$  with pressure increase. The correlation of the axial ratio with the alloy content and its change with pressure in In alloys and In itself are attributed to Brillouin-zone–Fermi-sphere interactions.

## 1. Introduction

The group III element In crystallizes in a body-centred tetragonal (bct) structure,  $tI2$ , space group  $I4/mmm$ . This structure represents a small distortion of a face-centred cubic (fcc) structure and is usually described as a face-centred tetragonal (fct) structure with an axial ratio  $c/a = 1.0758$  [1]. The bct–fct relations are:  $a_{fct} = a_{bct}\sqrt{2}$  and  $c_{fct} = c_{bct}$ . Under pressure In has been found to remain tetragonal up to about 45 GPa, showing a slight axial ratio increase with a flat maximum  $c/a = 1.09$  at around 24 GPa [2–4].

Alloying of In with group IV elements Pb or Sn results first in an increase in  $c/a$  of the fct phase and then a discontinuous decrease in axial ratio down to  $c/a < 1$  at the alloy content of 12–15% Pb or Sn [5]. These changes in axial ratio of the fct phase with the alloy content point to a correlation between the tetragonal distortion and the mean number of valence electrons,  $n$ , in the alloy. The electron concentration  $n = 3.12$ – $3.15$  for In alloys with 12–15 at.% Pb or Sn appears to be a critical value for the axial ratio of the fct phase, where it changes from  $c/a > 1$  to  $c/a < 1$ . The In–Pb alloys with more than 30 at.% Pb have an fcc structure, that changes under pressure to fct with  $c/a < 1$ , as has been shown in the recent study on In–Pb alloys with 40 and 60 at.% Pb [6].

One can speculate regarding a discontinuous fct–fct phase transition with a jump of the axial ratio that may occur under pressure in In–Pb alloys with electron concentration close to the critical value. Therefore, we have investigated In alloys with 10, 15, and 22 at.% Pb covering the region of critical valence electron concentration. The interest in this study is in gaining more understanding of the tetragonal structural distortion, in particular in the elemental In, and the physical reasons for the stability of the tetragonal phases in In and In alloys.

## 2. Experimental details

Alloys of In with 10, 15, and 25 at.% Pb were prepared by melting the appropriate amounts of the pure elements (5N purity). The alloys have been characterized at ambient conditions by means of x-ray diffraction and found to correspond to the literature data [5] while the measured atomic volumes are consistent with Vegard's law. The  $\text{In}_{90}\text{Pb}_{10}$  alloy has fct structure with  $c/a > 1$  whereas alloys  $\text{In}_{85}\text{Pb}_{15}$  and  $\text{In}_{78}\text{Pb}_{22}$  both have fct structure with  $c/a < 1$ .

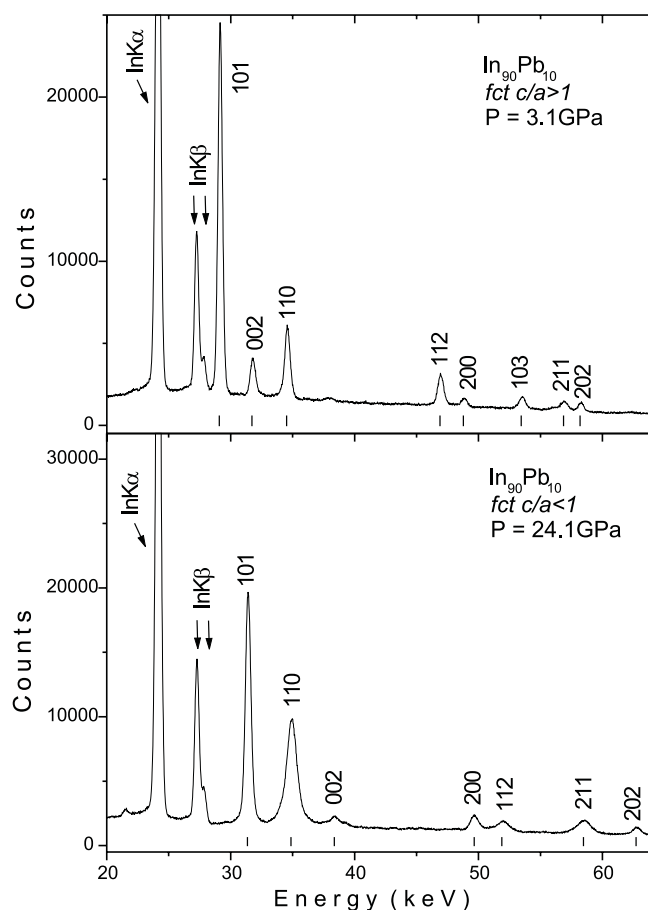
High-pressure studies were performed with diamond anvil cells [7] and energy-dispersive diffraction using synchrotron radiation at DESY, HASYLAB [8, 9]. The ruby luminescence technique [10] was used for pressure measurements with the non-linear ruby scale [11]. The alloy samples were loaded into the gasket hole with mineral oil as the pressure-transmitting medium or without any transmitting medium because of the low shear modulus of In and In-rich alloys. The high-pressure data for each of the three alloys were collected in 2–3 runs up to pressures of about 30 GPa in steps of about 3 GPa. In the case of a two-phase mixture, additional experiments were performed after annealing the alloy samples under pressure in the diamond anvil cell. Diffraction spectra were evaluated with the computer programs EDXPOW and XPOWDER [12].

## 3. Results

The fct  $c/a > 1$  phase of the  $\text{In}_{90}\text{Pb}_{10}$  alloy remains stable up to  $\sim 7$  GPa. At higher pressure, several additional diffraction peaks appear and grow with increasing pressure at the expense of the low-pressure phase peaks. Above  $\sim 20$  GPa the diffraction patterns are consistent with a new phase which is determined as fct,  $c/a < 1$ . Examples of diffraction patterns for both fct phases of  $\text{In}_{90}\text{Pb}_{10}$  are shown in figure 1. On pressure decrease, a reversible transformation occurs, also with a region of two-phase mixture.

Thus the  $\text{In}_{90}\text{Pb}_{10}$  alloy undergoes under pressure a phase transition from one fct to another fct structure with a discontinuous jump of the axial ratio from  $c/a \approx 1.09$  to  $c/a \approx 0.93$ . The pressure range of two-phase mixture is about 13–15 GPa from  $\sim 7$  to  $\sim 21$  GPa; it is difficult to determine precisely because the first strong diffraction peak (101) is common to both phases. Additional difficulties arise due to the easy deformation of In-rich alloys, which lead to the broadening of diffraction peaks and relatively low precision in the determination of peak positions and lattice parameters. The measured lattice parameters and atomic volumes at selected pressures are listed in table 1. No significant change in the atomic volume is found at this fct–fct transition.

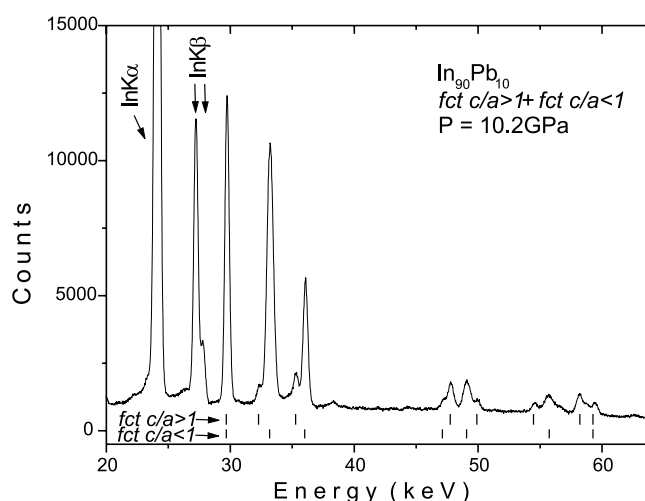
To check whether the two-phase mixture is a non-equilibrium state due to kinetic effects or an equilibrium state in a certain pressure range, sample annealing was performed under pressure at  $\sim 10$  GPa and  $150^\circ\text{C}$  for 18 h. After this annealing, strong recrystallization was observed and the pattern of the  $\text{In}_{90}\text{Pb}_{10}$  alloy taken at room temperature and  $P = 10.2$  GPa was consistent with two fct phases as shown in figure 2. This implies that coexistence of two fct phases with different  $c/a$  ratios is an equilibrium state for this alloy at  $\sim 10$  GPa [13].



**Figure 1.** EDXD spectra of the  $\text{In}_{90}\text{Pb}_{10}$  alloy collected under pressure with  $2\theta = 9.03^\circ$  ( $Ed = 7875 \text{ keV pm}$ ). The fluorescence peaks arising from In are marked by arrows. The diffraction patterns correspond to a single phase: fct,  $c/a > 1$  at  $P = 3.1 \text{ GPa}$ ; and fct,  $c/a < 1$  at  $P = 24.1 \text{ GPa}$ . The tick marks below the patterns show the calculated peak positions for each phase. The Miller indices are given for both tetragonal phases in the body-centred setting. The lattice parameters are listed in table 1.

The alloys of In with 15 and 22 at.% Pb have at ambient pressure an fct  $c/a < 1$  phase and do not show any phase transition in the pressure range studied ( $\sim 30 \text{ GPa}$ ). The fct phases for both alloys display a slight decrease in  $c/a$  with increasing pressure. Variations of  $c/a$  with pressure are very similar for the two alloys, differing only by a small shift in  $c/a$ . For the alloy with the higher valence electron concentration (or Pb content), a lower  $c/a$  value was observed at a given pressure.

The variation of the axial ratio with pressure for the fct phase is shown in figure 3, for all three alloys studied. The data for pure In [3] are shown for comparison, indicating a similarity in  $c/a$  behaviour (slight increase) for In and for the fct  $c/a > 1$  phase of the  $\text{In}_{90}\text{Pb}_{10}$  alloy in its stability region and even in the two-phase region up to  $\sim 20 \text{ GPa}$ . However, in contrast to the case for In, the tetragonal phase of  $\text{In}_{90}\text{Pb}_{10}$  displays a transition from  $c/a \approx 1.09$  to  $c/a \approx 0.93$  through the extended two-phase region ( $\sim 7\text{--}20 \text{ GPa}$ ).

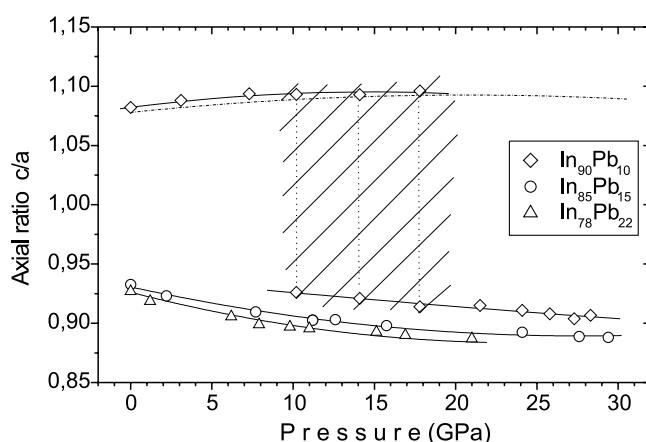


**Figure 2.** EDXD spectra of  $\text{In}_{90}\text{Pb}_{10}$  collected at  $P = 10.2$  GPa with  $2\theta = 9.03^\circ$  ( $E_d = 7875$  keV pm). The sample was annealed before exposure in the diamond anvil cell under pressure of  $\sim 10$  GPa at the temperature  $150^\circ\text{C}$  for 18 h. Fluorescence peaks from In are marked by arrows. The diffraction pattern corresponds to the mixture of two tetragonal phases: fct,  $c/a > 1$  and fct,  $c/a < 1$ . The tick marks below the pattern show calculated peak positions for each phase. The lattice parameters are listed in table 1.

**Table 1.** Structural characteristics of tetragonal phases in the In–Pb alloys at ambient and high pressures. All the phases have bct structure, space group  $I4/mmm$ , Pearson symbol  $tI2$ . Axial ratios  $c/a$  are given for the bct and fct settings.

Alloy content (at.%)	Pressure (GPa)	Lattice parameters for bct cell			$c/a$ (fct)	$V_{at}$ $10^6$ ( $\text{pm}^3$ )
		$a$ (pm)	$c$ (pm)	$c/a$		
$\text{In}_{90}\text{Pb}_{10}$	0	327.1(1)	500.6(2)	1.530	1.083	26.78
	3.1	322.4(1)	496.2(2)	1.539	1.088	25.80
	10.2	315.5(2)	487.7(3)	1.546	1.093	24.28
		333.9(3)	437.0(8)	1.309	0.926	24.35
	24.1	318.2(5)	409.9(7)	1.288	0.911	20.75
	28.3	317.7(5)	409.0(7)	1.288	0.911	20.64
$\text{In}_{85}\text{Pb}_{15}$	0	347.5(3)	458.4(7)	1.319	0.933	27.68
	13.9	328.7(1)	419.7(3)	1.277	0.903	22.67
	28.4	317.3(3)	398.3(8)	1.256	0.888	20.50
$\text{In}_{78}\text{Pb}_{22}$	0	347.4(2)	455.6(3)	1.311	0.927	27.99
	11.0	334.3(4)	421.3(8)	1.260	0.891	23.55
	21.0	329.1(5)	412.9(9)	1.255	0.887	22.35

It should be noted that the two-phase state of the  $\text{In}_{90}\text{Pb}_{10}$  alloy observed under pressure is a thermodynamic equilibrium, implying different phase compositions. This difference of phase content is expected to be within 3–5 at.%, as at ambient pressure [5]. Taking the atomic volumes for the pure components at  $\sim 10$  GPa as  $\sim 22 \text{ \AA}^3$  for In [3] and  $26 \text{ \AA}^3$  for Pb [14], one can estimate that the atomic volume difference for the phases within a range of 5 at.% should be less than  $0.2 \text{ \AA}^3$ , in agreement with our experimental data (see table 1).



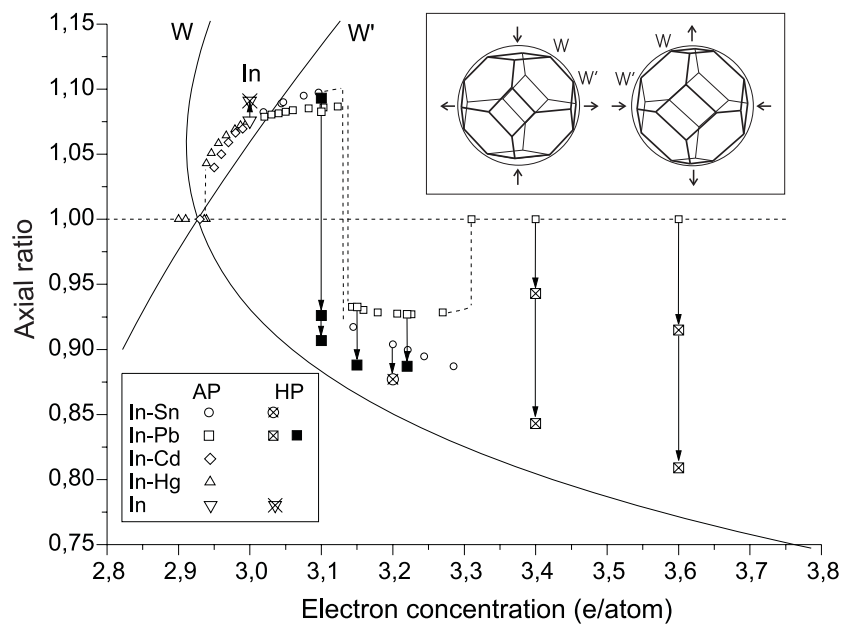
**Figure 3.** Variations of the axial ratio  $c/a$  with pressure for In alloys with 10, 15, and 22 at.% Pb. The axial ratio for the tetragonal phase is given in the fct setting to illustrate the relation to the fcc case ( $c/a = 1$ ). For comparison, the  $c/a$  data for pure In [3] are shown by a dash-dotted line. Vertical dashed lines connect two coexisting phases with different values of  $c/a$ . The hatched area indicates the two-phase region of the In<sub>90</sub>Pb<sub>10</sub> alloy. The solid curves connecting the experimental data are guides to the eye.

#### 4. Discussion

The present results form part of a general pattern for crystal structures in In alloys over the range of electron concentration from 2.9 (In–Hg, In–Cd) to 3.6 (In–Sn, In–Pb), which is summarized in figure 4. Axial ratios for tetragonal phases in the In–Pb and In–Sn alloys at ambient pressure (from [5]) show that a jump of  $c/a$  occurred near the critical value of the electron concentration  $n \approx 3.12$ .

Correlation of the tetragonal distortions in In alloy phases with the alloy electron concentration indicates a valence electron origin of these distortions. The fitting of the Brillouin zone (BZ) to the Fermi sphere (FS) provides minimization of the band-structure energy as suggested by Mott and Jones [15] for Hume-Rothery phases in the Cu–Zn and related alloys. It has been stated by Heine and Weaire [16] that ‘for polyvalent metals there are always many zone planes cutting the Fermi surface, and the contribution to the total energy from regions close to the intersection of two or more zone planes may lead to important effects’. Heine and Weaire [16] referred to the Svechkarev suggestion [17] that it is favourable for corners of the BZ to touch the FS. Two kinds of distortion, with either  $c/a > 1$  or  $c/a < 1$ , have been discussed by Svechkarev [17], when the FS touches the BZ corners of type W' or W, respectively, as shown in the inset to figure 4. Solid lines represent Svechkarev's plot—calculated values of  $c/a$  from the model when a free-electron-like FS for a given valence electron concentration is touching the BZ corners of type W or W'. Distortions with either  $c/a > 1$  or  $c/a < 1$  are realized at  $n < 3.12$  and  $n > 3.15$ , respectively.

Results on In<sub>90</sub>Pb<sub>10</sub> alloy in the present study show that the critical value of  $n$  for a jump from  $c/a > 1$  to  $c/a < 1$  is shifted under pressure toward the lower concentration of Pb. This indicates that under pressure, touching of the W-type corners to the FS became preferable over that of the W'-type corners. Distortions of fct  $c/a < 1$  phases increase under pressure, displaying a trend of approaching the W branch ( $c/a < 1$ ) of the Svechkarev plot of  $c/a$  versus  $n$ , as shown in figure 4.



**Figure 4.** Axial ratio versus electron concentration for fct phases in In alloys at ambient pressure from [5] (small open symbols), at high pressure from [6] (crossed symbols), and from the present work (solid symbols). Data on In at high pressure are taken from [3]. Vertical arrows show the change of  $c/a$  from the ambient-pressure value to a value at the highest pressure ( $\sim 30$  GPa) reached in the studies (present work and [6]). The solid curves represent the calculated distortion ( $c/a$  versus  $n$ ) for the case where the BZ corners (of type W and W') are in contact with the free-electron FS at a given  $n$  [17]. The BZs for fct structures with  $c/a > 1$  and  $c/a < 1$  for  $\text{In}_{90}\text{Pb}_{10}$  at  $\sim 10$  GPa are shown in the inset. Circles represent the FS corresponding to  $k_F$  for  $n \approx 3.1$  electrons/atom. Arrows drawn near BZ planes indicate plane shifts via tetragonal distortions that result in one of the planes of sets (200) or (002) moving to the FS and the BZ corners of W' type (left) or W type (right) approaching the FS.

The results obtained in the present work fit well to the previous observations under pressure of the fct–fct transition in the In–Pb alloys ( $\text{In}_{60}\text{Pb}_{40}$  and  $\text{In}_{40}\text{Pb}_{60}$ ) and the  $c/a$  decrease for the fct  $\text{In}_{80}\text{Sn}_{20}$  alloy [6], shown also in figure 4. The common picture of the In alloys is that the increase in valence electron concentration and pressure stabilizes the fct phase with  $c/a < 1$ . With increasing pressure the tetragonal distortion approaches the values of  $c/a$  given by Svechkarev's model. This indicates that the contribution to the crystal energy due to BZ–FS interactions is enhanced under high pressure.

High-pressure studies on In alloys prompt the question of whether in pure In a phase transition from fct  $c/a > 1$  to fct  $c/a < 1$  can occur under pressure. A previously observed structural transition in pure In above 45 GPa was explained as a tetragonal-to-orthorhombic distortion [4]. In the light of the present results, a different interpretation of the complex diffraction spectra for In above 45 GPa could be suggested, namely the coexistence of two different tetragonal phases with  $c/a \sim 1.1$  and  $c/a \sim 0.95$ . It should be noted that theoretical energy calculations for In [18] show two energy minima for two tetragonal phases with different  $c/a$  values that become very close in energy at compressions  $V/V_0 \approx 0.6$ – $0.7$ .

In contrast to a binary alloy, In, as a one-component material, cannot have an extended thermodynamically stable two-phase region with pressure variation at a given temperature. However, the small pressure gradient and deviatoric stress within the cell, in addition to

kinetical hindrance, may lead to the coexistence of these two tetragonal phases. A special balance between energy minima for two tetragonal phases in In [18] may result in a non-single state of In over a wide pressure range. To clarify these suggestions, it would be interesting to investigate under pressure In alloys with ~5 at.% Pb or Sn to search for a fct–fct transition, and to extrapolate the data on the axial ratio and transition pressure from present results on In<sub>90</sub>Pb<sub>10</sub> to pure indium.

## 5. Conclusions

An unusual phase transition is observed under pressure in the In<sub>90</sub>Pb<sub>10</sub> alloy without a significant volume change, where the crystal structure (space group) remains the same. The main feature of this transition is a jump in the axial ratio from  $c/a > 1$  to  $c/a < 1$  which seems to be controlled by the electronic subsystem.

Experimental results on  $c/a$  for fct phases obtained under pressure in In alloys with 10, 15, and 22 at.% Pb display a trend for  $c/a$  to approach the plot calculated for the touching of the BZ corners to the FS. These observations support the suggested model at least qualitatively, explaining the instability of the fcc structure with respect to tetragonal distortions in In and In alloys and the trends in the variation of  $c/a$  with electron concentration and with pressure.

## References

- [1] Villars P and Calvert L D 1985 *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (Metals Park, OH: American Society for Metals)
- [2] Vereshchagin L F, Kabalkina C C and Troitskaja Z V 1964 *Dokl. Akad. Nauk* **158** 1061 (Engl. transl. 1965 *Sov. Phys.–Dokl.* **9** 894)
- [3] Takemura K 1991 *Phys. Rev. B* **44** 545
- [4] Takemura K and Fujihisa H 1993 *Phys. Rev. B* **47** 8465
- [5] Pearson W B 1964 *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (New York: Pergamon)
- [6] Degtyareva O, Degtyareva V F, Porsch F and Holzapfel W B 2001 *J. Phys.: Condens. Matter* **13** 7295
- [7] Syassen K and Holzapfel W B 1975 *Europhys. Conf. Abstr. A* **1** 75
- [8] Grosshans W A, Düsing E F and Holzapfel W B 1984 *High Temp.–High Pressures* **16** 539
- [9] Otto J W 1997 *Nucl. Instrum. Methods Phys. Res. A* **384** 552
- [10] Forman R A, Piermarini G J, Barnett J D and Block S 1972 *Science* **176** 284
- [11] Mao H K, Bell P M, Shaner J W and Steinberg D J 1978 *J. Appl. Phys.* **49** 3276
- [12] Porsch F 1995 *EDXPowd* and *XPOWDER*—programs for evaluation of EDXD spectra (RTI, Paderborn, Germany)
- [13] The annealing temperature of the alloy In<sub>90</sub>Pb<sub>10</sub> at  $P = 10$  GPa was selected as  $T_{ann} = 150$  °C (423 K), in comparison with the temperature of melting for In at 10 GPa,  $T_{melt} \approx 700$  K, estimated from the  $T$ – $P$  phase diagram for indium in Young D A 1991 *Phase Diagrams of the Elements* (Berkeley, CA: University of California Press)  
For the In<sub>90</sub>Pb<sub>10</sub> alloy,  $T_{melt}$  is expected to be 750–800 K, so  $T_{ann}$  obeys an empirical metallurgical rule for the recrystallization temperature,  $T_{recr} \approx 0.5 T_{melt}$ , fairly well for recrystallization processes.
- [14] Schulte O 1994 *Thesis* Paderborn University
- [15] Mott N F and Jones H 1936 *The Theory of the Properties of Metals and Alloys* (London: Oxford University Press)
- [16] Heine V and Weaire D 1970 *Solid State Physics* vol 24 (New York: Academic) pp 342–5, 406–10
- [17] Svechkarov I V 1964 *Zh. Eksp. Teor. Fiz.* **47** 961 (Engl. transl. 1965 *Sov. Phys.–JETP* **20**)
- [18] Simak S I, Haeussermann U, Ahuja R, Lidin S and Johansson B 2000 *Phys. Rev. Lett.* **85** 142