an alternative way of looking at an old problem, has already lead Enting (1977c) to derive the relationship between the single- and triple-spin expectations for the Ising model on the honeycomb and triangular lattices far more simply than the existing derivation of Baxter (1975).

In terms of crystal growth the present findings are significant as they indicate that above a critical temperature we would expect binary systems to crystallize as disordered mixed crystals but below this temperature to tend to crystallize separately. In addition, since it is generally accepted that the critical temperature is dependent primarily on dimensionality (see Domb, 1974), the critical temperature for the introduction of disorder at growth would be expected to be lower than for the same system were it able to rearrange its constituent molecules to achieve energy minimization.

The authors have benefited from numerous discussions with Dr I. G. Enting.

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The Ordered State of In₃Te₄

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The composition of In_3Te_4 has been established as a single-phase material. Single crystals of this material have been prepared and its structure has been identified as tetragonal with lattice parameters $a_0 = b_0 = 6 \cdot 173$ and $c_0 = 12 \cdot 438$ Å. The stability of the structure has also been investigated.

Introduction

In a recent study on the ordered phases of In_2Te_3 (Karakostas & Economou, 1975) it was postulated that the high-temperature modification of the cubic phase on cooling separates into hypo- and hyperstoichiometric phases, with different long-range-order arrangements of the vacancies. This segregation occurs by the material passing through a transition state (Bleris, Karakostas, Stoemenos & Economou, 1976) where a short-order arrangement prevails.

The postulated hyperstoichiometric α-In_2Te_3-I, as

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it was called by Karakostas & Economou (1975), should have a structure within the range of stoichiometry of the compound In_3Te_4. From the electron diffraction patterns it was concluded that the phase should have a one-dimensional long-period superlattice with a tetragonal unit cell. The proposed structure for the In sublattice of α-In_2Te_3-I is given in Fig. 1(a), together with the lattice corresponding to the transmission electron diffraction patterns, with cubic cell indexing (Fig. 1b) and transformed to a tetragonal cell indexing (Fig. 1c).

Since the structure proposed for α-In_2Te_3-I and therefore assumed for In_3Te_4 was based on evidence which was not direct, we considered it important to investigate the In–Te system in the vicinity of the 3:4 composition range to confirm the existence of the tetragonal phase as a single independent stable one.
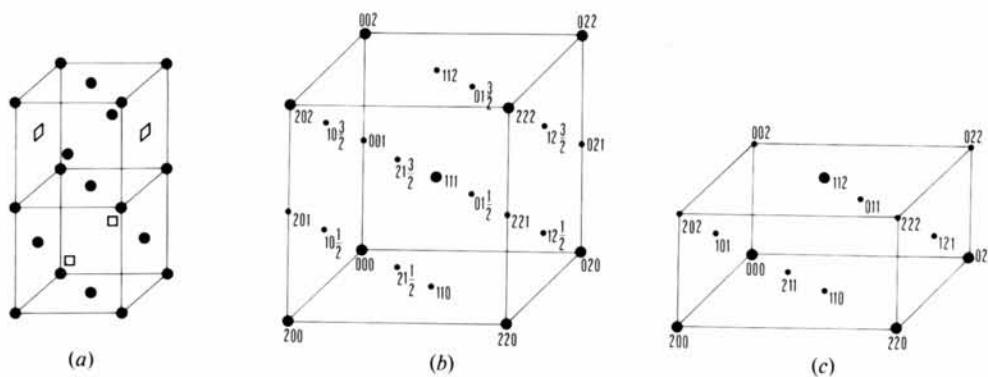
Fig. 1. (a) The unit cell of the long-period superlattice for the phase α-In_2Te_3-I (referring only to the In sublattice: dots are In atoms, squares In vacancies). (b) Cubic cell indexing. (c) Tetragonal cell indexing.

Experimental and crystal data

In order to obtain single-phase material we grew single crystals with a composition in the vicinity of the desired final product. For this we followed the same method used previously for In_2Te_3 (Karakostas & Economou, 1975) with the difference that in the initial charge the stoichiometric amounts of the elements corresponded to a composition In_3Te_4. Because the transformation from the β phase to the α phase was found to be a slow process, to assure perfection the growth ampoule was left at a temperature a little over 500°C for a week. The crystals obtained in this manner were similar in their main external features to the crystals of composition In_2Te_3 and, in order to obtain specimens for the electron microscope, the same procedure which was applied previously was followed.

The electron microscope transmission studies revealed that we were dealing with a single phase. In Fig. 2 diffraction patterns are presented corresponding to different sections. These diffraction patterns are similar in the general features to the ones obtained from areas in the segregated material of the α phase of In_2Te_3 (Karakostas & Economou, 1975) which was characterized as α-In_2Te_3-I, with the difference that the superstructure spots appear with different relative intensities. The variation in intensity of the super-structure spots may be attributed to the fact that this phase may exist over a wide range of composition, as is expected from the phase diagram of indium telluride (Shunk, 1964).

Material obtained from these crystals was used to perform X-ray powder analysis. This was done by using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1\cdot5417$ Å). The calculations were done by using least-squares analysis with the aid of program *PARAM* from the
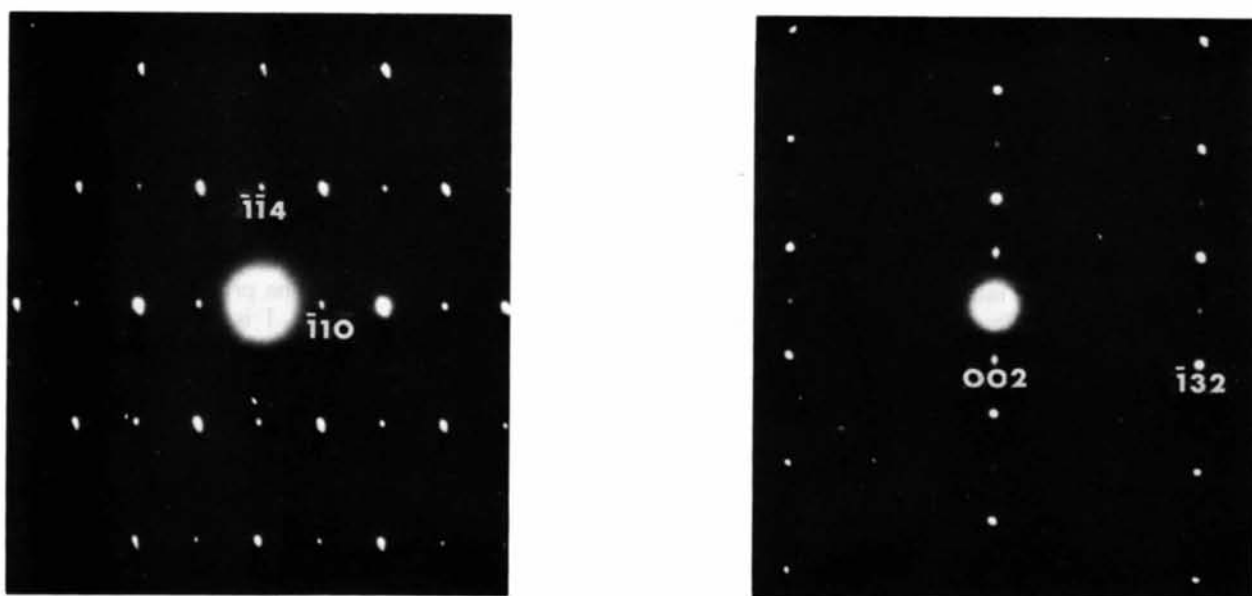

Fig. 2. Diffraction patterns obtained from single crystals of the phase In_3Te_4.

Table 1. *Indexing of X-ray powder diagrams of* In_3Te_4

I/I_1	d_{exp} (Å)	d_{calc} (Å)	$h k l$
75	3·5477	3·5729	1 1 2
75	3·4728	3·4420	0 1 3
100	3·1103	3·0866	0 2 0
40	3·0178	3·0063	1 1 3
20	2·6556	2·6952	1 2 1
10	2·3048	2·3074	0 1 5
50	2·1758	2·1826	2 2 0
40	2·0601	2·0594	2 2 2
40	1·9656	1·9522	1 3 0
40	1·8582	1·8626	1 3 2
20	1·4144	1·4168	3 3 2
30	1·3533	1·3476	2 4 2
30	1·2594	1·2617	2 4 4

$a_0 = 6\cdot173 \pm 0\cdot010$, $b_0 = 6\cdot173 \pm 0\cdot010$, $c_0 = 12\cdot438 \pm 0\cdot073$ Å

XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The results are presented in Table 1. From these results it is evident that the reflections obtained are compatible with a structure having a tetragonal unit cell with constants $a_0 = b_0 = 6\cdot173 \pm 0\cdot010$ and $c_0 = 12\cdot438 \pm 0\cdot073$ Å (*vs* $a_0' = 6\cdot158$ Å for the f.c.c. β-In_2Te_3).

Analysis of the results

From the data presented in the previous section it can be concluded that both TEM and X-ray powder analysis confirm that In_3Te_4 exists as a single-phase material. The stability of the structure, which is expected both from the relatively wide range of composition (57–60 at % Te), and from the slight deviation of the tetragonal from the cubic structure, indicates that the Te anions play a stabilizing role as in the case of the chalcopyrite structure (Phillips, 1973). Therefore we may conclude that we are basically dealing with a superstructure in the indium sublattice.

There are three stable ordered distributions of the indium vacancies possible in the In–V_{In} sublattice (V_{In} stands for In vacancies) and these give rise to superstructures compatible with the composition In_3–V_{In}. These superstructures are described with the following functions (Khachaturyan, 1973):

$$n_1(x,y,z) = \tfrac{1}{4} + \tfrac{1}{4}[\exp(2\pi ix) + \exp(2\pi iy) + \exp(2\pi iz)]$$

$$n_2(x,y,z) = \tfrac{1}{4} + \tfrac{1}{4}\exp(2\pi iz) + \tfrac{1}{4}\{\exp[\pi i(x + y + z)]$$
$$+ \exp[i\pi(x + y - z)]\}$$

$$n_3(x,y,z) = \tfrac{1}{4} + \tfrac{1}{4}\exp(2\pi iz) + \tfrac{1}{2}\cos \pi(2x + z). \qquad (1)$$

Only the third of these functions describes an ordered state which is characterized by a tetragonal superstructure with parameters for the unit cell $a = a_0$ and $c = 2a_0$ (Fig. 3a), which is compatible with the TEM observations and with the structure presented in Fig. 1. The space group of this In-V_{In} sublattice is $I4/mmm$.

This ordered form is oriented within the basic structure which has point group $m3m$ for the f.c.c. sublattice. Because $4/mmm \subset m3m$, the possible orderings of the tetragonal superstructure may be found by using the approach advanced by Van Tendeloo & Amelinckx (1974). Thus, by choosing the elements C_{4x}, $C_{4y} \notin 4/mmm$ we may write

$$\{m3m\} = \{4/mmm\} + C_{4x}\{4/mmm\} + C_{4y}\{4/mmm\}. \qquad (2)$$

This result shows that there are three possibilities for the ordering.

After the ordering of the In–V_{In} sublattice has been established, a possible structure of In_3Te_4 may be advanced. Such a structure is given in Fig. 3(b) with the atomic coordinates based on the assumption $c_0 \simeq 2a_0$.

In reality the z axis of the structure, described by the arguments presented above, is distinguished from the two other axes, since the actual ratio c/a differs from
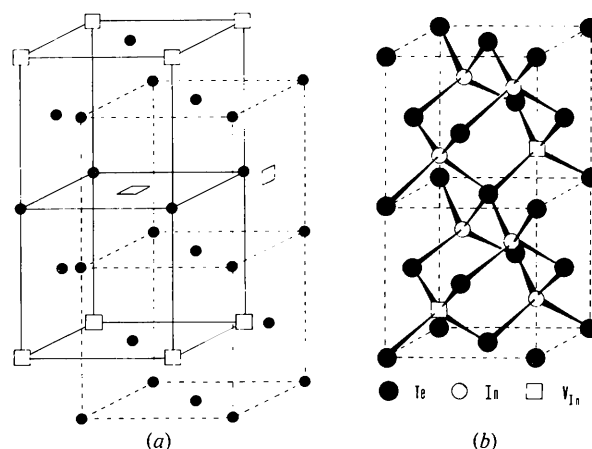

Fig. 3. (a) The unit cell of the proposed structure for In_3V_{In} sublattice (the cell presented with dotted lines corresponds to the cell of Fig. 1). (b) A possible ordering of the In_3Te_4 unit cell.
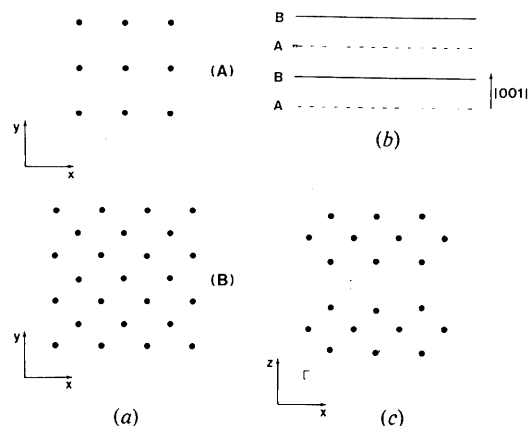

Fig. 4. The stacking of In atoms and In vacancies: (a) The two non-equivalent planes along the z direction. (b) The stacking order along the z direction. (c) The xz or yz equivalent planes.

the expected value of 2 by 0·014, that is $2 - c/a < 0$. By analysis of the structure proposed in Fig. 3(a) it is evident that the In atoms on successive xy planes are not equivalent. Thus the stacking of In atoms on these planes alternates along the z direction (Fig. 4a, b) with the In atoms experiencing second-order interactions either with In atoms or with vacancies; on the other hand, in the xz or yz equivalent planes each In experiences interactions with an equal number of In atoms and vacancies (Fig. 4c). Thus we expect the lattice constant to change less on the xy plane, which is what actually is observed (6·173 vs 6·158 for the cubic phase), while along the z direction the softening of the linkage $In-V_{In}$ leads to a small relaxation. In the case of In_2Te_3, if we sum the vacancies with zero valence, but count them per formula unit, the ratio e/a is equal to 4 ($\Sigma n_i v_i = 2·3 + 1·0 + 3·6 = 24$ and $\Sigma n_i = 2 + 1 + 3 = 6$) as expected for a tetrahedrally coordinated material. In the case of In_3Te_4 the ratio e/a is 4·12 ($\Sigma n_i v_i = 3·3 + 1·0 + 4·6 = 33$ and $\Sigma n_i = 3 + 1 + 4 = 8$). To restore the validity of the rule of 4, since the coordination remains unchanged although slightly distorted, it may be assumed that the electron–atom ratio in the In_3V_{In} sublattice is smaller than 3 per point, which requires one of the In atoms associated with the vacancy to become divalent. Such a compensation of charge, which actually is a resonance between In^{III} and In^{II} states, has been advanced previously in connection with the stability of the pyrrhotite structure (Van Landuyt & Amelinckx, 1972). From these arguments we may conclude that the energy contribution from the electron system is a second-order phenomenon which must contribute very little to the whole energy.

The small relaxation along the z direction due to the $In-V_{In}$ linkage is due to electrostatic interactions which introduce a shift among nearest-neighbour metal ions and metal vacancies. This view has been advanced by Phillips (1973) to account for the distortions in defect compounds with a certain degree of ionicity. The ionicity of a single In–Te bond is estimated to lie in the range 0·6–0·7 on the Phillips scale. This small relaxation has no rigorous effect on the energy of the $In-V_{In}$ sublattice, at least in the first approximation. Actually the total electrostatic Coulomb energy, i.e. the Madelung energy, is

$$E = - \frac{M(ze)^2}{r_0}, \tag{3}$$

where M is the Madelung constant. The total energy of the metallic sublattice, apart from the energy of the stable Te sublattice, can be regarded as a sum of E and the energy of the electron system E_{el}. Recently Soma & Umenai (1976) investigated the dependence of the

Madelung constant on small distortions (δ, δ') of the lattice parameters. In our case, if we assume a f.c.c. cell of the In_3V_{In} sublattice with half the volume of the proposed tetragonal cell, this cell is described by parameters $a_0 = b_0 = c_0 = 6·188$ Å. The deviation is $\delta \simeq -0·002$, as obtained from the relations

$$a = a_0(1 - 0·002) = 6·173$$
$$c = a_0(1 - 0·002)^{-2} = 6·219. \tag{4}$$

For this deviation the Madelung constant for the f.c.c. lattice differs very little from the value for the undistorted f.c.c. lattice, as is evident from the corresponding diagram presented by Soma & Umenai, but it nevertheless has a stabilizing effect, decreasing slightly the corresponding energy.

In conclusion we may state that the compound In_3Te_4 exists as a single-phase material with a tetragonal structure, as a result of long-range order of the vacancies. The vacancies introduce a relaxation, increasing the lattice constant along the z direction. The stabilization of the metallic sublattice of this phase seems to extend over a range of $In-V_{In}$ compositions. This variable composition has two results; first there is a filling of the space of the metallic sublattice with In atoms and second there is a continuous change of the e/a ratio. The range of stability of this phase is a matter for thermodynamic investigation.

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