Letters

Supporting evidence for the coincidence-ledge aspects of the CLD model of grain boundaries

In the coincidence-ledge aspects of the coincidence-ledge-dislocation (CLD) model [1, 2] one-layer unrelaxed hard-sphere modelling was used to show that the structure of high-angle tilt boundaries could be described in terms of *simple structural units*. In certain symmetric tilt coincidence boundaries, termed ideal coincidence boundaries, the ledge length is uniform so that the structure is perfectly periodic, and the shared atoms in the boundary at the ends of the units are exactly coincident. In these boundaries the structural units are defined by the ledges which enclose polygonal units of misfit. Between the misorientations at which the ideal coincidence boundaries occur, the boundary structure is made up of mixtures of units characteristic of adjoining ideal coincidence boundaries, or in certain misorientation ranges, of units characteristic of the crystal lattice. In these non-ideal symmetric tilt coincidence boundaries, the repeat unit is longer, and only boundary sites at the ends of the longer repeat units can be exactly coincident. The shared atoms in the interior of the repeat unit are in a compromise position between two nearly coincident lattice sites, that is, at "boundary coincidence" or near-coincidence sites.

It is the purpose of this letter to point out that the recent calculations by Hasson, Guillot, Baroux, and Goux (HGBG) [3] of the minimum energy configurations of ⟨100⟩ symmetric tilt boundaries in copper and aluminium provide support for the coincidence-ledge aspects of the CLD model. Both the CLD model and the computer modelling study of HBGB chose ⟨100⟩ symmetric tilt boundaries in fcc metals as examples. However, HGBG defined their misorientation θ_H as the angle between {100} planes rather than between {110} planes as was done in the CLD model for the definition of θ_C. Therefore, the θ values used in the two studies are complementary, i.e. $\theta_H = 90 - \theta_C$. Also HBGB chose to draw in {100} planes to connect the lattice points in their figures, rather than the {110} planes used in the figures of the CLD model. The computed boundary structures shown by HBGB in their fig. 6 (reproduced here as fig. 1) have $\theta_H = 16°45'$(should be 16°16'), 36°53', and 53°08', in which the boundary planes are of the form {710}, {310}, and {210}, respectively. These misorientations and boundaries correspond to those in the CLD model at $\theta_C = 73.7$, 53.1, and 36.9°, respectively.

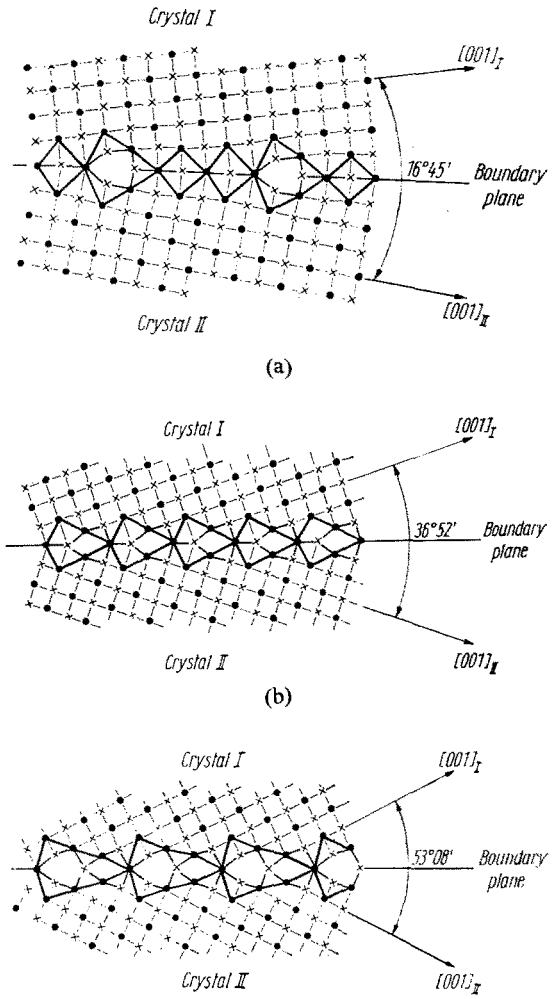

Figure 1 Computed structures of {100} fcc symmetric tilt boundaries from Fig. 6 of HGBG [3] with the {110} planes defining the ledges as in the CLD model drawn in the layer denoted by the filled circles; (a) the $\theta_H = 16°45'$ (should be 16°16'), $\theta_C = 73.7°$ boundary, {710} boundary plane, ledge pattern . . . |121| . . .; (b) The $\theta_H = 36°52'$, $\theta_C = 53.1°$ boundary, {310} boundary plane, ledge pattern . . .2222 . . .; (c) The $\theta_H = 53°08'$, $\theta_C = 36.9°$ boundary, {210} boundary plane, ledge pattern . . .3333 . . . .

In treating the structure of symmetric tilt boundaries, the CLD model developed a notation for expressing the pattern of structural units in terms of the length of the ledge in each structural unit. For example, in ⟨100⟩ fcc symmetric tilt boundaries the notation ...4444... indicates the ledge pattern in an ideal coincidence boundary at $\theta_C = 28.1°$ in which the ledge length is uniformly $4 \cdot a/2 \cdot \langle 110 \rangle$. The step height at the end of the ledge is always $1 \cdot a/2 \cdot \langle 110 \rangle$. In the notation ...|44344|..., the vertical bars delineate the longer repeat unit in a non-ideal coincidence boundary lying between the ...3333... $\theta_C = 36.9°$ and the ...4444... $\theta_C = 28.1°$ ideal coincidence boundaries. In boundaries with $\theta_C > 53.1°$, the "1" units in a pattern such as ...|121|... are aligned ledges of length $1 \cdot a/2 \cdot \langle 110 \rangle$. Since the step height is also $1 \cdot a/2 \cdot \langle 110 \rangle$, these aligned "1" ledges form square units which are units of a {100} plane, i.e. of the lattice. The ledge structure proposed in the CLD model [1] for the $\theta_C = 73.7°$, 53.1°, and 36.9° ⟨100⟩ fcc symmetric tilt boundaries were ...|121|..., ...2222..., and ...3333..., respectively.* Figs. 1a, b, and c of this paper show figs. 6a, b, and c of HGBG with the ⟨110⟩ planes (necessarily somewhat bent in the relaxed structures) drawn in one layer as used in the CLD model to define the ledges. As can be seen, the ledge pattern and the structural units in the computed structures are those proposed in the CLD model. Moreover, the relaxations from the atom positions in the CLD model are those one might intuitively expect. For example, in the $\theta_H = 53°08'$ ($\theta_C = 36.9°$) ...3333... boundary, the unrelaxed hard-sphere model shows that on one side of the coincidence atom the bond length across the boundary is too short (compression), and on the other side the bond length is too long (dilation). The calculations of HGBG show that the atoms in the region of compression shift outward away from the boundary and those in the region of dilation relax inward.

The relaxed structures show a series of shared atoms in the boundaries where either exact coincidence sites (ends of repeat units), or near-coincidence sites (interior of the longer repeat unit in the $\theta_C = 16°16'$ boundary) are expected. Initially HGBG [3] found, where they checked, that assuming $T \neq 0$† increased the computed enthalpy of the boundary, that is the shared sites at the ends of the repeat units were exact coincidence sites in the minimum energy configurations. However, they have found recently [4] that by varying T very slowly, the enthalpy could be reduced slightly by choosing T near 0.1 a_0 (a_0 = the lattice parameter). This refinement in the calculation does not alter the structural results, and changes the computed enthalpy by less than 5%. Thus it appears that in relaxed structures shared sites at the boundary will be found where expected on the basis of the CLD model, but that these shared sites will all be near-coincidence sites.

In fig. 1 the {110} planes defining the ledges at the boundary were drawn in only one layer in each boundary to avoid cluttering the figure. It can be determined easily by drawing the {110} planes in the second layer (denoted by crosses) that it is very nearly identical to the first layer, but displaced along the boundary. This is as expected, since {100} layers are displaced by $a/2 \cdot \langle 100 \rangle$ with respect to each other.

In developing the coincidence-ledge aspects of the CLD model, even though some suggestions were made as to how relaxation in the immediate vicinity of the boundary might take place, e.g. in the $\theta_C = 28.1°$ boundary by removal of one of a pair of overlapping atoms to give an alternating ledge structure, no attempt was made to predict in detail the way in which the structure in a real boundary might relax. It was recognized at the time that this would require a more sophisticated treatment such as that of HGBG. In spite of the apparent limitations of one-layer unrelaxed hard-sphere modelling there is surprisingly close agreement between the structures presented by HGBG and those proposed in the CLD model. This agreement, however, must obviously be treated cautiously. HGBG present structures for only three ⟨100⟩ boundaries in two fcc metals. These three boundaries, although they include both ideal and non-ideal coincidence misorientations, are all on one side of the ⟨100⟩ tilt spectrum $36.9° < \theta_c < 73.7°$ where the ledge lengths are short. This is where the unrelaxed hard-sphere model would be expected

*In fig. 1n of [1] the ledge notation and the misorientations are correctly shown. However, in making up the composite figure, the structural models for the repeat units in the $\theta_C = 67.4°$ ...|21|... and the $\theta_C = 73.7°$ ...|121|... boundaries were interchanged, as a count of the ledge pattern in the models will quickly show.

†T is the smallest vector joining two homologous sites. When $T \neq 0$, sites that would normally coincide exactly are translated with respect to each other by T.

to give the best results. In ⟨100⟩ fcc symmetric tilt boundaries when $\theta_C < 18.9°$, ledge lengths are long ($> 6 \cdot a/2 \cdot \langle 110 \rangle$) and extensive overlap of atoms in the long ledges in the unrelaxed model occurs. This suggests that in real boundaries coalescence of the ledges would occur to give a structure of isolated cores separated by regions of distorted single crystal. Weins, Gleiter, and Chalmers [5] have also computer modelled ⟨100⟩ symmetric tilt boundaries. Although most of their boundary structures agree with the CLD model, to the same degree as those of HGBG, not all do. The elastic anisotropy of cubic metals indicates that central force potentials, such as the Morse potential, are only approximate representations of metallic bonding. There is also a problem in recognizing absolute energy minima in the calculations, and entropy considerations have not yet been included.

Even with these reservations, the results of HGBG support the basic idea of the CLD model that grain boundaries are made up of a *limited number of small structural units* that are: (i) characteristic of certain *short period* special boundaries*, or characteristic of the lattice†; (ii) defined by ledges; (iii) bounded by shared sites; (iv) mixed in crystallographically appropriate patterns to form the longer repeat units of more complex boundaries lying between, or away from, the misorientations and/or inclinations at which the special boundaries occur. In relaxed structures the ledges may be slightly bent, the shared sites may be all near-coincidence sites and there may be extra or missing atoms in a unit. These relaxational features appear to modify, but not to basically alter, the structural features proposed in the CLD model. Chalmers and Gleiter [7] in a recent paper which retains the other features of the CLD model, suggested that translational relaxation will eliminate shared sites in the boundary. The results of HGBG indicate that this is not necessarily so.

The feature that the longer repeat units in boundaries away from short period boundaries are formed by mixing shorter, more-basic units characteristic of the neighbouring short period boundaries, or of the lattice, is important. This reduces the number of structural units needed to specify the boundary, and allows a continuous transition in structure and properties [1, 2] as the misorientation and/or inclination of the boundary changes.

Finally, it is of interest to note that a careful reading of the transition zone model of Hargreaves and Hills [8] reveals that it contains a number of features of the CLD model. They noted the existence of simple repeating structural units bounded by coincidence sites at special misorientations. If their [001] asymmetric tilt boundaries are viewed as [001] fcc boundaries (in one (001) layer, $[100]_{sc} = [110]_{fcc}$), these misorientations are $\theta_C = 53.1°, 22.6°, 16.3° \ldots$ to smaller θ_C, as given by their first formula. They also observed that between these coincidence misorientations, there would be "transition patterns" at a second series of misorientations given by a more general formula. Quite understandably in view of its time, their treatment overlooked certain points. Restriction of n to odd numbers in their first formula excludes certain of the ideal coincidence misorientations which are given by substituting even n in that formula. In addition they examined in detail only one of the repeat units, so that their concept of the structure of the repeat units and the transition in structure from one misorientation to another remained undeveloped, i.e. they did not recognize that the repeat patterns were made up of small basic units, which are mixed to effect the transition in structure. Also their relaxed zones on either side of the boundary are very wide in terms of today's thinking. Nevertheless their model must be counted as the first coincidence-structural unit model for grain boundaries.

References

1. G. H. BISHOP and B. CHALMERS, *Scripta Metallurgica* **2** (1968) 133.
2. *Idem*, *Phil. Mag.* **24** (1971) 515.
3. G. C. HASSON, J. B. GUILLOT, B. BAROUX, and C. GOUX, *Phys. Stat. Sol.* (a) **2** (1970) 551.
4. *Idem*, private communication.
5. M. WEINS, H. GLEITER, and B. CHALMERS, *J. Appl. Phys.* **42** (1971) 2639.
6. W. H. HARTT, G. H. BISHOP, and G. A. BRUGGEMAN, *J. Metals*, **21** (1969) 124A. Abstract of paper presented at 1969 Spring Meeting of TMS-AIME, Pittsburgh.
7. B. CHALMERS and H. GLEITER, *Phil. Mag.* **23** (1971) 1541.

*There are short period boundaries other than ideal coincidence boundaries, units of which may be structural elements in complex boundaries [6].

†For example the "1" units in a pattern such as . . . |121| . . . .

8. F. HARGREAVES and R. J. HILLS, *J. Inst. Metals.* **41** (1929) 257.

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Assignment of axes to arsenic and other rhombohedral crystals of the A7 structure type

Over the last decade, there has been much interest in the physical properties of the group V elements (arsenic, antimony and bismuth) and the literature abounds with publications on the subject. Recently, Akgöz and Saunders [1] have raised the question of the necessity for assigning a unique orthogonal axial set when describing such physical properties. Previous workers, Hatori [2], Kosevich [3], and Shetty and Taylor [4] were criticized for using an erroneous definition of a right-handed, orthogonal axial set which, it was claimed, results in incorrect assignment of the basic crystallographic directions. It is incumbent upon us to rebut or accept this criticism. The defence of our position is based on a fresh determination of the orientation of etch pits on cleaved complementary surfaces of an arsenic crystal. In order to clarify the point for future workers in the field, we present for the first time a concise and complete description of the crystallography with reference to three axial systems commonly used by previous workers. Our experimental work refers specifically to arsenic but the treatment and conclusions have direct applicability to other materials with the rhombohedral point group $\bar{3}m$.

The crystallographic data for arsenic are given in Table I. The original description of the structure by Bradley [5] was referred to a face-centred rhombohedral cell (fcr). The angles calculated by Bacon, Heckscher, and Crocker [6] also refer to this cell. The most recent and accurate determination of the crystal structure by Schiferl and Barrett [7] is referred to a primitive rhombohedral cell (rh) and a hexagonal cell (hex). The point group symmetry $\bar{3}\ 2/m$ and space group symmetry $R\bar{3}m$ remain unchanged in each description. An infrequently used body-centred rhombohedral cell [8] related to the primitive rhombohedral cell by the transformation $0\,1\,1/1\,0\,1/1\,1\,0$ is omitted from Table I.

Fig. 1 is a projection of the arsenic structure on the $(1\,1\,1)_{rh}$ plane. The three cells are shown together with pertinent crystallographic data. The origin lies in the paper and the positive directions of the three primitive rhombohedral axes, a_1, a_2 and a_3 are upwards. It must be stressed that there are three possible ways of assigning a_1, a_2 and a_3 in that any one of these directions can be designated a_1 but having done that, the choice for a_2 and a_3 is fixed. (The operation of the centre of symmetry results in another option which is considered later.) This set of rhombohedral axes or any one of the related axial sets is sufficient to set up a Cartesian axial system to describe any tensor property of materials crystallizing with the A7 structure

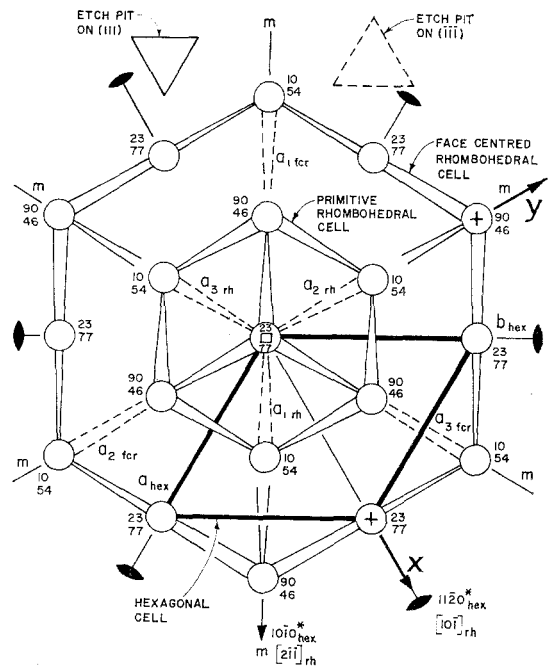

Figure 1 The rhombohedral arsenic structure projected onto $(1\,1\,1)_{rh}$. The atoms (open circles) are labelled with the values of their parameters (numerically $x = z$ for rhombohedral or hexagonal cells) referred to the origin (small square) in the centre; crosses (+) mark the lengths assigned to x and y in the Cartesian axial system.