Acknowledgments. This work was funded by an Australian Research Council grant (A39231020). We wish to thank Alexander Basman for help with a Russian translation.

References

Dimitriev, Y., Dimitrov, V., and Arnaudov, M. (1983) IR spectra and structures of tellurite glasses. *J. Mat. Sci.*, **18**, 1353–8.

Nakamoto, K. (1986) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed. Wiley-Interscience, New York.

Spiridonov, E. M. (1980) [Balyakinite, $CuTeO_3$, a new mineral from the zone of oxidation]. *Dokl. Akad. Nauk SSSR*, **253**, 1448–50 (in Russian).

Williams, S. A. (1981). Choloalite, $CuPb(TeO_3)_2.H_2O$, a new mineral. *Mineral. Mag.*, **44**, 55–7.

Yamaguchi, O., Tomihisa, D., and Shimizu, K. (1988) A new modified form of $TiTe_3O_8$. *J. Chem. Soc., Dalton Trans.*, 2083–5.

[*Manuscript received 5 October 1993*]

KEYWORDS: choloalite, synthesis, stoichiometry, tellurite.

Department of Chemistry,
University of Western Sydney, Nepean,
PO Box 10, Kingswood, N.S.W. 2747,
Australia.

D. W. POWELL
R. G. THOMAS
P. A. WILLIAMS

Department of Mineralogy,
Museum of Victoria,
328 Swanston Street,
Melbourne, Victoria 3000, Australia.

W. D. BIRCH

Department of Geology,
University of Melbourne,
Parkville, Victoria 3052, Australia.

I. R. PLIMER

MINERALOGICAL MAGAZINE, SEPTEMBER 1994, VOL. 58, PP. 508–512

Comments on 'An unusual octahedral diamond' by A. Yacoot and M. Moore

THE relative development of different crystallographic forms and their constituent faces during the growth history of a crystal has traditionally been studied by polishing successive crystal sections and etching them in an appropriate growth-texture-revealing reagent. Nowadays X-ray topography provides a widely applicable, non-destructive method, the diffraction contrast patterns recorded being sensitive to impurity zoning, which reveals the growth stratigraphy, and to differences in lattice perfection that are often found associated with material belonging to different growth sectors. Unfortunately, a recent application of the X-ray topographic technique to a natural diamond (Yacoot and Moore, 1992) incorrectly interprets the evidence and thereby misses genuine interesting and unusual features in the specimen concerned. Those features deserve proper description, which is here offered. Salient points are: (1)

the specimen belongs to the class of natural diamonds that exhibit mixed-habit growth in which non-faceted growth on hummocky surfaces that are roughly {100} in mean orientation occurs in combination with normal faceted growth on {111}); (2) unusually for diamonds in this class, the {111}-face growth sectors have suffered more post-growth dissolution than the near-{100}-orientation sectors (a possible explanation is suggested below); (3) interpretation (1) renders needless the complexity of a four-part sequence of alternating growth and dissolution epochs postulated by Yacoot and Moore; instead, a single growth epoch followed by some dissolution can account for both internal stratigraphy and present external morphology.

Consider first the characteristics of mixed-habit growth exhibited by natural diamonds. It was the remarkable etch patterns, abounding in curvilinear features, produced on polished diamond sections by Harrison and Tolansky (1964) and by Seal (1965) that led to the recognition (Frank, 1967) that during parts of their growth history the diamonds studied had been bounded by two forms, viz., non-faceted, hummocky, mean-{100}-orientation surfaces in addition to the normal {111} facets. [For brevity, the former, non-faceted, growth surfaces, together with the growth sectors underlying them, are called 'cuboid' (Moore and Lang, 1972)]. Diagrams explaining how the observed geometry of the etch patterns on polished sections, of cathodoluminescence images of such sections, and of the corresponding X-ray section topograph images, results from this mixed-habit growth are given by Lang (1974*a*, 1979), Suzuki and Lang (1976) and by Welbourn *et al.* (1989). The X-ray topographs published in these and other papers indicate that the relative development of {111} and cuboid forms, and their relative degrees of lattice perfection, can vary widely, both from specimen to specimen and within an individual crystal. (These and other characteristics of mixed-habit diamond growth are noted in a recent review (Lang *et al.*, 1992).) However, for present, diagnostic, purposes the most significant characteristics of cuboid growth are the curvilinear traces that cuboid growth surfaces make with intersecting plane surfaces (e.g. with an intersecting, thin, ribbon X-ray beam as used in recording X-ray section topographs), and, in particular, the prevalence of persistent re-entrants in cuboid growth surfaces and their traces. Good examples of such re-entrants appear in Fig. 8 of Moore (1988).

Turning to the specimen illustrated by Yacoot and Moore, note first that in their Fig. 1*a* the large apical protuberance pointing towards the observer is an octahedron in similar orientation to the central, larger octahedron. This is shown by the similarity of SEM contrast of their corresponding faces and the parallelism of their corresponding $<110>$ directions. One surmises, therefore, that it is this particular apical protuberance that is intersected on the right in the three X-ray section topographs, Figs. 1*d–f*; and such conclusion has been confirmed in private communication with the authors (whom the present writer thanks for this information, and for sending him a set of photographic prints of their figures). The X-ray images show that the smaller octahedron is a coherent parallel growth with the central octahedron. Parallel growth is not infrequent in diamond. The morphology in the present case is simple compared with some examples of parallel growth in Fig. 26 of Orlov (1977). It follows that the right-hand parts of the X-ray topographs contain no feature of particular interest. Attention can be concentrated on the protuberances appearing upper left and lower left in the topographs Figs. 1*d* and *e*. These protuberances are composed of cuboid growth.

The following drawings explain Yacoot and Moore's topograph images, albeit with some geometric idealisation. Their sections involve the half of the specimen nearer the observer, so the drawings Figs. 1*a* and *b* show only the near half of an octahedron that has (100) and$(0\bar{1}0)$ corner-truncating facets. This truncated octahedron idealises the shape of the crystal before post-growth dissolution (omitting the parallel growth occupying the volume towards $[00\bar{1}]$). The (100) and $(0\bar{1}0)$ growth sectors are drawn radiating from the octahedron centre; in actuality, they might have first developed at some radial distance between the central section, topograph Fig. 1*f*, and the section cut in topograph Fig. 1*e*. The relative development of the (100) and $(0\bar{1}0)$ sectors with respect to their surrounding octahedral sectors is drawn to make a reasonable match with topographs Figs. 1*d* and *e*. The geometry is idealised to show a constant $<111>/<100>$ growth velocity ratio, which gives rise to {100} growth sectors in the form of uniformly expanding, square-based pyramids. An X-ray section topograph cutting parallel to an octahedral plane (which is $(1\bar{1}\bar{1})$ in the present case) and passing through or close to the crystal's growth nucleus would make at most only small cross-sectional-area intersections with such (100) and $(0\bar{1}0)$ growth pyramids. Absence in topograph Fig. 1*f* of cuboid growth banding such as is seen in the [100] and $[0\bar{1}0]$ protuberances cut in topographs Figs. 1*d* and *e* accords with the construction shown here. The latter topographs do make significant intersections with the cuboid growth sectors, similar in size to those formed by the plane of section that is indicated in drawing Fig. 1*b*. The growth stratigraphy that would be revealed in the left half of a section located as in Fig. 1*b* is sketched in Fig. 2*a*. To make the basic pattern clear, Fig. 2*a* is drawn showing planar growth surface traces in the cuboid growth sectors. Replace these planar traces by curvilinear ones (with a persistent re-entrant in the case of the [100]-direction growth sector), remove the outermost zone of octahedral growth by dissolution, round-off the protruding cuboid growth sectors, and there results Fig. 2*b*, which makes a good match with the observed X-ray topographic images. Note that it is a mass of dislocations, radiating outwards roughly in the direction [0$\bar{1}$0] (on the evidence of topographs Figs. 1*d* and *e*) that is obscuring the curvilinear growth horizons in the [0$\bar{1}$0] cuboid growth sector. However, this dislocation trajectory direction is itself evidence that the local growth direction is roughly [0$\bar{1}$0] rather than normal to an octahedral face. In the [100] protuberance the sequence of curving growth surface traces, all similarly oriented, and filling the whole volume of the protuberance, is geometrically incompatible with that protuberance being a remnant of a dissolved octahedron on the vertex of the central (major) octahedron, as suggested by Yacoot and Moore. Indeed, such manifestation of curved traces, taking the form of arcs meeting in a pronounced and persistent re-entrant, denies faceted growth in the volume concerned. (Note also that in Yacoot and Moore's SEM image (Fig. 1*b*) of a dodecahedral protuberance some weak terracing can be discerned surrounding the cube-axis apex pointing towards the observer, revealing outcrops of the cuboid growth surfaces.)

Regarding the absence of cuboid growth along [00$\bar{1}$], and the presence of parallel octahedral growth instead, it is, of course, unknown what local chemical differences in the matrix surrounding the growing crystal might have been responsible for this feature. However, it is relevant to note the geometrical possibility that the stage of initiation of cuboid growth at other apices occurred after parallel growth surrounding the [00$\bar{1}$] apex had commenced its development. Recall that whereas X-ray topograph Fig. 1*e* shows that cuboid growth was well established in [100] and [0$\bar{1}$0] directions at a radial distance from the central octahedron nucleus of 0.5 (cosec 35.26°)

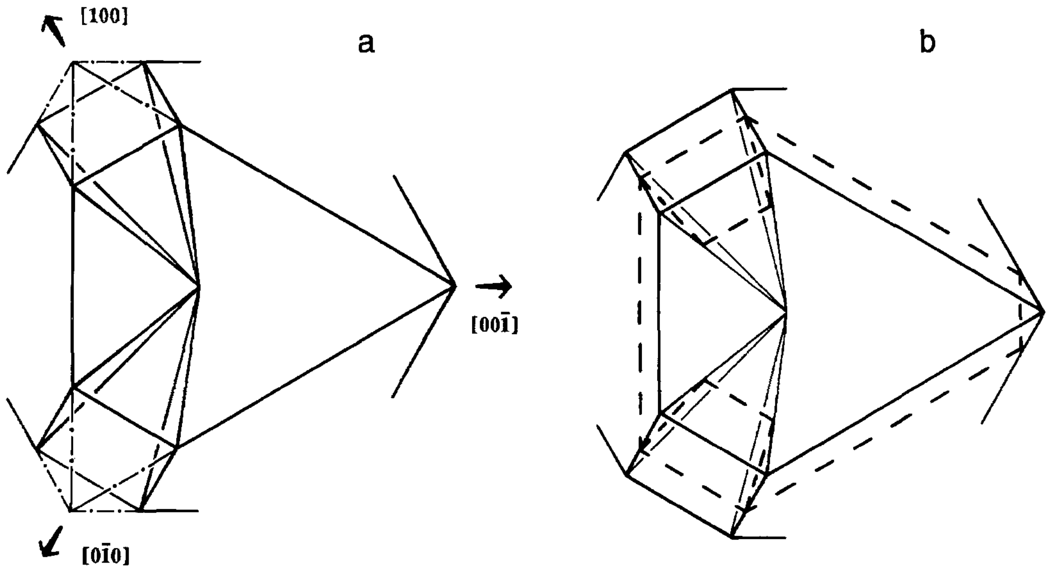

FIG. 1. Projection of external edges and of internal growth sector boundary edges of the near half of a regular octahedron having (100) and (0$\bar{1}$0) cube corner facets terminating [100] and [0$\bar{1}$0]-direction growth pyramids. Cube axes coming out of plane of drawing towards observer are indexed to correspond to those adopted by Yacoot and Moore: direction [1$\bar{1}\bar{1}$] points towards observer. (*a*) Chain lines indicate the edges of octahedron corners removed by truncation by (100) and (0$\bar{1}$0) faces. (*b*) Interrupted lines indicate intersections with the truncated octahedral external surface and with the internal cube growth sector boundaries made by a planar section parallel to (1$\bar{1}\bar{1}$) and located two-thirds of the distance from the octahedron centre to its (1$\bar{1}\bar{1}$) face.

mm = 0.87 mm, the radial distance at which these cuboid growth facets *first* appeared need not have been much less. The X-ray topographs do not disclose at what radial distance the geometry of the [00$\bar{1}$] apical region of the central octahedron first became modified by the parallel octahedral growth, but the present relative sizes and positions of the major and minor octahedra suggest that it may well have been less than 0.87 mm. Hence the configuration of growth facets in the neighbourhood of the [00$\bar{1}$] apex might already have been dissimilar to the configurations surrounding the [100] and [0$\bar{1}$0] apices at the growth stage when cuboid faces on the latter pair first appeared.

Finally, an explanation for the present shape of the diamond is proposed. All available evidence indicates that diamond takes up more nitrogen impurity on {111} facets than on cuboid facets. Laboratory experiments with oxidising agents on diamonds having inhomogeneous content of nitrogen impurity show preferential etching of the more nitrogen-rich material. If the outermost zones of {111}-faceted growth of the present specimen had been rich in nitrogen impurity, and post-growth dissolution had occurred under oxidising conditions, then these zones would have been preferentially removed, leaving the cuboid growth sectors protruding. Furthermore, the dodecahedral shape of the latter can also be plausibly explained, drawing upon previous observations of mixed-habit diamonds. Out of 13 specimens illustrated by Suzuki and Lang (1976), in 9 (including those that had suffered least dissolution) the X-ray topographs showed that cuboid growth had been superseded by {111}-faceted growth in the outermost growth zones preserved within the present crystal volumes. The specimen probably most nearly corresponding to Yacoot and Moore's diamond in an earlier stage of the latter's history is Specimen C1, whose near-(001) (and hence 4-fold symmetrical) central section appears in Fig. 3 of Suzuki and Lang (1976), and also in reviews (Lang, 1974*b*, Fig. 5; 1979, Fig. 14.13) and in a text on X-ray topography (Tanner, 1976, Fig. 6.2). In Specimen C1 high integrated X-ray intensity from outermost {111}-faceted growth zones is evidence for high density of nitrogen-containing lattice defects (too dense for individual resolution X-ray-topographically). In the same growth epoch, the cuboid growth sectors were completely grown out, tapering to zero cross-section area as

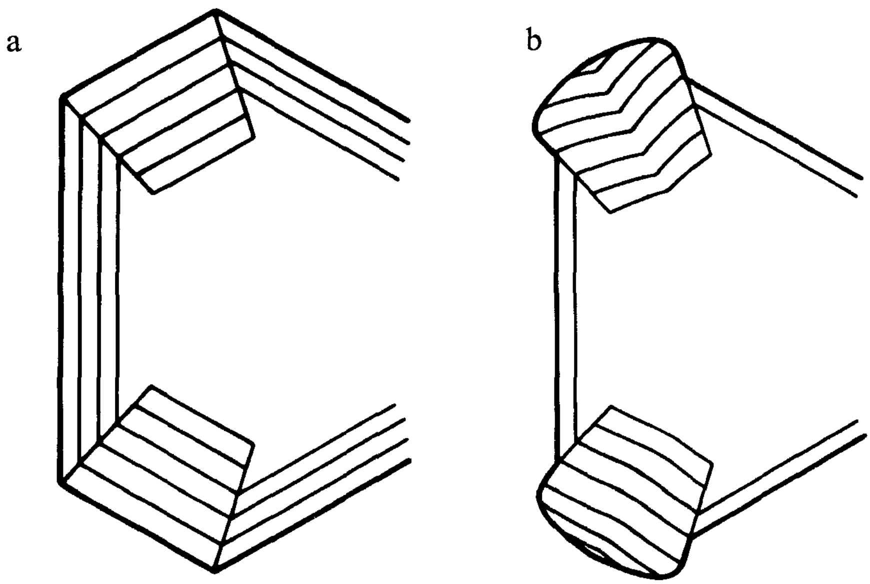

FIG. 2. Growth stratigraphy that would be revealed in the left half of (1$\bar{1}\bar{1}$) section cut as in Fig. 1b. For simplicity, traces of {111} facets are drawn only in outer zones of the crystal. [In the X-ray topographs the 4$\bar{4}$0 diffracted beam leaves the crystal in a direction rotated $20\frac{1}{2}°$ from [1$\bar{1}\bar{1}$] towards [00$\bar{1}$], but this produces no significant distortion of observed relative to predicted images.] (*a*) Original shape of section of Fig. 1*b*, with faceted growth in cube growth sectors. (*b*) Expected growth surface traces on reduced section area following post-growth dissolution. Cuboid growth present.

outward-pointing pyramids, axis $<100>$, with the orientation of growth sector boundary surfaces between cuboid growth and its surrounding {111}-faceted growth sectors approaching tangency with the {111} faces of the latter. If cuboid growth sectors terminated in this fashion by near-{111} surfaces in the vicinity of their apices were left protruding by preferential removal of their surrounding octahedral growth sector material, and were themselves subjected to dissolution, a roughly dodecahedral shape of the outward-pointing surfaces of these protuberances is expected to result (Moore and Lang, 1974).

References

Frank, F. C. (1967) In *Proc. International Industrial Diamond Conf., Oxford. Vol.1. Science* (J. Burls, ed.) pp. 119–35, Industrial Diamond Information Bureau, London.

Harrison, E. R. and Tolansky, S. (1964) *Proc. R. Soc. Lond.* A, **279**, 490–6.

Lang, A. R. (1974*a*) *Proc. R. Soc. Lond.* A, **340**, 233–48.

Lang, A. R. (1974*b*) *J. Cryst. Growth*, **24/25**, 108–15.

Lang, A. R. (1979) In *The Properties of diamond* (J. E. Field, ed.) Chapter 14, pp. 425–69, Academic Press, London.

Lang, A. R., Moore, M. and Walmsley, J. C. (1992) In *The Properties of Natural and Synthetic Diamond* (J. E. Field, ed.) Chapter 5, pp. 215–58, Academic Press, London.

Moore, M. (1988) *Industrial Diamond Review*, **48**, 59–64.

Moore, M. and Lang, A. R. (1972) *Phil. Mag.*, **26**, 1313–25.

Moore, M. and Lang, A. R. (1974) *J. Cryst. Growth*, **26**, 133–9.

Orlov, Yu. L. (1977) *The Mineralogy of the Diamond*, Wiley, New York.

Seal, M. (1965) *Amer. Mineral.*, **50**, 105–23.

Suzuki, S. and Lang, A. R. (1976) *Diamond Research*, 1976, 39–47, Industrial Diamond Information Bureau, Ascot, Berks.

Tanner, B. K. (1976) *X-ray Diffraction Topography*. Pergamon, Oxford.

Welbourn, C. M., Rooney, M.-L. T. and Evans, D. J. F. (1989) *J. Cryst. Growth*, **94**, 229–52.

Yacoot, A. and Moore, M. (1992) *Mineral. Mag.*, **56**, 111–3.

[*Manuscript received 15 October 1993.*]

KEYWORDS: diamond, non-faceted growth, X-ray topography.

H. H. Wills Physics Laboratory,
University of Bristol,
Royal Fort,
Tyndall Avenue,
Bristol BS8 1 TL, UK

A. R. LANG