Table 4 for Schoknecht and Göttlicher are (mostly) positive and (mostly) negative, respectively: their magnitudes are large in both cases. Jansen & Freeman (1986) report calculated values larger than the experimental values by Schoknecht (1957), in particular for the 555, 771 and 777 reflections for which they find the largest discrepancies (28, 45 and 101%). These differences between our results and those of Jansen & Freeman are clearly due to the DW factors used.

3. Concluding remarks

Our results appear to indicate that whenever good room-temperature data are available [LiF and KCl: Schmidt *et al.* (1985), NaF: Howard & Jones (1977)] the agreement between the structure factors calculated with the DW theory and the experimental values is generally very good and the few large discrepancies for NaF can be attributed to deficiencies of the experimental data. For NaCl, one cannot draw any definite conclusion owing to the lack of good experimental data.

Our results show that there does not seem to be any need to call into question the validity of the DW theory, as Jansen & Freeman (1986) appear to propose.

We should finally note that the low-temperature diffraction experiments suggested by Jansen & Freeman (1986) are not only technically difficult but would not eliminate the problem of taking into account the vibrational effects of the zero-point motions, which still involve contributions from all lattice frequencies.

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The Morphology of Calaverite ($AuTe_2$) from Data of 1931. Solution of an Old Problem of Rational Indices

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Abstract

The anomalous high-index faces (*hkl*) of the mineral calaverite ($Au_{1-x}Ag_xTe_2$) measured goniometrically in the year 1931 by Goldschmidt, Palache & Peacock [*Neues Jahrb. Mineral.* (1931), **63**, 1-58] are re-interpreted and related to the wave vector **q** of the displacive incommensurate modulation which was recently found in the crystal structure. All crystal faces (including the high-index ones) can be given four low indices (*hklm*), using **q** as a fourth basis vector. From this an almost hundred-year-old anomaly in crystal morphology is in principle solved.

1. Introduction

The present investigation started from a suggestion made in 1984 by J. D. H. Donnay to one of the authors at the XIII International Congress of Crystallography in Hamburg in 1984 to reconsider the problem of

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non-applicability of the law of rational indices to crystal growth forms of calaverite $Au_{1-p}Ag_pTe_2$ ($p < 0{\cdot}15$) (Smith, 1902; Goldschmidt, Palache & Peacock, 1931).

Classically (Bravais–Friedel) the morphology of crystals is related to the existence of a crystal lattice. This crystal lattice is even implicitly suggested by Haüy's law of rational indices. The latter can be extended to the use of four or more rational indices in order to describe the crystal forms of modulated crystals (Janner, Rasing, Bennema & van der Linden, 1980; Dam & Janner, 1983, 1986). The fact that the number of indices can be larger than three reflects the fact that the number of fundamental periodicities can also be larger than three, which is a key concept for the understanding of crystal faces. Hence, in the description of crystal morphology one is not necessarily restricted to the three periodicities generating a three-dimensional space lattice. In the one-dimensional modulated case the modulation wave vector $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$ has to be added as a fourth basic vector to the three ones of the undistorted reciprocal-lattice unit cell: $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$. Any crystal face of a one-dimensionally modulated crystal is then labeled by the *four* indices ($hklm$) of the corresponding face normal given by $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$. The use of four indices is closely related to the superspace approach as introduced for incommensurately modulated crystals by de Wolff (1977) and Janner & Janssen (1977, 1980). Indeed, the presence of fundamental periodicities in a given crystal does not mean that the structure is periodic in space. One can eventually restore the familiar lattice periodicity by embedding the crystal in a larger space, the superspace, with as many dimensions as there are fundamental periodicities. In Dam & Janner (1986) the details of this approach are explained and applied to the morphology of the modulated phases of the crystal tetramethylammonium tetrachlorozincate $[(CH_3)_4N]_2ZnCl_4$. The most recent experimental result of morphological research on that compound is the observation of a roughening of a satellite orientation ($hklm$) upon a change of the modulation wave vector $\mathbf{q}$ as a function of temperature (Dam, 1985). Note that superspace embedding is necessary for a symmetry characterization in terms of Euclidean space groups, but not if that is not required. Indeed, in the present paper we will stick to the three-dimensional description.

In a previous paper on the morphology of calaverite (Dam, Janner & Donnay, 1985) a first partial re-indexing of a number of crystal faces was given, taking advantage of the electron diffraction results of Van Tendeloo, Gregoriades & Amelinckx (1983) and Van Tendeloo, Amelinckx & Gregoriades (1984). Their diffraction patterns show the existence of extra so-called satellite spots around the main reflections of the basic reciprocal lattice, revealing that the crystal is modulated by a periodic lattice distortion, which is incommensurate with respect to a basic structure having $C2/m$ symmetry. The appearance of the extra diffraction spots is mainly due to a displacive modulation of the gold–tellurium distances (Schutte, Dam, Janner & de Boer, 1987; Schutte & de Boer, 1988). Taking the existence of that modulation into account, we give a full re-interpretation of the morphology of this famous anomalously behaving mineral. It will be shown that the morphology can be consistently described by four indices, labeling the observed faces in the way indicated above. No new measurement has been performed: the present analysis is fully based on the morphological data collected in 1931 by Goldschmidt, Palache & Peacock, hereafter denoted GPP. Using three indices (hkl) only, GPP needed at least four interpenetrating lattices, and, even so, they were unable to index all forms occurring in natural calaverite. In the present four-indices ($hklm$) approach, one single set of reciprocal wave vectors (the same as the ones appearing in the Fourier analysis of the crystal structure in terms of four fundamental periodicities a^*, b^*, c^* and q) is sufficient for characterizing all the forms observed. Accordingly, the faces of calaverite are oriented parallel to fronts of the Fourier waves of its crystal structure.

The relevance of the present paper can be seen in the consistent indexing of the full set of faces measured by GPP on calaverite. In a previous paper on this subject (Dam, Janner & Donnay, 1985) only less than half of the faces had been indexed. One has to realize that for partial sets GPP were also able to assign low indices. That is the way they presented their morphological data. The problem was that they were unable, as other investigators before them, to do so for the full set of crystal growth forms. The present investigation is therefore essential for ensuring the validity of the four-indices approach presented in the 1985 paper mentioned above.

2. Historical review

2.1. *Morphological investigations on calaverite*

The first detailed morphological account of calaverite was given by Penfield (1895) after the mineral had been first identified by Genth (1868). The latter author characterizes the (Au, Ag)Te_2 compound as a soft brittle substance without a well defined cleavage plane. Penfield describes the crystal morphology as having essentially triclinic point symmetry. His article was quickly followed by two extensive and detailed studies by Smith (1902, 1903) and by Penfield & Ford (1902). These papers describe an amazingly rich variety of forms of which only a few could be indexed with three small integers. From the low-index forms, both papers identified a monoclinic lattice. The cell constants revealed that this lattice is pseudo-orthorhombic ($\beta = 90{\cdot}13°$) and bears a remarkable similarity to that of sylvanite, another $(Au, Ag)Te_2$ compound with an Ag/Au ratio of approximately 1. Nevertheless, the configurational symmetry of the morphology as a whole appeared to have a $2/m$ point-group symmetry. Penfield & Ford therefore chose the monoclinic lattice to describe the morphology, though they have to admit: 'Die Krystalle scheinen geradezu einen Widerspruch gegen einige Gesetze der Krystallographie darzubieten'.

An alternative for the high indices necessary in the Penfield & Ford description of crystal forms is given by Smith (1903). He examined a large number of crystals, which all showed a pronounced prismatic habit with many small crystal faces on top. (An example taken from the GPP paper is shown in Fig. 3.) The 135 crystal forms he could identify forced him to assume at least three independent lattices (one monoclinic and two triclinic). To account for the monoclinic $2/m$ configurational symmetry of the crystal morphology Smith (1903) assumed that the triclinic lattices are twinned. That brings the total number of lattices to five: 'Thatsächlich scheinen fünf verschiedene Gitter da zu sein, welche incongruent, aber nicht von einander unabhängig sind' (Smith, 1903). Two other important statements from Smith are cited by Penfield & Ford (1902): 'Unless, however, the crystals are regarded as triclinic twins, it is impossible to obtain simple indices' and, as he did not find any re-entrant angles, 'there must be an extraordinarily intimate penetration'. Apart from this special kind of twinning, Smith identified two new twin laws in addition to the one already reported by Penfield & Ford.

The dilemma of either giving up important crystallographic laws or assuming an otherwise indistinguishable twinning occupied many crystallographers in the following 30 years. These researches remained unpublished as they failed to reconcile the experimental evidence with the accepted laws of crystallography. Finally, all these efforts resulted in a joint paper by GPP, based on the morphological data of 105 crystals of finest quality. Confirming in essence the results of Smith and Penfield & Ford, GPP have to admit that it is not possible to choose an axis system such that the majority of forms can be described by simple rational indices. They resort to a description which requires not less than four distinct and independent lattices, one monoclinic and three triclinic, a fifth being degenerate (see Fig. 1). Therefore even this does not allow one to describe all forms satisfactorily. At the end the law of rational indices is abandoned with the statement that 'das Gesetz der Rationalen Indices ... nicht ein allgemeines Gesetz ist'. Only with an *ad hoc* extension to the so-called law of complication do GPP satisfy themselves with their four-lattice description. They do not deal with the physical meaning of this extension, which seems to say nothing more than that the construction of four interpenetrating lattices is now allowed. The morphological literature on calaverite was temporarily concluded by a preliminary communication of Donnay (1935). He proposed a new kind of twinning due to a deformation of the crystal structure. At the same time X-ray crystallography gradually took over.

2.2. *X-ray and electron diffraction studies on calaverite*

The first Weissenberg photographs made by Tunell & Ksanda (1935) confirmed the monoclinic (sylvanite-like) lattice as the basic structural one. Excluding any orthorhombic groups, they proposed the $C2/m$ space group. In a subsequent paper (Tunell & Ksanda, 1936) the morphological unit cell was established. Also, extra so-called 'adventive' diffraction spots were observed, which could not be ascribed to planes of the structural lattice, unless the monoclinic unit cell was enormously expanded. An attempt to correlate these adventive spots with the high-index faces was only partly successful. Donnay himself, however, verified on the photographic records of

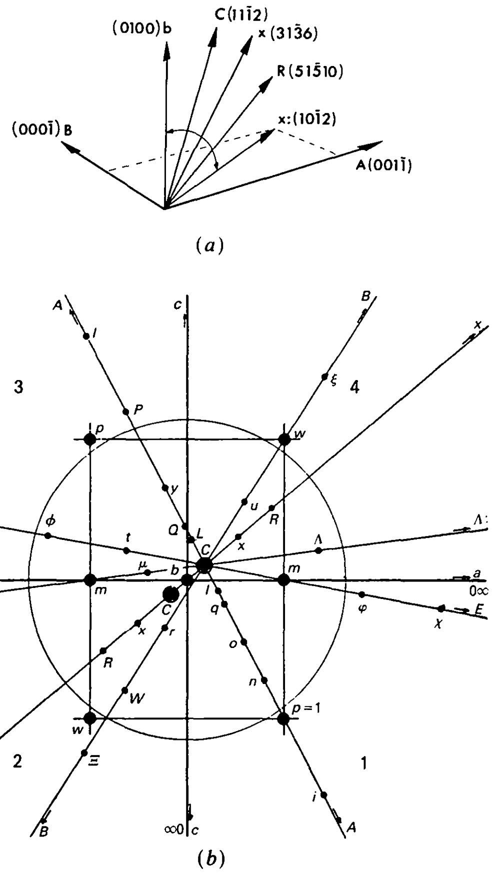

Fig. 1. (*a*) The axes of the Miller bases of Table 1 plotted in one drawing. The indices *hklm* indicate the direction $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$. (*b*) The same axes indicated in a gnomonic projection as reproduced from Fig. 7 of GPP.

Tunell & Ksanda the correspondence in orientation between those 'aberrant spots' and the crystal faces having 'complicated indices' (Donnay, 1935). The structure determination by Tunell & Pauling (1952) confirmed the space group formerly obtained, acknowledging that it disregards the extra diffraction spots and therefore describes an average structure only. In 1964 M. J. Buerger called the attention of de Wolff (1984) to a possible analogy between calaverite and γ-Na_2CO_3 whose incommensurately modulated character had just been recognized (Brouns, Visser & de Wolff, 1964). Recent work by Pertlik (1984) led to other conclusions. He proposed a *Pc* or even a *P*1 space group; he did not mention the extra spots though. The *Pc* structure determination also describes, as he states, an average structure only, which otherwise should be indicated by a *P*1 space group.

The modulated nature of calaverite was first acknowledged by Sueno, Kimata & Ohmasa (1979). The adventive spots were identified as satellite reflections with a wave vector normal to the $(30\bar{4})$ lattice plane. Still, the structure was again interpreted in terms of a *P*1 space group and an enlarged supercell.

Shortly afterwards, Van Tendeloo, Gregoriades & Amelinckx (1983) presented their impressive electron microscope high-resolution images and the corresponding electron diffraction results. They confirmed the Tunell & Pauling monoclinic centred lattice as the basic one, on which a displacive incommensurate modulation along the *b* axis is superposed involving mainly the gold atoms. The basic unit cell of calaverite is correspondingly the same as that of sylvanite. The difference lies in the modulation which is commensurate in the case of sylvanite, with wave vector $\mathbf{q} = [0{\cdot}5\ 0\ 0{\cdot}5]^*$, whereas in calaverite slight deviations in length and orientation yield an incommensurate **q** vector oriented approximately along $[202]^*/4{\cdot}5$.

The diffraction studies reviewed are rather confusing as far as the relative sign of the $\mathbf{a}^*$ component in the **q** vector is concerned. The morphological analysis presented by Dam, Janner & Donnay (1985) required $\mathbf{q} = [-0{\cdot}41\ 0\ 0{\cdot}45]^*$. An X-ray structure determination of natural calaverite by Schutte & de Boer (1988; Schutte, Dam, Janner & de Boer, 1987) confirmed the basic structure of Tunell & Pauling (1952) with space group $C2/m$ and the modulation wave vector given by $\mathbf{q} = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*$ with $\alpha = -0{\cdot}408$ and $\gamma = 0{\cdot}448$, the modulation parameters being practically temperature independent. The (3 + 1)-dimensional superspace group appears to be $C2/m(\alpha, 0, \gamma)(0s)$ and the displacive modulation indeed has amplitude mainly along the unique *b* axis (of the basic structure). These displacements give rise to a variation of the local octahedral tellurium configuration around the gold atoms from a nearly linear to a nearly planar square one for the nearest neighbours. One also observes a concentration modulation of silver at gold positions with maxima at the linear configuration sites (Schutte & de Boer, 1988). This supports the idea of a combined modulated valence state for Au between those of Au^+ and Au^{3+} as anticipated by de Groot, Gutfreund & Weger (1987). In order to test this interpretation *ab initio* electronic band structure calculations on pure $AuTe_2$ are in progress (Krutzen, 1988).

It is interesting to note that the analogy between calaverite and anhydrous sodium carbonate suggested by Buerger is now confirmed in the sense that both compounds share the same superspace symmetry group. All these results were not yet known at the moment when the present investigation was practically concluded. A preliminary version of this paper can be found in the PhD thesis of Dam (1986).

3. The morphology of calaverite

3.1. *A re-indexing of crystal faces*

A large portion of the calaverite morphology could be re-indexed quite easily. Satellite face normals were obtained by adding $m\mathbf{q}$ to the normals of the main faces (*hkl*) expressed in the reciprocal-lattice basis vectors of the monoclinic structure, as reported by Dam, Janner & Donnay (1985). The face normals $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ were thus described in terms of four integers (*hklm*). The corresponding spherical angles were then compared with those obtained by goniometric measurements. Identification was mostly straightforward. Conversely, with the face indices known, it was then possible to determine the orientation of the modulation wave vector **q** showing the best fitting with the accurate experimental data supplied by GPP. One then obtains for the modulation vector: $\mathbf{q} = [-0{\cdot}4095\ldots\ 0\ 0{\cdot}4492\ldots]^*$. For comparing observed with calculated face orientation the approximative value $\mathbf{q} = [-0{\cdot}41\ 0\ 0{\cdot}45]^*$ has been used in combination with a pseudo-orthorhombic lattice as in our previous publication. This is more appropriate than to use the monoclinic lattice because in the morphological studies cited the monoclinic angle β was found to vary a little from sample to sample. It is not straightforward to give (*hklm*) indices to satellite faces which are not associated with an identified main (*hkl*0) face.

The problem has been approached in two ways. First, all spherical angles ρ(obs.), colatitude measured from $\mathbf{b}^*$, and φ(obs.), longitude measured from $\mathbf{a}^*$, obtained from observation were transformed to fractional indices (*h*1*l*). Then $m\mathbf{q}$ is added to each of these fractional coordinates, until one is close enough to the orientation of a vector of the basic reciprocal lattice. Though this (*h*1*l*0) coordinate, to be called the 'origin' from now on, does not represent a face normal, still the satellite face can now be indicated as (*h*1*lm*). In order to keep *m* as low as possible (*i.e.* $m < 15$) one is sometimes forced to assume that $k \neq 1$. The $(hkl0)$ origins are then of course found by adding $(m\mathbf{q})/k$ to the fractional coordinate of each satellite face.

The second approach consisted of making a list of the orientation of all reciprocal vectors having integral coordinates h, k, l, m smaller than five when expressed with respect to $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ and $\mathbf{q}$ which (because of incommensurability) are linearly independent of the integers. All but a few satellite faces can then be identified by comparing these values with the corresponding GPP list of spherical coordinates. Some ambiguities could be resolved by assuming that the satellite wave vectors lying in a given zone $\mathbf{k}(hklm) \times \mathbf{q}$ will usually belong to one and the same $(hkl0)$ origin.

Both methods yield surprisingly unique and corresponding results for most faces because $(hkl0)$ origins have to be situated in the zone spanned by $\mathbf{k}(hklm) \times \mathbf{q}$ *and* have to lie at a distance $m\mathbf{q}$ separated from $\mathbf{k}(hklm)$. The few remaining ones have been identified by combining the two methods. The result is presented in Table 1 and in Figs. 2 and 3.

3.2. *Discussion of Table* 1

All 92 crystal forms numbered according to GPP are re-indexed with respect to the single set of four basic vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ and $\mathbf{q}$. In most cases only relatively small integers occur in the indices and the difference between observed and calculated orientation given in terms of the spherical angles ρ and φ as in GPP is surprisingly small. In a few cases, however, the difference is definitely larger, *e.g.* for forms no. 15, 54, 72, 74, 75. Also, the high indices that one gets for m in a few cases are a bit suspicious. Note, by the way, that these high values for m require a very accurate determination of $\mathbf{q}$, so that in these cases the angular deviations are understandable. Conversely, the excellent agreement between the modulation parameters α and γ following from these morphological identifications and those obtained from X-ray diffraction represents an additional check. In addition, a simple extension of Friedel's law of the morphological importance of crystal faces expressed in terms of small wave vectors $\mathbf{k}(hklm)$ makes plausible the appearance of fairly large m values compatible with the requirement of small $\mathbf{k}$. Still, the majority of forms is quite easily provided with remarkably low indices, especially when comparing with any other single lattice interpretation. For one case, that of the face φ of no. $42 = (11\bar{3}6)$, we find only a plausible form at the angle $\varphi = -163°28'$ and not $+163°28'$ as indicated in the GPP table. In view of the position of the face φ one finds in Table III of GPP's paper, it is fairly safe to assume that there is a mistake in sign for the value of the angle $\varphi(\text{obs.})$ originally indicated by GPP. Accordingly that value has been changed in Table 1.

Also in the case of the face y of no. 15 we might be dealing with an erroneously given value for $\varphi(\text{obs})$. For the same face Smith (1903) reports $\varphi(\text{obs.}) = 104°04'$ and $\rho(\text{obs.}) = 30°21$, which is in much better agreement with our $(11\bar{2}3)$ assignment.

The Miller indices in the third column are derived by GPP on the basis of their interpretation in terms of four lattices spanned by the reciprocal vectors C, x, R and b, respectively, together with the common two A and B. These lattices are briefly indicated by ABC, ABx, ABR and ABb. We remark that A, B, C, x, R and b denote at the same time an observed crystal face (representative of the form) and a corresponding reciprocal wave vector normal to it. The four lattice bases are separately indicated in the table using GPP's notation for each set of forms. For the last eight forms no lattice at all is provided. From our indexing it follows that these eight forms belong to the lattice ABx: which is degenerate as A, B and x: are coplanar, all being perpendicular to b. Note furthermore that b, C, x, R and x: lie in the same zone $[0{\cdot}10, 0, -0{\cdot}18]$ (the zone is indicated in fractional coordinates of the basic monoclinic lattice abc). The relation between the axes of the Miller bases is sketched in Fig. 1. Substituting for each of the reciprocal vectors A, B, C, x, R, b and x: the corresponding $hklm$ indices, one is surprised to find that our interpretation is fully compatible with the Miller indices given in Table 1. The difference in the two approaches is that at the cost of one single extra base vector, one set only of 'fundamental reciprocal vectors' is needed. The structural meaning of the relative orientation of the five lattices given above with respect to the zone $[0{\cdot}10, 0, -0{\cdot}18]$ is not yet clear.

The *hklm* indices reported in Table 1 do not take into account any possible symmetry extinction conditions which follow from applying to superspace the ideas originally developed by Donnay & Harker (1937). In the crystal form of $[(CH_3)_4N]_2ZnCl_4$ (TMA-ZC), we have observed morphological forbidden indices corresponding to the X-ray extinction conditions due to the superspace symmetry group of this compound (Dam & Janner, 1986) on the basis of the TEM results of Van Tendeloo *et al.* (1983). For calaverite we proposed (Dam, Janner & Donnay, 1985) the superspace group denoted by $C2/m(\alpha\ 0\ \gamma)(0s)$ for which the conditions of reflection are (de Wolff, Janssen & Janner, 1981) $h + k = 2n$ and $h0lm$, $m = 2n$. From GPP and Penfield & Ford (1902) we already know that all forms have a $2/m$ configurational symmetry, which is in agreement with the external point group of the proposed superspace group. The C-centring condition $h + k = 2n$ is fulfilled for most of the forms. In a few cases, *e.g.* {0100}, {1010} or {0102} one would have to double all indices to conform to the centring condition, but this cannot be deduced from these forms without a comparative study of their 'morphological importance' (MI).

Table 1. *Re-interpretation of the morphological data of Goldschmidt, Palache & Peacock (GPP) on calaverite*

The first three columns give the GPP symbols for each form, the Miller representation being based on four different lattices; the fifth degenerate Miller basis* is added by us. The observed spherical angles φ and ρ with respect to $\mathbf{a}^* = (1000)$ and $\mathbf{b}^* = (0100)$, correspondingly, are given in columns four and five. Our *hklm* assignment is based on the basic monoclinic lattice $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ in the orthorhombic approximation and on the modulation vector $\mathbf{q} = [-0{\cdot}41\ \ 0\ \ 0{\cdot}45]^*$ treated as a fourth basic vector. Adding $\Delta\varphi$ and $\Delta\rho$ to the observed values one obtains the computed spherical angles according to our (*hklm*) assignment.

GPP	Miller basis *ABC*			C_1 forms			*hklm* assignment	
No.	GPP	Miller	φ(obs.)	ρ(obs.)	$\Delta\varphi$	$\Delta\rho$	*hklm*	MI
1	*C*	001	−38°30′	8°03′	17′	−05′	$11\bar{1}2$	103
2	*B*	010	−57 05	90 00	−11	00	$000\bar{1}$	48
3	*A*	100	62 12	90 00	04	00	$001\bar{1}$	60
4	*E*	110	9 50	90 00	−02	00	$001\bar{2}$	57
5	*c*	$1\bar{1}0$	89 54	90 00	06	00	0010	84
6	*V*	610	54 36	90 00	12	00	1010	4
7	*l*	103	20 34	11 46	−07	−05	$33\bar{2}5$	1
8	*q*	102	32 37	15 42	11	−03	$22\bar{1}3$	92
9	*o*	101	47 07	28 05	07	−05	1101	131
10	*n*	302	52 01	38 49	16	−20	2211	8
11	*p*	201	54 43	46 50	05	−07	1110	139
12	*i*	301	57 12	58 07	07	−10	$112\bar{1}$	23
13	*L*	$\bar{1}03$	−83 32	13 48	18	05	$33\bar{4}7$	2
14	*Q*	$\bar{1}02$	−92 53	18 10	12	−08	$22\bar{3}5$	7
15	*y*	$\bar{1}01$	−101 12	30 24	−2°48	−14	$11\bar{2}3$	39
16	*P*	$\bar{2}01$	−110 39	48 18	03	−15	$11\bar{3}4$	19
17	*I*	$\bar{3}01$	−113 01	58 49	06	−03	$11\bar{4}5$	2
18	*u*	011	−52 58	30 58	05	−04	$11\bar{1}1$	65
19	*w*	021	−54 58	46 49	10	−06	$11\bar{1}0$	72
20	ξ	031	−55 43	56 47	10	−02	$11\bar{1}\bar{1}$	6
21	*r*	$0\bar{1}1$	114 41	18 26	10	04	$11\bar{1}3$	50
22	*W*	$0\bar{2}1$	119 20	38 29	05	04	$11\bar{1}4$	22
23	Ξ	$0\bar{3}1$	120 21	51 21	17	13	$11\bar{1}5$	2
24	τ	122	−26 54	28 29	47	−02	$22\bar{1}1$	1
25	ι	$\bar{1}22$	−72 02	37 07	15	−07	$22\bar{3}3$	1
26	*m*	111	−0 04	31 30	04	−03	1100	122
27	θ	121	−24 33	43 32	12	−06	$110\bar{1}$	13
28	σ	131	−35 16	53 41	14	−01	$110\bar{2}$	1
29	υ	$1\bar{1}1$	81 51	38 21	07	−06	1102	18
30	*G*	$1\bar{2}1$	96 46	49 36	05	07	1103	4
31	κ	$1\bar{3}1$	103 38	58 05	26	04	1104	2
32	*M*	$\bar{1}11$	−83 36	44 00	11	−09	$11\bar{2}2$	24
33	*s*	$\bar{1}31$	−70 22	61 26	−12	02	$11\bar{2}0$	3
34	*t*	$\bar{1}\bar{1}1$	−155 57	23 14	−08	−03	$11\bar{2}4$	44
35	Θ	$\bar{1}\bar{2}1$	160 57	34 08	23	00	$11\bar{2}5$	11
36	Σ	$\bar{1}\bar{3}1$	145 34	46 55	13	17	$11\bar{2}6$	1
37	*d*	211	28 54	44 38	03	−03	$111\bar{1}$	19
38	ϕ	221	4 22	48 15	05	−05	$111\bar{2}$	16
39	γ	231	−12 56	54 24	24	01	$111\bar{3}$	1
40	*g*	$2\bar{1}1$	73 55	52 43	04	−06	1111	17
41	*D*	$\bar{2}\bar{1}1$	−134 51	42 36	14	−10	$11\bar{3}5$	4
42	Φ	$\bar{2}\bar{2}1$	−163 28	43 00	−17	−04	$11\bar{3}6$	17
43	Γ	$\bar{2}\bar{3}1$	173 41	48 47	−11	15	$11\bar{3}7$	1
44	α	321	22 23	56 00	04	−07	$112\bar{3}$	1
45	χ	331	6 03	58 24	04	−01	$112\bar{4}$	1
46	*f*	$3\bar{1}1$	70 29	61 35	05	−07	1120	38

GPP	Miller basis *ABx*			C_2 forms			*hklm* assignment	
No	GPP	Miller	φ(obs.)	ρ(obs.)	$\Delta\varphi$	$\Delta\rho$	*hklm*	MI
47	*x*	001	−38°05′	23°00′	−08′	−12′	$31\bar{3}6$	42
48	*e*	101	19 42	32 04	45	15	$31\bar{2}5$	10
49	ω	201	39 48	47 25	01	−07	$31\bar{1}4$	12
50	*X*	$\bar{1}01$	−84 10	36 48	20	−14	$31\bar{4}7$	3
51	Ω	$\bar{2}01$	−98 07	50 52	06	−03	$31\bar{5}8$	3
52	Ψ	011	−48 37	41 23	24	−17	$31\bar{3}5$	9
53	*K*	021	−51 25	53 25	03	−18	$31\bar{3}4$	1
54	ψ	$0\bar{1}1$	57 08	8 12	1°26	28	$31\bar{3}7$	9
55	*k*	$0\bar{2}1$	108 11	28 30	01	13	$31\bar{3}8$	17
56	Λ	111	−11 35	40 38	−11	−16	$31\bar{2}4$	9
57	*Z*	121	−27 39	50 48	09	−07	$31\bar{2}3$	2
58	Π	$1\bar{1}1$	60 58	34 37	29	02	$31\bar{2}6$	10
59	*O*	$1\bar{2}1$	85 20	44 55	06	07	$31\bar{2}7$	4
60	λ	$\bar{1}\bar{1}1$	−115 09	21 48	−1 07	−39	$31\bar{4}8$	5
61	*z*	$\bar{1}\bar{2}1$	174 03	22 43	04	17	$31\bar{4}9$	18
62	Δ	211	15 12	48 21	27	00	$31\bar{1}3$	2
63	ρ	221	−3 52	53 21	08	−09	$31\bar{1}2$	16
64	*j*	$2\bar{1}1$	61 37	50 50	11	07	$31\bar{1}5$	7

Table 1 (*cont.*)

GPP	Miller basis *ABx*			C_2 forms			hklm assignment	
No.	GPP	Miller	φ(obs.)	ρ(obs.)	$\Delta\varphi$	$\Delta\rho$	*hklm*	MI
65	*U*	$2\bar{2}1$	77 10	56 36	12	−05	$31\bar{1}6$	1
66	δ	$\bar{2}\bar{1}1$	−116 51	42 58	−16	−10	$31\bar{5}9$	2
67	*H*	$\bar{2}\bar{2}1$	−146 10	39 33	−1 01	−52	$31\bar{5}10$	1
68	*h*	321	14 05	58 44	−15	−14	3101	1
69	β	331	−0 18	61 22	18	03	3100	2
70	*F*	$3\bar{1}1$	61 40	60 08	17	24	3104	1

GPP	Miller basis *ABR*			C_3 forms			hklm assignment	
No.	GPP	Miller	φ(obs.)	ρ(obs.)	$\Delta\varphi$	$\Delta\rho$	*hklm*	MI
71	*R*	001	−39°03′	35°33′	50′	−31′	$51\bar{5}10$	6
72	*S*	101	1 30	39 00	1°35	−15	$51\bar{4}9$	1
73	π	201	25 17	49 49	1 02	−14	$51\bar{3}8$	1
74	η	$0\bar{1}1$	−11 23	17 27	3 09	−36	$51\bar{5}11$	2
75	*u*	$\bar{1}\bar{2}1$	−143 36	13 35	−3 35	−05	$51\bar{6}13$	13
76	*T*	211	5 00	53 48	42	−1°10	$51\bar{3}7$	1
77	ν	$2\bar{2}1$	66 29	54 34	35	07	$51\bar{3}10$	1
78	*N*	$\bar{2}\bar{1}1$	−100 37	46 06	−49	−35	$51\bar{7}13$	1
79	ε	$\bar{2}\bar{2}1$	−125 40	37 39	−1 02	−30	$51\bar{7}14$	1

GPP	Miller basis *ABb*			C_0 forms			hklm assignment	
No.	GPP	Miller	φ(obs.)	ρ(obs.)	$\Delta\varphi$	$\Delta\rho$	*hklm*	MI
80	*b*	001	0°00′	0°00′	00′	00′	0100	34
81	*J*	102	62 12	15 15	04	−10	$021\bar{1}$	14
82	*Y*	$0\bar{2}1$	122 38	42 57	05	−05	0102	5
83	μ	112	9 58	14 17	−10	00	$021\bar{2}$	31
84	ζ	212	37 08	25 23	−18	−12	$022\bar{3}$	7

	Miller basis* *ABx*:			CC_2 forms			hklm assignment	
No.	GPP	Miller	φ(obs.)	ρ(obs.)	$\Delta\varphi$	$\Delta\rho$	*hklm*	MI
85	*a*	111	0°00′	90°00′	00′	00′	1000	14
86	*e*:	421	32 10	90 00	38	00	$10\bar{3}\bar{4}$	2
87	ω:	101	47 03	90 00	11	00	1001	7
88	Π:	$1\bar{1}2$	72 40	90 00	−17	00	$20\bar{1}4$	15
89	*Z*:	$\bar{2}3\bar{1}$	167 11	90 00	16	00	$\bar{1}0\bar{1}3$	10
90	*K*:	011	−53 09	90 00	16	00	$10\bar{1}1$	5
91	*x*:	001	−38 34	90 00	36	00	$10\bar{1}2$	16
92	Λ:	112	−7 05	90 00	14	00	$20\bar{1}2$	79

Stronger is the case of {0223} = no. 84, where {0220} is the only possible origin of this satellite instead of {0110}. For the superspace glide condition *h*0*lm*, $m = 2n$ such morphological evidence is lacking. Only by doubling the indices of the CC_2 forms does one obtain an even *m*. In principle one can also apply the Bravais–Friedel law, which states that the MI of a crystal face increases with increasing interplanar distance *d*(*hkl*). In the modulated case that corresponds to increasing Fourier wave front distance *d*(*hklm*). As noted by Dam, Janner & Donnay (1985) this relation seems to hold in calaverite. On the other hand it is not quantitative enough to allow us to distinguish between $C2/m(\alpha 0\gamma)(0s)$ and $C2/m(\alpha 0\gamma)(00)$ which lacks the condition *h*0*lm* $m = 2n$. The X-ray structure determination mentioned above (Schutte & de Boer, 1988) indicates that $C2/m(\alpha 0\gamma)(0s)$ is the correct superspace group of calaverite, a result in full agreement with the morphological observations.

The satellite faces on calaverite are very large and numerous compared with the satellite faces found on TMA-ZC (Dam & Janner, 1986). Thus the high order of some of the satellite indices *m* is not fully clarified despite the plausibility from the point of view of the Bravais–Friedel law. The problem of the high-order satellite faces is coupled to that of their (*hkl*0) 'origins'; indeed if *d*(*hklm*) has to be large (according to Bravais–Friedel), a high index *l* requires a high-order satellite index *m*.

While dealing with the morphology of modulated TMA-ZC (Dam & Janner, 1986), we related the stability of satellite faces to the presence of (*hkl*0) *F* faces, *i.e.* thermodynamically stable faces of the basic crystal structure. The calaverite morphology makes this assumption questionable. Are the non-existent (*hkl*0) origins *F* faces which are just too weak to show up, or is there no such connection between (*hkl*0) and (*hklm*) faces? In Table 1, 31 of the 82 satellite faces are related to an (*hkl*0) origin which is present as a crystal face. The summed MI of these 31 satellite faces covers over 50% of the summed MI of all (*hklm*) faces. This observation points to some relation between the stability of a certain series of satellite faces (*hklm*) and the stability of the corresponding (*hkl*0) origin.

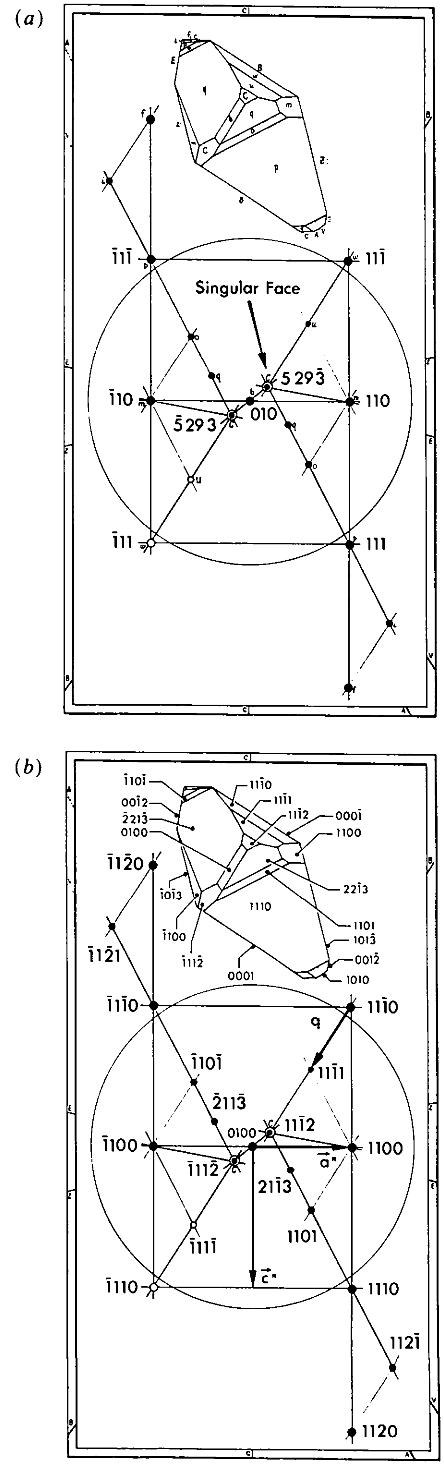

Fig. 2. Relation between the old and the new approach to the morphology of calaverite. (*a*) Crystal faces of identification and corresponding gnomonic projection according to GPP (Table VI). The Miller indices *hkl*, referred to the monoclinic basic structure (unique axis *b*), have been added for comparison. (*b*) Same situation re-interpreted using four indices *hklm* and taking into account the additional incommensurate modulation vector **q**. The high-indices singular face *C* with (5 29 3̄) now appears as a low-indices satellite face (1 1 1̄ 2).

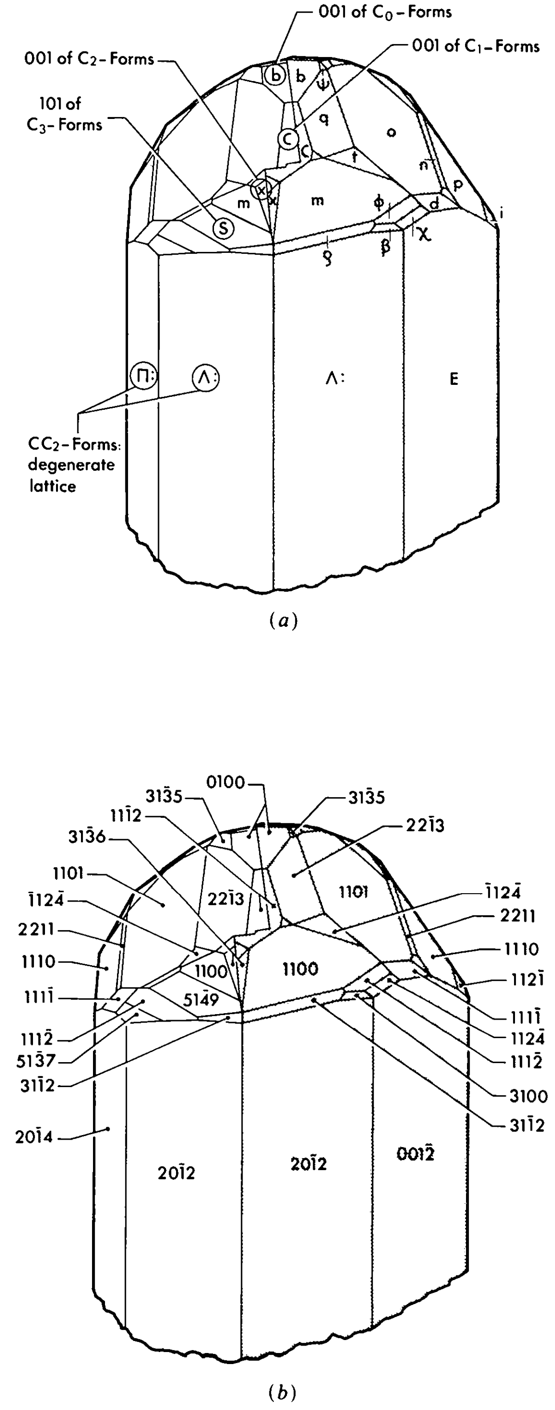

Fig. 3. A typical calaverite twin crystal reproduced from GPP (Table X). The prismatic axis is the monoclinic one. (*a*) For indexing the faces of this one crystal according to GPP five different lattices are required. These are spanned by *ABb* (C_0 forms), *ABC* (C_1 forms), *ABx* (C_2 forms), *ABR* (C_3 forms) and *ABx*: (CC_2 forms), the latter being degenerate (see also Fig. 1). (*b*) Same crystal with faces labelled by indices *hklm* in terms of the four fundamental periodicities of the structure: a^*, b^*, c^* of the monoclinic lattice and *q* of the modulation wave vector. Note that the satellite faces ($m \neq 0$) dominate above the basic ones ($m = 0$).

To answer the question whether all derived $(hkl0)$ origins are in fact F faces, a detailed study of the morphology resulting from the bond strength in the calaverite crystal structure is required. This is not a simple task, even if at present one knows the atomic structure of calaverite, because the microscopic structure of the macroscopically flat faces of an incommensurate crystal is still obscure.

4. Concluding remarks

We still have only a partial understanding of the morphology of calaverite. Nevertheless, the complete indexing of the 92 independent forms of calaverite observed in nature shows the power of the application of the (incommensurate) modulation wave vector as a fourth base vector. The reason for the stability of the satellite faces (see Fig. 3) and the role which the so-called $(hkl0)$ origins plays remain unclear, though the extended classical geometrical laws of crystal morphology seem to hold within a reasonable approximation.

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Reduced Cells Based on Extremal Principles

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Abstract

It is known that the Buerger cell, $a+b+c=\text{abs min}$, is ambiguous. Uniqueness is usually achieved by an additional system of inequalities which leads to the generally accepted Niggli cell. However, this system is rather unusual and does not suggest any geometrical meaning for the Niggli cell. In this paper four types of unique cells originating from the Buerger cell are introduced by means of simple conditions which have an extremal character. Any of these cells may stand for a reduced cell and has an express geometrical property. One of the four types coincides with the Niggli cell, which is thus given a geometrical interpretation. Systems of inequalities are shown that allow recognition of the cell of any type and algorithms are

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