Incommensurate Morphology of Calaverite ($AuTe_2$) Crystals

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The existence of large-sized satellite faces on crystals of the mineral calaverite ($Au_{1-x}Ag_xTe_2$) is reported. These anomalous high-index faces can be related directly to the wave vector **q** of the displacive incommensurate modulation recently found in the crystal structure. If we extend the classical morphological law of rational indices to include **q** as a fourth basic vector, the high-index faces can be described by four low integers ($hklm$).

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In the past two centuries the determination of lattice parameters and crystal symmetry from the morphology of crystals has been a powerful research program. The subsequent development of x-ray crystallography made this branch of crystallography go out of fashion. Still, the persistence of a few anomalies deserves attention. One of them is found in calaverite, which together with sylvanite and krennerite belongs to a class of related gold-silver tellurides; calaverite contains up to 15-at.% Ag. In 1931 Goldschmidt, Palache, and Peacock[1] (GPP) published an extensive morphological research on calaverite, a mineral which had already puzzled the mineralogists during the preceding century. After compiling the morphological data of 105 of the finest-quality single crystals found in nature, they were not able to give an adequate classical description of the morphology. Though the crystal morphology allows for a $2/m$ point-group symmetry, only 10 out of the 92 crystal forms (i.e., sets of symmetry-equivalent crystal faces $\{hkl\}$) constituting the rich morphology could be indexed as $\{hkl\}$'s with h, k, and l low integers. After discarding all trivial error sources, such as twinning, GPP had to admit that inevitably the law of rotational indices is not a general law. This statement deprives crystallography of its historical basis!

The reason for the failure was sought in a badly understood "singular" crystal structure. Four years later, one of us[2] (J.D.H.D.) tried to recover the validity of the law of rational indices by attempting to solve the problem in terms of a new type of twinning. This paper was dubbed a "preliminary communication" and now, fifty years later, we all want to look at the problem from the point of view of incommensurability.

As early as 1979 Sueno, Kimata, and Ohmasa[3] proposed a modulated structure for calaverite. Their x-ray studies were followed by a number of electron-microscope studies on the (Au,Ag)Te_2 compounds.[4] With use of pure $AuTe_2$ for calaverite, the electron-microscope diffraction pattern shows a beautiful series of satellite spots, which reveal the modulated incommensurate structure. Around the main diffraction spots, satellites up to the sixth order could be observed. The main diffraction spots are consistent with the $C2/m$ space group, as determined earlier by Tunell and Pauling.[5] The displacement of Au atoms along [010] forms the main contribution to the modulation wave. The orientation of the modulation wave vector could not be determined precisely. The diffraction pattern shows that it deviates slightly from [202]* and has a wavelength of $4.5d_{202}$. Sylvanite ($AuAgTe_4$), on the other hand, appears to be commensurately modulated with $\lambda = 4d_{202}$. Note that in the paper of Van Tendeloo, Gregoriades, and Amelinckx[4] a left-handed coordinate system has been used. With respect to the coordinate system defined by Tunell and Pauling adopted here, the direction of **q** is near $[\bar{2}02]^*$.

Already in 1936 Tunell and Ksanda,[6] in a study of the x-ray diffraction pattern of calaverite, found some extra (so-called adventive) spots that could not be ascribed to the structural lattice. They suggested a relation with the high-index faces but did not go into any detail. Here we intend to show that with the new structural information a large part of the morphology of calaverite can be described in a consistent way that shows a close connection between the crystal form and the periodic displacive modulation.

In previous publications it has been shown that the morphology of modulated crystals is determined not only by the lattice periodicity of the average structure, but also by the additional periodicity of displacive modulation waves.[7,8] By extending classical morphological laws, we can index a crystal face by four integers ($hklm$) indicating the Fourier wave vector $\mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ normal to it. For $m \neq 0$ these Fourier vectors, which can be associated with satellite diffraction spots, explicitly reveal the relation between the modulation wave and the satellite faces. These observations can be consistently described in the superspace approach which was introduced for the characterization of the diffraction pattern of incommensurate crystals by de Wolff, Janner, and Janssen.[9] In particular, from the absence of second-order satellites in the net plane of $h0l$ reflections reported by Van Tendeloo, Gregoriades, and Amelinckx,[4] it is possible to identify the superspace group of calaverite as $C2/m(\alpha,0,\gamma)(\bar{1},s)$. With the assumption that the three-dimensional part of the four-dimensional point group determines configurational morphology, the set of symmetry related faces, i.e., the crystal form, is indicated by the braces of the $\{hklm\}$ symbol (in this case indicating a $2/m$ point-group symmetry).

From the morphology of Rb_2ZnBr_4 crystals grown in the incommensurate phase,[10] the relative length of the modulation wave could be determined from the orientation of the satellite faces $(hklm)$ with respect to the main faces $(hkl0)$. Furthermore, it appeared that for $[(CH_3)_4N]_4ZnCl_4$ one single superspace group characterizes the symmetry consistent with what is known about structure and morphology of its various modulated phases.[11] In all these experiments, however, the observed satellite faces had very small sizes (up to a single one), and the limited number of observations prevented the testing of morphological laws.

Quite different is the situation with calaverite, for which not less than 1849 very accurate observations have been made[1] on more than a hundred crystals involving 92 different forms, 82 of which appear to be of satellite character.

The morphology as described by GPP can be reindexed in the following way. As a basic lattice we take a pseudo-orthorhombic instead of a monoclinic lattice ($\beta = 89° 48'$). The base vectors $\mathbf{a} = 7.19$ Å, $\mathbf{b} = 4.40$ Å, and $\mathbf{c} = 5.07$ Å[4] were combined with a wave vector $\mathbf{q} = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*$ (with $\mathbf{q}$ near $[\bar{2}02]^*/4.5$) to span the "integer space" generated by the $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, $\mathbf{q}$ of our $(hklm)$ indexing. Reinterpreting in this way the very important "singular" face C, we arrive at $\{11\bar{1}2\}$ instead of GPP's high index $\{5\,29\,\bar{3}\}$. In turn, on the basis of the experimentally observed orientation of C, this indexing allows for the refined determination of the modulation wave vector:

$$\mathbf{q} = [-0.4095\ldots, 0, 0.4492\ldots] \sim [-0.41, 0, 0.45].$$

Many satellite forms $\{hklm\}$ can now be constructed by adding multiples m of $\mathbf{q}$ to the normal vectors of the so-called main forms $\{hkl0\}$, i.e., those observed forms which can be indexed classically with three integers $\{hkl\}$, even in an incommensurate phase. Here as main forms we take GPP's low-index forms, the so-called S forms listed in their Tabelle 1. In Table I the thus obtained satellite forms $\{hklm\}$ which are actually observed, are indicated by their index m with respect to the corresponding main forms $\{hkl0\}$ (neglecting for the moment possible superspace-group extinction conditions). The alphabetical description and the morphological importance (in parenthesis) given in GPP of the high-index faces is indicated in the last column.

In this way 31 of the 82 high-index forms can be reinterpreted as $\{hklm\}$'s. Satellite forms up to the sixth order [see, e.g., $(\bar{1}12\bar{6})$ or the Σ face] are found, and one observes from Table I a general tendency of the main forms to have more satellites the more morphologically important that they are. On the other

TABLE I. Reinterpretation of a part of Goldschmidt, Palache, and Peacock's high-index faces on calaverite. The GPP symbol of the so-called main forms are given in column 1. Related to these main forms, which are reinterpreted as $\{hkl0\}$ in column 2, are the so-called satellite forms $\{hklm\}$ whose order m is indicated in column 3. The corresponding GPP symbol of these series of satellite faces is given in column 4 (e.g., $h = \{3101\}$ and $g = \{1111\}$). Morphological importance (MI) is indicated in parentheses in terms of the number of times such a set of faces was found by GPP in their sample of 105 crystals.

Main forms $\{hkl0\}$		Related satellite forms $\{hklm\}$	
GPP(MI)	$hkl0$	m	GPP's letter (MI)
$\beta(2)$	3100	1 4	$h(1)$ $F(1)$
$f(3)$	1120	−1 −3 −4	$i(23)$ $\alpha(1)$ $\chi(1)$
$p(139)$	1110	1 −1 −2 −3	$g(17)$ $d(19)$ $\phi(16)$ $\gamma(1)$
$m(122)$	1100	4 3 2 1 −1 −2	$\kappa(2)$ $G(4)$ $\upsilon(18)$ $0(131)$ $\theta(13)$ $\sigma(1)$
$s(18)$	$11\bar{2}0$	2 3 4 5 6	$M(24)$ $y(39)$ $t(44)$ $\theta(11)$ $\Sigma(1)$
$w(72)$	$11\bar{1}0$	−1 1 2 3 4 5	$\xi(6)$ $u(65)$ $C(103)$ $r(50)$ $W(22)$ $\Xi(2)$
$b(5)$	0100	2	$Y(5)$
$a(14)$	1000	1	ω:(7)
$c(5)$	0010	−1 −2	$A(60)$ $E(57)$
$V(6)$	$\bar{1}0\bar{1}0$	3	z:(10)

hand, rare main forms such as {0010} can be surrounded by the frequently observed satellite faces $(001\bar{1}) = A$ and $(001\bar{2}) = E$.

From Table I we can conclude that the stability of {*hkl*0} is an important factor for the satellite morphology. A restriction on *m* is that it be not too large an integer. Finally, it can be seen that, around a single {*hkl*0}, the decreases of the morphologic importance (MI) with *m* is not linear; this observation suggests that $d_{\{hklm\}}$ too is a relevant morphological factor, despite the fact that the distance now is not one between net planes in a lattice, but one between fronts of Fourier matter waves.

In Table II some few examples are given of comparison between the observed orientational angles (GPP) and those calculated on the basis of our *h,k,l,m* indexing for the parameter values given above. The agreement is astonishing if one remembers that the crystals measured are native minerals. This shows the power of classical crystallography, whose modern extension reveals how profound an effect subtle periodic lattice distortions of the microscopic structure can have on the macroscopic crystal morphology.

The morphological importance of satellite faces is directly recognized on a drawing reproduced from GPP (Tafel X), which shows a twin comparison of a left-handed and a right-handed crystal. Both main faces (*hkl*0) and satellite faces (*hklm*) can be found, when

TABLE II. Examples of indexing calaverite crystal faces. The letter symbol and the spherical angles $\phi_{\rm obs}$ and $\rho_{\rm obs}$ are those reported by GPP in 1931. The calculated values are based on the *hklm* indices in the last column and a modulation vector $\mathbf{q} = [-0.41\ 0\ 0.45]^*$.

GPP symbol	$\phi_{\rm obs}$	$\rho_{\rm obs}$	$\phi_{\rm cal}$	$\rho_{\rm cal}$	*hklm*
C	−38° 30′	08°03′	−38° 13′	07° 58′	$11\bar{1}2$
B	−57° 05′	90° 00′	−57° 16′	90° 00′	$000\bar{1}$
A	62° 12′	90° 00′	62° 16′	90° 00′	$001\bar{1}$
M	−83° 36′	44° 00′	−83° 25′	43° 51′	$11\bar{2}2$
u	−52° 58′	30° 58′	−52° 53′	30° 54′	$11\bar{1}2$

comparing GPP's lettering in Fig. 1(a) with those in Fig. 1(b). The enormous prismatic faces Λ:, Π:, and *E* show the morphological importance of satellite faces as habit-controlling factors. Satellite faces Λ: and Π: can be described as $\Lambda{:} = (20\bar{1}2)$ and $\Pi{:} = (20\bar{1}4)$, the difference being that now $(20\bar{1}0)$ is not an observed main face. In a subsequent paper it will be shown that the complete crystal morphology can be described in terms of combinations of four low indices {*hklm*}.

In conclusion, it can be said that the classical law of rational indices still holds for incommensurate crystals, provided the correct number of indices is used (four in the case of calaverite). This reveals the sensitivity of

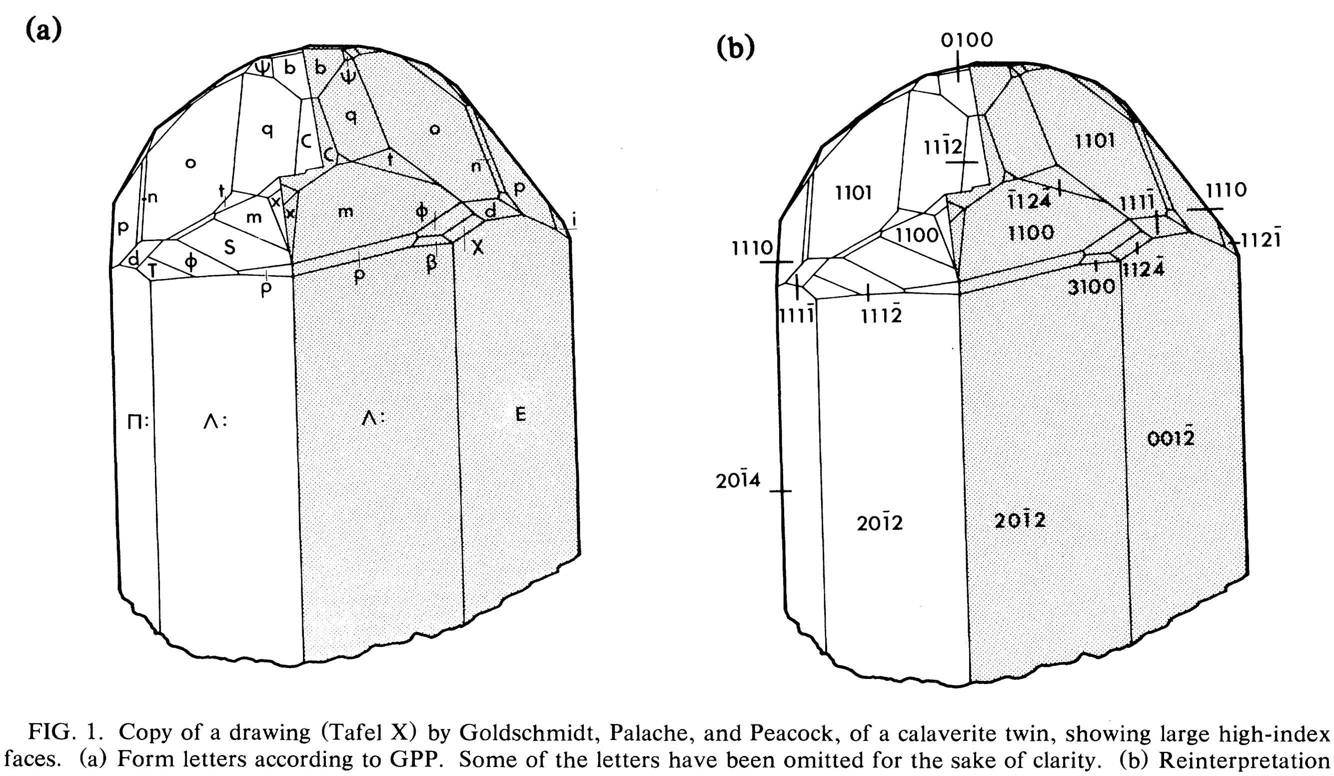

FIG. 1. Copy of a drawing (Tafel X) by Goldschmidt, Palache, and Peacock, of a calaverite twin, showing large high-index faces. (a) Form letters according to GPP. Some of the letters have been omitted for the sake of clarity. (b) Reinterpretation in terms of four-index symbols using the modulation wave as a fourth basic periodicity.

crystal morphology to the periodicity of atomic interactions. After a closer analysis of the laws governing the appearance of satellite faces, we hope to get some idea about the nature of their microscopic structure. Note however, that for an incommensurate satellite face the Bravais concept of a high reticular density of the parallel net plane is completely lost. Thus the investigation of the surface of satellite faces opens a new field of experimental research.[12]

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[1]V. Goldschmidt, Ch. Palache, and M. Peacock, Neues Jahrb. Mineral. Geol. Palaeont., Ref., Beil.-Bd. **63**, 1 (1931).

[2]J. D. H. Donnay, Ann. Soc. Geol. Belg. **18**, B222 (1935).

[3]S. Sueno, M. Kimata, and M. Ohmasa, in *Modulated Structures—1979,* AIP Conference Proceedings No. 53, edited by J. M. Cowley, J. B. Cohen, M. B. Salamon, and B. J. Wuensch (American Institute of Physics, New York, 1979), p. 333.

[4]G. Van Tendeloo, P. Gregoriades, and S. Amelinckx, J. Solid State Chem. **50**, 321 (1983), and **50**, 335 (1983), and **53**, 281 (1984).

[5]G. Tunell and L. Pauling, Acta Crystallogr. **5**, 375 (1952).

[6]G. Tunell and C. J. Ksanda, J. Wash. Acad. Sci. **26**, 507 (1936), and **26**, 509 (1936).

[7]A. Janner, Th. Rasing, P. Bennema, and W. H. van der Linden, Phys. Rev. Lett. **45**, 1700 (1980).

[8]B. Dam, A. Janner, P. Bennema, W. H. van der Linden, and Th. Raising, Phys. Rev. Lett. **50**, 849 (1982).

[9]P. M. De Wolff, Acta Crystallogr., Sect. A **33**, 493 (1977); A. Janner and T. Janssen, Phys. Rev. B **15**, 643 (1977); P. M. de Wolff, T. Janssen, and A. Janner, Acta Crystallogr., Sect. A **37**, 625 (1981).

[10]B. Dam and A. Janner, Z. Kristallogr. **165**, 247 (1983).

[11]B. Dam and A. Janner, Acta Crystallogr., Sect. A (to be published).

[12]B. Dam, Phys. Rev. Lett. (to be published).