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The Vicissitudes of the Low-Quartz Crystal Setting or the Pitfalls of Enantiomorphism

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To I. Koda, who in 1929 *first proposed to use coordinate systems of both hands*

Based on a literature study, the following proposals endeavour to combine the advantages of previous conventions for setting low-quartz crystals: (1) Knowing that symmetry axes are parallel to the edges of the smallest hexagonal cell, place *Oz* along the 3-axis and *Ox*, *Oy*, *Ou* along the *macroscopic* 2-axes. (2) Direct the polar axes positively toward the *s* and *x* faces, if present, or toward the positive charge developed on extension by piezoelectric test. (3) Match the hand of the coordinate system to that of the structural screw; thus, the right-handed coordinate system (RHCS) for the known right screw (RS) of laevorotatory quartz. (4) Let the coordinate axis that *coincides* with a 2-axis *in the structure* be *Ox*[100]. These rules result in both enantiomorphs obeying Lang's mnemonic rule and being in the $r(+)$ setting, in which $\{10\bar{1}1\}$ symbolizes the major rhombohedron *r*, defined by $I_{\rm obs}(10\bar{1}1) > I_{\rm obs}(01\bar{1}1)$. Low quartz has only one structure. It should be published only for the RS ($P3_121$) and in the RHCS: anyone can visualize the LS enantiomorph by plotting the atomic coordinates in the LHCS. This policy should apply to any enantiomorphous substance with known absolute configuration. If a crystal structure, determined in the RHCS, turns out to have a LS, transform to LHCS and publish the new coordinates, which also fit the *standard RS in RHCS*, but add, 'Known only as LS' or 'Observed as LS'.

Introduction

Various settings have been used in the literature for the description of low quartz, and several attempts at uniformization have been made. Colliding interests of the parties involved have hampered progress. Proposed conventions have conflicted on many points: (1) What criterion will identify a crystal as 'right' or 'left' and, concomitantly, how to express the optical rotatory power [Biot (1817) *vs* Herschel (1822) conventions], and whether it is possible to correlate the hand of the screw axis ('geometrical or structural helix') with that of the 'optical helix'; (2) the hand of the coordinate system; (3) the sense of the rotation that will define a screw rotation; (4) whether to adopt the *r* or the *z* setting, that is, giving the symbol $\{10\bar{1}1\}$ to the 'major rhombohedron' *r* or to the 'minor rhombohedron' *z*; (5) how to orient the polar twofold axes; (6) what to call the coordinate axis that is chosen to coincide with a twofold axis in the crystal structure (*x*, *y* or *u*). Committees have disagreed on whether to use a single (right-handed) coordinate system for both right and left quartz, or one system for right quartz and the other for left quartz; in the latter choice, an additional question comes up at the present time, now that it is possible to determine the absolute configuration of an enantiomorph – should the hand of the coordinate system match that of the geometrical helix or that of the optical helix? Finally a number of misprints in key publications increased the confusion. None of the above difficulties, which deal mostly with matters of convention, would by itself create any problem. Taken together, however, they lead to so many possibilities that they constitute a real obstacle to the mastering of the literature.

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Abbreviations. Terminology. Synonymy

LS: *Left screw.* Left-handed helix. Left-handed screw axis.
RS: *Right screw.* Right-handed screw axis.

l: *laevo.* Laevorotatory (plane of polarization rotated *counter-clockwise*, as seen when facing the source of light: Biot's convention). The laevorotatory power is given the *minus* sign in the chemical literature.
d: *dextro.* Dextrorotatory (clockwise rotation, *plus* sign).

Quartz *l*: *Quartz laevo.* Left quartz, 'left-hand quartz' (optical and morphological designation). Correlated with RS in low quartz.
Quartz *d*: *Quartz dextro.* Right quartz, 'right-hand quartz' (optical and morphological designation). Correlated with LS in low quartz.

LHCS: *Left-handed coordinate system.*
RHCS: *Right-handed coordinate system.*

Pos. rot.: *Positive rotation.* In either coordinate system, sense of the $2\pi/3$ rotation about *Oz* that brings *Ox* on to *Oy*.
Neg. rot.: *Negative rotation.* Sense of the $2\pi/3$ rotation that brings *Oy* on to *Ox*.

LH rot.: *Left-hand rotation* (thumb up). Clockwise rotation. Pos. rot. in LHCS. Neg. rot. in RHCS.
RH rot.: *Right-hand rotation* (thumb up). Counter-clockwise rotation. Pos. rot. in RHCS. Neg. rot. in LHCS.

r rhombohedron: 'Major rhombohedron' of morphology. Designated *R* by Cady (1946).
z rhombohedron: 'Minor rhombohedron' of morphology. The faces of *z* are usually smaller than those of *r*; they are sometimes dull on natural crystals, very commonly so on synthetic ones, whereas *r* faces have high vitreous luster. Net planes that are parallel to *z* faces give less intense X-ray reflections than those which are parallel to *r* faces. The *z* rhombohedron was called *r* by Cady.

r settings: Settings with indexing $r\{10\bar{1}1\}$ and $z\{01\bar{1}1\}$.
z settings: Settings with indexing $r\{01\bar{1}1\}$ and $z\{10\bar{1}1\}$. Lang's (1965) 'obverse setting' is an *r* setting; his 'reverse setting' is a *z* setting.

(+) settings: Settings in which the twofold axis along which the *Ox* coordinate axis is chosen develops a (+) charge at its positive end on extension (stretching).
(−) settings: Settings in which the same piezoelectric test develops a (−) charge.

r(+), *z*(−), *r*(−), *z*(+): Complete symbols for the four settings that are considered either in one coordinate system (two settings with RS, two with LS) or in one screw (two settings in RHCS, two in LHCS). See Figs. 1.1–8.

How to select a crystal setting for low quartz

The crystal lattice of low quartz is known to be hexagonal, with lattice symmetry $6/m\,2/m\,2/m$. The coordinate axes must be chosen along the edges of the smallest hexagonal cell; the *z* axis is taken along the 3-axis, and the *x*, *y*, *u* axes along the shortest lattice vectors in the (0001) net plane. The crystal point group having been determined as 321 (not 312), the *x*, *y*, *u* axes coincide with the macroscopic 2-axes; as they join opposite edges of the only hexagonal prism *m*, they are easy to recognize morphologically. They are polar: how should they be oriented? Two methods are available. (1) The morphological method. – If the crystal has good morphological development, the answer is immediate. By 'good development' we mean either the presence of both the usual trigonal trapezohedron *x* and trigonal dipyramid *s*, or the presence of *s* without *x*, provided the major rhombohedron *r* can be distinguished from the minor one *z*. The small faces *x* and *s* are situated *to the left* of an *r* face on a *laevo* crystal (Fig. 2*b*), to the right on a *dextro* crystal (Fig. 2*a*); they are in zone between an *m* face and a *z* face. The trigonal trapezohedron *x* has three upper faces, and so has the dipyramid *s*. The coordinate axes *Ox*, *Oy*, *Ou* are to be directed positively from the origin toward the prism edges that are below the *s* faces. (2) The piezoelectric test. – If morphology is of no avail, the crystal is stretched between two opposite prism edges, thus in the direction of a coordinate axis. The end that acquires a plus (+) charge on extension is to be taken as positive. This convention, used by the radio engineers (IRE, 1949), yields the same result as that of the morphologists. Macroscopically the setting is now completely determined, except for the hand of the coordinate system.

Let us now turn to structural considerations and project the crystal structure onto the (0001) plane. The six silicon atoms that are projected around the origin outline a ditrigon, in either enantiomorph (Fig. 1.1 or 1.2), whose more obtuse angles point toward the positive ends of the polar axes, in accordance with Lang's (1965) useful mnemonic rule. Since a laevo crystal of low quartz happens to have a right structural screw (de Vries, 1958), we use a RHCS in Fig. 1.2, corresponding to Fig. 2(*b*), and a LHCS in Fig. 1.1, which goes with Fig. 2(*a*). In each case the crystal is in an *r*(+) setting, which means that the rhombohedra are indexed $r\{10\bar{1}1\}$, $z\{01\bar{1}1\}$. On Figs. 1.1 and 1.2 three large dots indicate the location of the faces $x(6\bar{1}\bar{5}1)$, $s(2\bar{1}\bar{1}1)$, in the zone between $r(10\bar{1}1)$ and $z(1\bar{1}01)$.

The space group is known: for the enantiomorph that contains a right screw (RS), it is $P3_121\text{–}D_3^4$ (*IT*, 1952, p. 257).* In it (Fig. 1.2) three 2-axes intersect the *z* axis in points *c*/3 apart. One of them (which one does not matter) is picked as the origin, and the 2-axis that passes through it is chosen as the *x* axis. (This choice departs from that of *IT*; it has been found more convenient in practice and has been endorsed by all but two workers in the field.) A $2\pi/3$ screw rotation in the positive sense (RH rot.) brings *Ox* to coincidence with the 2-axis at $z = c/3$; the second power of the operation yields the 2-axis at $z = 2c/3$. Lines drawn through *O* parallel to these two 2-axes will be the *Oy* and *Ou* coordinate axes, respectively. The dextro enantiomorph (Fig. 1.1), the one with the LS, is shown as the mirror image of that with the RS (Fig. 1.2), as regards both the crystal structure and the coordinate system.

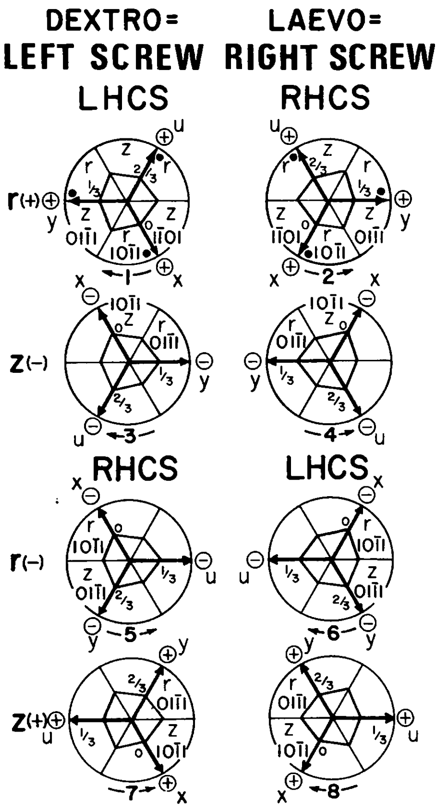

Fig. 1.1–8. Various choices of coordinate axes on a left screw and a right screw. The two screws are shown as mirror images of each other. Either screw remains the same from top to bottom of the page: only the orientation of the coordinate system changes by rotation around *Oz*. Arrow shows sense of positive rotation. Settings symbols tell which rhombohedron (*r* or *z*) is indexed {10$\bar1$1} and which charge (+ or −) develops at the positive end of each polar coordinate axis on extension. Heights above *O* of polar 2-axes in the structure are shown as fractions of *c*.

Previous settings

The various settings that have been used in the past can be described by noting which of the rhombohedra, *r* or *z*, is indexed {10$\bar1$1}, and whether the polar axes point toward the + or the − charges that are observed in the piezoelectric test. The short-hand symbols *r*(+), *z*(−), *r*(−), *z*(+) are applicable to LS and RS settings; hence a total of eight figures are presented (Figs. 1.1–8), to which reference will be made in the following sections.

Table 1. *Various descriptions of low-quartz structure*

Atomic positions	Atomic sites	Setting	LS (*d*)	RS (*l*)	Fractional coordinates (× 100)
$P3_121\text{–}D_3^4$			LHCS	RHCS	
Si 3(*a*)2:	$u,0,0$ $0,u,\frac{1}{3}$ $\bar{u},\bar{u},\frac{2}{3}$	*r*(+)	Fig. 1.1	Fig. 1.2	Si: 47 0 0 0 47 33 53 53 67
O 6(*c*)1:	x,y,z $\bar{y}, x-y, z+\frac{1}{3}$ $y-x, \bar{x}, z+\frac{2}{3}$ $x-y, \bar{y}, \bar{z}$ $\bar{x}, y-x, \bar{z}+\frac{2}{3}$ $y, x, \bar{z}+\frac{1}{3}$				O: 41 27 88 73 14 21 86 59 55 14 73 12 59 86 79 27 41 45
		z(−)	Fig. 1.3	Fig. 1.4	Si: 53 0 0 47 47 67 0 53 33 O: 59 73 88 27 86 21 14 41 55 86 27 12 41 14 79 73 59 45
$P3_221\text{–}D_3^6$			RHCS	LHCS	
Si 3(*a*)2:	$u,0,0$ $0,u,\frac{2}{3}$ $\bar{u},\bar{u},\frac{1}{3}$	*r*(−)	Fig. 1.5	Fig. 1.6	Si: 53 0 0 0 53 67 47 47 33
O 6(*c*)1:	x,y,z $\bar{y}, x-y, z+\frac{2}{3}$ $y-x, \bar{x}, z+\frac{1}{3}$ $x-y, \bar{y}, \bar{z}$ $\bar{x}, y-x, \bar{z}+\frac{1}{3}$ $y, x, \bar{z}+\frac{2}{3}$				O: 59 73 12 27 86 79 14 41 45 86 27 88 41 14 21 73 59 55
		z(+)	Fig. 1.7	Fig. 1.8	Si: 47 0 0 0 47 67 53 53 33 O: 41 27 12 73 14 79 86 59 45 14 73 88 59 86 21 27 41 55

Nota bene: In all settings *Ox*[100] is chosen along the twofold axis through the origin. The space-group symbols are used in Schoenflies's sense, as they appear in Table 2. Heading abbreviations are explained in the *Introduction*.

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* *Internationale Tabellen zur Bestimmung der Kristallstrukturen* and *International Tables for X-ray Crystallography* are both abbreviated as *IT*, with appropriate dates.

The arrow drawn under each figure indicates the rotation sense that is used to define a screw rotation: since *Oz* is directed toward the observer, the hand of the coordinate system is immediately obtained by noting which hand (thumb up) closes in the direction of the arrow: LH rot., LHCS (Fig. 1.1), for instance. On our figures the rotation sense is the positive sense, dictated by the coordinate system itself, which brings *Ox* on to *Oy* by the shortest route. One would assume that such an obvious choice would be general; in fact, we have found out that the opposite convention has also been used.

The symbolism of threefold screw axes

Crystallographers nowadays use the right-handed coordinate system (RHCS) almost exclusively. Until the turn of the century, and even well into the XXth century, however, the LHCS was standard. Schoenflies (1891) used the LHCS and the corresponding positive rotation, that is, LH rot.; in his second book (Schoenflies, 1923) he changed over to the RHCS, with the concomitant positive rotation (RH rot.).

With the positive sense of rotation imposed by our present coordinate system (RHCS), the hand of a threefold screw axis (screw, for short) is indicated by the subscript: 3_1 symbolizes a right screw (RS), 3_2 a left screw (LS). The Hermann–Mauguin symbol 3_1 stands for all three powers 0, 1, 2 of the screw rotation $A(2\pi/3, \mathbf{c}/3)$, which combines a RH rotation through $2\pi/3$ around the axis with a positive translation $\mathbf{c}/3$ along it. Symbol 3_2 defines a LS, by means of the same RH rotations, but with associated translations 0, $2\mathbf{c}/3$, $4\mathbf{c}/3$. As $4\mathbf{c}/3$ implies $\mathbf{c}/3$ (by lattice translation $-\mathbf{c}$), the three equivalent points could equally well be generated at heights 0, $c/3$, $2c/3$, and in that sequence, simply by reversing the sense of the rotation from RH to LH, and the 3_2 (with RH rot.) could thus be symbolized '3_1 with LH rot.'.

In a LHCS the LH rotation *is* the positive rotation. In Schoenflies (1891), therefore, space group C_3^2 contained a LS, that is, a '3_1 with LH rot.', while C_3^3 contained a RS, that is, a '3_2 with LH rot.'. Likewise, in point group 321, D_3^4 (Table 1 and Fig. 1.1), having C_3^2 as a subgroup, included a LS, whereas D_3^6 (Table 1 and Fig. 1.6), with C_3^3 as a subgroup, possessed a RS.

When Schoenflies (1923) went over from LHCS to RHCS, all enantiomorphous space groups changed hand: C_3^2 was redefined as $P3_1$ with RH rotation, so that its former LS turned into a RS; C_3^3, as $P3_2$ with RH rot., acquired a LS. The supergroups, D_3^4–$P3_121$ and D_3^6–$P3_221$ thus contain a RS and LS, respectively. This usage has been that of *IT* ever since they first appeared in 1935. Note that a Schoenflies symbol does not characterize the nature of the screw: it is the synonym of a Hermann–Mauguin symbol, whose meaning depends on the conventional sense in which the rotations are performed.

Summarizing these results we see (Table 1) that symbol 3_1, which once meant a LS in a LHCS (Fig. 1.1) (Schoenflies, 1891), now denotes a RS in a RHCS (Fig. 1.2) (Schoenflies, 1923; *IT*, 1935, 1952), while 3_2 went from RS in LHCS (Fig. 1.6) to LS in RHCS (Fig. 1.5).

In the case of low quartz, as in the case of any merohedry where a form of the holohedry splits into two or more complementary forms,[*] there is an additional ambiguity: the coordinate axes may be chosen in two different ways, corresponding to the *r* and *z* settings (see *Terminology*, above). Additional drawings are necessary (Figs. 1.3, 1.4 and 1.8, 1.7, respectively).

Friedel's presentation of the space-group symbols

Friedel (1926, pp. 145–222) presents an extended account of the second version of Schoenflies's (1923) *Crystal Structure Theory* and describes all 230 space groups with appropriate figures. He uses the RHCS throughout. His symbols for symmetry axes look like prototypes of those now standard in *IT*. In particular he uses a symbol that resembles the *IT* symbol for 3_2 and generates a LS (his Fig. 243). He uses a peculiar terminology, in which the axis represented by this symbol is called a '*right helical* axis with translation $c/3$ (or left helical axis with translation $2c/3$)' (Friedel, 1926, p. 148). This axis is our '3_1 with a *LH rot.*' [or our 3_2 (with RH rot.)]. The name applied by Friedel presumably stems from the Biot (1817) convention for optical activity (*dextro*) or from the mineralogists' usage ('*right* quartz'), explaining the change of hand.

In addition Friedel keeps the original Schoenflies (1891) symbol C_3^2, which did contain a LS ('3_1 with LH rot.') in the LHCS used at the time, but had changed hand when it was redefined by Schoenflies (1923) as a RS with the same pitch in the RHCS (= present $P3_1$).

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[*] In point group 321, where the lattice is hexagonal, an $\{h0\bar{h}l\}$ hexagonal dipyramid of the holohedry ($6/m\,2/m\,2/m$) splits into two *complementary* (or correlative) rhombohedra; for instance, $\{10\bar{1}1\}$ splits into $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$, whose interplanar distances are equal, $d(10\bar{1}1) = d(01\bar{1}1)$. In point group 32, where the lattice is rhombohedral, however, $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$ are the same two forms as in the holohedry ($\bar{3}\,2/m$) – they are *not* complementary rhombohedra, but distinct forms, with different interplanar distances; they must be symbolized $\{10\bar{1}1\}$ and $\{03\bar{3}3\}$ in the obverse setting (see *IT*, 1952, Fig. 2.5.3), or $\{01\bar{1}1\}$ and $\{30\bar{3}3\}$, respectively, in the reverse setting, as $-h + k + l$ or $h - k + l$ must be divisible by 3 depending on the orientation of the coordinate axes with respect to the lattice. This lattice criterion, familiar to X-ray diffractionists, is of course an expression of the law of Bravais; it was rediscovered, from morphological observations alone, by Ungemach (1935) who probably was the first crystallographer to use the *multiple indices*, in the four-index (rhombohedral) symbols, to express the relative frequencies of occurrence of the crystal forms observed on a rhombohedral species.

The combination of these two features in Friedel's nomenclature led to a compound confusion: both Schoenflies (1923) and Friedel (1926) could state that C_3^2 contains a 'right screw axis', which for the former was a RS in the redefined C_3^2 (our $P3_1$), but for the latter was a *dextro* axis in the original C_3^2 (our $P3_2$)!

We deem it worthwhile to present this short analysis of Friedel (1926) in view of the tremendous influence that this book and its reprinted edition (1964) have exerted on French-reading crystallographers over half a century.

Wyckoff's reversal of the rotation sense

In the classical work *The analytical expression of the results of the theory of space groups* (Wyckoff, 1922), the LHCS was still in use,* but the sense of the rotation chosen for plotting equivalent points was the negative one, that is to say, the RH rotation. Inasmuch as the hand of the screw depends only on the sense of rotation (the translation component of a screw rotation being always taken as positive along Oz), D_3^4 (and C_3^2) were interpreted as containing, instead of a LS '3_1 with LH rot.' (Figs. 1.1, 1.3) as in Schoenflies (1891), a RS '3_1 with RH rot.' (Figs. 1.8, 1.6, with arrows reversed), while D_3^6 (and C_3^3) contained, instead of a RS '3_2 with LH rot.' (Figs. 1.8, 1.6), a LS '3_2 with RH rot.' (Figs. 1.1, 1.3, with arrows reversed).

Wyckoff's usage of 1922 thus deceivingly corresponds to that of the *IT*, to the extent that a given screw is described by the same rotation sense and by the same Schoenflies and Hermann–Mauguin symbols (Table 2); since the hand of the coordinate system differs, however, the set of atomic coordinates does not appear in the same place in Table 1. The *IT* do not accept the LHCS at all, so that some of the above symbols have no official interpretation in a LHCS at the present time. It is obvious, nevertheless, that the mechanism of the Hermann–Mauguin symbols is applicable in either a LHCS or a RHCS, whether the rotation is taken as positive or negative.

When Wyckoff, in his second edition (1930), switched from LHCS to RHCS, he again adopted the negative rotation,* here a LH rot., so that D_3^4 (and C_3^2) acquired a '3_1 with LH rot.', that is a LS (Figs. 1.7, 1.5, with arrows reversed), while D_3^6 (and C_3^3) acquired a '3_2 with LH rot.', that is a RS (Figs. 1.2, 1.4, with arrows reversed). Wyckoff (1930) and Schoenflies (1891) thus associate the same screw with the same space-group *symbol*, despite the fact that they use different coordinate systems. The same is true for Schoenflies (1923) and Wyckoff (1922). In either the old or the new coordinate system (Table 2), Wyckoff reverses the hand that had been associated by Schoenflies with a given space-group symbol. For example Wyckoff's D_3^4–$P3_121$ of 1930 is effectively a synonym of D_3^6–$P3_221$ of *IT*.

In his description of the low-quartz crystal structure, Wyckoff (1931, 1948, 1963) considers a LS (quartz *d*) in a RHCS, $z(+)$ setting, and LH rotation (Fig. 1.7

Table 2. *Space-group symbols* (*in Schoenflies notation and Hermann–Mauguin translation*) *used by various authors, in the different settings, to express either screw in either coordinate system with either rotation sense*

For the set of atomic coordinates corresponding to any setting, see Table 1. Note that, in a given coordinate system, a given screw described in a given setting has the same set of atomic coordinates in Wyckoff as in Schoenflies; the space group too is the same, only its symbol is different.

	LHCS			RHCS		
		Pos. rot LH rot.	Neg. rot. RH rot.		Pos. rot. RH rot.	Neg. rot. LH rot.
Setting	Screw and figure	Schoenflies (1891)	Wyckoff (1922)	Screw and figure	Schoenflies (1923) and *IT*	Wyckoff (1930)
	LS			RS		
$r(+)$	Fig. 1.1	D_3^4–$P3_121$	D_3^6–$P3_221$	Fig. 1.2	D_3^4–$P3_121$	D_3^6–$P3_221$
$z(-)$	Fig. 1.3			Fig. 1.4		
	RS			LS		
$r(-)$	Fig. 1.6	D_3^6–$P3_221$	D_3^4–$P3_121$	Fig. 1.5	D_3^6–$P3_221$	D_3^4–$P3_121$
$z(+)$	Fig. 1.8			Fig. 1.7		

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* As a matter of fact, in all systems other than the hexagonal, Wyckoff (1922) used the RHCS in the Introduction (Ch. I and II) and the LHCS in the Tables; in the hexagonal system, however, the LHCS was used throughout the book (with the single exception of Fig. 34, where the RHCS can only be a misprint).

* Burckhardt (1946; 1966) charges *all* the crystallographers with reversing the rotation sense of the RHCS. After describing the space groups C_3^2–$P3_1$ and C_3^3–$P3_2$ by means of the RH rot., as does Schoenflies (1923), he states, 'An Stelle der Rechtsdrehung betrachten die Kristallographen die durch ($y-x$, $\bar{x}$, z) erzeugte Linksdrehung' [LH rot.], and he goes on, '$P3_1$ wird durch eine Linksschraubung der Ganghöhe 1/3 erzeugt'. This description fits Wyckoff (1930) perfectly.

with arrow reversed).* The corresponding atomic coordinates (Table 1) are found under $P3_121$–D_3^6, which is the present-day designation. This conflict of conventions has created confusion, as some authors equated Wyckoff's 'D_3^4' with the $P3_121$ of *IT* (Parthé, 1964; Arnold, 1962), obviously overlooking the LH rot. used by Wyckoff. The coordinates given by Wyckoff apply to Fig. 1.7; they would also apply to Fig. 1.8: the two settings are mirror images of each other, with both the crystal structure and the coordinate axes being reflected. The four sets of numerical atomic coordinates are presented in Table 1, to correspond to the four settings of the LS (Figs. 1.1, 1.3, 1.5, 1.7) and of the RS (Figs. 1.2, 1.4, 1.6, 1.8). Each screw has two settings in each coordinate system.

How to use Table 1

The usefulness of Table 1 is that it permits the setting of any published description of quartz to be readily identified. Not counting the eight variants due to the Wyckoff rotation convention, which only changes the designation of the space group, and restricting the designation of the 2-axis that passes through the origin to $Ox[100]$, there are eight different ways of describing the low-quartz structure. Any one of several sets of data identifies the description: (1) the atomic coordinates, with the hand of the screw or that of the coordinate system; (2) the complete setting, $r(+)$, $z(-)$, $r(-)$ or $z(+)$, with the hand of the screw or that of the coordinate system; (3) a half-setting, r, z, $(+)$ or $(-)$, with the space group and the hand of the screw or that of the coordinate system; (4) a half-setting, with both the hand of the screw and that of the coordinate system.

We shall now assign the previous descriptions of low quartz to the appropriate settings and figures.

(1) Gibbs (1926) published perspective drawings that display a RS; the X-ray diffracted intensities obey $I(10\bar{1}1) > I(01\bar{1}1)$, indicating an r setting; the RHCS, then standard in Bragg's laboratory (Bragg & Gibbs, 1925), proves the setting to be $r(+)$, which is shown on Fig. 1.2.

(2) Ewald & Hermann (*Strukturbericht*, 1931, Fig. 76, p. 166) use a RHCS. The space group that is figured is $P3_221$, so that the screw axis is a LS. The atomic coordinates reported are those given by Wyckoff (1931), *viz.* $u = 0{\cdot}46$, $x = ca\ 0{\cdot}5$, $y = ca\ 0{\cdot}3$, $z = +0{\cdot}1_1$. It follows that the structure is described in the setting $z(+)$ of Fig. 1.7.

(3) IRE (1945) (in Cady, 1946, p. 408, Fig. 76). The *laevo* crystal is in the setting of Fig. 1.8; the *dextro* crystal, in that of Fig. 1.7. Both are $z(+)$ settings. (Note that the Y axis of the IRE rectangular system of coordinates coincides with our reciprocal axis y^*.)

(4) IRE (1949, p. 1384, Fig. 10). The *laevo* crystal corresponds to Fig. 1.2; the *dextro*, to Fig. 1.5. Both are in r settings, $(+)$ and $(-)$ respectively. (The Y axis of IRE coincides with the y^* of our RHCS.)

(5) A. de Vries (1958) uses a *laevo* crystal, a fact established optically and confirmed morphologically. He obviously uses a RHCS. From the measurements of X-ray diffraction intensities, we learn that $I(\bar{1}101)$ is stronger than $I(1\bar{1}01)$ or, equivalently, $I(10\bar{1}1) > I(01\bar{1}1)$; this establishes an r setting. This case is that of Fig. 1.2, setting $r(+)$. Indeed the method of anomalous scattering (Bijvoet, 1949), applied by de Vries, yielded space group $P3_121$, to which the atomic coordinates published by Brill, Hermann & Peters (1939) had been adapted for the purpose of intensity calculations.

(6) Parthé (1964) states atomic coordinates which, in conjunction with the RHCS, require the setting of Fig. 1.7, $z(+)$, LS in RHCS, space group $P3_221$. Parthé's symbol 'D_3^4–$P3_121$' is that of Wyckoff (1930).

(7) The following authors all describe the low-quartz structure in the $z(+)$ setting of Fig. 1.7:

Wyckoff (1931) as 'D_3^4'; Wei (1935); Brill, Hermann & Peters (1942); Wyckoff (1948); Young & Post (1962); Smith & Alexander (1963); Wyckoff (1963); Zachariasen & Plettinger (1965); Megaw (1973); Le Page & Donnay (1976).

What to call the twofold axis through the origin

So far we have followed the convention adopted by almost all the crystallographers who had to describe the low-quartz structure, *viz.* to take $Ox[100]$ along the twofold axis through O. Note that any three points of intersection of the screw axis with three consecutive twofold axes are crystallographically equivalent, so that the choice is not really one between *different* origins; it is only a choice between labels (Ox,Oy,Ou) to tack on to the twofold axis with which one of the coordinate axes will coincide. We have found one example of a paper in which this axis turned out to be Oy (Wooster, 1953) and one in which it was deliberately chosen as $Ou[\bar{1}\bar{1}0]$ to be in agreement with the setting used in *IT* (1952) (Burnham, 1965).

Case of Oy on the twofold axis through O

Wooster (1953, p. 73, Figs. 8 and 9) deals with a LS, as can be gathered from his Fig. 9, which shows a crystal with the x and s faces in *dextro* position. His

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[*] Lang (1965) attributed Wyckoff's LH rotation to a LHCS (with implied positive rotation), a situation that would correspond to our Fig. 1.3 and would require other atomic coordinates (shown in Table 1). The transformation 'Fig. 1.3 - from - Fig. 1.7' is 100/110/001 for the direct axes; whence 110/010/001 for the coordinates. This transformation is a reflection in a plane normal to twofold axis Ox $(.m'.)$ or the inversion $\bar{1}'$, either of which relates the two enantiomorphous crystals in a Brazil twin.

other figure is a projection of the structure on to (0001); on it the twofold axes are identified by their heights $0,\frac{1}{3},\frac{2}{3}$, and the corresponding coordinate axes are unconventionally and openmindedly labelled *OR*, *OQ*, *OP′*, respectively. Minus (–) charges are known to develop at *R*, *Q*, *P′*, on extensions parallel to the twofold axes. The figure shows that the positive directions *OR*, *OQ*, *OP′* run outwards from the less obtuse angles of the projected silicon ditrigon. (We set *OP′* = –*OP*.)

Accepting the face indexing on Wooster's Fig. 9, we must take *OQ* as *Ox*, *OR* as *Oy*, *OP′* as *Ou*. This is an *r*(–) setting corresponding to our Fig. 1.5 after its RHCS has been rotated 120° clockwise around *Oz*, so that *Oy* will be the twofold axis at height zero. If, however, we give other assignments to *OR*, *OQ*, *OP′*, we can make Wooster's Fig. 8 correspond to any one of our four LS settings. Setting *OR* = *Ox*, *OP′* = *Oy*, *OQ* = *Ou*, leads to our Fig. 1.5; reversing the three axes gives Fig. 1.7. Taking *OR′* = *Ox*, *OQ′* = *Oy*, *OP* = *Ou*, gives Fig. 1.1; reversing the three axes, Fig. 1.3.

Case of Ou on the twofold axis through O

Burnham (1965) describes his structure as follows: the space group is $P3_121$ of *IT* (1952) [hence a RS in a RHCS]; the 2-axis through the origin is [$\bar{1}\bar{1}0$] [so that we can label the heights $\frac{1}{3}$ and $\frac{2}{3}$ of the other two axes]; the silicon atoms are in position 3(*a*) at *u*,*u*,0, with *u* = 0·47 (we can now draw the projected ditrigon of silicon atoms around the origin).

The more obtuse angles of the ditrigon point in the directions $O\bar{u}$, $O\bar{x}$, $O\bar{y}$, thus locating the + charges that develop in the pyroelectric test (Lang's rule, 1965). These + signs also indicate which edges of the hexagonal prism *m*{$10\bar{1}0$} are surmounted by the *x* and *s* faces. As the space group contains a RS, we are dealing with a *laevo* crystal and we can identify the *r* face to the right of the edge marked (+). This is the case of our Fig. 1.4 after its RHCS has been rotated 120° counterclockwise around *Oz*, so that *Ou* will be the 2-axis at height zero. The relabelling of the faces of the two rhombohedra, required by the rotation of the RHCS, does not alter the relative orientation of the *r* and *z* faces on Fig. 1.4. The Burnham setting thus turns out to be a *z*(–) setting, and the intensity of the $01\bar{1}1$ reflection should have been greater* than that of $10\bar{1}1$. The atomic coordinates are listed as: *u* = 0·47, *x* = 0·41, *y* = 0·14, *z* = 0·12 (quoted here approximately, to facilitate comparison with Table 1). The Si coordinates, 0·47,0·47,0, correspond to 0·47,0·47,0·67, in the setting of Fig. 1.4 (Table 1); the oxygen coordinates, given above, correspond to 0·41,0·14,0·79. In both cases the difference in the *z* value is $\frac{2}{3}$, which is explained by the transformation of coordinate axes.

According to Burnham, matrix 100/$1\bar{1}0$/001 transforms the coordinates in his setting to those of previous authors. Indeed the silicon coordinates become 0·47,0,0, and those of oxygen, 0·41,0·27,0·12, which are those found in setting *z*(+) of Fig. 1.8 (Table 1); the RS is here referred to a LHCS, and the space group must be interpreted as '$P3_221$ with LH rot.'. The coordinates of Fig. 1.8 are also those of Fig. 1.7; they properly describe a LS in a RHCS with space group $P3_221$. Smith & Alexander (1963) were actually dealing with this case (Fig. 1.7).

Reversing the sense of the polar axes in Burnham's setting and stating the Si coordinates as 0·53,0·53,0·67 would lead to an *r*(+) setting obeying the *IT* (1952, vol. I, p. 257) convention. The near-unanimity of the workers who have described the low-quartz structure, however, speaks in favor of [100], instead of [$\bar{1}\bar{1}0$], as the 2-axis through the origin. This minor change would make Fig. 1.2 standard.

Matrix $0\bar{1}0$/$1\bar{1}0$/001 will transform coordinates from the Burnham setting, modified as stated, to the setting *r*(+) of Fig. 1.2. Matrix 010/$\bar{1}10$/001 transforms coordinates from the original setting of Burnham directly to that of Fig. 1.2.

Discussion and conclusion

We have seen the two principal conventions that have been proposed: the *r* convention, advocated by mineralogists, and the (+) convention, resting on the piezoelectric test, most useful to radio engineers. We have seen that setting *z*(+) has been chosen by most workers in the field of quartz crystal structure. IRE (1949) and Lang (1965) recommend the *r* settings (Figs. 1.2, 1.5). Megaw (1973) says she is following Lang's recommendations, but her own description of the quartz structure ends up in the *z*(+) setting:* her Fig. 11-23 enables the reader to check the atomic coordinates against the list in our Table 1, which places a LS in our Fig. 1.7.

Summing up, we see that a RS (*laevo*) crystal, in the RHCS, can be set in an *r*(+) setting, which satisfies both conventions, but that a LS cannot obey both conventions in the RHCS, no more than can a RS in the LHCS. The RS in the RHCS (Fig. 1.2) gives the *r*(+) setting, which should satisfy everybody. The LS in the RHCS, neither in its *r*(–) setting (Fig. 1.5) nor in its *z*(+) setting (Fig. 1.7), can be satisfactory. The price we have to pay for insisting on using only one coordinate

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* This information was not given in the *Year-Book* report (Burnham, 1965), but has courteously been provided by Professor Burnham (private communication): '$|F_o(01\bar{1}1)| = 49$, $|F_o(10\bar{1}1)| = 41{\cdot}8$'.

* The reason for this outcome may be that she used the Lang rule to orient the coordinate axes *x*, *y*, *u*, making them 'run outwards from the more obtuse corners of the distorted hexagon', oblivious of the fact that in the *r* setting 'in $P3_221$ they run outwards from the more acute corners' (Lang, 1965, last sentence).

system, *viz.* the RHCS, may be too high. [We crystallographers are blamed for this practice, which is referred to in the literature as the 'standard crystallographic practice' (IRE, 1949).] Let us consider the feasibility of reverting to the use of both systems.

Matching the hand of the coordinate system to that of the screw

A crystal of LS (*dextro*) quartz is placed (Fig. 2*a*) next to a RS (*laevo*) crystal (Fig. 2*b*). As drawn, the two crystals are seen to be mirror images of each other in a plane $(1\bar{2}10)_0$, passed through the origin perpendicularly to the *y* axis; this plane is a twin plane $(.m'.)$ in the Brazil twin. Let the crystal of Fig. 2(*b*) be crystal I of the twin; the crystal of Fig. 2(*a*) is then exactly the same as what crystal II of the twin would be. (The two crystals here are not united in any twin: they are independent, but the relation is identical.) What difference does it make if we refer crystal II to a RHCS instead of a LHCS (as we have assumed in this paper)? To find out, we have repeated the crystal of Fig. 2(*a*) to the right of Fig. 2(*b*). Crystal II has a LHCS in Fig. 2(*a*), a RHCS in Fig. 2(*c*).

The small *x* and *s* faces that occur on the right side of crystal II are physically similar, in all their properties, to the *x* and *s* faces that appear on crystal I, even though they occur here on the left side of the drawing. This fact deserves to be brought out, not obscured, by the symbolism: it will be if crystal II is referred to a LHCS, which matches the hand of its LS, simply by reflecting the RHCS of crystal I in $(1\bar{2}10)_0$ as well as crystal I itself (*cf.* Figs. 1.2 and 1.1). Faces *x* and *s* thus retain their own symbols (Fig. 2*a*). In contrast when crystal II is described in a RHCS (Fig. 2*c*), its *x* and *s* faces acquire new symbols, $(51\bar{6}1)$ and $(11\bar{2}1)$ respectively, which characterize faces of a different trigonal trapezohedron and a different trigonal dipyramid! An elegant solution to this vexing problem has been found in the symbolism of twinning, where a face of crystal I and its reflected counterpart in crystal II are given the same Miller indices, the two symbols being distinguished by the underlining of the symbol of the face that belongs to crystal II. We submit that this practice should be adhered to whether the two enantiomorphous crystals are united in a twin or exist independently of each other.

Describing a RS in a RHCS and a LS in a LHCS should appeal to structural crystallographers and crystal morphologists alike; the scheme would also have great simplifying value for radio engineers, as explained by Cady[*] (1946). The first issue of the *Standard for Piezoelectric Crystals* (IRE, 1945) already provided for the use of both coordinate systems. At that time, four years before the advent of the method for determining the absolute configuration of an enantiomorph (Bijvoet, 1949) and thirteen years before it was applied to low quartz (de Vries, 1958), the members of the IRE committee could only go by the sign of the optical activity and they recommended a RHCS for a *dextro* crystal and a LHCS for a *laevo*. Four years later (IRE, 1949) the *Standard* was revised, reverting to the single RHCS for the description of both enantiomorphs (Figs. 1.2, 1.5). This decision is still in force at the present time.[†]

Now, one generation later, this question might be broached again. Insofar as low quartz is concerned, the enantiomorph with the RS, in a RHCS, can be accepted as standard (Fig. 1.2). The latest refinement of

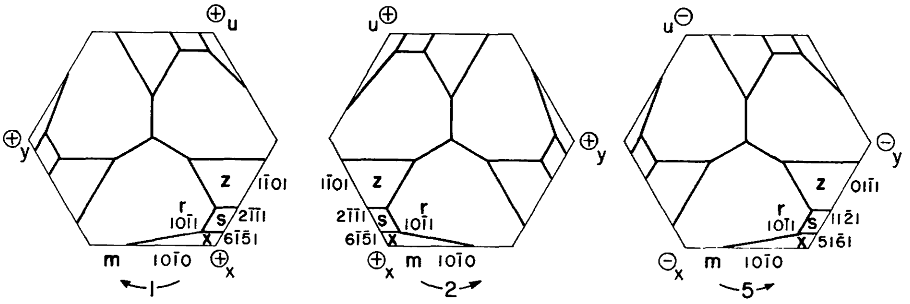

Fig. 2. Idealized crystal drawings of low-quartz crystals in orthogonal projection on (0001). Arrows show correspondence with Figs. 1.1, 1.2, 1.5, respectively. The RS (*laevo*) in a RHCS (*b*) is between two LS's (*dextro*), one in a LHCS (*a*), the other in a RHCS (*c*). Note the symbols of *x* and *s* faces on (*a*) [same as on (*b*)] and on (*c*) [different from those on (*b*)]. The *x* forms (and the *s* forms) on all three drawings are *physically similar*: the use of the wrong coordinate system on (*c*) leads to a misleading indexing [whose only usefulness is to show with which reflections of crystal I (*b*) the $6\bar{1}\bar{5}1$ and $2\bar{1}\bar{1}1$ reflections of crystal II (*a*) will coalesce on an X-ray film taken from a Brazil twin].

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[*] According to Cady (1946, p. 407) the recommendation to use both coordinate systems was first made by Koda (1929).

[†] An IEEE 'Standard on Piezoelectricity' is now being prepared by the Subcommittee on Piezoelectric Crystals, A. H. Meitzler, Chairman, in which general rules for the setting of *any* piezoelectric crystal are to be recommended, to supersede the 1949 conventions (Meitzler, 1977, private communication).

the low-quartz structure has been cast in that form (Le Page, 1978). The numerical values of the coordinates being the same for the LS in a LHCS (Fig. 1.1), it will never be necessary to publish data on LS quartz – they will be understood.

This approach leads to the concept of *a single crystal structure* for low quartz, to be conventionally described in space group $P3_121$ with a RHCS. If observations and measurements were made on a LS, an accompanying statement would be, 'Observations made on a LS'. If a new compound is described, in which only the LS enantiomorph is known, the investigation would, of course, be conducted in a LHCS, but the results would be recorded in the RS format,* with the additional note, 'Only the LS is known'.

Professors F. C. Frank, A. C. Lang (Cardiff) and A. Pabst (Berkeley) reviewed the manuscript critically. Professor John Clark (US Naval Postgraduate School) facilitated access to the 1935 *International Tables* and the 1891 Schoenflies reference; Professors C. Frondel and Charles W. Burnham (Harvard University) helped in obtaining information from the 1923 Schoenflies reference. Professor P. P. Ewald contributed his copy of Wyckoff's 1922 edition.

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APPENDIX I

Structural screw *vs* optical helix

The first X-ray determination of an absolute configuration, that of the sodium rubidium tartrate (Bijvoet, 1949; Peerdeman, Bommel & Bijvoet, 1951), established the correlation between the right-handed screw (RS) and the right-handed 'optical helix', which shows laevorotatory character. Wooster (1953) thought that the above correlation might turn out to be general.

Some experimental results on low quartz (de Vries, 1958; Zachariasen, 1965) sustained Wooster's position, but two isostructural compounds, $NaBrO_3$ and $NaClO_3$, were shown (Beursken-Kerssen, Kroon, Endeman, van Laar & Bijvoet, 1963) to have rotatory powers of opposite signs, contrary to Ramachandran's (1951) theoretical results. Cinnabar, HgS, whose structure (Mauguin, 1923; Lundborg-Aurivillius, 1950) crystallizes in the same space group as low quartz, had its absolute configuration determined by Seifert (1963) and confirmed by Auvray (1976): the LS of D_3^6–$P3_221$ was found in a *laevo* crystal. Auvray also confirmed the LS in a *dextro* crystal of low quartz. The correlation between the hand of the screw axis and the sign of the rotatory power is thus not general: it must be determined anew for each optically active crystalline substance.

APPENDIX II

Table of errata et corrigenda

Wyckoff (1922)

p. 18, Fig. 16: Angle α should be $(OX,OY) = (OY,OZ)$, not the angle between OX (or OY) and the threefold axis.

p. 44, Fig. 34: *instead of* OY, *read* $O\bar{Y}$. (This RHCS is the only one we found for hexagonal coordinate axes. *Cf.* Fig. 26, p. 36, which has a LHCS, to which many references are made in the book.)

p. 36, line 10: *instead of* 60°, *read* 30°. (Fig. 26, though incorrectly drawn, is correctly labelled.)

Mauguin (1931)

p. 554, Table D_3: Mauguin gives the concordance between Schoenflies 1930 symbols and his own.

in D_3^3–$C3_212 = H3_121$ *instead of* 3_2, *read* 3_1

in D_3^5–$C3_112 = H3_221$ *instead of* 3_1, *read* 3_2

(The screw axes are correctly symbolized in the H setting. The letter C was used at the time to denote the primitive hexagonal cell; H designates the triple cell.)

IT (1935)

In C_6^4–$P6_2$ and C_6^5–$P6_4$ the RS and LS screw-axis symbols on the figures were interchanged; this error was corrected in *IT* (1952).

IRE (1949)

p. 1384, Section 1.11, 2nd paragraph, last sentence: Note that 'regarding one form as the crystallographic inversion of the other rather than as its mirror image' does not alter the fact that it *is* its mirror image! It is not clear why, 'under this convention' (to use a RHCS for either form), inversion should be preferable to reflection since both operations lead to the same form.

p. 1386, Section 1.14, 2nd paragraph, line 3: In the explanation of Table I, *delete* '*m* an axis in a plane of symmetry'. (Such an axis would not be defined in direction; Table I gives no example of such an axis.)

p. 1385, Table I, col. 2: *instead of* $\bar{6}m2$, *read* $\bar{6}2m$. (The 2s are taken as coordinate axes and so should appear in second position in the symbol.)

p. 1386, col. 1, lines 4 up to 2 up: In the orthorhombic system the c axis is *not* the first, but the third, to be identified.

p. 1385, Table I, col. 2: *instead of* $2mm$, *read* $mm2$.

p. 1386, Section 1.15, lines 5 to 6: *instead of* internal structural properties, *read* macroscopic properties.

Lundborg-Aurivillius (1950)

p. 1415, line 9: *instead of* D_3^4 or D_3^6 *read* D_3^6 or D_3^4.

p. 1418, Fig. 1: The x and y axes must be interchanged to represent a RHCS. The RH rot. is implied. The LS is our present 3_2 in D_3^6 (see our Fig. 1.5).

Instead of D_3^4 *read* D_3^6 *and vice-versa.*

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* In a paper on absolute structure determination in space groups $P4_132$ and $P4_332$, Van der Biest & Thomas (1977) insist on the necessity of using a LHCS for indexing the reflections, even though the atomic coordinates used refer to the RHCS 'standard in crystallography'.

Frondel (1962)

p. 12, Fig. 6, *legend: interchange* left-handed *and* right-handed
p. 15, line 8 up: *instead of* red to violet *read* violet to red
line 5 up: *instead of* violet to red *read* red to violet
line 2 up: *instead of* inward *read* outward*
line 1 up: *instead of* outward *read* inward*

p. 18, under 'Structural Crystallography', line 4: The atomic positions are said to be 'in D_3^4–$C3_12$'. This symbol is that used in Wyckoff's second edition (1930); this space group has been designated D_3^6–$C3_22$ since 1935 (*IT*, 1935) and D_3^6–$P3_221$ since 1952 (*IT*, 1952). [Note that the heights of the 2-axes in *IT* must be increased by $\frac{1}{3}$ in order to agree with Wyckoff's Fig. 9, in which the 2-axis in direction [100] is at height zero.]

p. 49, lines 14, 16, 18, 29: *instead of* pyramid *read* dipyramid.

Arnold (1962)

p. 468, line 11: Where Arnold announces his result that the high-quartz structure is simulated by low-quartz Dauphiné twins, the space group of high quartz is given as D_6^4–$P6_222$ and that of low quartz as D_3^4–$P3_121$: *instead of* D_3^4–$P3_121$ *read* D_3^6–$P3_221$. ($P3_121$ is a subgroup of D_6^5–$P6_422$, as was pointed out by Megaw, 1973, p. 267.)

Seifert (1963)

p. A16, line 4 up of abstract; *instead of* D_3^6–$P3_121$ (RS) *read* D_3^4–$P3_121$ (RS).

Parthé (1964)

p. 139: *instead of* D_3^4–$P3_121$ *read* D_3^6–$P3_221$. [Parthé obviously quotes the Wyckoff (1930) symbol.]

Lang (1965)

p. 290, col. 1, third paragraph:

lines 10–13 and reference to Wyckoff (1922): We confirm Lang's conclusion (based on Figs. 17, p. 19 and 26, p. 36) that Wyckoff used a LHCS to express the equivalent points. The three triplets of coordinates (x,y,z; $y-x$, $\bar{x}$, z; $\bar{y}$, $x-y$, z) that are listed on p. 20 (D_3, for twofold axes U_a, parallel to which the coordinate axes are taken) belong to points P, P_2, P_1 on the figure of p. 19, and *in that counterclockwise order*. Wyckoff thus used the RH rot., that is, the negative sense for the plane XY of the LHCS.

lines 13–15: The reason why *IT* (1935) made no comments on their RHCS reversing the hand of Wyckoff's LHCS of 1922, probably was that the LHCS had already been given up by Schoenflies in 1923 and by Wyckoff in 1930 (*cf.* our Table 2).

line 8 up to line 1, col. 2: In Wyckoff's (1931) description of the structure of quartz the coordinates are those of the $z(+)$ setting in a RHCS (our Fig. 1.7), but with LH rot. Wei (1935) kept Wyckoff's RHCS in his drawing; *Wyckoff's LS remained a LS*, but the space group that was called 'D_3^4' ($P3_121$) with LH rot. by Wyckoff became D_3^6 ($P3_221$) with the proper RH rot. of the RHCS. The 'unconventional' orientation found in Wei can thus be traced back to Wyckoff's own description of 1931.

p. 290, first paragraph: The use of the terms *obverse* and *reverse* to designate the r and z settings can be justified by analogy with the case of a rhombohedral lattice. Note, however, that in (hexagonal) low quartz the difference between major and minor rhombohedra is a structural and fortuitous one, whereas it is reticular and systematic (*cf.* footnote p. 587) in *any* crystal with a rhombohedral lattice, where it is also more striking and more constant.

Le Page & Donnay (1976)

p. 2457, footnote: Superseded by present paper.

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* Errata communicated by Professor J. A. Weil, University of Saskatchewan. [The convergent light test is correctly stated in IRE, (1949, p. 1386, col. 1, lines 4–6).]

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X-ray Study of the Atomic Charge Densities in MgO, CaO, SrO and BaO*

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Accurate X-ray structure factors of CaO, SrO and BaO were measured at 293 K from single crystals and analysed together with the data of Sanger [*Acta Cryst.* (1969), A**25**, 694–702] on MgO. The oxygen ion is seen to suffer an average compression and a fourth-order cubic harmonic type deformation, as compared to the atomic superposition model, yielding a lower average charge density in the surrounding region and a charge transfer from [111] to the [100] direction. These features strengthen with increasing atomic number of the cation. Mg and Ca show a weak broadening. About nine electrons are localized around the oxygen position. The tenth electron of O^{2-} is more widely distributed. The electron counts of the cation correspond most closely to Mg^+, Ca^{2+}, Sr^{2+} and Ba^{2+}. The results confirm the dominance of ionic character and increase of ionicity with increasing atomic number of the cation.

Introduction

By their chemical nature, the alkaline earth oxides should lie between the covalent III–V compounds and the alkali halides with ionic character. Experimental study of their electronic structure is therefore expected to yield information on the bonding mechanism in cases where neither of these simple models works well.

This paper refers to the series MgO, CaO, SrO and BaO with NaCl structure. General chemical and dielectric considerations (Phillips, 1970) indicate strong dominance of ionic character comparable to the alkali halides, increasing from MgO to BaO. The oxides show, however, slightly more covalent character than the corresponding fluorides with same core configuration (Son & Bartels, 1972).

Theoretical consideration of the bonding in these crystals meets difficulties since the doubly ionized oxygen is not stable in the free state, the stabilization resulting from its bonding into the crystal lattice. Furthermore, theoretical models in lattice dynamics seem not to give a satisfactory explanation of spectroscopic results, especially in the case of SrO and BaO (Galtier, 1973; Montaner, 1974; Rieder, Weinstein, Cardona & Bilz, 1973).

The electronic state of the oxygen in MgO has been subject to several theoretical calculations (Yamashita & Kojima, 1952; Watson, 1958; Suzuki, 1960; Tokonami, 1965; Yamashita & Asano, 1970) and to

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