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$La_2I_2SiO_4$, a New Type of Rare Earth Halogenosilicate

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The preparation and crystal structure determination of $La_2I_2SiO_4$ is reported. Two modifications, triclinic a- and monoclinic m-$La_2I_2SiO_4$, are found, which can be described as stacking variants of a layered structure. The relations between them are discussed on the basis of the OD terminology introduced by Dornberger-Schiff. © 1993 Academic Press, Inc.

Introduction

Preparative chemistry in the field of rare earth halides is heavily affected by the tendency to unwanted side reactions with impurities in the surrounding "inert" atmosphere or with container materials such as silica. Very often thermodynamically extremely stable oxides, oxyhalides, or silicates result as major contaminants in such syntheses. In the course of our studies on lanthanum iodides we have found an iodide—silicate phase of lanthanum of hiterto unknown stoichiometry—$La_2I_2SiO_4$—as a byproduct resulting from melting and sublimation of LaI_3 in silica ampules. Our efforts to synthesize this compound intentionally, the determination of its crystal structure, and a crystallographic interpretation of the structural topology are summarized in this paper.

Experimental

LaI_3, SiO_2, and LaOI were used as starting materials in different synthesis routes. LaI_3 was prepared by slow thermal decomposition of LaI_3-hydrates and subsequent sublimation at temperatures above 750°C in Ta-containers under vacuum. SiO_2 was formed in an active form by drying silicic acid at temperatures up to 500°C. LaOI was prepared by melting stoichiometric mixtures of LaI_3 and La_2O_3 at 800°C for 1 day.

Following a scheme proposed by Corbett (*1*, *2*) we tried a synthesis of $La_2I_2SiO_4$ by fusing stoichiometric amounts of triiodide and silica according to the reaction

$$2\ LaI_3 + 2\ SiO_2 \rightarrow La_2I_2SiO_4 + SiI4;$$

however, it took weeks at 800°C until the strongest lines of the new compound could be detected in the X-ray diagrams. A reaction according to the synthesis of $La_3Cl(SiO_4)$ (*3*) i.e.,

$$2\ LaOI + SiO_2 \rightarrow La_2I_2SiO_4,$$

was also not successful.

The best results were achieved by the reaction

$$2\ LaI_3 + 2\ La_2O_3 + SiO_2 \rightarrow 3\ La_2I_2SiO_4,$$

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where LaOI "in statu nascendi" reacts better with silica. For the synthesis of a well crystallized product, the finely crystalline compound was kept in excess LaI_3 for several weeks at 800°C.

The $La_2I_2SiO_4$ crystals were separated mechanically from the adhering LaI_3 matrix. They quickly decompose in air and cleave very easily, and it takes care to mount undistorted crystals in a capillary for the X-ray investigation.

Structure Determination

Crystals about 120 × 100 × 30 μm in size were sealed in a glass capillary under an Ar atmosphere. Unit cell dimensions were determined on a HUBER diffractometer (*4*) using Mo$K\alpha$ radiation. Buerger precession photographs helped to confirm the space group. Three out of four crystals showed triclinic symmetry $P\bar{1}$ (a (anorthic)-$La_2I_2SiO_4$). The second space group could be determined as $P2_1/c$ (m (monoclinic)-$La_2I_2SiO_4$); however, additional extinctions showing a pseudosymmetry (an *a* glide plane with the normal parallel *b*, see Discussion) were at first confusing. Precession photographs of the *hkO* zones of both modifications seem identical. A complex twinning pattern could be ruled out by the inspection of *Okl* zones.

Details of data collection are summarized in Table I. The structure could be solved with direct methods and difference Fourier syntheses using the SHELX (SHELXS) package (*5*). Due to the irregular form of the crystals, an empirical correction for absorption had to be applied (DIFABS) (*6*). This procedure improved the standard deviations of the positional parameters considerably and ensured positive definite temperature factors and reasonable Si–O distances and angles (*7*). However, the poor quality of the crystals (as seen in streaking of reflections) is reflected in the temperature factors, namely of the SiO_4 groups, and in the *R* values (see Discussion). The structural parameters are given in Table II.

TABLE I

LATTICE PARAMETERS AND DETAILS OF DATA COLLECTION

Compound lattice parameters	a-$La_2I_2SiO_4$	m-$La_2I_2SiO_4$
a[pm]	847.9(4)	847.4(3)
b[pm]	857.4(4)	857.8(4)
c[pm]	1195(2)	2236(3)
α[°]	99.6(1)	90
β[°]	108.3(2)	92.6(1)
γ[°]	90.1(1)	90
Space group	$P\bar{1}$	$P2_1/c$
Cell volume	812.1	1624.0
Θ scan range [°] (Mo$K\alpha$)	4–25	3–25
Regions of reciprocal space	$\pm h\ k\ l$, $\pm\ h\ -k\ -l$	$\pm h\ \pm k\ \pm l$
Number of independent reflections	1035	1401
R/R_w (%)	7.8/6.0	7.6/5.6

Note. Numbers in brackets are standard deviations referring to the last digits.

Discussion

The two modifications of $La_2I_2SiO_4$ have a very similar layered structure. I and La atoms and SiO_4 groups are separated into different layers which make up a sandwich-like package in the sequence I–La–SiO_4–La–I. The SiO_4 groups are oriented in such a way that half of them in a layer point in one direction along *c* with one of their apices and the other half in the reverse direction. a- and m-$La_2I_2SiO_4$ differ only by the way these sandwiches are stacked in the *c*-direction. The features of a half-sandwich I–La–SiO_4 are shown in Fig. 1 in a projection on the *a*, *b*-plane, and Figs. 2a,b show a sideview of both modifications to illustrate the difference in stacking.

Coordination polyhedra in rare earth silicates tend to be quite irregular because of

TABLE II

STRUCTURAL PARAMETERS OF a- AND m-$La_2I_2SiO_4$

m-$La_2I_2SiO_4$

Atom	x	y	z	B
La(1)	0.3773(2)	0.9356(2)	0.1537(1)	—
La(2)	0.8768(2)	0.7975(2)	0.1537(1)	—
La(3)	0.2405(2)	0.8059(2)	0.3133(1)	—
La(4)	0.7402(2)	0.9291(2)	0.3136(1)	—
I(1)	0.6662(3)	0.0498(2)	0.0703(1)	—
I(2)	0.1646(3)	0.6842(3)	0.0700(1)	—
I(3)	0.6340(3)	0.5442(3)	0.0792(2)	—
I(4)	0.1374(3)	0.1924(3)	0.0780(2)	—
Si(1)	0.038(1)	0.063(1)	0.2363(6)	174(22)
Si(2)	0.467(1)	0.172(1)	0.2628(6)	191(22)
O(1)	0.368(3)	0.191(3)	0.795(1)	400(74)
O(2)	0.416(3)	0.995(2)	0.270(1)	259(59)
O(3)	0.079(3)	0.243(3)	0.233(1)	296(61)
O(4)	0.055(2)	0.028(2)	0.310(1)	177(56)
O(5)	0.857(3)	0.037(3)	0.216(1)	345(68)
O(6)	0.870(2)	0.067(2)	0.797(1)	244(60)
O(7)	0.644(2)	0.192(2)	0.286(1)	167(54)
O(8)	0.456(2)	0.202(3)	0.191(1)	249(61)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	186(11)	224(12)	270(17)	−12(8)	45(10)	7(11)
La(2)	168(11)	229(12)	234(17)	6(8)	28(10)	−3(11)
La(3)	201(11)	193(12)	305(18)	−18(8)	35(10)	−6(12)
La(4)	172(11)	222(12)	265(17)	10(8)	30(10)	−7(11)
I(1)	271(14)	326(15)	300(21)	13(11)	24(12)	36(14)
I(2)	240(13)	158(15)	262(20)	−6(10)	47(11)	−18(14)
I(3)	506(17)	371(16)	319(23)	14(12)	−89(15)	7(15)
I(4)	481(17)	377(16)	328(23)	67(12)	−142(15)	−13(15)

a-$La_2I_2SiO_4$

Atom	x	y	z	B
La(1)	0.7771(4)	0.7744(4)	0.8074(3)	—
La(2)	0.2773(4)	0.6360(4)	0.8076(3)	—
La(3)	0.4263(4)	0.1582(4)	0.8727(3)	—
La(4)	0.9283(4)	0.2819(4)	0.8738(3)	—
I(1)	0.4040(4)	0.8487(5)	0.6403(4)	—
I(2)	0.9030(4)	0.4833(4)	0.6399(4)	—
I(3)	0.4426(5)	0.3449(5)	0.6566(4)	—
I(4)	0.9484(5)	0.9933(5)	0.6596(4)	—
Si(1)	0.200(2)	0.940(2)	0.972(2)	232(41)
Si(2)	0.299(2)	0.456(2)	0.027(2)	123(34)
O(1)	0.259(4)	0.934(3)	0.117(3)	201(88)
O(2)	0.145(3)	0.111(3)	0.963(3)	63(83)
O(3)	0.364(4)	0.901(4)	0.924(3)	377(109)
O(4)	0.349(3)	0.632(3)	0.040(3)	94(75)
O(5)	0.077(4)	0.790(3)	0.904(3)	219(91)
O(6)	0.425(4)	0.331(4)	0.101(3)	289(100)
O(7)	0.139(4)	0.439(4)	0.069(3)	282(98)
O(8)	0.241(4)	0.387(4)	0.882(3)	269(97)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	182(14)	132(24)	224(29)	31(13)	62(17)	28(20)
La(2)	182(14)	173(25)	213(30)	20(14)	65(17)	21(20)
La(3)	207(15)	161(25)	199(29)	−4(14)	68(17)	19(20)
La(4)	191(15)	146(24)	225(30)	14(14)	56(18)	12(20)
I(1)	205(17)	345(30)	261(33)	−7(17)	24(20)	67(23)
I(2)	258(18)	298(31)	248(34)	8(18)	66(20)	6(24)
I(3)	623(3)	345(32)	329(36)	87(23)	262(28)	13(25)
I(4)	550(28)	327(33)	366(38)	31(22)	261(27)	46(26)

Note. Anisotropic parameters U_{ij} (given in pm^2) were refined for La and I; standard deviations refer to the last digits.

the great differences between the geometry of a silicate group on one hand and the coordinative needs of the large rare earth cations on the other. The point symmetry of the SiO_4 group is therefore mostly reduced to 1 (*7*, *8*). In the iodosilicates the deviations of O–Si–O angles from $\bar{4}3m$ symmetry are stronger than all others known so far (*7*, *8*) (up to 13°). They can be expected because of the great size differences of the ligands O and I. However, it must be admitted that the positional parameters of the oxygen atoms may not be as certain as in comparable structure determinations due to the poor quality of the data sets. The coordination polyhedra of La(1) and La(2) are quite similar (in both modifications), and the same is true for those around La(3) and La(4). The geometry and concatenation of these types of polyhedra is illustrated in Figs. 3a and b.

Having emphasized the similarities, let us now discuss the differences of the two modifications. The "elementary unit" common to both consists of a half-sandwich I–La–$(SiO_4)/_2$ as illustrated in Fig. 2a. These units are expanded differently along *c* in the two structures. The two halves of the sandwich are interconverted by inversion elements $\bar{1}$ in a-$La_2I_2SiO_4$ and by 2_1 elements in m-$La_2I_2SiO_4$. We have mentioned pseudoextinctions above; pseudosymmetries are therefore detected in the list of the positional parameters. We find "local" glide planes relating parts of the structure in m-$La_2I_2SiO_4$ in $y = \frac{1}{8}$ and $\frac{5}{8}$, and in a-$La_2I_2SiO_4$ perpendicular to [010] in $y = \frac{4}{10}$ and $\frac{9}{10}$—i.e. incompatible even with the crystal system—and these findings are typical for substances classified as OD structures.

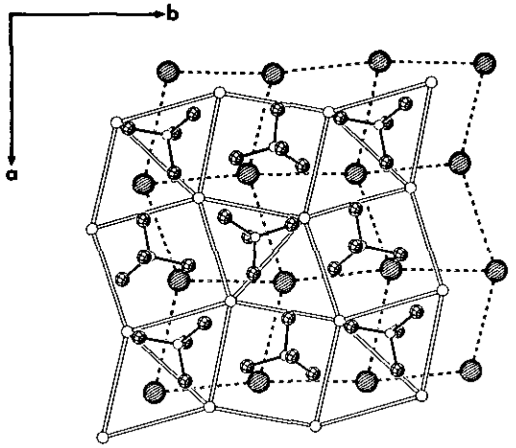

FIG. 1. The sequence of layers I–La–SiO_4 as viewed perpendicular onto the (001) plane. Dotted line: net of I; open line: net of La.

The Interpretation of a- and m-$La_2I_2SiO_4$ in the Terminology of OD Structures

According to Dornberger-Schiff (*9*) structural arrangements are termed "OD (order–disorder) structures" when they can be described by layer-like units for which different stacking operations are possible without having to change the symmetry relation between adjacent units. In such cases, several closely related structures are possible which may indeed be found in nature. The polymorphs created by varying the stacking operation can be completely ordered systems; however, polytypic disorder is also very common. The term OD alludes to the relative order of layers with respect to immediately adjacent layers (local or partial order) and the possibility of missing long range order (disorder).

The symmetry elements found in both structures are schematically represented in Figs. 4a,b, where they act on simplified structural elements for better clarity. Within the unit cell additional symmetry elements are added which relate only parts of the structure ("partial symmetry operations"), but which are not elements of the corresponding space group. The set of all symmetry operations relevant to one structure has the algebraic structure of a groupoid which we can imagine as an imperfect group. To be a group the symmetry elements describing only local symmetry would have to create

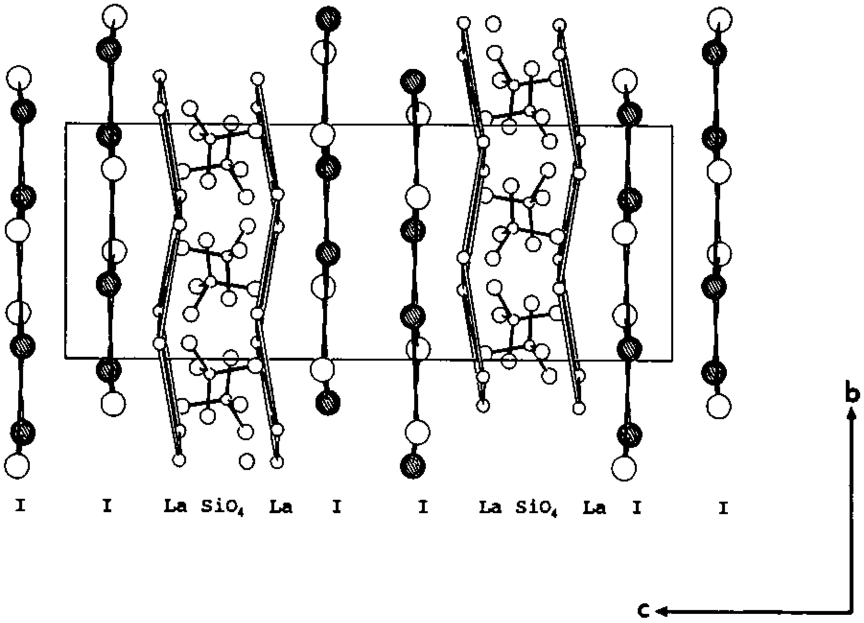

FIG. 2a. The structure of m-$La_2I_2SiO_4$ viewed along [$\bar{1}$00].

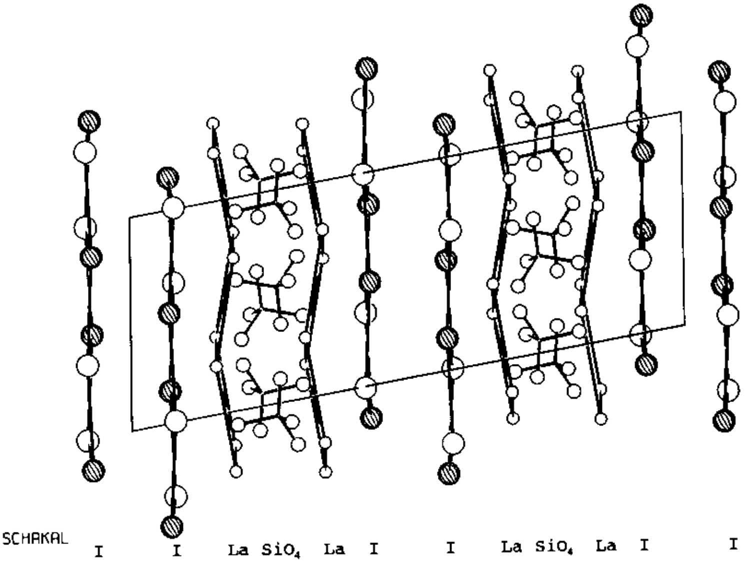

FIG. 2b. The structure of a-$La_2I_2SiO_4$ viewed along [$\bar{1}$00]. For better comparison the cell is doubled in the *c* direction.

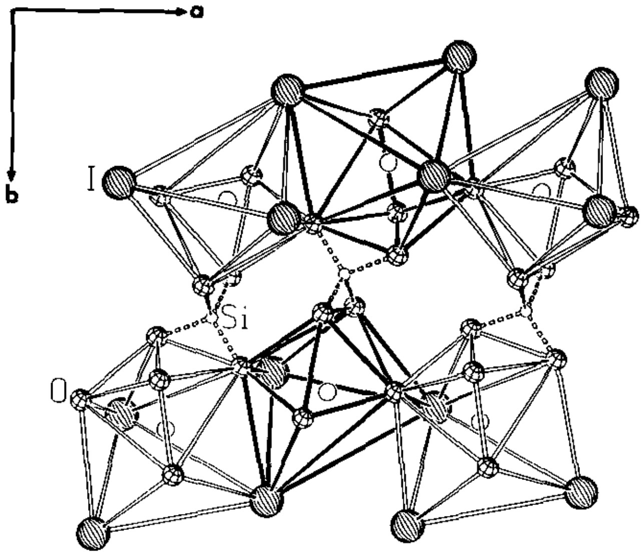

FIG. 3a. The catenation of coordination polyhedra around La(1) (bold lines) and La(2).

additional ones—all possible products—with those of the ordinary space group of total symmetries, which are not present in the structure however. Following a formalism described elsewhere (*10*), the layer sequence I–La–SiO_4–La–I can be defined as an OD layer for which the plane space group $P12_1/a$ (1) holds (the direction of missing periodicity is given in parentheses). Adjacent OD layers are related by an inversion $\bar{1}$ as stacking operation, and they form equivalent OD layer pairs (so called "equivalent regions" (ERs) (*10*)).

The OD groupoids—as mentioned above—describe the complete symmetry of each of the structures, and they both belong

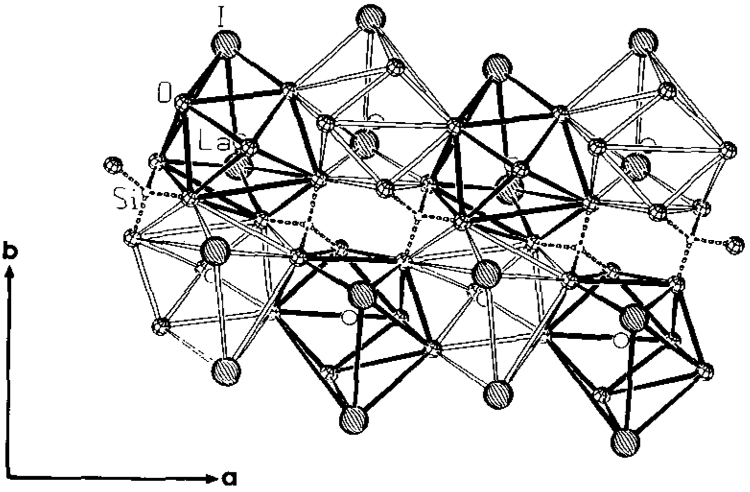

FIG. 3b. The catenation of coordination polyhedra around La(3) (bold lines) and La(4).

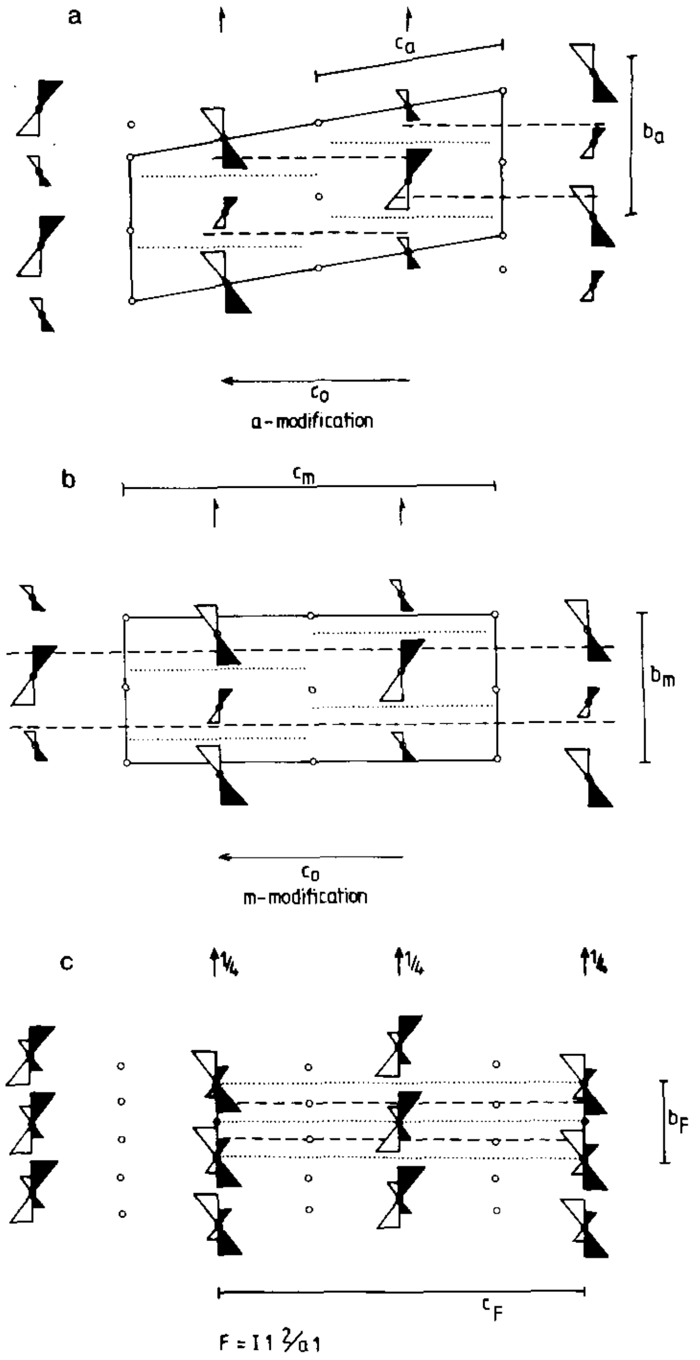

FIG. 4. Elements of symmetry and pseudo symmetry in a-$La_2I_2SiO_4$ (a), m-($La_2I_2SiO_4$ (b), and the fictive family group (c). The triangles symbolize tetrahedra representing the "elementary unit": an empty triangle stands for a tetrahedron with one of its vertices pointing upwards, a full triangle for a tetrahedron pointing downwards; large triangles symbolize tetrahedra with their basic face in $x = \frac{1}{2}$.)

to the same "family" (*11*, *12*) for which a notation can be given as

$$\begin{array}{l} P12_1/a\,(1) \\ \{1 \quad 1\,(\bar{1})\}. \end{array}$$

(The first line gives the type of the layer group and the second the stacking operation. This family belongs to the so-called category Ia (*13*); i.e., there are nonpolar layers, and there is a stacking operation within each layer pair transforming the whole pair into itself.)

Completing the groupoids to a group would give a fictive space group F called the family group. Here

$$F = I12/a1$$

with $a_F = a$, $b_F = b/2$, and $c_F = 2\,c_0$, where a and b are the basic vectors of an OD layer and c_0 is the vector perpendicular to the layers with the length of the distance between their centres. Figure 4c shows the fictive arrangement of the simplified structural elements as it is produced by this symmetry group.

Given a pair of OD layers, the number Z of possibilities for a third layer, i.e., the number of noncongruent layer triples, can be derived as the index of the symmetry group common to two adjacent layers in the subgroup of so-called τ-operations of one layer, (i.e., the group of all symmetry operations of the layer not converting it upside down). In our case

$$Z = |\,P\ 1\ a\ (1) : P\ 1\ 1\ (1)\,| = 2$$

i.e, there are two kinds of OD layer triples, and they are nonequivalent. All triples of the m-modification are equivalent to one kind, those of the a-modification to the other kind. Structures consisting of both kinds of triples are possible; however, they are of a lower degree of order. In fact both structures can be classified as being of "maximum degree of order" (MDO) (*14*, *15*). It can be shown that there are Z—in our case 2—nonequivalent MDO structures in families of category Ia, and here they are represented by the m- and the a-modification.

With these descriptions in mind it is surprising—and at the same time convincing—that we have found just these two modifications. Other OD arrangements with a lower degree of order are certainly possible, as are more or less random stacking constellations. However, these would reflect a loss in translational symmetry down to the situation where diffuse streaks appear in the reciprocal lattice in the latter case. (We may have missed such examples when picking "good" crystals for the structure determination.) In such cases the symmetry of the family group mentioned above is reflected in the pattern of the sharp reflections.

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