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Complex Copper(II) Fluorides

IV. Crystal Structure of $Ba_6Cu_{11}F_{34}$: First Evidence of Trinuclear Edge-Sharing Units and Defective NaCl-Type Blocks in Crystal Chemistry of Fluorides[1]

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Single crystals of $Ba_6Cu_{11}F_{34}$ were isolated from a melt corresponding to the composition 25 BaF_2–75 CuF_2. They are triclinic: $P\bar{1}$, $a = 7.490(1)$ Å, $b = 10.031(2)$ Å, $c = 10.271(3)$ Å, $\alpha = 82.98(2)°$, $\beta = 73.88(2)°$, $\gamma = 70.42(2)°$, $Z = 1$. The structure was determined from 3604 independent reflections using the program SHELX ($R = 0.054$, $R_w = 0.052$). The three-dimensional network is built from units of three edge-sharing octahedra connected by complex groups of octahedra. All the copper octahedra are elongated and the barium ions exhibit 11- or 12-fold coordination. The structural relations to $Ba_6Zn_7F_{26}$ and $Ba_2Ni_3F_{10}$ are discussed.

Introduction

In the binary systems BaF_2–MF_2 with M = Co,Ni,Cu,Zn (*4*), numerous compounds are formed for a molar ratio $r = M/\mathrm{Ba} > 1$: e.g., $Ba_6M_7F_{26}$ with M = Cu,Zn; $Ba_2M_3F_{10}$ with M = Co,Ni,Zn (*5, 7*); and $Ba_2M_7F_{18}$ with M = Ni,Cu,Zn. From what is presently known, it may be assumed that all these compounds could belong to a series of general formula: $Ba_6M_nF_{12+2n}$ with n odd. After the structural determination of $Ba_6Zn_7F_{26}$ ($r = 1.16$, $n = 7$) (*6*) and $Ba_2Ni_3F_{10}$ ($r = 1.5$, $n = 9$) (*7*), we are now investigating phases corresponding to higher r values and we describe in this paper the hitherto unknown compound $Ba_6Cu_{11}F_{34}$ ($r = 1.83$, $n = 11$) in order to illustrate the structural recurrence in this family of fluorides.

Experimental

By cooling a melt corresponding to the composition 25 BaF_2–75 CuF_2, shapeless single crystals of a new phase were isolated. These crystals correspond to a stoichiometry 6 BaF_2–11 CuF_2 as determined from the resolution of the structure. Several attempts of direct synthesis from the stoichiometric amounts at temperatures up to 600°C always led to a mixture of two phases: $Ba_6Cu_7F_{26}$ and $Ba_2Cu_7F_{18}$, even after quenching the tubes in cold water. The homologous $Ba_6M_{11}F_{34}$ phases (with M = Ni,Zn) could not be isolated. In Table I we

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[1] For parts I to III, see Refs. (*1–3*).

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TABLE I

CALCULATED X-RAY POWDER PATTERN (Cu$K\alpha$)

h	k	l	θ	D_{calc}	I_{calc}
0	1	0	4.68	9.4460	1
1	0	0	6.48	6.8271	1
0	1	−1	6.59	6.7145	6
1	1	0	6.69	6.6131	4
1	0	1	6.88	6.4259	4
1	1	1	6.99	6.3326	3
0	0	2	8.99	4.9310	15
1	1	−1	9.01	4.9172	3
0	2	0	9.39	4.7230	3
1	−1	1	9.50	4.6669	9
1	2	0	9.58	4.6279	2
1	0	2	9.67	4.5862	5
1	1	2	9.67	4.5849	1
1	2	1	9.72	4.5610	1
0	1	2	10.01	4.4302	11
0	1	−2	10.28	4.3146	2
0	2	1	10.28	4.3142	3
0	2	−1	10.55	4.2072	8
1	−1	−1	10.84	4.0973	5
1	2	−1	11.40	3.8962	16
1	−1	2	11.75	3.7815	7
1	2	2	11.76	3.7793	3
2	1	1	11.93	3.7271	5
2	1	0	12.38	3.5936	58
1	0	−2	12.39	3.5893	4
1	1	−2	12.62	3.5264	8
2	0	1	12.67	3.5122	7
0	2	2	12.84	3.4671	2
2	2	1	13.00	3.4235	8
2	0	0	13.04	3.4135	53
1	−2	0	13.05	3.4124	9
2	1	2	13.14	3.3883	12
0	2	−2	13.26	3.3572	26
1	−2	1	13.36	3.3329	2
1	0	3	13.47	3.3071	58
0	0	3	13.55	3.2873	53
1	3	0	13.58	3.2803	4
1	3	1	13.63	3.2683	100
2	0	2	13.87	3.2129	15
1	−1	−2	13.90	3.2068	33
2	2	2	14.08	3.1663	21
0	3	0	14.16	3.1487	19
0	1	3	14.22	3.1362	27
1	−2	−1	14.26	3.1266	48
2	1	−1	14.34	3.1092	9
1	2	−2	14.50	3.0770	19
0	1	−3	14.51	3.0744	14
0	3	1	14.74	3.0279	34
2	0	−1	14.88	2.9996	14
2	−1	1	14.98	2.9807	49
1	3	−1	14.99	2.9774	5
0	3	−1	15.02	2.9719	11
1	−1	3	15.11	2.9551	6
1	−2	2	15.12	2.9523	39
1	3	2	15.13	2.9505	4
2	−1	0	15.25	2.9283	1
2	2	−1	15.35	2.9091	25
2	3	1	15.55	2.8739	40
2	1	3	15.66	2.8539	53
2	−1	2	16.06	2.7836	3
0	2	3	16.33	2.7398	12
2	0	3	16.33	2.7395	2
1	0	−3	16.54	2.7062	11
0	3	2	16.62	2.6935	3
1	1	−3	16.75	2.6723	8
0	2	−3	16.84	2.6583	8
0	3	−2	17.13	2.6158	24
2	1	−2	17.36	2.5818	4
1	−3	0	17.46	2.5674	2
2	3	−1	17.67	2.5375	7
1	−3	1	17.74	2.5274	2
1	3	3	17.75	2.5263	4

give the indexing of the pattern obtained from the program LAZY PULVERIX (*8*) using the atomic coordinates of the refinement.

No symmetry element appears on Laue patterns and the precession photographs show no systematic absences among the reflections: the space group is hence triclinic. Intensity data were collected on a CAD4 Nonius diffractometer. The crystallographic characteristics are reported in Table II. Corrections for Lorentz and polarization effects were applied and the refinement used the program SHELX (*9*) without any absorption correction owing to the lack of faces of the crystal. Atomic scattering factors for Ba^{2+}, Cu^{2+}, and F^- ions were taken from the International Tables for X-Ray Crystallography (*10*). Anomalous dispersion corrections were applied.

Structure Determination

The heavy atoms were localized using

TABLE II

EXPERIMENTAL DATA FOR A $Ba_6Cu_{11}F_{34}$ CRYSTAL

Symmetry: triclinic ($P\bar{1}$)
Cell parameters: a = 7.490(1) Å, b = 10.031(2) Å, c = 10.271(2) Å,
α = 82.98(2)°, β = 73.88(2)°, γ = 70.42(2)°
V = 698.1 Å^3, Z = 1
Molar weight: 2168.99 g, Density: 5.15 g · cm^{-3}
Crystal dimensions: shapeless (mean length: 0.020 mm)
Linear absorption coefficient: 167 cm^{-1} (Mo-$K\alpha$)
Operating features:
Radiation: Mo (λ = 0.71069 Å) monochromator: graphite
Scan mode: ω, sweep: 0.9 + 0.4 tg(2θ)°
Scanning speed: (20.1166/NV)° · mn^{-1} with NV integer
Range measured: $2° < \theta < 35°$
$-11 \leq h \leq 11$, $-16 \leq k \leq 16$, $0 \leq l \leq 16$
Reflections measured: total 3763
independent 3604
Refined parameters in $P\bar{1}$ group: 233
Secondary extinction factor: 2.0(2) × 10^{-7}
Residual peak height: 1.8 e$^-$/Å^3

TABLE III

ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a]

Atom	X/A	Y/B	Z/C	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Ba1	0.7874(1)	0.3632(1)	0.6499(1)	137(2)	105(2)	108(2)	−30(2)	−33(2)	−37(2)	0.79
Ba2	0.3609(1)	0.0930(1)	0.7181(1)	147(2)	105(2)	148(2)	−45(2)	−54(2)	−28(2)	0.90
Ba3	0.3296(1)	0.3444(1)	0.0271(1)	169(2)	116(2)	110(2)	−34(2)	−25(2)	−65(2)	0.89
Cu1	0	0	$\frac{1}{2}$	129(6)	98(6)	110(6)	−41(5)	−19(5)	−49(5)	0.75
Cu2	0.1840(2)	0.4838(1)	0.7064(1)	108(4)	77(4)	136(5)	−10(3)	−43(3)	−33(3)	0.72
Cu3	0.2626(2)	0.2561(1)	0.3821(1)	129(4)	85(4)	106(4)	−32(3)	−29(3)	−29(4)	0.73
Cu4	0.6989(2)	0.2547(1)	0.2799(1)	119(4)	97(5)	123(5)	−41(3)	−44(3)	−30(3)	0.75
Cu5	0.8978(2)	0.2532(1)	0.9775(1)	114(4)	109(4)	101(4)	−32(3)	−38(3)	−32(4)	0.72
Cu6	0.8120(2)	0.9905(1)	0.8176(1)	123(4)	77(4)	120(4)	−31(3)	−35(3)	−32(3)	0.71
F1	0.5758(9)	0.6435(7)	0.2627(7)	152(25)	167(27)	266(31)	−10(23)	−82(22)	−44(22)	1.33
F2	0.4391(8)	0.8858(6)	0.1070(6)	159(24)	155(26)	186(26)	−56(20)	−52(20)	−38(20)	1.14
F3	0.0763(9)	0.3959(7)	0.2953(6)	152(25)	188(28)	222(28)	−33(22)	−68(21)	−29(22)	1.31
F4	0.0547(8)	0.8774(6)	0.7003(6)	160(25)	157(26)	181(27)	−48(21)	−60(21)	−4(21)	1.19
F5	0.8515(9)	0.8519(6)	0.9922(6)	161(25)	193(28)	215(28)	−19(22)	−102(22)	−34(22)	1.28
F6	0.3268(9)	0.6168(6)	0.0764(6)	184(25)	126(24)	172(26)	−20(20)	−83(20)	−38(20)	1.07
F7	0.1889(10)	0.3891(7)	0.5208(6)	241(9)	227(30)	188(27)	−131(23)	−33(23)	−75(25)	1.46
F8	0.7176(9)	0.1489(7)	0.1345(6)	228(29)	175(28)	207(28)	−79(22)	−62(23)	−60(23)	1.36
F9	0.1243(10)	0.6011(7)	0.9009(6)	308(33)	249(31)	156(27)	−118(23)	−89(24)	−67(26)	1.55
F10	0.1052(9)	0.1394(6)	0.5363(6)	201(25)	149(25)	180(26)	−32(20)	−53(20)	−105(22)	1.11
F11	0.4562(8)	0.3812(6)	0.2511(6)	139(24)	152(25)	182(26)	−28(20)	−62(20)	−31(20)	1.08
F12	0.0678(9)	0.3487(7)	0.8013(7)	181(27)	188(29)	304(34)	17(25)	18(24)	−116(24)	1.60
F13	0.0591(9)	0.8723(7)	0.1673(6)	213(27)	182(27)	173(26)	−58(21)	−59(21)	−109(22)	1.18
F14	0.3214(8)	0.1357(6)	0.2312(5)	183(25)	145(24)	123(24)	−27(18)	−33(19)	−69(20)	1.00
F15	0.2426(8)	0.8972(6)	0.3827(6)	140(24)	169(26)	200(27)	−79(21)	−36(20)	−40(21)	1.16
F16	0.4987(8)	0.1410(6)	0.4304(6)	154(24)	160(25)	168(25)	−1(20)	−64(20)	−57(20)	1.07
F17	0.7025(9)	0.3807(6)	0.4035(6)	222(26)	147(25)	162(25)	−43(20)	−47(20)	−104(21)	1.12

[a] The vibrational coefficients are relative to the expression $T = \exp(-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12}))$ with standard deviations in parentheses and U_{ij} values ×10^4.

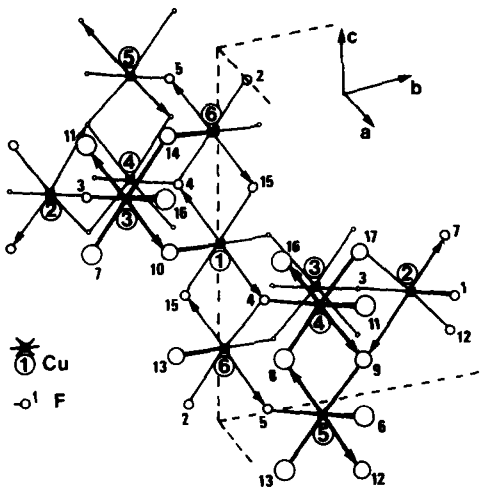

FIG. 1. "Sticks and balls" model of the basic unit in $Ba_6Cu_{11}F_{34}$. Numbers refer to the type of atom as given in Table III. Sticks with arrows indicate the two long distances of the CuF_6 octahedra.

the "$P1$" method described by Abrahams (*11*). First, the refinement of the structure was performed in the noncentric $P1$ space group. From a three-dimensional Patterson map, 4 barium positions were obtained and refined ($R = 0.35$). Then successive Fourier maps revealed 2 other barium ions and 11 copper sites leading to the $Ba_6Cu_{11}F_{34}$ formulation. At this stage, an inversion center appeared relating 3 pairs of Ba^{2+} ions and 5 pairs of Cu^{2+}, the eleventh copper atom being located on the inversion center.

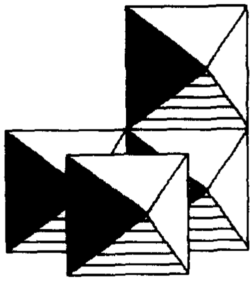

FIG. 2. Idealized perspective view of a four-membered satellite in $Ba_6Cu_{11}F_{34}$ (see text).

The corresponding atomic parameters were refined in the centrosymmetric space group with isotropic temperature factors to $R = 0.14$. The F^- ions were located from a new Fourier synthesis and the refinement easily converged to $R = 0.080$. When applying anisotropic thermal motion, the reliability factor fell to $R = 0.054$ ($R_w = 0.052$). The final refined positions and thermal parameters are listed in Table III. The list of the structure factors may be obtained on request to one of the authors (G.F.).

Discussion of the Structure

Two main features arise from the examination of the three-dimensional structure: (i) the original basic building unit; if compared to the corresponding units in $Ba_6Zn_7F_{26}$ (*6*) and $Ba_2Ni_3F_{10}$ (*7*), it forms an interesting step in the building of the rutile struc-

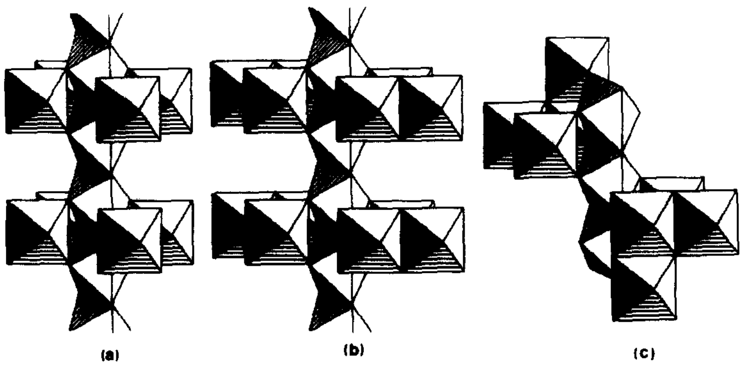
(a) (b) (c)

FIG. 3. Evolution of the shape of the satellites grafted on a rutile chain in $Ba_6Zn_7F_{26}$ (a), $Ba_2Ni_3F_{10}$ (b), and $Ba_6Cu_{11}F_{34}$ (c).

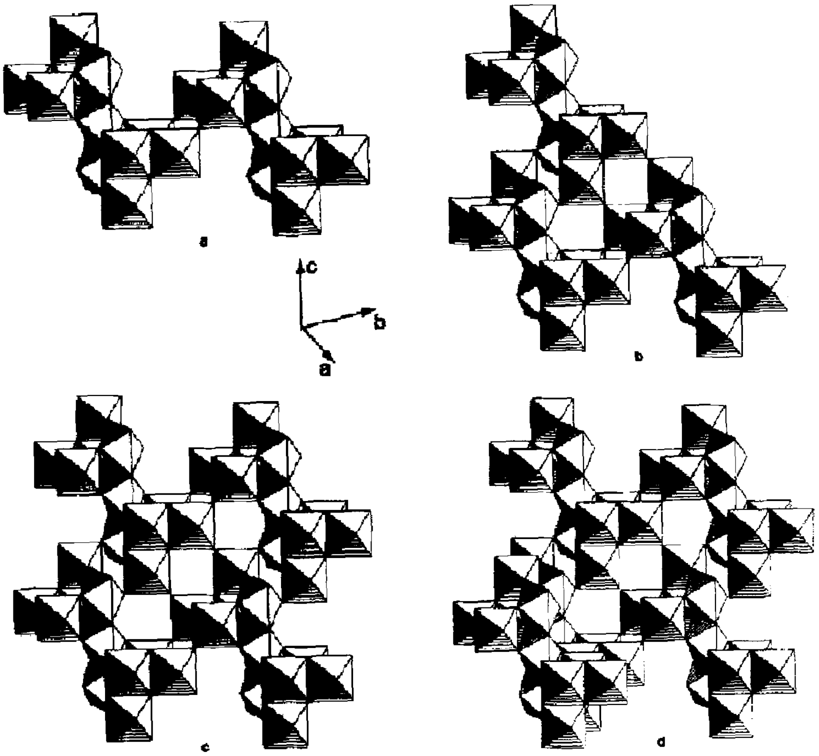

FIG. 4. Illustration of the connection of two (a), three (b), four (c), and five (d) idealized basic units to form the 3-D network.

ture. (ii) the connection of these units which leads to the appearance of new entities in the crystal chemistry of fluorides; these entities can be considered as defective NaCl blocks.

The basic unit (Fig. 1) is built up from 11 copper octahedra and is centered on (Cu1) which occupies a center of symmetry. The central part of this unit consists of a linear trimeric cluster of 3 edge-sharing octahedra

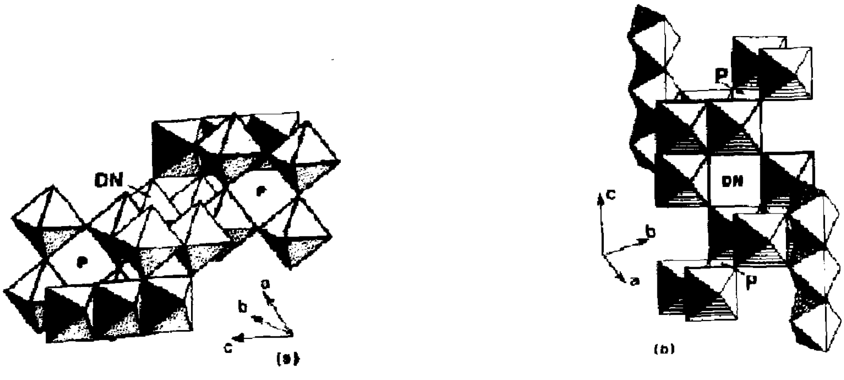

FIG. 5. Two idealized perspective views of basic units linked by (F12) ions. Beside the trimers, appear perovskite-type squares (P) in (a) and defective NaCl-type blocks (D.N.) in (b).

(Cu6–Cu1–Cu6) almost parallel to the *c* axis of the cell. As far as we know, it is the first example of such an arrangement in fluoride chemistry. However the existence of similar trimers was previously reported in the structure of $Co_3(AsO_4)_2$ (*12*). Two complex groups (hereafter called satellites) related to each other by the center of symmetry are grafted on this trimer. Every satellite is made of 4 octahedra (Cu2–Cu3–Cu4–Cu5) which lie in 2 quasi-orthogonal planes (respectively, perpendicular and parallel to the *c* axis), thus forming a "folded double L" shape (Figs. 1 and 2). In each satellite, 3 octahedra (Cu2–Cu4–Cu5) share edges around the common F9 fluorine. The fourth octahedron (Cu3) is corner-shared to (Cu2) via the F3 ion. Each satellite is connected to the central trimer by 4 corners (F4–F5–F10–F14). The structural evolution in the $Ba_6M_nF_{12+2n}$ family may be understood by considering the environment of the rutile chains (Figs. 3a–c):

—in $Ba_6Zn_7F_{26}$ ($n = 7$), single octahedra are connected to an infinite rutile chain;

—in $Ba_2Ni_3F_{10}$ ($n = 9$), 1 supplementary octahedron connects 2 satellites of the previous structure, one by edge-sharing, the other by corner-sharing, in a plane normal to the rutile chain. This gives the L shape of the satellites within the $Ba_2Ni_3F_{10}$ structure;

—in $Ba_6Cu_{11}F_{34}$ ($n = 11$), a fourth octahedron is inserted in the "L" satellite to which it is linked by an edge. However, the reason why the infinite rutile chain breaks into a trimer in this structure is not yet understood.

To build the three-dimensional network, several basic units link corners in a rather complicated way (Figs. 4a–d). However, attention must be paid to the connection of two basic units via the (F12) fluorine atoms of their satellites; beside the linear trimers two types of blocks appear (Figs. 5a and b): perovskite-type squares and complex groups of six octahedra (Fig. 5b) which can be described as defective NaCl blocks (Fig. 6). Once again, it is the first time that such an arrangement is encountered in the structures of 3*d* transition metal fluorides.

TABLE IV

INTERATOMIC DISTANCES (Å) IN COPPER OCTAHEDRA

2 × Cu1–F15:	1.910(6)		
2 × Cu1–F10:	1.935(7)	⟨Cu1–F⟩	2.058(95)
2 × Cu1–F04:	2.329(6)		
Cu2–F12:	1.882(5)	Cu3–F07:	1.910(6)
Cu2–F01:	1.910(5)	Cu3–F16:	1.920(6)
Cu2–F03:	1.922(6)	Cu3–F14:	1.943(5)
Cu2–F17:	1.926(6)	Cu3–F03:	1.945(6)
Cu2–F07:	2.218(6)	Cu3–F10:	2.169(6)
Cu2–F09:	2.302(6)	Cu3–F11:	2.283(6)
⟨Cu2–F⟩	2.027(83)	⟨Cu3–F⟩	2.028(72)
Cu4–F08:	1.884(7)	Cu5–F05:	1.911(6)
Cu4–F17:	1.909(7)	Cu5–F06:	1.925(5)
Cu4–F11:	1.914(6)	Cu5–F13:	1.954(8)
Cu4–F04:	1.925(6)	Cu5–F09:	1.973(8)
Cu4–F16:	2.317(6)	Cu5–F08:	2.200(6)
Cu4–F09:	2.560(8)	Cu5–F12:	2.220(6)
⟨Cu4–F⟩	2.084(130)	⟨Cu5–F⟩	2.030(64)
Cu6–F02:	1.881(6)	Cu1–Cu6:	3.178(5)
Cu6–F04:	1.944(6)	Cu2–Cu4:	3.061(6)
Cu6–F13:	1.969(9)	Cu4–Cu5:	3.049(6)
Cu6–F14:	2.033(8)	Cu2–Cu3:	3.753(8)
Cu6–F05:	2.155(5)		
Cu6–F15:	2.294(6)		
⟨Cu6–F⟩	2.046(68)	Mean ⟨Cu–F⟩	2.045

As indicated in Table IV and Fig. 1, every copper octahedron presents four short and two long distances: this elongation is due to the Jahn–Teller effect. The mean Cu–F distance (2.045 Å) is close to the sum of ionic radii (*13*) but in the Cu4 octa-

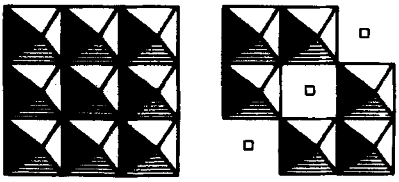

FIG. 6. NaCl-type block (left) and defective block as encountered in $Ba_6Cu_{11}F_{34}$ (right).

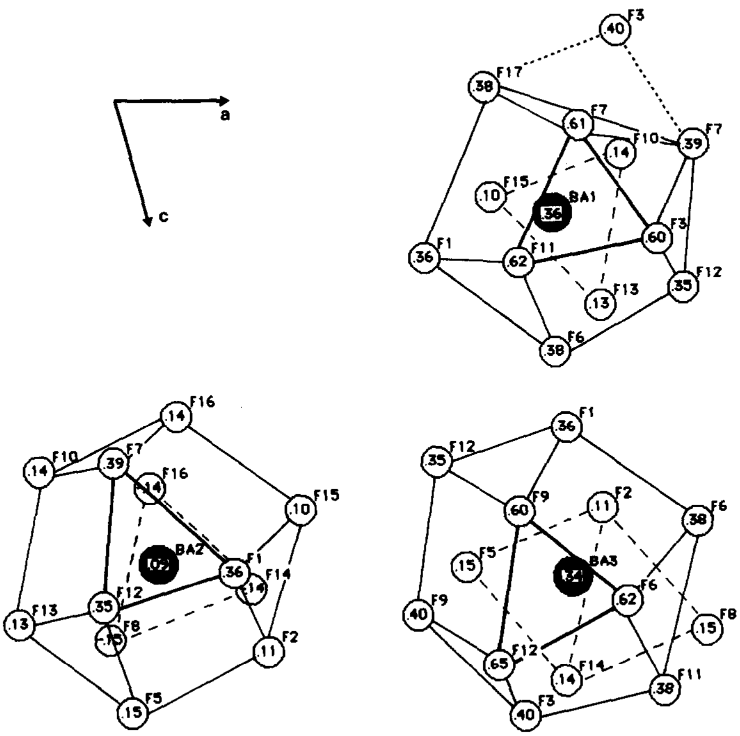

FIG. 7. (010) projections of barium polyhedra. The y coordinate is inside the circle. The number beside the circle indicates the type of atom corresponding to Table III.

TABLE V

INTERATOMIC DISTANCES (Å) IN BARIUM POLYHEDRA

Ba1 polyhedron		
Ba1–F01: 2.639	Ba1–F07: 2.887	
Ba1–F06: 2.713	Ba1–F12: 2.899	
Ba1–F11: 2.722	Ba1–F13: 2.953	
Ba1–F17: 2.748	Ba1–F07: 3.016	⟨Ba1–F⟩ 2.834(67)
Ba1–F10: 2.754	Ba1–F03: 3.083	
Ba1–F15: 2.763	(Ba1–F03: 3.720)	
Ba2 polyhedron		
Ba2–F16: 2.697	Ba2–F16: 2.885	
Ba2–F02: 2.705	Ba2–F15: 2.892	
Ba2–F12: 2.801	Ba2–F10: 2.923	
Ba2–F14: 2.817	Ba2–F13: 2.952	⟨Ba2–F⟩ 2.903(99)
Ba2–F08: 2.844	Ba2–F05: 2.979	
Ba2–F01: 2.875	Ba2–F07: 3.464	
Ba3 polyhedron		
Ba3–F06: 2.637	Ba3–F01: 2.859	
Ba3–F02: 2.646	Ba3–F03: 2.871	
Ba3–F14: 2.779	Ba3–F09: 2.883	
Ba3–F05: 2.791	Ba3–F09: 3.140	⟨Ba3–F⟩ 2.915(117)
Ba3–F11: 2.825	Ba3–F08: 3.307	
Ba3–F06: 2.831	Ba3–F12: 3.416	
	(Ba3–F12: 3.708)	

Note. All estimated standard deviations less than 0.007 Å.

hedron, the Cu4–F9 distance is very long: 2.56 Å. However, a calculation of bond valence distributions indicates that the valence sum rule (*14*, *15*) is well obeyed by all ions in the structure.

The Ba2 cations adopt a 12-fold coordination with an hcp type environment. Ba1 is (11 + 1)-fold coordinated (the distance Ba1–F3 is considerably larger than the average bond length). Its polyhedron derives from a fcc close-packed environment, like the Ba3 one which is more distorted since its coordination number is 12 + 1 (Fig. 7). The close-packed layers are stacked along the b axis. The mean Ba–F distances (Table V) correspond to the sum of the ionic radii (*13*) and the packing fraction is 0.583 (0.611 when Cu^{2+} ions are included). The structural study of phases with higher values of r = M/Ba is presently in progress.

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References

1. M. Samouël, A. de Kozak, J. Renaudin, M. Leblanc, and G. Ferey, *Rev. Chim. Min.* **22,** 64 (1985).
2. J. Renaudin, Y. Calage, M. Samouël, A. de Kozak, M. Leblanc, and G. Ferey, *Rev. Chim. Min.* **22,** 74 (1985).
3. J. Renaudin, Y. Laligant, M. Samouël, A. de Kozak, and G. Ferey, *J. Solid State Chem.* **62,** 158 (1986).
4. M. Samouël, *Rev. Chim. Min.* **8,** 533 (1971) and references therein.
5. H. G. von Schnering, *Z. Anorg. Allgem. Chem.* **353,** 1 (1967).
6. J. Renaudin, M. Samouël, M. Leblanc, A. de Kozak, and G. Ferey, *J. Solid State Chem.* **59,** 103 (1985).
7. M. Leblanc, G. Ferey, and R. de Pape, *J. Solid State Chem.* **33,** 317 (1980).
8. K. Yvon, W. Jeitschko, and E. Parthe, *J. Appl. Crystallogr.* **10,** 73 (1977).
9. G. M. Sheldrick, "SHELX: A Program for Crystal Structure Determination," Cambridge (1976).
10. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974).
11. S. C. Abrahams, *J. Chem. Phys.* **46**(6), 2052 (1967).
12. N. Krishnamachari and C. Calvo, *Canad. J. Chem.* **48,** 881 (1970).
13. R. D. Shannon, *Acta Crystallogr. A* **32,** 751 (1976).
14. I. D. Brown and R. D. Shannon, *Acta Crystallogr. A* **29,** 266 (1973).
15. I. D. Brown, *Chem. Soc. Rev.* **7,** 353 (1978).