



Article The Crystal Structure of Bornite Cu₅FeS₄: Ordered Fe and Split Cu

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Abstract: The crystal structure of bornite with ideal formula Cu_5FeS_4 from the Saishitang skarn copper deposit in Qinghai Province, along with bornite from the Yushui spouting hydrothermal copper deposit in Guangdong Province and the Bofang sandstone copper deposit in Hunan Province, has been refined by single-crystal X-ray diffraction with R1 = 0.0259-0.0483 (I > 2σ) and 0.0338-0.1067for 2732 to 3273 unique reflections. As represented by the Saishitang sample, it is orthorhombic with a Pbca space group and unit cell parameters a = 10.97016(18) Å, b = 21.8803(4) Å, c = 10.9637(2) Å, V = 2631.61(8) Å3 and Z = 16. The structure is composed of sulfur layers parallel to the (0 1 0) lattice plane with interstices occupied by metal atoms. The Fe atoms occupy two tetrahedral sites with full occupancy, but the Cu atoms are all partially distributed over 20 paired sites, split from 10 sites with a distance ranging from 0.24 Å to 0.54 Å. The Fe-S tetrahedra are not split with Fe-S lengths from 2.2609 Å to 2.3286 Å (average 2.2997 Å). The Cu-S lengths in pyramidal triangles are from 2.218 Å to 2.397 Å (average 2.288 Å), whereas the Cu-S tetrahedra are strongly distorted, with great variations in Cu-S lengths from 2.224 Å to 2.604 Å (average 2.391 Å). The orthorhombic unit cell is stacked from 16 1a-type (5.5 Å) cubes; each cube has one tetrahedrally-coordinated Fe atom, five split from 3- to 4-coordinated Cu atoms, and two vacancies, i.e., 5Cu_{III-IV}+Fe_{IV}+2[]+4S. The phenomenon of site-splitting of Cu atoms may provide for a more accurate structure of bornite, allowing for a better understanding of its magnetic properties and ore-formation conditions.

Keywords: crystal structure; site splitting; order-disorder; bornite; sulfide

1. Introduction

Study of the crystal structure of bornite (Cu₅FeS₄) first began in the 1950s and three types of structure have been reported for different stability temperatures, including the cubic *Fm*-3*m* 1a-type (a = 5.50 Å) for the high-temperature form found above 228 °C [1,2], the cubic *Fm*-3*m* 2a-type for the intermediate form of 170–235 $^{\circ}$ C [3–5] and the orthorhombic Pbca 2a-4a-2a-type for the low-temperature form below 200 °C [6,7]. In addition, the cubic *Fm*-3*m* 4a-type [8] and the rhombohedral R3m type [2] were also proposed for the intermediate form. In the early reported structure [7], the metal atoms are mixed over tetrahedral or triangular sites, which seems to disagree with the highly stoichiometric composition of bornite (Cu₅FeS₄) and the common knowledge that isomorphic substitution between Cu and Fe is quite limited in nature. Martinelli et al. first identified tetrahedral sites that were fully occupied by Fe in *Pbca* bornite at 275° K and observed a structural transition from *Pbca* to *Pca*₂₁ at 65° K using synchrotron powder X-ray diffraction data [9]. However, a study of single crystal X-ray diffraction is still needed to clarify the locations of Fe and Cu atoms in the structure to satisfy the stoichiometric Cu_5FeS_4 in natural bornite. Inspired by this, we collected bornite samples from different localities representative of the skarn, spouting hydrothermal and sandstone copper deposits in China, and carried out structural determination experiments using single-crystal X-ray diffraction.



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2. Samples and Experimental Methods

The bornite samples were collected from the Saishitang skarn copper deposit in Qinghai Province, the Yushui spouting hydrothermal porphyry copper deposit in Guangdong Province and the Bofang sandstone copper deposit in Hunan Province. The polished sections of the samples were observed using a Leica DM2500p microscope manufactured by Shimadzu company of Japan (Figure 1). In Saishitang, bornite is associated with stannoidite, chalcopyrite and cobaltite in a matrix of andradite. In Yushui, betekhtinite, chacocite and stromeyerite are disseminated in massive bornite. In Bofang, bornite, along with tetrahedrite, is disseminated in a matrix of chalcopyrite. The compositions were analyzed with a Shimadzu-1720 electron probe microanalyzer (EPMA) at accelerating voltage 15 kV, beam current 10 nA and beam size 1 μ m. Pure materials of Cu, Ag and FeS₂ were used as standards for the quantification of Cu (K α), Ag (L α), Fe (K α) and S (K α) using ZAF correction. Five points were analyzed for each of the three samples and the average weight percent and empirical formula are shown in Table 1, which indicates a stoichiometric formula Cu₅FeS₄.



Figure 1. Photomicrographs showing occurrences and mineral associations of bornite. (**a**) Agglomerate of bornite, chalcopyrite, cobaltite and stannoidite filling intergranular space of andradite (Sample no. KD56a04) from the Saishitang skarn copper deposit. (**b**) Massive bornite with disseminated betekhtinite, chalcocite and stromeyerite (Sample no. Yus04) from the Yushui spouting hydrothermal copper deposit. (**c**) Euhedral bornite grains in colloidal chalcopyrite and tetrahedrite (Sample no. TGT1202b) from Tonggutang of the Bofang sandstone copper deposit.

Deposits		Element wt%					<i>apfu.</i> (Total Atoms = 10)			
		S	Fe	Cu	Ag	Total	S	Fe	Cu	Ag
Saishitang	average	25.38	11.64	61.48	0.59	99.09	4.01	1.06	4.90	0.03
(N = 5)	stdev	0.54	0.10	0.43	0.41	0.39	0.06	0.01	0.06	0.02
Yushui	average	25.21	11.17	62.46	0.34	99.47	3.98	1.04	4.97	0.02
(N = 5)	stdev	0.32	0.25	0.62	0.08	0.39	0.03	0.01	0.07	0.01
Bofang	average	25.82	11.91	62.59	0.03	100.34	4.02	1.06	4.92	0.00
(N = 5)	stdev	0.22	0.26	0.44	0.02	0.53	0.03	0.02	0.03	0.00

Table 1. EPMA analyses of bornite. Calculated composition ratio for each element is based on the Cu_5FeS_4 formula.

The single-crystal diffraction data were collected using a Rigaku XtaLAB Synergy-DW diffractometer with microfocus sealed Mo and Cu anode tubes at 50 kV and 1 mA. According to the crystal size and X-ray tube intensity, the exposure time per frame was 20, 10 and 80 s, respectively, for the samples from Saishitang, Yushui and Bofang. The experimental data were treated with CrysAlisPro and all reflections were indexed on the basis of an orthorhombic (pseudotetragonal) unit cell (Table 2). The intensity data were corrected for X-ray absorption using the Rigaku program ABSPACK. The systematic absence of reflections is suggestive of the space group *Pbca*. The crystal structure was

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then solved for the space group *Pbca* with SHELXT [10] and refined with SHELXL [11], both included in the freeware Olex2 [12]. The structure model and site labels of Koto and Morimoto were adopted, in which the split M sites are distinguished by *a* and *b* (Table 2) [7]. The positions of atoms and anisotropic displacement parameters were refined with full occupancies for S and Fe, and free occupancies for Cu at split sites (Table 3). The structures were illustrated with the freeware VESTA [13].

 Table 2. Summary of crystal data and refinement results for bornite.

Crystal Data			
Sample source	Saishitang	Yushui	Bofang
Empirical formula	Cu ₅ FeS ₄	Cu ₅ FeS ₄	Cu ₅ FeS ₄
Formula weight	501.79	501.71	501.99
Crystal size/mm ³	$0.09\times0.08\times0.07$	$0.04\times0.035\times0.03$	$0.03\times0.02\times0.01$
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	Pbca	Pbca	Pbca
Temperature °K	293	293	293
a Å	10.97016(18)	10.95863(16)	10.9639(7)
b Å	21.8803(4)	21.8673(4)	21.8774(12)
c Å	10.9637(2)	10.9569(2)	10.9593(6)
V Å ³	2631.61(8)	2625.67(8)	2628.7(3)
Z	16	16	16
$\rho_{calc} g/cm^3$	5.066	5.077	5.074
μ/mm^{-1}	19.163	45.839	19.194
Data collection			
Instrument	Rigaku Synergy	Rigaku Synergy	Rigaku Synergy
Radiation (λ Å)	Μο Κα (0.71073)	Cu Kα (1.54184)	Μο Κα (0.71073)
2θ range $^{\circ}$	5.26 to 56.53	8.086 to 154.668	5.262 to 56.552
Absorption correction	ABSPACK	ABSPACK	ABSPACK
Reflections collected	67,413	11,787	19,144
Independent reflections	3273	2732	3272
Reflections with $I > 2\sigma(I)$	2645	2258	1768
Rint	0.0345	0.0203	0.0564
Rsigma	0.0135	0.0271	0.0426
Indices range of <i>h</i>	$-14 \le h \le 14$	$-7 \le h \le 13$	$-14 \le h \le 14$
Indices range of <i>k</i>	$-29 \le k \le 29$	$-27 \le k \le 27$	$-28 \le k \le 29$
Indices range of <i>l</i>	$-14 \le l \le 14$	$-13 \le l \le 13$	$-11 \le l \le 14$
Refinement			
No. of parameters, restraints	283, 0	283, 0	282, 0
R1, wR2 $[I > 2\sigma(I)]$	0.0259, 0.0748	0.0299, 0.0749	0.0483, 0.1060
R1, wR2 (all data)	0.0338, 0.0792	0.0396, 0.0796	0.1067, 0.1284
Goodness-of-fit	1.023	1.041	1.013
Δρmax, Δρmin (e^{-} Å ⁻³)	1.15, -0.71	0.54, -0.60	2.02, -0.73

Site	Atom/Occup.	x	y	z	U_{eq}	U^{11}	U^{22}	U ³³	U ²³	U^{13}	U^{12}
S1	S _{1.00}	0.00400(6)	-0.00082(2)	0.25260(5)	0.0153(2)	0.0153(3)	0.0152(3)	0.0156(3)	-0.0018(2)	0.0007(2)	0.0008(2)
S2	S _{1.00}	0.00255(5)	0.25026(2)	0.25351(6)	0.0157(2)	0.0160(3)	0.0161(3)	0.0150(3)	0.0012(2)	-0.0015(2)	0.0019(2)
S3	S _{1.00}	0.24441(5)	0.12678(3)	0.25587(6)	0.0149(2)	0.0155(3)	0.0155(3)	0.0138(3)	-0.0006(2)	0.0011(2)	0.0019(2)
S4	S _{1.00}	0.25185(5)	0.00161(3)	0.50844(5)	0.0152(2)	0.0154(3)	0.0145(3)	0.0156(3)	-0.0014(2)	-0.0002(2)	-0.0016(2)
S5	S _{1.00}	0.00092(6)	0.12814(3)	0.49451(6)	0.0155(2)	0.0144(3)	0.0165(3)	0.0157(3)	0.0008(2)	0.0020(2)	-0.0015(2)
S6	S _{1.00}	-0.00676(6)	0.12238(3)	-0.00617(6)	0.0152(2)	0.0144(3)	0.0155(3)	0.0156(3)	-0.0022(2)	-0.0014(2)	-0.0010(2)
S7	S _{1.00}	0.25509(5)	0.12286(3)	0.74808(6)	0.0158(2)	0.0160(4)	0.0163(3)	0.0150(3)	-0.0018(2)	0.0024(2)	-0.0001(2)
S8	S _{1.00}	0.24376(5)	0.24817(3)	0.49624(5)	0.0151(2)	0.0156(3)	0.0143(3)	0.0154(3)	-0.0017(2)	-0.0003(2)	-0.0013(2)
M1a	Cu _{0.665(36)}	0.12769(51)	0.05825(18)	0.37157(36)	0.0258(5)	0.0293(12)	0.0216(7)	0.0265(6)	-0.0034(8)	-0.0032(7)	-0.0037(6)
M1b	Cu _{0.335(36)}	0.14591(164)	0.05270(60)	0.36457(95)	0.0337(14)	0.0280(29)	0.0402(26)	0.0330(21)	0.0188(18)	-0.0127(16)	-0.0129(19)
M2a	Cu _{0.555(25)}	0.10702(27)	0.06453(17)	0.62799(37)	0.0315(5)	0.0278(8)	0.0346(7)	0.0320(8)	0.0063(6)	-0.0044(10)	-0.0121(11)
M2b	Cu _{0.445(25)}	0.09920(56)	0.05726(37)	0.61058(90)	0.0441(9)	0.0474(18)	0.0426(15)	0.0424(18)	0.0217(12)	0.0258(12)	0.0256(12)
МЗа	Cu _{0.441(27)}	0.39174(39)	0.06319(30)	0.36114(74)	0.0364(9)	0.0355(14)	0.0404(12)	0.0333(16)	-0.0142(10)	-0.0108(13)	0.0212(15)
M3b	Cu _{0.559(27)}	0.39210(31)	0.05648(23)	0.37724(50)	0.0336(6)	0.0340(11)	0.0418(10)	0.0251(9)	-0.0126(7)	0.0126(10)	-0.0147(12)
M4	Fe _{1.00}	0.37625(3)	0.06010(2)	0.63211(3)	0.0129(1)	0.0129(2)	0.0127(2)	0.0131(2)	0.0006(1)	0.0001(1)	0.0000(1)
M5	Fe _{1.00}	0.11933(3)	0.18967(2)	0.37289(3)	0.0131(1)	0.0132(2)	0.0131(2)	0.0132(2)	0.0001(1)	-0.0002(1)	0.0004(1)
M6a	Cu _{0.433(24)}	0.13093(47)	0.19273(36)	0.64528(38)	0.0391(8)	0.0459(12)	0.0291(14)	0.0421(15)	0.0122(11)	0.0295(15)	0.0116(9)
M6b	Cu _{0.567(24)}	0.12080(31)	0.18330(24)	0.64253(23)	0.0334(6)	0.0361(7)	0.0336(11)	0.0304(8)	-0.0116(9)	-0.0116(11)	0.0106(6)
M7a	Cu _{0.435(25)}	0.38411(47)	0.18556(29)	0.35932(36)	0.0330(8)	0.0373(12)	0.0323(13)	0.0295(12)	0.0149(14)	-0.0123(14)	-0.0110(8)
М7b	Cu _{0.565(25)}	0.37318(43)	0.19490(33)	0.35581(35)	0.0367(6)	0.0297(8)	0.0396(14)	0.0407(13)	-0.0153(9)	0.0193(10)	-0.0170(8)
M8a	Cu _{0.669(22)}	0.37928(29)	0.19057(22)	0.61967(30)	0.0239(4)	0.0256(5)	0.0156(11)	0.0304(6)	-0.0027(5)	-0.0003(6)	-0.0004(5)
M8b	Cu _{0.331(22)}	0.38490(69)	0.20084(59)	0.61229(74)	0.0335(15)	0.0382(18)	0.0195(28)	0.0427(19)	-0.0080(15)	-0.0235(17)	0.0048(13)
M9a	Cu _{0,305(30)}	0.13393(59)	0.06582(29)	0.87871(62)	0.0273(8)	0.0224(12)	0.0297(12)	0.0298(13)	-0.0019(17)	0.0011(11)	-0.0049(16)
M9b	Cu _{0.695(30)}	0.15070(68)	0.07260(30)	0.89771(75)	0.0434(9)	0.0386(13)	0.0456(12)	0.0459(15)	0.0266(10)	0.0220(11)	0.0219(9)
M10a	Cu _{0.243(18)}	0.36553(68)	0.06889(33)	0.11586(59)	0.0301(10)	0.0298(17)	0.0273(16)	0.0333(14)	-0.0015(14)	0.0013(15)	-0.0072(13)
M10b	Cu _{0.757(18)}	0.33485(52)	0.08299(24)	0.09033(45)	0.0461(10)	0.0511(13)	0.0447(12)	0.0425(11)	-0.0241(9)	0.0268(10)	-0.0271(11)
M11a	Cu _{0.363(27)}	0.13149(42)	0.18117(21)	0.11239(41)	0.0275(8)	0.0325(10)	0.0297(11)	0.0205(13)	0.0023(11)	-0.0032(10)	-0.0015(14)
M11b	Cu _{0.637(27)}	0.14964(75)	0.17138(41)	0.09043(87)	0.0520(12)	0.0499(15)	0.0548(16)	0.0514(18)	0.0321(14)	-0.0312(13)	-0.0344(12)
M12a	Cu _{0.221(26)}	0.36837(74)	0.18403(35)	0.88087(76)	0.0287(10)	0.0268(17)	0.0307(15)	0.0287(17)	-0.0003(16)	0.0010(17)	-0.0014(18)
M12b	Cu _{0.779(26)}	0.34422(66)	0.17387(29)	0.90399(63)	0.0442(11)	0.0457(14)	0.0427(12)	0.0442(13)	-0.0230(10)	-0.0243(12)	0.0238(11)

Table 3. Fractional atomic coordinates and displacement parameters (Å²) of atoms in bornite from Saishitang.

3. Results and Discussion

The samples of bornite from the three localities all show the same structure, although the refinement R1 varies from 0.0259 in the Saishitang samples to 0.0483 in those from Bofang (for reflections with $I > 2\sigma(I)$) due to different crystal qualities (Table 2). The structure is comparable to those of Koto and Morimoto and Martinelli et al., but differs from the former due to the separate occupation of Fe and Cu, and differs from the latter in terms of the site-splitting of Cu atoms [7,9]. The coordinates and displacement parameters of atoms in bornite, represented by those of the Saishitang samples (.cif files of the other two localities are contained within the supplementary materials and are available as needed) are listed in Table 3, with selected bond distances and angles shown in Table 4. The results reveal that the two tetrahedral sites (M4 and M5) are uniquely occupied by Fe atoms without splitting. Cu atoms, however, are partially distributed over 20 paired sites, which are split from 10 M sites. The site-splitting is indispensable as it rapidly improves R1 from 0.0764, and the residual peaks from $3.79/-3.80 \text{ e}^{-\text{Å}-3}$ before splitting to 0.0259 and $1.15/-0.71 e^{-} A^{-3}$ after splitting. To confirm the lack of Fe-Cu mixed occupation, a refinement of free occupancy for all cation sites was also tried and the results indicated that the occupancies of Fe at M4 and M5 range from 0.998 to 1.006, and that the sum occupancies of Cu at split M sites vary between 0.975 and 0.997 for all three samples, in almost perfect agreement with stoichiometric Cu₅FeS₄ with negligible Fe-Cu mixing.

Table 4. Selected bond lengths and angles of bornite.

Fe-S tetrahedron										
M4(Fe)-	Distance		Angle		M5(Fe)-	Distance		Angle		
S1	2.2701(7)				S2	2.2609(6)				
S7	2.2954(7)	110.77(3)			S5	2.2975(7)	111.05(3)			
S4	2.3105(7)	111.52(3)	108.32(3)		S8	2.3087(7)	110.43(3)	108.61(3)		
S6	2.3261(7)	111.16(3)	107.33(2)	107.58(3)	S3	2.3286(7)	111.19(3)	107.85(3)	107.58(2)	
Average	2.3005		109.45		Average	2.2989		109.45		
Cu-S pyramidal triangles (including M1b 2b 7b 8b 9b 10b 11b 12b)										
M1b-	Distance		Angle		M10b-	Distance		Angle		
S4	2.2557(117)				S4	2.2665(15)				
S3	2.2837(91)	118.22(64)			S5	2.2716(16)	121.98(6)			
S1	2.3025(89)	117.98(45)	113.74(34)		S3	2.2796(16)	118.42(7)	119.49(6)		
Average	2.2806		116.65		Average	2.2726		119.96		
Cu-S distorted tetrahedra (including M1a 2a 3a 3b 6a 6b 7b 8a 9a 10a 11a 12a)										
M1a-	Distance		Angle		M10a-	Distance		Angle		
S1	2.2831(41)				S5	2.3133(47)				
S3	2.3445(46)	112.18(17)			S4	2.3291(49)	117.49(24)			
S4	2.3755(49)	113.98(17)	111.24(22)		S3	2.3929(57)	113.29(26)	111.59(26)		
S5	2.4677(47)	109.14(22)	101.95(15)	107.54(15)	S1	2.5911(105)	104.16(30)	102.46(28)	106.27(26)	
Average	2.3677		109.34		Average	2.4066		109.21		

The crystal structure of bornite is composed of layers of S atoms parallel to (010) with interstices filled by metal atoms (Figure 2), as described for cubic 1a-, 2a-type bornite and orthorhombic 2a4a2a-type bornite [1,2,4,7]. The interlayer distance of the S-layer in bornite is 2.735 Å and the 12 closest S-S lengths range from 3.734 Å to 3.989 Å (average 3.841 Å). This is similar to the S-S lengths of 3.878-3.889 Å reported for the cubic 1a-type, 2a-type bornite and the orthorhombic bornite, but bigger than the layer interval (2.603 Å) and the S-S length (3.719 Å) in chalcopyrite [5].

The Fe atoms independently occupy the two tetrahedral sites with full occupancy, but the Cu atoms are partially distributed over 20 paired sites with occupancies from 0.22 to 0.78 split from 10 fully occupied sites (Table 3, Figure 2). The Fe-S tetrahedra are slightly distorted, as indicated by the small variations (2.2609 Å to 2.3286 Å, average 2.2997 Å) of Fe-S lengths and angles (109.5° for ideal tetrahedron) (Table 4). Cu atoms occupy 20 split sites of two types. One is 3-coordinated in pyramidal triangles including *M1b*, *M2b*, *M7b*, *M8b*, *M9b*, *M10b*, *M11b*, and *M12b*. The other is 4-coordinated in strongly distorted tetrahedra

including *M*1*a*, *M*2*a*, *M*3*a*, *M*3*b*, *M*6*a*, *M*6*b*, *M*7*b*, *M*8*a*, *M*9*a*, *M*10*a*, *M*11*a*, and *M*12*a* (Table 4). The splitting distances in the split Cu atoms vary from 0.24 Å (between *M*1*a* and *M*1*b*) to 0.54 Å (between *M*10*a* and *M*10*b*). The Cu-S lengths in pyramidal triangles range from 2.218 Å to 2.397 Å (average 2.288 Å), and Cu atoms are off the triangle plane with the Cu-S interbond angles from 104.7° to 123.3° (average 117.4°). The Cu-S lengths in distorted tetrahedra range from 2.224 Å to 2.604 Å (average 2.391 Å) and the Cu-S interbond angles vary between 97.22° and 118.59° (average 109.19°), as shown in Table 4. In comparison to the structure formed without the splitting of Cu sites, the Fe-S lengths observed in tetrahedra (*M*4 and *M*5) are from 2.2582 Å to 2.3173 Å (average 2.2924 Å). The Cu-S length in pyramidal triangles (*M*9, *M*10, *M*11, and *M*12) varies from 2.272 Å to 2.331 Å (average 2.299 Å), and the Cu-S length in distorted tetrahedra (*M*1, *M*2, *M*3, *M*6, *M*7, and *M*8) varies from 2.254 Å to 2.545 Å (average 2.383 Å). Therefore, site-splitting may increase the degree of distortion of both pyramidal triangles and tetrahedra, as shown by the greater variation in Cu-S lengths, while the Fe-S tetrahedra remain relatively unchanged.



Figure 2. The crystal structure of bornite, showing the sites and the anisotropic displacement ellipsoids in the unit cell. (a) without site splitting of Cu atoms. (b) with site splitting of Cu atoms. (c) S layers parallel to (010) showing each S atom with its 12 closest neighbors.

In the literature, the structure of orthorhombic bornite was stacked from fully filled antifluorite 1*a* cubes and half-filled sphalerite 1*a* cubes [4,14]. Following this, we numbered each position of the 8 interstices in the 1*a*-type (5.5 Å) cube from 1–8 consisting of four face-centered S atoms. The cube was labeled 1, 1' to 8, 8' according to the position of the Fe atom and the setting of the two possible vacancies for the same position of Fe in the cube (Figure 3c). As such, the 2*a*-4*a*-2*a* orthorhombic unit cell of bornite is a building block of 16 cubes of the 1*a* type each with a number 1, 1' to 8, 8' (Figure 3a–c). In each cube, five Cu atoms are located in 10 paired sites split from three tetrahedral and two pyramidal triangle sites (Figures 2 and 3). Thus, the cube chemistry may be written as $5Cu_{III-IV}+Fe_{IV}+2[]+4S$ in accordance with the stoichiometric formula Cu_5FeS_4 . Similarly, the crystal structure of chalcopyrite is a 1*a*-1*a*-2*a* stacking supercell of the cubes labelled as 2–7 and 4–5 according to the position number of Fe in the cube, which contains two Fe atoms and two Cu atoms in the tetrahedral interstices, together with four fixed vacancies (i.e., $2Cu_{IV} + 2Fe_{IV} + 4[] + 4S$), as shown in Figure 3d–f.

The bond valence sums for Fe atoms at *M*4 and *M*5 range from 2.48 to 2.49 whereas the bond valence sums for Cu atoms at various sites vary between 0.92 and 1.02. These are comparable to those of chalcopyrite (2.74 for Fe, 1.19 for Cu) and are indicative of the



valence states of Fe³⁺ and Cu⁺ as shown by similar Mössbauer data (I.S. 0.12–0.53, Q.S., 0–0.50) of bornite and chalcopyrite [15].

Figure 3. Cube stacking models for the structure of bornite (**a**–**c**) and chalcopyrite (**d**–**f**) [5]. (**a**,**d**) Fe-S and Cu-S tetrahedra and Cu-S triangles in the unit cell. (**b**,**e**) cube stacking prism with cube labels indicating the position of Fe and the vacancy. (**c**,**f**) example cubes showing the locations of Fe atoms, Cu atoms, and the vacancy in the 8 interstitial sites of F-centered S atoms.

4. Conclusions and Implications

From this single-crystal X-ray diffraction study of samples from a number of different deposits we confirmed the orthorhombic structure of bornite, the separate occupation of Fe at two tetrahedral sites, and the partial occupation of Cu over 20 paired sites split from 10 fully occupied sites with negligible Fe-Cu mixing. We also proposed a model of a building block of 16 cubes of the 1*a* type with exact indication of the position of Fe and Cu atoms in the cube as well as any vacancies in accordance with the stoichiometric formula Cu_5FeS_4 .

Bornite is an important metal sulfide in various copper deposits and has been described and studied for over 100 years [16–18]. The phenomenon of site-splitting of Cu atoms in orthorhombic *Pbca* bornite may also exist in bornite with different structure types alongside other sulfides. This may provide evidence of a more accurate structure of bornite and could lead to a better understanding of its magnetic properties and ore-formation conditions [19–21]. **Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10 .3390/cryst11121495/s1.

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