The Canadian Mineralogist
Vol. 50, pp. 423-430 (2012)
DOI : 10.3749/canmin.50.2.423

THE CRYSTAL STRUCTURE OF ROXBYITE, $Cu_{58}S_{32}$

William G. MUMME[§] and Robert W. GABLE

CSIRO Process Science and Engineering, Box 312, Clayton South, Victoria 3169, and School of Chemistry,
University of Melbourne, Parkville, Victoria, 3010, Australia

Václav PETŘÍČEK

Institute of Physics, ASCR v.v.i., Na Slovance 2, CZ–182 21 Praha, Czech Republic

Abstract

Roxbyite is triclinic, space group $P\overline{1}$, with unit-cell dimensions *a* 13.4051(9), *b* 13.4090(8), *c* 15.4852(3) Å, α 90.022(2), β 90.021(2), γ 90.020(3)°. The crystal structure was solved using 12190 independent intensity data with $I > 4\sigma(I)$, out of some 43652 unique reflections measured with a single-crystal diffractometer. There are 58 different Cu atoms and 32 different S atoms in the structure. Refinement using isotropic temperature-factors yielded $R_w = 0.079$. The number of parameters refined was 372. Because the crystal used is twelve-fold rotationally twinned about **a**, 12 twin-volume parameters were invoked. The structure was determined after transformation of an initial model obtained for a unit cell four times larger, also with space group *P*, with *a* 30.9625, *b* 30.9727, *c* 13.4051 Å, α 90.007, β 89.972, γ 119.994° and with a composition $Cu_{228}S_{128}$. This larger cell, which was determined by the instrumental software during data collection, actually results from complicated multiple twinning of the true cell defined above. The structure of roxbyite is based on a hexagonal-close-packed framework of sulfur atoms with the copper atoms occupying these layers, all having triangular coordination. Other layers sandwiched between the close-packed sulfur layers consist purely of double, or split, layers of Cu atoms. Some of these Cu atoms have two-fold linear coordination, but mostly they have three- and four-fold coordination to the sulfur atoms in the close-packed layers that lie above and below them. The crystal structure of roxbyite bears a strong kinship to those of low chalcocite and djurleite.

Keywords: roxbyite, crystal structure, multiple twins, low chalcocite, djurleite.

Introduction

Roxbyite, $Cu_{1.74–1.82}S$, was reported as a new copper sulfide mineral occurring in the Olympic Dam deposit at Roxby Downs, South Australia, by Mumme *et al.* (1988). A presumed close structural relationship with high and low chalcocite (Evans 1971, 1979b) and djurleite $Cu_{1.96}$ S (Evans 1979a, 1979b) was also discussed. The single-crystal Weissenberg X-ray films of roxbyite at first indicated an orthorhombic symmetry with a strong superimposed hexagonal pseudosymmetry, but the presence of some intensity variations between what would be equivalent reflections for an orthorhombic cell suggested that it is more probably monoclinic (*C*2/*m*, *Cm* or *C*2), with an orthogonal cell having as parameters **a** 53.79, **b** 30.90, **c** 13.36 Å, β 90°. A further reason for initially choosing this cell is that it is related metrically to the unit cell of djurleite. Djurleite had previously been found by Evans to be monoclinic $P2_1/c$, with a nearly orthogonal cell, **a** 26.897, **b** 15.745, **c** 13.565 Å, β 90.13°.

We have determined the crystal structure of roxbyite, and report here the results of our investigation of the type-locality material.

Experimental Details

The crystal of roxbyite used to collect Weissenberg film data in 1988 was now used for (two) data collections using single-crystal diffractometers situated in the School of Chemistry, University of Melbourne. The first was made using the Oxford Diffraction XcaliburS difractometer. A total 93189 reflections were collected, with 12424 unique and a Rmerge value of 0.24 for the presumed monoclinic symmetry. Attempts were made to solve the structure in *C*2/*m*, with close-packed layers of sulfur atoms containing triangularly coordinated Cu atoms alternating with split Cu-only layers, as in the

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[§] *E-mail address*: william.mumme@csiro.au structure of djurleite. As discussed, the close-packing was originally assumed to be normal to **a** ≈ 53 Å. As this approach proved to be unsatisfactory, closer attention was given to Patterson function calculations, which indicated that the layering is more probably normal to the **c** ≈ 13 Å axis.

A partial structure still based on that of djurleite was determined, but with only four layers of close-packed sulfur, with Cu in triangular coordination interleaved with four intermediate double (or puckered) layers of Cu in more distorted three- and four-fold coordinations. However, the limited number of reflection data with respect to number of atoms (with only 1322 reflections having I > 4σI) caused the refinement to stall, even though the Fourier maps calculated by JANA (Petříček *et al.* 2006) were well defined, and suggested that the modeling was progressing in the right direction.

At this stage, a second set of data (Table 1) was collected using the newly acquired Oxford Diffraction SuperNova diffractometer. Fewer data (82771 reflections) were collected, but with greatly improved counting statistics. Notably, for this cycle of data collection, the pseudohexagonal cell **a** 30.9625, **b** 30.9727, **c** 13.4051 Å, α 90.007, β 89.972, γ119.994° (**a** = **b** 30.97, **c** = 13.41 Å, α = β 90°, γ 120°) was chosen by the instrumental software (CRYSALISPRO 2010) as the preferred cell rather than a monoclinic or orthorhombic cell. However, for hexagonal lattice type *P*, the R_{int} was very high (0.221), whereas the data analysis showed that, of all the possible lattice-types raised, including hexagonal and *C*-centered monoclinic, the R_{int} = 0.076 for triclinic symmetry was lowest. With still some doubt about the true symmetry, we decided to continue the refinement with this triclinic cell, hopefully solve the structure in $P\overline{1}$, and later test for possible higher symmetry.

TABLE 1. ROXBYITE: DATA COLLECTION AND REFINEMENT DETAILS

Ideal formula	$Cu_{58}S_{32}$		
Crystal data			
Unit-cell parameters (triclinic cell)			
a, *b*, *c* (Å)	13.4090(8), 13.4051(9), 15.4852(3)		
α, β, γ (°)	90.022(2), 90.021(2), 90.020(3)		
Z	2	Space group	$P\overline{1}$
Calculated density	5.62 g cm^{-3}		
Data collection			
Temperature (K)	293	λ (Cu*K*α, Å)	1.5418
Crystal size (mm)	0.174 × 0.10 × 0.03		
Collection mode	omega scan, Δω = 1.0°		
Count time per frame	150 seconds		
$2\theta_{max}$ (°)	60.98		
Cell parameters used for data collection			
a, *b*, *c* (Å)	30.9625, 30.9727, 13.4051		
α, β, γ (°)	90.007, 89.972, 119.994		
No. unique reflections	43652		
No. reflections, *I* > 4σ(*I*)	12190		
Absorption correction	Gaussian (indexed crystal faces)		
μ (mm^{-1})	34.2	T_{min}	0.049
T_{max}	0.432	R_{merge} (observed)	0.076
Refinement			
No. of parameters refined	372		
Rw_{obs}, *I* > 4σ(*I*)	0.079	Rw_{obs}, all data	0.079
GOF	2.40		
Twinning	Twelve-fold rotation around *a*		
Twin-volume fractions	0.149(5), 0.0904(16), 0.0511(14), 0.0731(16), 0.1059(17), 0.0315(14), 0.1532(18), 0.0509(14), 0.0896(16), 0.0745(16), 0.0298(14), 0.1012(17)		
$\Delta\sigma_{min}$, $\Delta\sigma_{max}$ (e/Å^3)	-2.66, +3.45		

DETERMINATION OF PART TWINNING IN ROXBYITE

It was now possible to progress from the previous partial refinement in monoclinic *C*2/*m*, transposed to the new triclinic cell, by using large damping constraints, Fourier mapping and (there being eventually 356 atoms in total) least-squares refinements in selected groups of atoms. The improvements in the R value agreements were invariably incremental, although Fourier mapping continued to give quite clear images of both the sulfur–copper framework and the intermediate copper layers. With R ≈ 0.40, and with a complete close-packed network of sulfur (only) and about 75% of the possible Cu atoms identified, initially six-fold rotational twinning about **c** was introduced to mimic any possibility of hexagonal symmetry.

At the very first stage, the R agreement improved considerably. It became possible to gradually improve the value to an R of 0.076, with 12190 reflections with I > 4σI. As the six twin volumes varied considerably in magnitude, it seemed that the true symmetry of roxbyite is triclinic, and therefore we eventually refined the coordinates and isotropic temperature-factors of all the atoms together with twelve twin parameters required for $P\overline{1}$. Fourier mapping using the CONTOUR facility in JANA was critical in eventually finding all the Cu atoms.

At this stage, we had now determined a crystal structure for roxbyite based on a triclinic, but nearly equivalent hexagonal cell, $P\overline{1}$, with α 30.962, *b* 30.973, *c* 13.045 Å, α 90.007°, β 89.972°, γ 119.994°, which contained 228 Cu and 128 S independent atoms. As such, this structure was found to have the predicted relationships to the structures of low and high chalcocite and djurleite based on hexagonal close-packing of sulfur layers. However, rather than the original suggestion by Mumme *et al.* (1988) that the close-packing in roxbyite is normal to the **a** axis (53 Å), *i.e.*, approximately eight times the axis normal to close-packing in high chalcocite, **c** = 6.72 Å, four times that in low chalcocite, **c** = 13.494 Å, and twice that in djurleite, **a** = 26.879 Å, the close-packing in this model of roxbyite was actually determined to be equivalent to that found in low chalcocite, having only four close-packed layers per cell repeat along **c**.

DETERMINATION OF THE DEFINITIVE TWINNING IN ROXBYITE

A survey of the Cu–S bonds in the $Cu_{228}S_{128}$ model showed that a significant number of Cu atoms, both in 3- and 4-fold coordinations, had bonds shorter than 2.2 Å, many not much greater than 2.0 Å. Further to this, many S atoms had negative temperature-factors. These anomalies were factors leading to the further analysis of a partial Patterson map (by V.P.) based on the 12190 reflections with I > 4σI. Apart from the peak at the origin, two more peaks at (1/4,–1/4,0), and (1/2,1/2,0) were observed that have a height almost as great as the origin peak. This observation implies that the lattice can be transferred to one four times smaller by the matrix transformation, *a*' = (1/4,–1/4,0) ; *b*' = (0,1,0) ; *c*' = (0,0,1), resulting in a cell with *a* 13.409, *b* 30.973, *c* 13.405 Å, α 90.007, β 89.980, γ 150.002°. When this lattice transformation is carried out, it is found that only 142 of the weaker I > 4σI reflections are discarded from the original 12190 (~1.0%) described by the twin domains in the structure determined for $Cu_{228}S_{128}$. Furthermore, the discarded reflections are described by the $Cu_{228}S_{128}$ model with R > 30%, and are therefore basically not contributing to this model.

The four-times-smaller cell can be further reduced to a nearly orthogonal one with *a* 13.4051, *b* 13.4090, *c* 15.4842 Å, α 90.0215, β 90.0210, γ 90.0202°, by the overall transformation *a*" = *c*, *b*" = –1/4*a* + 1/4*b*, *c*" = –1/2*a*–1/2*b*. Subsequently, by transforming the $Cu_{228}S_{128}$ structure model to the above cell four times smaller, with $P\overline{1}$ symmetry, and merging all the resulting equivalent atoms, a satisfactory refinement of the structure for roxbyite of R = 0.079 is achieved with twelve twin matrices, a total of 90 atoms, and a composition $Cu_{58}S_{32}$. It may be noted that the transformations described above now result in the orientation of the true cell for which the close packed S layers are normal to the **a** axis. Figure 1 illustrates the twinning in roxbyite.

Atom coordinates and temperature factors for this structure are given in Table 2; bond lengths are given

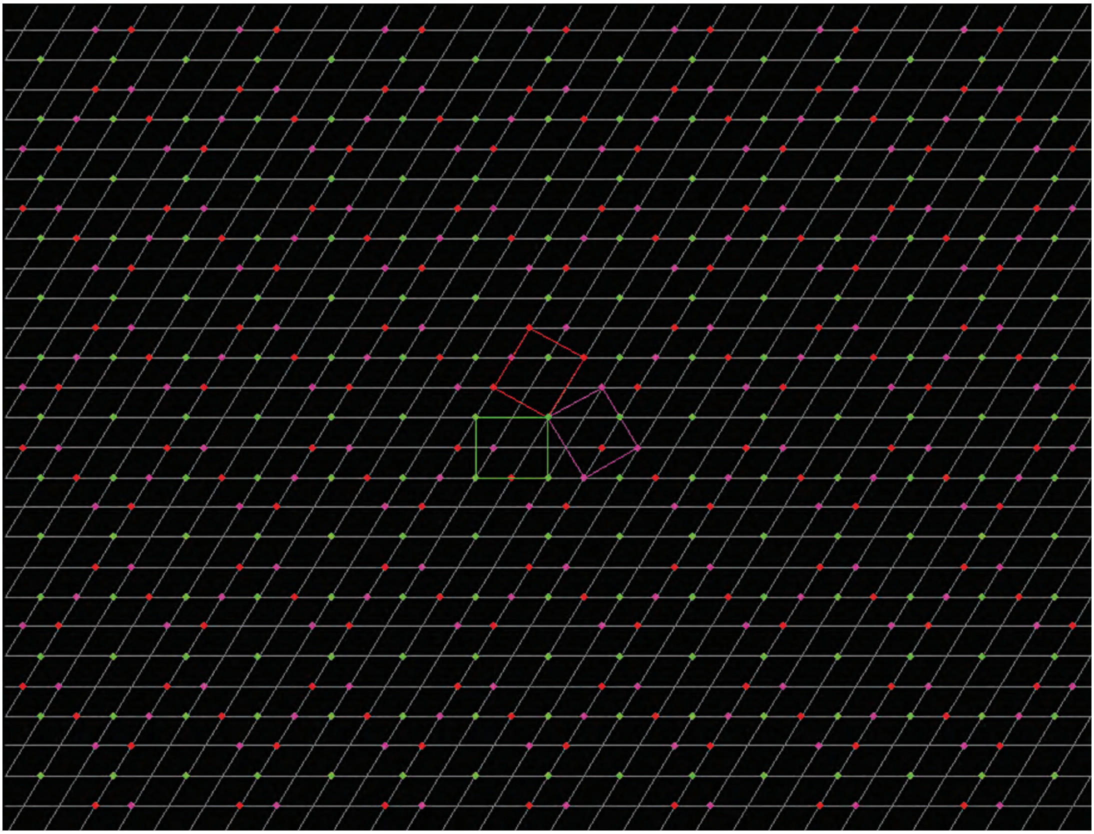

FIG. 1. Twinning in roxbyite, viewed along **a**.

TABLE 2. REFINED COORDINATES AND ISOTROPIC TEMPERATURE–FACTORS OF ATOMS IN ROXBYITE

	x	*y*	*z*	U_{iso} (Å^2)		*x*	*y*	*z*	U_{iso} (Å^2)
Cu1	0.0328(5)	0.1474(5)	0.3739(6)	0.0213(14)	Cu46	0.3856(8)	0.5043(11)	0.7513(9)	0.025(3)
Cu2	0.0225(6)	–0.4368(6)	0.8817(6)	0.0262(18)	Cu47	0.3736(6)	0.0091(8)	0.5079(7)	0.026(2)
Cu3	0.0332(7)	0.3117(8)	0.9668(6)	0.028(2)	Cu48	0.3672(6)	0.0091(7)	0.2397(5)	0.0236(17)
Cu4	0.0377(6)	–0.6735(6)	0.4932(5)	0.0274(17)	Cu49	0.4651(6)	–0.8156(7)	0.9696(5)	0.0303(19)
Cu5	0.0398(6)	0.3203(7)	0.2612(6)	0.0204(17)	Cu50	0.4706(7)	0.1860(7)	0.2827(6)	0.0288(19)
Cu6	0.0306(6)	0.3211(6)	0.7703(5)	0.0175(16)	Cu51	0.4562(6)	0.1793(7)	0.7502(7)	0.0300(19)
Cu7	0.0338(5)	0.1377(5)	0.8773(7)	0.0195(15)	Cu52	0.4679(6)	–0.8064(6)	0.4590(5)	0.0156(15)
Cu8	0.0242(6)	–0.4295(6)	0.3645(6)	0.031(2)	Cu53	0.4681(4)	–0.0872(4)	0.8646(4)	0.0108(13)
Cu9	0.0467(4)	0.1038(5)	0.1297(6)	0.0180(13)	Cu54	0.4711(5)	–0.0761(6)	0.3660(5)	0.0253(17)
Cu10	0.0394(5)	–0.8931(5)	0.6241(6)	0.0194(14)	Cu55	0.4630(6)	0.3803(5)	0.3737(7)	0.0258(17)
Cu11	0.1406(6)	–0.2565(7)	0.6229(9)	0.028(2)	Cu56	0.4510(5)	–0.6307(6)	0.6290(8)	0.0322(18)
Cu12	0.1067(8)	0.9937(10)	0.9990(11)	0.028(3)	Cu57	0.4662(6)	0.3746(6)	0.8686(9)	0.036(2)
Cu13	0.1180(6)	–0.5059(8)	0.7365(6)	0.034(2)	Cu58	0.4598(5)	–0.6304(6)	0.1217(8)	0.0320(18)
Cu14	0.1319(8)	–0.5078(10)	0.0100(8)	0.036(2)	S1	0.1217(10)	0.1669(12)	0.0075(9)	0.017(3)
Cu15	0.1444(6)	–0.2548(7)	0.1285(8)	0.025(2)	S2	0.3718(8)	0.5873(10)	0.6277(10)	0.008(3)
Cu16	0.1288(6)	–0.0048(6)	0.2509(6)	0.0195(19)	S3	0.1208(7)	0.4183(8)	0.8745(8)	0.003(2)
Cu17	0.1112(7)	0.9946(8)	0.7519(8)	0.019(2)	S4	0.3611(6)	0.1012(6)	0.1170(6)	0.0014(17)
Cu18	0.1196(7)	–0.2543(8)	0.8722(6)	0.021(2)	S5	0.1226(8)	0.9073(9)	0.8717(11)	0.010(3)
Cu19	0.1055(9)	–0.0052(10)	0.5010(10)	0.032(3)	S6	0.3871(10)	0.0783(12)	0.3744(14)	0.024(4)
Cu20	0.2153(7)	0.3053(9)	0.7139(7)	0.034(2)	S7	0.3730(9)	–0.4111(10)	0.1283(10)	0.005(3)
Cu21	0.2231(6)	–0.6203(6)	0.4746(5)	0.0258(17)	S8	0.1252(8)	–0.0932(9)	0.3729(10)	0.008(3)
Cu22	0.2139(8)	–0.1957(9)	0.4665(7)	0.039(2)	S9	0.3611(7)	0.1013(7)	0.6268(8)	0.0067(19)
Cu23	0.2114(7)	–0.4469(8)	0.1668(7)	0.029(2)	S10	0.3725(10)	–0.1622(11)	0.2518(10)	0.008(3)
Cu24	0.2190(7)	–0.8986(7)	0.3772(7)	0.046(2)	S11	0.3716(10)	0.5823(10)	0.8689(10)	0.020(4)
Cu25	0.2120(8)	–0.1930(9)	0.2839(7)	0.031(2)	S12	0.1416(9)	–0.5887(9)	0.1380(8)	0.023(3)
Cu26	0.2219(8)	0.3066(10)	0.0359(8)	0.041(3)	S13	0.1134(9)	0.1703(10)	0.7437(9)	0.010(3)
Cu27	0.2349(6)	0.3745(7)	0.2912(6)	0.0329(18)	S14	0.3983(10)	0.0801(11)	0.8731(11)	0.024(3)
Cu28	0.2176(8)	–0.4398(9)	0.3797(6)	0.036(2)	S15	0.3672(9)	–0.1627(10)	0.7594(9)	0.005(3)
Cu29	0.2090(8)	0.5529(9)	0.5797(7)	0.037(2)	S16	0.3832(10)	0.5819(10)	0.3685(10)	0.019(4)
Cu30	0.2934(7)	0.6941(9)	0.9688(7)	0.034(2)	S17	0.1384(9)	0.4126(9)	0.6098(8)	0.021(3)
Cu31	0.2853(7)	–0.5775(7)	0.8785(7)	0.045(2)	S18	0.3693(11)	0.1573(13)	0.0066(12)	0.017(3)
Cu32	0.2904(8)	–0.3062(10)	0.7823(7)	0.037(2)	S19	0.3833(10)	0.3380(11)	0.4953(9)	0.016(3)
Cu33	0.2862(7)	–0.7983(8)	0.2086(7)	0.032(2)	S20	0.3818(10)	0.3369(12)	0.9935(9)	0.018(4)
Cu34	0.2804(7)	–0.8019(8)	0.5386(6)	0.031(2)	S21	0.1239(10)	0.1713(10)	0.2464(8)	0.006(3)
Cu35	0.2949(7)	–0.0535(7)	0.0856(6)	0.0260(19)	S22	0.3731(10)	0.8446(12)	0.4987(10)	0.011(3)
Cu36	0.2693(8)	0.1278(9)	–0.0383(7)	0.048(3)	S23	0.1322(10)	–0.3378(12)	0.2582(11)	0.013(3)
Cu37	0.2735(7)	0.8795(7)	0.2252(6)	0.039(2)	S24	0.1241(13)	0.1645(16)	0.5033(12)	0.027(4)
Cu38	0.2906(8)	–0.0526(9)	–0.3323(7)	0.035(2)	S25	0.3845(10)	0.3310(11)	0.2525(8)	0.008(3)
Cu39	0.2860(12)	–0.0575(15)	–0.1287(11)	0.074(4)	S26	0.1311(12)	–0.0928(14)	–0.3710(12)	0.024(4)
Cu40	0.3674(5)	–0.2399(6)	0.6282(7)	0.0150(17)	S27	0.3693(8)	0.3348(9)	0.7550(8)	0.005(2)
Cu41	0.3703(6)	–0.2396(7)	0.1226(8)	0.024(2)	S28	0.1294(13)	0.6539(14)	0.4985(13)	0.025(4)
Cu42	0.3836(8)	–0.2442(10)	0.3745(7)	0.030(2)	S29	0.1136(8)	–0.5836(8)	0.3740(11)	0.008(2)
Cu43	0.3738(7)	–0.4994(8)	0.0060(6)	0.029(2)	S30	0.1281(13)	0.6621(14)	0.7485(13)	0.022(4)
Cu44	0.3920(7)	–0.4949(10)	0.2511(11)	0.028(3)	S31	0.1362(10)	0.9078(12)	0.1293(11)	0.020(4)
Cu45	0.3887(8)	0.5042(10)	0.5009(9)	0.028(3)	S32	0.1316(11)	–0.3410(12)	0.0042(11)	0.016(4)

in Table 3. A table of structure factors and a cif file are available from the Depository of Unpublished Data, MAC website [document Roxbyite CM50_423]. An indexed powder pattern of the XRD data previously reported in Mumme *et al.* (1988) is now given in Table 4.

DESCRIPTION OF THE STRUCTURE

The crystal structure of roxbyite as presented here contains 58 independent Cu atoms. The structure has Cu in coordinations very similar to those of djurleite and low chalcocite, with threefold (triangular) coordination being the most usual. The Cu–S distances are listed in Table 3.

The distribution of the atoms in roxbyite is illustrated in Figures 2–4. Figure 2 shows the hexagonal-close-packed layers of sulfur atoms on edge viewed along **b**. In roxbyite, there are two different types of S layers, at x = ~1/8 and 3/8, and three types of interlayer arrangements of Cu atoms, scattered around x = 0, ¼ and ½. Views normal to the different sulfur layers are given in Figures 3a and 3b, together with Figure 4, a similar view, but showing a composite of the two, three and four-fold bonding between the split Cu (only) layer x = ~1/4, and the sulfur layers at x = ~1/8 and 3/8.

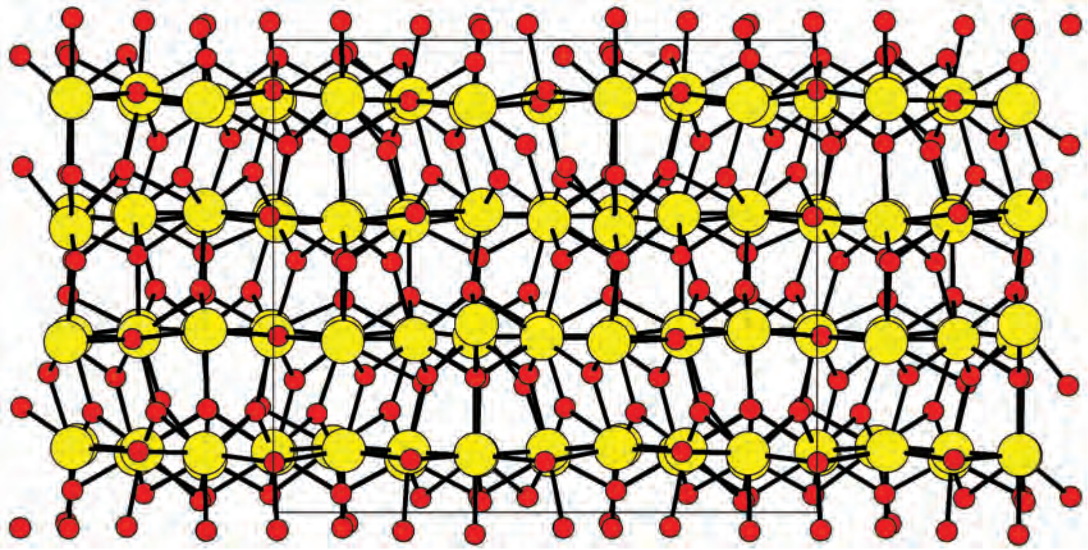

FIG. 2. Distribution of atoms in roxbyite viewed along the **b** axis. Small filled circles represent Cu, large filled circles represent S. The origin is at the lower left, at 0, –0.5, –0.5; **a** is the vertical axis, and **c** is horizontal.

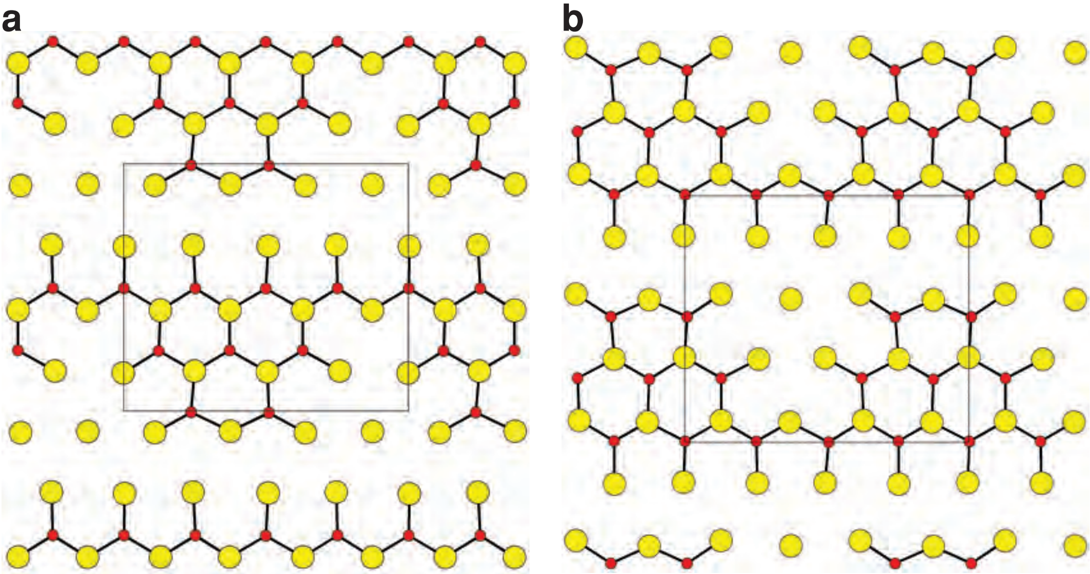

FIG. 3. The distribution of atoms in roxbyite in (a) layer x = ~1/8, and (b) layer x = ~3/8, viewed along **c**. Notation as in Figure 2. The origin is at the lower left, at 0, –0.5, –0.5; the **b** axis is vertical, and the **c** axis horizontal.

Figures 3a and 3b also illustrate how, in both of the close-packed layers at x = ~1/8 and 3/8, pseudo-hexagonal Cu_6S_{12} groups (disposed, with approximate three-fold local symmetry, about a central Cu, thus forming Cu_7S_{12} units overall) are further linked by linear Cu_2S_3 groups to form continuous chains running, in parallel, along **c**.

There are 40 independent Cu atoms located between the S layers, mostly in triangular sites, but six are in distorted tetrahedral coordinations, and four are in what

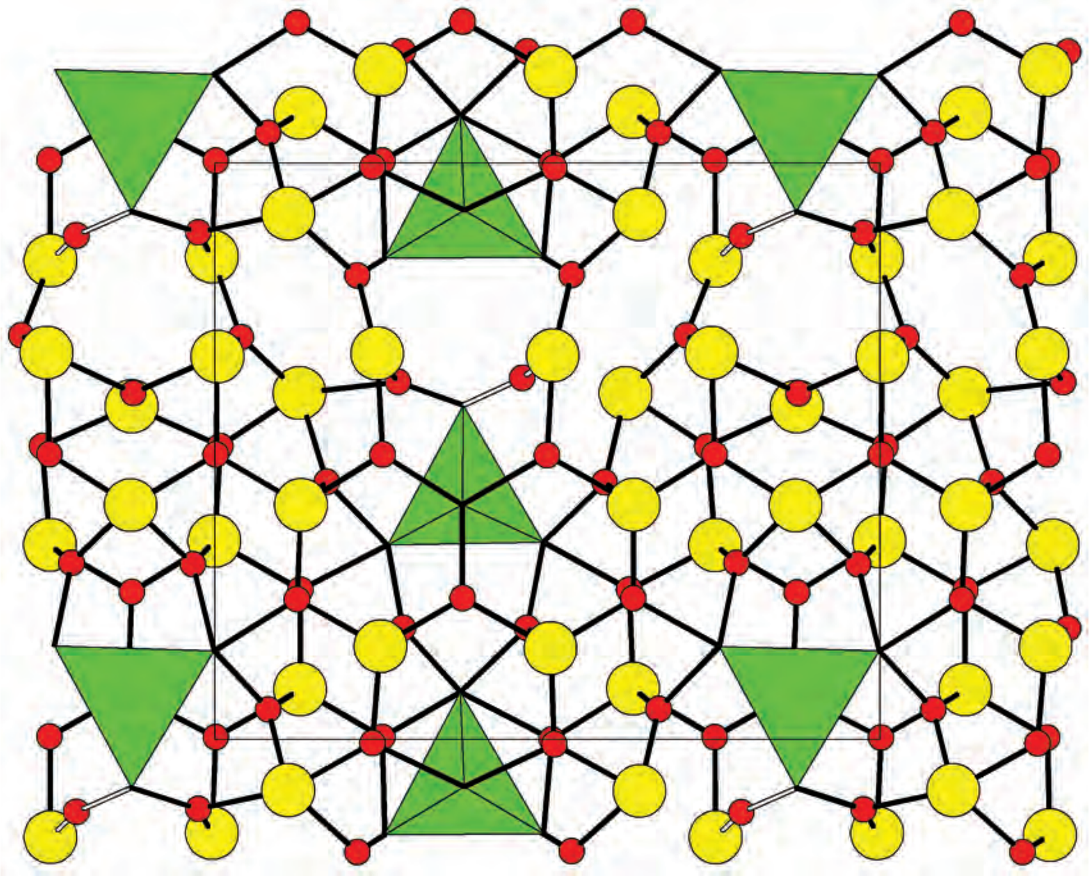

FIG. 4. Composite of the distribution of Cu atoms in layer x = ~1/4, together with Cu and S atoms in layers x = ~1/8 and 3/8. Some tetrahedrally coordinated CuS_4 groups are shaded, together with mostly triangular CuS_3 groups. Several Cu atoms in near-linear two-fold coordination are also shown with open bonds. Notation as in Figure 2. The origin is at the lower left, at 0, –0.5 –0.5; the **b** axis is vertical, and the **c** axis, horizontal.

may best be described as two-fold linear coordinations. The valences of Cu required for charge balance in roxbyite, $Cu^{1+}_{52}Cu^{2+}_{6}S_{32}$, indicate a preference for a tetrahedral environment for Cu^{2+} in roxbyite. The average bond-lengths for all of these coordinations fall in the range 2.16–2.44 Å; in comparison, the average Cu–S distance in djurleite is 2.29 Å (Evans 1979a, 1979b).

Twinning has been reported as prevalent in djurleite by both Takeda *et al.* (1967) and Evans (1979a, 1979b), and in fact Evans did not attempt a structure solution of djurleite until he first obtained an untwinned crystal. The crystal structure of roxbyite reported here is determined from a multiply twinned crystal with triclinic symmetry, $P\bar{1}$. However the refinement converged to a respectable agreement value, and the composition $Cu_{58}S_{32}$, or $Cu_{1.81}S$, lies in the reported compositional range for roxbyite (Mumme *et al.* 1988). Higher symmetry, particularly monoclinic (because the R_{int} for a two-fold axis along the **c** direction in the true cell is 5.5%) has been tested, but not found.

CONCLUDING REMARKS

The crystal structure of roxbyite, although based on a simple close-packed arrangement of sulfur atoms, is again just as complex in its entirety as are the crystal structures of low chalcocite and djurleite. Hopefully, its structure will provide another link in the overall understanding of the principles by which these as well as other well-known, well-defined minerals in the Cu–S system, such as analite ($Cu_{1.75}S$), geerite ($Cu_{1.6}S$), spionkopite ($Cu_{1.39}S$) and yarrowite ($Cu_{1.12}S$), form in

TABLE 3. BOND LENGTHS (Å) IN POLYHEDRA IN ROXBYITE

Cu1-S21	2.344(16)	Cu16-S8	2.230(17)	Cu31-S3	2.208(14)	Cu46-S2	2.22(2)
Cu1-S24	2.36(2)	Cu16-S21	2.364(16)	Cu31-S11	2.439(16)	Cu46-S11	2.11(2)
Cu1-S26	2.315(18)	Cu16-S31	2.221(19)	Cu31-S20	2.483(18)	Cu46-S27	2.284(19)
				Cu31-S27	2.511(15)		
Cu2-S3	2.351(13)	Cu17-S5	2.200(19)			Cu47-S6	2.27(2)
Cu2-S12	2.246(15)	Cu17-S13	2.359(17)	Cu32-S11	2.285(19)	Cu47-S9	2.224(15)
		Cu17-S26	2.25(2)	Cu32-S15	2.211(18)	Cu47-S22	2.209(19)
Cu3-S1	2.362(18)			Cu32-S30	2.28(2)		
Cu3-S3	2.339(15)	Cu18-S5	2.167(16)			Cu48-S4	2.269(12)
Cu3-S32	2.288(18)	Cu18-S30	2.22(2)	Cu33-S4	2.199(14)	Cu48-S6	2.30(2)
		Cu18-S32	2.357(19)	Cu33-S21	2.291(16)	Cu48-S10	2.305(17)
Cu4-S17	2.531(15)			Cu33-S25	2.280(18)		
Cu4-S24	2.47(2)	Cu19-S8	2.32(2)			Cu49-S14	2.233(18)
Cu4-S28	2.259(19)	Cu19-S24	2.29(3)	Cu34-S9	2.173(14)	Cu49-S18	2.320(17)
Cu4-S29	2.427(17)	Cu19-S26	2.33(2)	Cu34-S19	2.422(18)	Cu49-S20	2.360(18)
Cu5-S12	2.644(15)			Cu34-S24	2.21(2)		
		Cu20-S13	2.314(17)			Cu50-S6	2.31(2)
Cu5-S21	2.306(16)	Cu20-S17	2.394(16)	Cu35-S4	2.307(13)	Cu50-S15	2.291(15)
Cu5-S29	2.384(17)	Cu20-S27	2.196(14)	Cu35-S18	2.23(2)	Cu50-S25	2.309(17)
Cu5-S30	2.269(19)			Cu35-S31	2.293(17)		
		Cu21-S17	2.421(15)			Cu51-S9	2.524(15)
Cu6-S3	2.399(14)	Cu21-S19	2.242(15)	Cu36-S1	2.167(18)	Cu51-S10	2.309(15)
Cu6-S13	2.344(15)	Cu21-S29	2.196(16)	Cu36-S14	2.299(19)	Cu51-S14	2.448(19)
Cu6-S23	2.238(16)					Cu51-S27	2.389(15)
		Cu22-S8	2.324(17)	Cu37-S9	2.588(15)		
Cu7-S1	2.367(17)	Cu22-S22	2.257(18)	Cu37-S13	2.298(15)	Cu52-S6	2.297(19)
Cu7-S13	2.369(16)	Cu22-S28	2.36(2)	Cu37-S14	2.326(17)	Cu52-S19	2.314(17)
Cu7-S31	2.361(15)					Cu52-S22	2.289(16)
		Cu23-S7	2.298(16)	Cu38-S9	2.356(15)		
Cu8-S17	2.227(14)	Cu23-S12	2.166(16)	Cu38-S15	2.292(17)	Cu53-S4	2.315(10)
Cu8-S23	2.514(18)	Cu23-S23	2.296(19)	Cu38-S26	2.28(2)	Cu53-S14	2.435(15)
Cu8-S28	2.75(2)					Cu53-S15	2.346(14)
Cu8-S29	2.394(13)	Cu24-S6	2.276(17)	Cu39-S5	2.24(2)	Cu53-S18	2.573(19)
		Cu24-S21	2.570(17)	Cu39-S14	2.38(2)		
Cu9-S1	2.305(17)	Cu24-S24	2.48(2)	Cu39-S15	2.48(2)	Cu54-S6	2.360(17)
Cu9-S5	2.273(12)			Cu39-S18	2.57(2)	Cu54-S9	2.278(12)
Cu9-S21	2.269(15)	Cu25-S8	2.246(17)			Cu54-S10	2.491(16)
		Cu25-S10	2.246(17)	Cu40-S2	2.318(15)	Cu54-S22	2.662(17)
Cu10-S8	2.215(12)	Cu25-S23	2.25(2)	Cu40-S15	2.280(17)		
Cu10-S13	2.266(16)			Cu40-S22	2.304(19)	Cu55-S2	2.256(13)
Cu10-S24	2.32(2)	Cu26-S1	2.35(2)			Cu55-S19	2.240(17)
		Cu26-S12	2.373(17)	Cu41-S7	2.301(16)	Cu55-S25	2.250(17)
Cu11-S26	2.20(2)	Cu26-S20	2.278(18)	Cu41-S10	2.254(19)		
Cu11-S28	2.27(2)			Cu41-S18	2.29(2)	Cu56-S16	2.317(15)
Cu11-S30	2.24(2)	Cu27-S25	2.174(16)			Cu56-S19	2.298(18)
		Cu27-S29	2.146(15)	Cu42-S10	2.201(18)	Cu56-S27	2.285(16)
Cu12-S1	2.33(2)			Cu42-S16	2.333(18)		
Cu12-S5	2.30(2)	Cu28-S16	2.246(17)	Cu42-S22	2.267(19)	Cu57-S7	2.210(14)
Cu12-S31	2.36(2)	Cu28-S23	2.592(19)			Cu57-S20	2.298(19)
		Cu28-S28	2.52(2)	Cu43-S7	2.232(18)	Cu57-S27	2.251(16)
Cu13-S3	2.367(16)	Cu28-S29	2.381(15)	Cu43-S11	2.390(18)		
Cu13-S17	2.263(16)			Cu43-S20	2.206(19)	Cu58-S11	2.355(15)
Cu13-S30	2.26(2)	Cu29-S2	2.351(16)			Cu58-S20	2.286(18)
		Cu29-S17	2.156(17)	Cu44-S7	2.22(2)	Cu58-S25	2.322(17)
Cu14-S12	2.264(18)	Cu29-S28	2.14(2)	Cu44-S16	2.09(2)		
Cu14-S32	2.24(2)			Cu44-S25	2.34(2)		
		Cu30-S11	2.397(18)				
Cu15-S23	2.30(2)	Cu30-S18	2.27(2)	Cu45-S2	2.27(2)		
Cu15-S31	2.183(18)	Cu30-S32	2.287(18)	Cu45-S16	2.30(2)		
Cu15-S32	2.25(2)			Cu45-S19	2.23(2)		

copper ores and synthetic systems as compositionally related, but discrete minerals and phases.

DEDICATION

This paper is dedicated to Emil Makovicky on the occasion of his official retirement. One of us (WGM) acknowledges both his kind friendship and fruitful collaboration over the course of over 30 years. Best wishes, Emil.

TABLE 4. ROXBYITE: X-RAY POWDER-DIFFRACTION DATA

I	d_{obs}	d_{calc}	*h*	*k*	*l*	I	d_{obs}	d_{calc}	*h*	*k*	*l*	I	d_{obs}	d_{calc}	*h*	*k*	*l*
10	4.78	4.82	0	$\bar{1}$	$\bar{3}$	25	2.532	2.530	$\bar{5}$	0	2	100	1.934	1.935	0	0	$\bar{8}$
15	4.24	4.23	1	3	0			2.531	5	0	2			1.933	6	0	$\bar{4}$
		4.24	$\bar{3}$	1	0	15	2.451	2.453	$\bar{2}$	$\bar{5}$	1	10	1.894	1.893	7	1	0
5	3.90	3.91	2	$\bar{1}$	$\bar{3}$	85	2.372	2.372	1	$\bar{2}$	$\bar{6}$	90	1.859	1.860	4	$\bar{3}$	$\bar{6}$
20	3.59	3.59	1	$\bar{1}$	$\bar{4}$			2.371	2	$\bar{1}$	$\bar{6}$			1.860	4	3	6
55	3.35	3.35	2	$\bar{3}$	2			2.370	4	$\bar{2}$	$\bar{4}$			1.858	6	$\bar{2}$	$\bar{4}$
		3.35	4	0	0			2.371	2	4	4			1.858	6	2	4
5	3.16	3.16	$\bar{3}$	3	0			2.373	$\bar{2}$	4	4	10	1.794	1.794	6	1	5
		3.15	3	3	0	10	2.299	2.298	$\bar{5}$	3	0			1.793	2	$\bar{2}$	8
30	3.00	3.00	2	$\bar{2}$	$\bar{4}$			2.298	$\bar{3}$	5	0			1.792	5	$\bar{2}$	$\bar{6}$
		3.00	2	2	4	10	2.239	2.237	0	$\bar{3}$	$\bar{6}$	30	1.675	1.673	8	0	0
		3.00	$\bar{4}$	2	0	15	2.174	2.173	5	$\bar{1}$	$\bar{4}$	10	1.652	1.651	4	7	1
60	2.862	2.861	1	3	4			2.179	6	1	1			1.650	$\bar{4}$	$\bar{7}$	1
		2.858	3	$\bar{1}$	$\bar{4}$			2.178	$\bar{6}$	$\bar{1}$	1	25	1.628	1.628	2	$\bar{4}$	$\bar{8}$
		2.862	$\bar{1}$	3	4	10	2.121	2.122	2	$\bar{3}$	$\bar{6}$			1.628	2	4	8
45	2.628	2.626	$\bar{5}$	1	0			2.121	3	$\bar{2}$	$\bar{6}$	5	1.581	1.581	3	6	6
		2.625	5	1	0									1.579	$\bar{6}$	6	0

Least-squares refinement of the X-ray powder data listed in Table 3 of Mumme *et al.* (1988), under the heading *Diffractometer reaction product*, yielded the following triclinic unit-cell dimensions: *a* 13.387(4), *b* 13.395(6), *c* 15.481(9) Å, α 89.80(6), β 89.98(4), γ 90.08(3)°.

ACKNOWLEDGEMENTS

We gratefully acknowledge the generous help of Dr. Ian Grey (CSIRO) in preparing this manuscript.

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Received April 13, 2011, revised manuscript accepted January 10, 2012.