Am-79-1164

American Mineralogist, Volume 64, pages 1265-1271, 1979

Structure and symmetry of CuS_2 (pyrite structure)

HUBERT E. KING, JR.[1] AND CHARLES T. PREWITT

Department of Earth and Space Sciences
State University of New York
Stony Brook, New York 11794

Abstract

X-ray diffraction data collected on a single-crystal specimen of CuS_2 show that despite its optical anisotropy CuS_2 apparently has the cubic pyrite structure, with $a = 5.7891(6)$A. Precession and Weissenberg photographs fail to reveal any reflections which violate the requirements for space group $Pa3$. Such reflections, however, were observed in four-circle diffractometer measurements, but they are shown to result from multiple diffraction effects. Refinement of the structure in space group $Pa3$ using 209 intensity data gives a weighted residual of 0.014 and $x(S) = 0.39878(5)$. A comparison of the refined structure with other pyrite structures suggests that copper in CuS_2 has a formal valence of 2+ and three antibonding electrons. Also, the CuS_6 octahedron is only slightly distorted, which is in contrast with the square-planar coordination usually found for Cu^{2+}.

Introduction

Disulfides of the transition elements Mn through Zn crystallize in the pyrite structure. The Mn, Fe, Co, and Ni members of this group occur as minerals, and their structures have been refined. CuS_2 and ZnS_2 are not found in nature, but they have been synthesized at high temperatures and pressures. This paper reports the results obtained in a study of the crystal structure and optical properties of CuS_2.

CuS_2 is of interest for two reasons. First, its crystal chemistry is unique. Nakai *et al.* (1978) have shown through X-ray photoelectron spectroscopy that most copper sulfides contain only Cu^+; however, our crystal-chemical evidence indicates that copper in CuS_2 is divalent. The copper is coordinated by six sulfur atoms in a trigonal antiprism slightly distorted from an octahedron, rather than in its usual square-planar coordination. Second, optical evidence for non-cubic symmetry has been reported (Taylor and Kullerud, 1972), but not explained in terms of the crystal structure. Similar, but less intense, optical effects have been reported for FeS_2 (Stanton, 1975; Gibbons, 1967). These authors disagree as to whether the anisotropy is entirely a surface feature or intrinsic to the crystal structure. There is also disagreement with respect to the X-ray diffraction studies on FeS_2. Finklea *et al.* (1976) found no deviations from cubic symmetry, but Bayliss (1977) concluded that at least some pyrite crystals are triclinic. Because optical anisotropy has always been observed for CuS_2 we decided to investigate its crystal structure to provide further information on this intriguing problem.

Experimental

The CuS_2 crystal used is a small ($0.13 \times 0.12 \times 0.08$ mm) rectangular prism selected from material reported by Bither *et al.* (1968). Although polished sections of these crystals are anisotropic in reflected light, long-exposure precession and Weissenberg photographs failed to reveal any diffraction spots which are inconsistent with the requirements for space group $Pa3$. This crystal was mounted on a Picker four-circle diffractometer and its lattice parameters were determined from twelve automatically-centered reflections using Mo$K\alpha$ radiation. The least-squares refinement of the orientation matrix (Tichý, 1970) provides an unconstrained estimate of all unit-cell lengths and angles; with the precision obtained, the geometry of the cell is cubic with $a = 5.7891(6)$A. This value agrees well with previous determinations using X-ray powder diffraction techniques: $a = 5.7898$A (Bither *et al.*, 1968) and $a = 5.7897$A (Taylor and Kullerud, 1972).

[1] Present address: IBM T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York, 10598.

0003-004X/79/1112-1265$02.00

H,2,0
0 898E 900 3
H,4,0
0 157 156 1
H,6,0
0 77 76 3
H,8,0
0 371 363 2
H,0,0
2 848E 845 4
H,2,0
2 759 763 4
H,4,0
2 441 440 3
H,6,0
2 292 292 2
H,0,0
4 156 155 2
H,2,0
4 441 437 3
H,4,0
4 717 721 4
H,6,0
4 537 531 3
H,0,0
6 83 76 3
H,2,0
6 297 292 2
H,0,0
8 373 363 2
H,1,1
1 452 446 3
H,2,1
1 381 -368 3
H,3,1
1 785 791 4
H,4,1
1 164 -161 1
H,5,1
1 772 764 3
H,6,1
1 129 126 2
H,7,1
1 372 367 2
H,8,1
1 130 130 2
H,1,1
2 375 -368 3
H,2,1
2 129 125 1
H,3,1
2 116 116 2
H,4,1
2 51 52 3
H,5,1
2 273 271 1
H,6,1
2 57 -50 3
H,7,1
2 54 54 4
H,1,1
3 773 782 4
H,2,1
3 455 -451 3
H,3,1
3 541 539 3
H,4,1
3 219 -218 1
H,5,1
3 302 301 2
H,6,1
3 182 182 2
H,7,1
3 251 247 2
H,1,1
4 161 -161 2
H,2,1
4 254 -257 2
H,3,1
4 58 60 3
H,4,1
4 135 -133 2
H,5,1
4 136 137 2
H,6,1
4 105 100 2
H,7,1
4 35 20 6
H,1,1
5 759 757 5
H,2,1
5 15* 12 7
H,3,1
5 298 301 2
H,4,1
5 16* 13 8
H,5,1
5 41 39 5
H,6,1
5 17* -2 8
H,1,1
6 129 126 2
H,2,1
6 185 -186 2
H,3,1
6 33 -42 6
H,4,1
6 91 -90 3
H,5,1
6 114 -114 3
H,1,1
7 369 367 3
H,2,1
7 258 253 2
H,3,1
7 252 247 2
H,4,1
7 130 126 3
H,0,1
8 18* 0 9
H,1,1
8 131 130 3
H,0,2
0 837E 836 3
H,2,2
0 742E 745 4
H,4,2
0 434 438 3
H,6,2
0 288 292 2
H,1,2
1 375 -366 3
H,2,2
1 126 125 1
H,3,2
1 451 -449 3
H,4,2
1 257 -257 2
H,5,2
1 14* 12 7
H,6,2
1 185 -186 2
H,7,2
1 249 253 2
H,0,2
2 759 758 4
H,1,2
2 126 125 1
H,2,2
2 676 679 4
H,3,2
2 156 156 1
H,4,2
2 488 485 3
H,5,2
2 15* -14 7
H,6,2
2 334 332 2
H,7,2
2 97 -95 3
H,1,2
3 113 116 2
H,2,2
3 153 156 1
H,3,2
3 165 162 1
H,4,2
3 363 -363 2
H,5,2
3 15* 3 7
H,6,2
3 255 -259 2
H,7,2
3 94 -93 3
H,0,2
4 427 437 3
H,1,2
4 48 52 3
H,2,2
4 483 485 3
H,3,2
4 68 66 3
H,4,2
4 496 496 3
H,5,2
4 34 -14 5
H,6,2
4 353 351 2
H,1,2
5 272 271 2
H,2,2
5 15* -14 8
H,3,2
5 378 381 3
H,4,2
5 16* 1 8
H,5,2
5 17* -13 8
H,6,2
5 18* 15 9

H,0,2
6 284 292 2
H,1,2
6 56 -50 4
H,2,2
6 330 332 2
H,3,2
6 76 -73 3
H,4,2
6 352 351 2
H,5,2
6 17* -3 9
H,1,2
7 52 54 5
H,2,2
7 95 -95 3
H,3,2
7 71 70 4
H,1,3
1 775 770 4
H,2,3
1 117 116 2
H,3,3
1 539 533 4
H,4,3
1 53 60 3
H,5,3
1 298 301 2
H,6,3
1 34 -42 5
H,7,3
1 244 247 2
H,1,3
2 450 -449 3
H,2,3
2 155 156 1
H,3,3
2 163 162 1
H,4,3
2 69 66 3
H,5,3
2 378 381 2
H,6,3
2 74 -73 3
H,7,3
2 74 70 3
H,1,3
3 525 536 4
H,2,3
3 162 162 2
H,3,3
3 495 497 4
H,4,3
3 87 84 2
H,5,3
3 392 396 2
H,6,3
3 61 -65 5
H,1,3
4 214 -218 2
H,2,3
4 359 -363 3
H,3,3
4 87 84 2
H,4,3
4 188 -188 2
H,5,3
4 187 188 2
H,6,3
4 142 147 2
H,1,3
5 292 301 2
H,2,3
5 16* 3 8
H,3,3
5 397 396 3
H,4,3
5 16* -5 8
H,5,3
5 376 380 2
H,1,3
6 181 182 2
H,2,3
6 262 -259 2
H,3,3
6 65 -65 4
H,4,3
6 129 -123 3
H,1,3
7 251 247 2
H,2,3
7 94 -93 3
H,2,4
0 431 433 3
H,4,4
0 709 708 4
H,6,4
0 523 527 2
H,1,4
1 155 -161 1
H,2,4
1 48 52 3
H,3,4
1 216 -218 2
H,4,4
1 133 -133 2
H,5,4
1 15* 13 7
H,6,4
1 91 -90 3
H,7,4
1 127 126 2
H,0,4
2 434 437 3
H,1,4
2 251 -257 2
H,2,4
2 490 482 3
H,3,4
2 360 -362 3
H,4,4
2 502 493 3
H,5,4
2 15* 1 8
H,6,4
2 348 351 2
H,1,4
3 56 60 3
H,2,4
3 64 66 3
H,3,4
3 89 84 2
H,4,4
3 188 -188 2
H,5,4
3 16* -5 8
H,6,4
3 126 -123 2
H,0,4
4 709 715 4
H,1,4
4 134 -133 2
H,2,4
4 494 494 3
H,3,4
4 185 -188 2
H,4,4
4 129 131 3
H,5,4
4 17* 7 8
H,1,4
5 134 137 2
H,2,4
5 16* -14 8
H,3,4
5 192 188 2
H,4,4
5 17* 7 9
H,5,4
5 18* -18 9
H,0,4
6 528 528 3
H,1,4
6 100 100 3
H,2,4
6 345 351 2
H,3,4
6 144 147 2
H,1,4
7 18* 20 9
H,1,5
1 747 742 4
H,2,5
1 266 270 2
H,3,5
1 296 300 2
H,4,5
1 134 137 2
H,5,5
1 42 39 5
H,6,5
1 108 -114 3
H,1,5
2 14* 12 7
H,2,5
2 32 -14 5
H,3,5
2 15* 3 7
H,4,5
2 16* -14 8
H,5,5
2 16* -13 8
H,6,5
2 17* -3 9
H,1,5
3 294 300 2
H,2,5
3 380 380 3
H,3,5
3 402 395 3

```
    H,4,5           H,0,6           H,4,6           H,2,7
 3 194  188 2   0  70   76 3   2 352  350 2   1  55   54 4
    H,5,5           H,2,6           H,5,6           H,3,7
 3 381  379 2   0 284  290 2   2  17*  15 9   1 242  246 2
    H,1,5           H,3,6           H,1,6           H,4,7
 4  15*  13 8   0  17*   0 8   3  40  -42 5   1  17*  20 8
    H,2,5           H,4,6           H,2,6           H,0,7
 4  16*   1 8   0 524  523 3   3  78  -73 3   2  16*   0 8
    H,3,5           H,1,6           H,3,6           H,1,7
 4  16*  -5 8   1 120  126 2   3  73  -65 4   2 249  252 2
    H,4,5           H,2,6           H,4,6           H,2,7
 4  17*   7 9   1  47  -50 4   3 146  147 2   2  93  -95 3
    H,5,5           H,3,6           H,0,6           H,3,7
 4  18* -18 9   1 180  182 2   4 513  527 3   2  91  -93 3
    H,1,5           H,4,6           H,1,6           H,1,7
 5  61   39 4   1  99  100 3   4  92  -90 3   3 246  246 2
    H,2,5           H,5,6           H,2,6           H,2,7
 5  17* -13 8   1  17*  -2 8   4 352  350 2   3  76   70 3
    H,3,5           H,0,6           H,3,6           H,0,7
 5 382  379 2   2 289  291 2   4 126 -123 3   4  17*   0 9
    H,4,5           H,1,6           H,1,6           H,1,7
 5  18* -18 9   2 185 -185 2   5 114 -114 3   4 129  126 3
    H,1,5           H,2,6           H,2,6           H,0,8
 6  18*  -2 9   2 333  331 2   5  18*  -3 9   0 359  360 2
    H,2,5           H,3,6           H,1,7
 6  35   15 7   2 256 -259 2   1 356  364 2

  251 REFLECTIONS PROCESSED.
SIGMA(FO)* 10. IS PRINTED INSTEA¬@OF PHASE ANGLE.
>
```