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Structure and symmetry of CuS_2 (pyrite structure)

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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 *Pa*3. 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 *Pa*3 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 × 0.12 × 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 *Pa*3. 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).

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