

A NOTE ON THE OXIDATION STATE OF IRON IN CUBANITE

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In a recent publication (Fleet 1970), a bonding model for cubanite (CuFe_2S_3) was developed to account for the juxtaposition of the Fe atoms across shared tetrahedral edges. By analogy with chalcopyrite (CuFeS_2), Cu was assumed to be present in the Cu^+ state and the Fe in the Fe^{3+} state. However, this simplification did not take into account the recent Mössbauer work on cubanite and, accordingly, may lead to some confusion as to the oxidation state of the Fe in cubanite. It is hoped that the following comments, together with those of Knop, Huang & Woodhams (1970), will clarify the situation.

In cubanite both Cu and Fe atoms are in tetrahedral coordination with S; the Fe coordination tetrahedra are arranged to share a common edge. By the molecular orbital bond theory, if two valency electrons are allocated to each metal-S σ bond and Cu is assumed to have the $3d^{10}$ configuration, there remain eleven valency electrons per formula unit to be distributed between the d -levels of the two Fe atoms. For the equivalent ionic model, then, one Fe atom per formula unit would be trivalent and one would be divalent.

The Mössbauer spectra of cubanite at 77°K and 295°K are consistent with this model (Greenwood & Whitfield 1968); the chemical isomer shift is intermediate between that expected for Fe^{2+} and Fe^{3+} ions in tetrahedral coordination. However, only a single six-line hyperfine spectrum is observed (two superimposed spectra are to be expected for distinct Fe^{2+} and Fe^{3+} states) and Greenwood & Whitfield interpret this to imply that there is a rapid electron exchange between the Fe^{2+} and Fe^{3+} ions. Earlier Imbert & Wintenberger (1967) had obtained similar Mössbauer data for cubanite from a mixture of cubanite and chalcopyrite. However, the cubanite spectrum at 4°K is little different from that at 300°K and this observation would seem to preclude a rapid exchange between distinct Fe^{2+} and Fe^{3+} states. The extra $3d$ electron must be associated in some molecular way with both of the adjacent Fe atoms; a situation that a purely ionic bonding model cannot accommodate. In

this regard, Hulliger (1968) suggested that the extra half electron per Fe atom occupies an incompletely-filled d -band.

It was hypothesised earlier (Fleet 1970) that the juxtaposition of the Fe tetrahedra possibly resulted from spin pairing of singly occupied ϵ orbitals across the shared edges. However, the nearest Fe-Fe distance (2.82Å) is greater than that calculated for the ideal structure (2.65Å), which is not intuitively in accord with this model. An alternative hypothesis was suggested, in which the one ϵ orbital (d_{z^2}), projected along the interatomic direction, is destabilized, resulting in spin pairing in the other ϵ orbital ($d_{x^2-y^2}$); the π bonding contribution between the spin paired orbital and the surrounding S atoms stabilizes the configuration. This reappraisal of the oxidation state of the Fe in cubanite does not invalidate these arguments but does give more support to the latter one. In this, the extra $3d$ electron would occupy the destabilized d_{z^2} orbitals which now adopt a molecular role located immediately below, or within, the conduction band. The apparent stretching of the observed Fe-Fe distance over the ideal distance results from the occupation of this molecular orbital.

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