Cu(II) IN OCTAHEDRAL SITES IN SPHALERITE

P. G. MANNING[1]

ABSTRACT

A spectrophotometric investigation has been made of the Cu environment in Cu-doped ultra-high purity sphalerite. A *d-d* absorption band was observed at 11,000 cm^{-1}, the spectral position and intensity of which are indicative of octahedrally bound Cu(II). No tetrahedrally bound Cu was detected. It is concluded that the Cu is located interstitially.

INTRODUCTION

A number of investigations have been reported in recent years (Low & Weger, 1960; Dvir & Low, 1960; Pappalardo & Dietz, 1961; Pappalardo, 1961; Weakliem, 1962; Slack, 1963; Coblentz, quoted by Slack) that describe the doping of oxide and sulphide crystals with transition metal impurities. Much of the work has dealt with sphalerite and wurtzite and other minerals with similar cubic and hexagonal structures. In all studies with minerals of the sphalerite or wurtzite type, the impurity metal was shown to occupy the substitutional tetrahedral sites. Tetrahedrally bound Fe(II), for example, is characterized by an intense absorption in the infrared at 3μ. The present study was initiated by observations in these laboratories that Fe-containing sphalerites are often opaque. The absorption in the visible region of the spectrum can be resolved into a number of bands characteristic of Fe^{3+} in octahedral sites (Ballhausen, 1962). It is hoped to publish this work in the near future in conjunction with some Mössbauer (R. H. Goodman, private communication) and electrical (J. D. Keys and T. Baleshta, private communications) observations. The present publication reports work done on the Cu-sphalerite system. Cu(II) in octahedral sites has a simple and characteristic absorption spectrum, and the confirmation (or otherwise) of the interstitial siting of impurity atoms should present little difficulty.

EXPERIMENTAL PROCEDURE

Synthetic ultra-high purity sphalerite crystals were purchased from the Eagle-Picher Company, Miami, Oklahoma. The crystals were colourless and showed a very low degree of birefringence. No sphalerite-wurtzite twinning was observed.

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[1] Senior Scientific Officer, Mineral Physics Section, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa 4, Canada.

Crystals, 5 mm × 5 mm × ~ 1 mm, were coated with copper in an Edwards High Vacuum Coating Unit Model 6E2, purchased from Edwards High Vacuum, P.O. Box 515, Cumberland Avenue, Burlington, Ontario. The coated crystals were baked under 3 mm argon in quartz tubes for 2–3 days at 700 °C. The doped sphalerite was either dark-brown or opaque, depending on the Cu concentration. Spectra were obtained, where necessary, by the thinning down of the crystal. The spectrophotometer was a Beckman DK2A.

Oscillator strengths were calculated from the equation (Ballhausen, 1960):

$$f = 4.6 \times 10^{-9} \times \epsilon_{\max} \times \nu_{\frac{1}{2}},$$

where $\epsilon_{\max}$ is the extinction coefficient and $\nu_{\frac{1}{2}}$ the width (in cm^{-1}) of the band at $\frac{1}{2}$ maximum.

DISCUSSION

Two representative room-temperature spectra of Cu-doped sphalerite are shown in Figure 1. The crystals containing high Cu concentrations (> 0.01%) were black, due presumably to the energy absorption associated with electronic transitions from the valence band to impurity levels. A prominent shoulder is evident on the low energy side (~ 11,000 cm^{-1}) of the intense absorption in the visible region, but the spectrum is then featureless to beyond 5 microns.

Absorption bands due to *d-d* transitions in Cu(II) systems are generally observed in the range 5,000–15,000 cm^{-1}. Cu(I), being a d^{10} ion, does not exhibit *d-d* bands. The predicted absorption band ($^2E_g \rightarrow {}^2T_{2g}$) for tetrahedrally bound Cu(II) is at 6045 cm^{-1} (Pappalardo, 1961), and the bands for Cu-doped ZnO and CdS are observed experimentally at 5800 cm^{-1} and 6400 cm^{-1} respectively (Pappalardo & Dietz, 1961). Cu(II) in distorted tetrahedral (squashed) environments absorbs at ~ 9,000 cm^{-1}. Octahedrally bound Cu(II) is well characterized by an absorption band at 12,000 cm^{-1}; the band is broad and contains two components that are usually difficult to resolve. Pappalardo & Dietz (1961) suggested that S lies between O and F in the spectrochemical series; and their experimental studies of transition metals in CdS confirmed the weaker ligand field of S as against O. The absorption band of Cu(II) octahedrally surrounded by six sulphur atoms would therefore be expected to lie at a lower energy than that of Cu(II) in an octahedral oxygen environment.

The spectra reproduced in Figure 1 may be interpreted on the basis of octahedrally sited Cu(II). The oscillator strength of the Cu(II) *d-d* band in tetrahedral sites in CdS is 2.10^{-4}, and there seems little reason for supposing that this value does not apply to tetrahedrally bound Cu in the

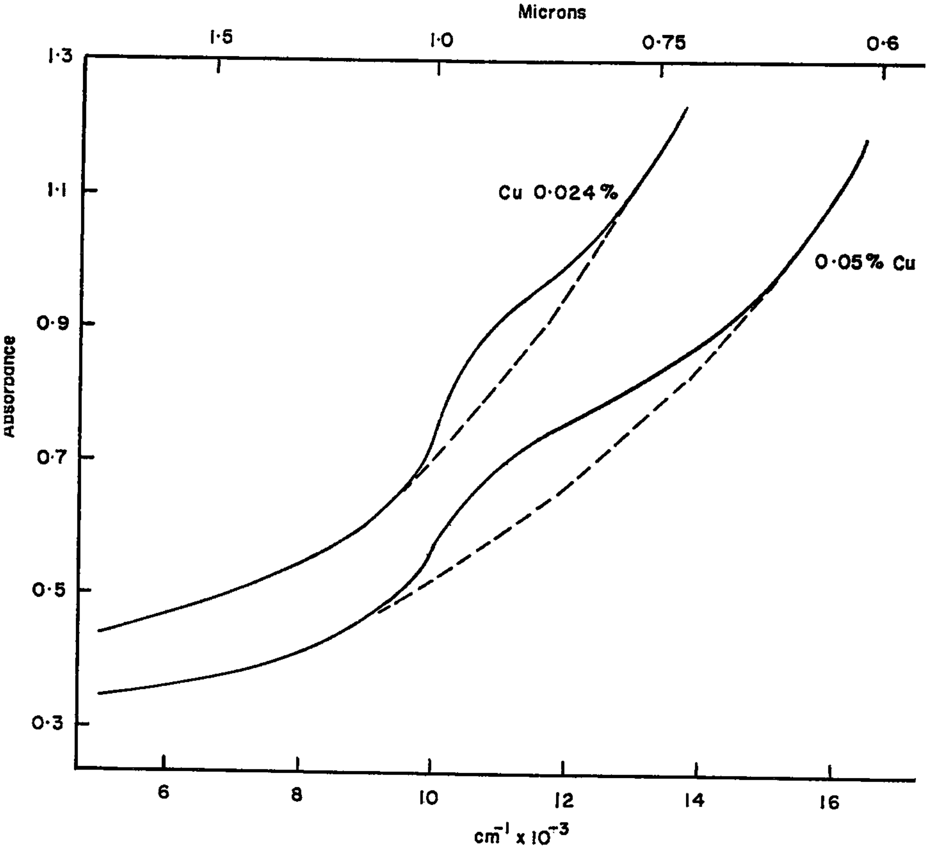

FIG. 1. Absorption spectra of Cu-doped sphalerites. Absorbance values refer to 0.024% Cu curve. For 0.05% Cu curve, add 0.5 absorbance units.

analogous sphalerite system. At the doping levels studied here, the *d-d* bands due to substitutional Cu would be readily detectable. The absence of any detectable band at either 6,000 cm^{-1} or 9,000 cm^{-1} indicates that only a small fraction, if any, of the copper has entered substitutionally. The position of the broad band at 11,000 cm^{-1} is in excellent agreement with that expected for Cu(II) in octahedral S fields, and assuming that all the Cu is present as octahedral Cu(II), $f \sim 10^{-4}$. This f value (an average for 4 different crystals) is reasonable for Cu(II) *d-d* bands, and its slightly smaller value compared with the f factor for tetrahedral Cu(II) in CdS is also to be expected (from symmetry considerations). For example, the f values for octahedral $CuCl_4.2H_2O^{2-}$ and tetrahedral $CuCl_4^{2-}$ in acetone are 10^{-3} and 2.10^{-3} respectively (G. H. Faye, private communication). It seems reasonable to conclude, therefore, that the Cu is present as Cu(II) in octahedral (interstitial) sites in sphalerite. As far as we know, this is the first reported occurrence of interstitial cations in sphalerite.

The ligand field stabilisation energy (LFSE) is a small factor in the overall energy of formation of a complex. The elevation in energy of the *d*-orbitals as a whole is $\sim$ 30 ev whereas *d*-orbital splittings are $\sim$ 1–3 ev. For a d^9 cation, the position in the spectrum of the *d-d* absorption is a direct measure of the splitting (Δ) of the t_{2g} and e_g orbitals. The LFSE for Cu(II) in octahedral sites is $3/5 \times \Delta$ and in tetrahedral sites $3/5 \times 4/9 \times \Delta$. Hence, because $\Delta \sim 11{,}000\ \text{cm}^{-1}$ and 1 kcal/mole = 350 cm^{-1}, LFSE (octahedral sites) – LFSE (tetrahedral sites) $\sim$ 10 kcal/mole. The calculation shows that if Cu(II) does sit interstitially, it will occupy the octahedral holes. The more electronegative Cu forms stronger bonds with ligands than does Zn and it would be expected that the Cu dopant would occupy the substitutional sites. All previous studies of transition metal doping of wurtzite or sphalerite have reported only substitutional siting of the impurities.

An examination under a microscope showed that the less highly doped, dark brown crystals were of uniform coloration. Segregation of the Cu as copper sulphides may be eliminated because octahedrally bound Cu(II) does not occur in copper sulphides. It would seem, therefore, that the Cu(II) occupies, randomly, the interstitial octahedral sites in sphalerite. It is readily conceivable that the interstitial Cu atoms coordinate to the S atoms, so that the closest neighbour S atoms are 5-coordinate. If the Cu atoms lie at the centre of undistorted sphalerite interstitial sites, the Cu-S bond lengths are 2.74 Å. This value is considerably larger than the Cu-S bond lengths (2.3 Å) in chalcopyrite (Pauling & Brockway, 1932) and cubanite (Azaroff & Buerger, 1955). It would seem, therefore, that the interstitial holes in sphalerite will tend to be reduced in size upon Cu occupation. If the Cu-S bonds (for interstitial Cu) are of comparable strength to the (substitutional) Zn-S bonds, the LFSE calculation would suggest that the Cu would occupy the energetically more favourable octahedral sites. The S atoms would, therefore, seem to be "true" 5-coordinate which further suggests that S can use its 3*d* orbitals in the bonding.

It was shown in an earlier publication (Manning, 1965) that the Cu-O bonds in cupric acetate and glycolate complexes in solution are of low covalent character, and the *d-d* bands for oxygen-bonding ligands of this type are at similar energies to the $Cu(OH_2)^{2+}$ band. With increasing covalent character of a bond, the *d-d* absorption bands shift to higher energies. This effect is apparent in pyrite, FeS_2, where the ligand field is strong enough to pair off the $3d^6$ electrons in the t_{2g} orbitals. Hence, $\Delta > 15{,}000\ \text{cm}^{-1}$ (Tanabe & Sugano, 1954). However, the *d-d* band for $Fe(OH_2)_6^{2+}$ is at 10,000 cm^{-1} (Jorgensen, 1954), corresponding to $\Delta \sim$

10,000 cm^{-1}; and the position in the spectrum of the 3-micron absorption of tetrahedral Fe(II) in ZnS (Low & Weger, 1960) and CdS (Pappalardo & Dietz, 1961) is reasonably consistent with the relative strengths of octahedral and tetrahedral fields. Mössbauer experiments (R. H. Goodman, private communication) confirm the high covalency of Fe-S bonds in pyrite. Since the Cu(II) absorption peak is not shifted to higher energies relative to the copper oxygenated-ligand complexes, it would seem that the Cu-S bonds in sphalerite are of low covalent character.

CONCLUSION

Interpretations of the absorption spectrum of Cu-doped sphalerite indicate that the Cu, as Cu(II) occupies the octahedral interstitial sites. The metal-sulphur bonds are of low covalent character.

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