OPTICAL ABSORPTION STUDIES OF THE MIXED-ION (Cu AND Al) DOPING OF SPHALERITE

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The theoretical and experimental aspects of *d-d* absorption spectra are now sufficiently well understood that spectrophotometry may be considered a useful tool in the diagnosis of the valence state and location of transition metal ions. The recent observation (Manning, 1966) of a well-defined absorption band with a maximum at 11,000 cm^{-1} in the spectrum of Cu-doped sphalerite was taken as evidence for the interstitial (octahedral) siting of Cu(II). Many earlier workers have used optical absorption methods to show that transition metals substitute for the parent metal ion in ZnS or CdS (Low & Weger, 1960; Pappalardo & Dietz, 1961; Pappalardo, 1961; Weakliem, 1961; McClure, 1963).

The aim of the present work is to determine whether the presence of other cations can influence the valence state or siting of Cu in sphalerite. Electron transfer (metal → Cu) and metal-metal ion pairing are two of the more obvious possible mechanisms. Aluminum has been chosen as the "other" metal because of its well known electron donor properties.

Experimental details

Synthetic crystals of ultra-high-purity sphalerite were coated with a film of the relevant metal in an Edwards High Vacuum Coating Unit Model 6E2. The coated crystals were annealed—at 500° C in some experiments and 800° C in others—in quartz tubes under 3 mm argon. Five hours were allowed for the thermal diffusion of both the Cu and Al at 800° C and one day at 500° C. The crystals were then lightly polished and examined spectrophotometrically. In this work, the ultra-high-purity sphalerite was doped first with Cu, and these dark-brown crystals were then doped with Al. Runs with three sphalerite crystals (denoted X, Y and Z) are described. A Cu-doped sample is designated X-1, and a Cu/Al-doped sample, X-2. The selected ultra-high-purity sphalerite crystals were colourless and showed a low degree of birefringence. No sphalerite-wurtzite twinning was observed. The crystals were purchased from the Eagle-Picher Company, Miami, Oklahoma.

Discussion of results

Extinction coefficients have been calculated from the expression

$$\epsilon = A/Cl$$

where A is the absorbance at peak maximum, C is the cation concentration in moles/litre and l is the crystal thickness in cm.

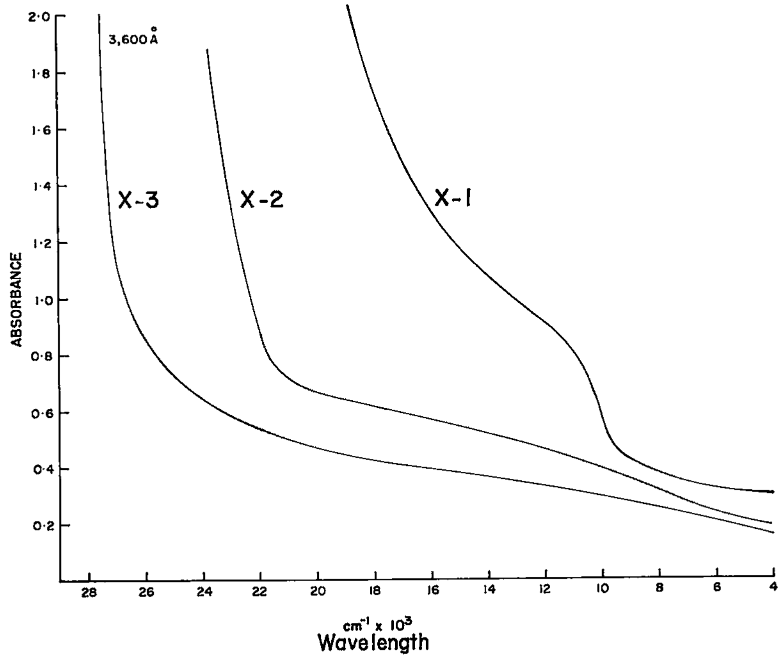

FIG. 1. Absorption spectra of sphalerites doped with Cu (X-1) and Cu-and-Al (X-2 and X-3). Crystal thickness = 1.25 mm. Concentration of Cu in all crystals = 0.009%. Concentration of Al in X-3 = 0.018% Temp. = 800° C.

Spectrum X-1 in Figure 1 is that of a Cu-doped sphalerite. The absorption band at ~11,000 cm^{-1} (900 mμ) is characteristically that of octahedrally-bonded Cu(II). The extinction coefficient of this band is ~100, a value that is reasonable for spin-allowed *d-d* bands. This ϵ value is somewhat greater than that measured earlier (Manning, 1966) for octahedrally-bonded Cu(II) in sphalerite. This variation in ϵ could indicate varying amounts of Cu(I) in sphalerite. The band marks the electronic transition $^2T_2 \rightarrow {}^2E(D)$. Tetrahedrally-bonded Cu(II) would be expected to have a stronger *d-d* band at ~6,000 cm^{-1} (Pappalardo & Dietz, 1961). The 11,000 cm^{-1} band in spectrum X-1 is superimposed on the shoulder of a more intense absorption that reaches into the red region of the spectrum. This intense band is very likely a manifestation of electronic transitions from the valence band to Cu(II) impurity levels, and accounts largely for the dark-brown colour of the crystals. The thinning of a dark-brown crystal by a factor of 5 showed that there was a uniform distribution of Cu in the crystal.

The doping of sample X-1 with Al gave a crystal of spectrum X-2. The 11,000 cm^{-1} Cu(II) band has disappeared and the absorption edge has moved to considerably higher energies. A fragment of crystal X-2 had an

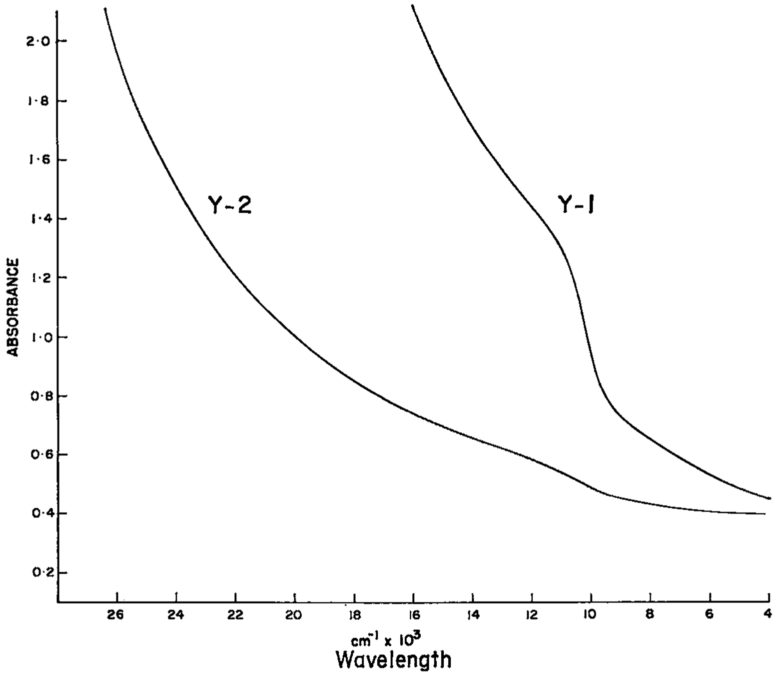

FIG. 2. Absorption spectra of sphalerites doped with Cu (Y-1) and Cu-and-Al (Y-2). Copper concentration = 0.018%. Crystal thickness = 1.25 mm. Temp. = 500° C.

aluminum content of ~0.008%. Spectrum X-2 is featureless apart from a very broad absorption in the visible region. This weak band was also observed in sphalerite doped only with Al, and we feel that this general absorption is unconnected with the Cu(II). Moreover, this band has none of the characteristics associated with Cu(II) *d-d* bands. For example, a weak Cu(II) *d-d* band is well resolved on a generally "sloping" background in spectrum Y-2 in Figure 2.

The Al doping of X-2 at 800° C gave a sphalerite of spectrum X-3 (Fig. 1). It is apparent that crystal X-3 is colourless and that the fundamental absorption edge is now close to that of undoped sphalerite. Furthermore, the general absorption in the visible is considerably weaker than in X-2. The thicknesses of samples X-1 and X-3 were 1.25 mm and 1.23 mm respectively, so that the thinning of the crystal may be ignored in comparing the spectra in Figure 1. There is no trace of the 11,000 cm^{-1} Cu(II) band in X-3. The Al content of X-3 is 0.018%. We may conclude, therefore, that the introduction of Al into a Cu-doped sphalerite causes a reduction of Cu(II) → Cu(I).

The spectra in Figures 2 and 3 tell a very similar story. Y-1 and Z-1 are the Cu-doped sphalerites and Y-2 and Z-2 are the Cu-and-then-Al-doped

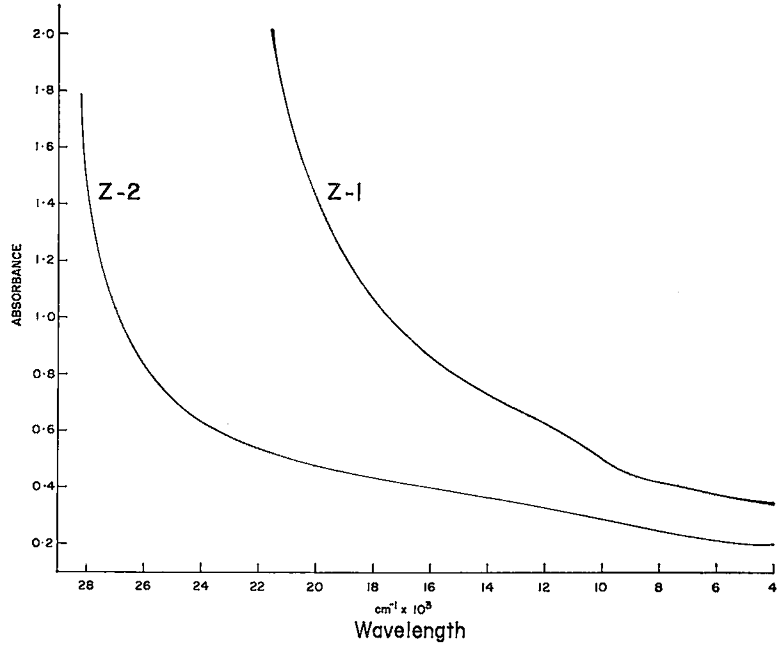

FIG. 3. Absorption spectra of sphalerites doped with Cu (Z-1) and Cu-and-Al (Z-2). Cu concentration = 0.005%. Al concentration = 0.013%. Crystal = 1.5 mm thickness. Temp. = 800° C.

samples. The intensity of the 11,000 cm^{-1} Cu(II) band in Y-2 is $\sim$20% of the same band in Y-1. In separate experiments, it was found that the Cu-doped sphalerites remained unchanged (spectrally) on re-annealing at 800° C for several days. This is to be expected because the Cu-doping experiments, themselves, involve an annealing treatment.

It would seem, therefore, that the doping with Al of a Cu-doped sphalerite causes the disappearance of the octahedrally-bonded Cu(II) band. Because no strong absorption appears at 6,000 cm^{-1} that can be attributed to tetrahedrally-bonded Cu(II) (Pappalardo & Dietz, 1961) it can be said that the octahedrally-bonded Cu(II) present in the Cu-doped sphalerite has been reduced to Cu(I) through the introduction of Al.

Because of its three valence electrons, Al often adopts the role of electron donor. The number of free electrons available per Al atom presumably depends on the location of the Al atom in the sphalerite crystal. For interstitially located Al, there will be three available electrons per atom, and for substitutional Al, one available electron per atom. Also, it is conceivable that a large fraction of the Cu in the originally Cu-doped sphalerite is Cu(I). It would seem, therefore, that it is not possible to determine unequivocally the number of electrons per Al atom donated to

Cu(II). Nevertheless, the spectra in Figure 1 and the chemical analyses of X-1 and X-3 indicate that at least one electron per Al atom is transferred to Cu(II).

The Cu(I) is probably located in a tetrahedral site. Tetrahedral is the preferred coordination of Cu(I) (Cotton & Wilkinson, 1967), and no authenticated octahedrally-coordinated Cu(I) complexes are known. In view of the highly covalent character of the bonds and also the stabilities of Cu(I) oxides and sulphides (Cotton & Wilkinson, 1967), it is probable that the Cu(I) is located substitutionally. The interstitial → substitutional exchange reaction could take place in a cation diffusion mechanism.

Based on the reactions suggested in this work, it would appear that Cu(II) in substitutional and interstitial sites in sphalerite is a strong electron acceptor. The role of such electron transfer reactions in determining the structures of copper sulphides might well be worthy of some study.

Conclusion

The doping with Al of a sphalerite containing octahedrally-bonded Cu(II) causes the reduction of Cu(II) to Cu(I). It is suggested that Cu(II) in substitutional and interstitial sites in sphalerite forms a strong electron acceptor state.

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