ABSORPTION SPECTRA OF Fe(III) IN OCTAHEDRAL SITES IN SPHALERITE

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ABSTRACT

Thin sections of natural Fe-containing sphalerite have been examined spectrophotometrically in the energy range 10,000–30,000 cm^{-1} (1μ–0.3μ). Specimens of 6.15 per cent Fe content (by weight) and of 100 micron thickness were a reddish-brown in colour. The thin sections were structurally isotropic showing no birefringence. The absorption in the specified energy range was resolved into a number of bands characteristic of octahedrally bound Fe(III). The presence of substitutional Fe(II) was confirmed by an intense absorption in the infrared at 3 microns, and it is concluded that the Fe is distributed between the interstitial (octahedral) and substitutional (tetrahedral) sites in sphalerite.

INTRODUCTION

The *d-d* absorption bands of Fe(II) in tetrahedral (substitutional) sites in sphalerite and CdS are observed in the infrared at ~3 microns (Low & Weger, 1960); Pappalardo & Dietz, 1961). These bands are sufficiently far out in the infrared that the crystals are colourless. However, sphalerites that have a high Fe content ($>1\%$) are black, while thin sections of the crystals are reddish-brown. The black sphalerites are remarkable in that large single crystals are readily available from natural sources.

Natural sphalerite crystals of low Fe content from Santander, Spain, were also studied. The crystals contained ~0.035 per cent total Fe and were orange to brown in colour. These colours are reminiscent of hydrolyzed Fe^{3+} in octahedral environments in aqueous solutions. It is conceivable, therefore, that the opacity of the Fe-containing sphalerites is due to octahedrally bonded Fe^{3+}, *i.e.*, interstitially located Fe^{3+}. However, Fe^{3+} in tetrahedral sites also absorbs strongly in the visible (Friedman, 1952). In this paper, therefore, thin sections of the Fe-containing sphalerites have been examined spectrophotometrically. The absorption bands in the visible region of the spectrum have been resolved and characterized so that the absorbing cation and its immediate environment can be deduced.

The present study is also of academic interest. Ballhausen (1962) has pointed out that a measure of disagreement exists among different authors on the assignments of bands in the absorption spectra of Fe^{3+} complexes. Ballhausen (1962) has reviewed the published data and his "composite"

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spectrum of octahedral Fe^{3+} is given in Table 1. We have been able to confirm Ballhausen's assignments.

EXPERIMENTAL PROCEDURES

Sphalerites of high Fe content were kindly donated by Dr. J. A. Mandarino of the Royal Ontario Museum, Toronto, Ontario. These black crystals originated from Timmins, Ontario (Museum Cat. No. M22550) and Chihuahua, Mexico (M 22377). Crystals of the Santander sphalerite were obtained from H. R. Steacy, curator of the National Mineral Collection, Geological Survey of Canada, Ottawa. Thin sections of the Timmins and Chihuahua sphalerites were structurally isotropic and showed no birefringence. *X*-ray powder diffraction patterns corresponded to sphalerite, and did not reveal the presence of any extra phases. Wet chemical and spectrographic analyses of these crystals are given in Table 2.

TABLE 1. ABSORPTION BANDS (cm^{-1}) OF OCTAHEDRALLY COORDINATED FE(III).

Excited level*	Ballhausen (1962)	Dvir & Low (1960)	Schlaefer (1955)	Rabinowitch & Stockmeyer (1942)
$^4T_{1g}$	12,300		12,000	
	14,200	14,200		14,300
$^4T_{2g}$	17,500	17,500	18,500	18,200
	20,000	20,000		
$^4E_g, {}^4A_{1g}$	23,000	23,600	24,500	24,600
$^4T_{1g}$	26,500	26,500		
		(27,300)	(27,500)	

*For energy level diagrams, see Tanabe & Sugano (1954).

TABLE 2. ANALYSES OF NATURAL SPHALERITES, WEIGHT PER CENT

Impurity	Chihuahua	Timmins
Cd	0.62	0.26
Fe	14.35	6.15
Mn	0.50	n.d.
Co	n.d.	n.d.
Ni	n.d.	0.005
Cu	0.005	n.d.
Ca		0.03
Mg		0.01
Si		0.48

n.d. = not detected.

Crystal slabs of size 5 cm × 1 cm × 1 mm were cut from the parent crystals by means of a 0.003 inch tungsten wire saw. One side was polished and mounted, in transparent cement, on quartz slides. The open side was then polished down to the desired thickness. The crystals were of sufficiently good quality that 20μ sections could be easily obtained. The absorption spectra were determined using a Beckman DK2A spectrophotometer. Crystals of 100μ thickness were reddish brown, and a number of peaks in the red end of the spectrum were resolvable. The higher-energy peaks were resolved by the further thinning down of the sections. The spectra were run at room temperature.

RESULTS AND DISCUSSION

Figures 1 and 2 show the spectra of thin sections of the Timmins sphalerite (6.15 per cent Fe by weight). The Chihuahua material (14.3 per cent Fe) gave a similar absorption spectrum, indicating that the

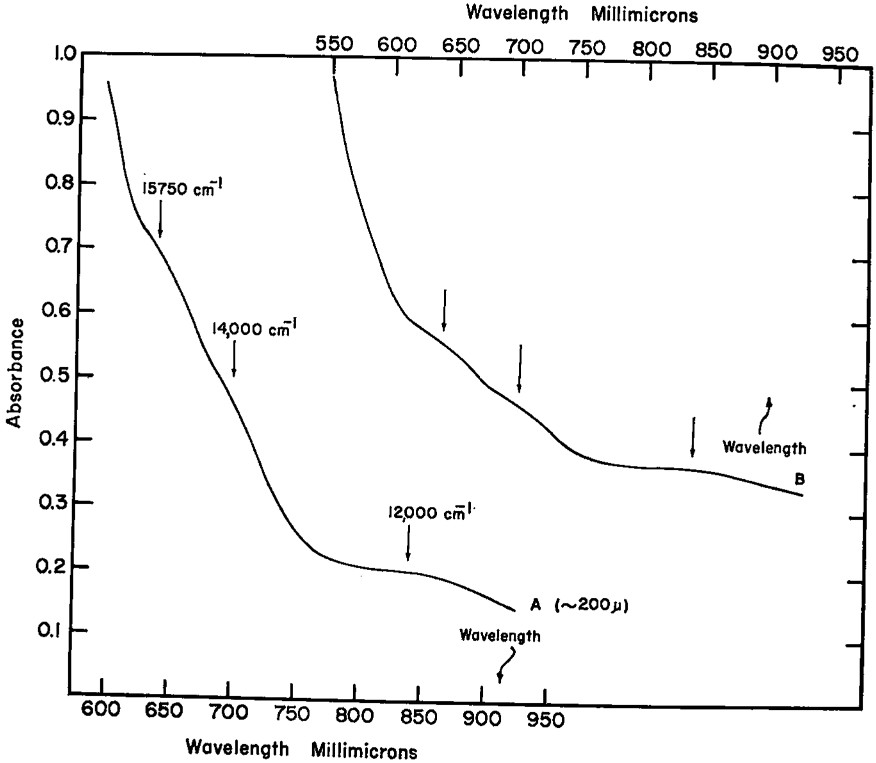

FIG. 1. Absorption spectra of Timmins sphalerite. Energy range 10,000–16,000 cm^{-1}.

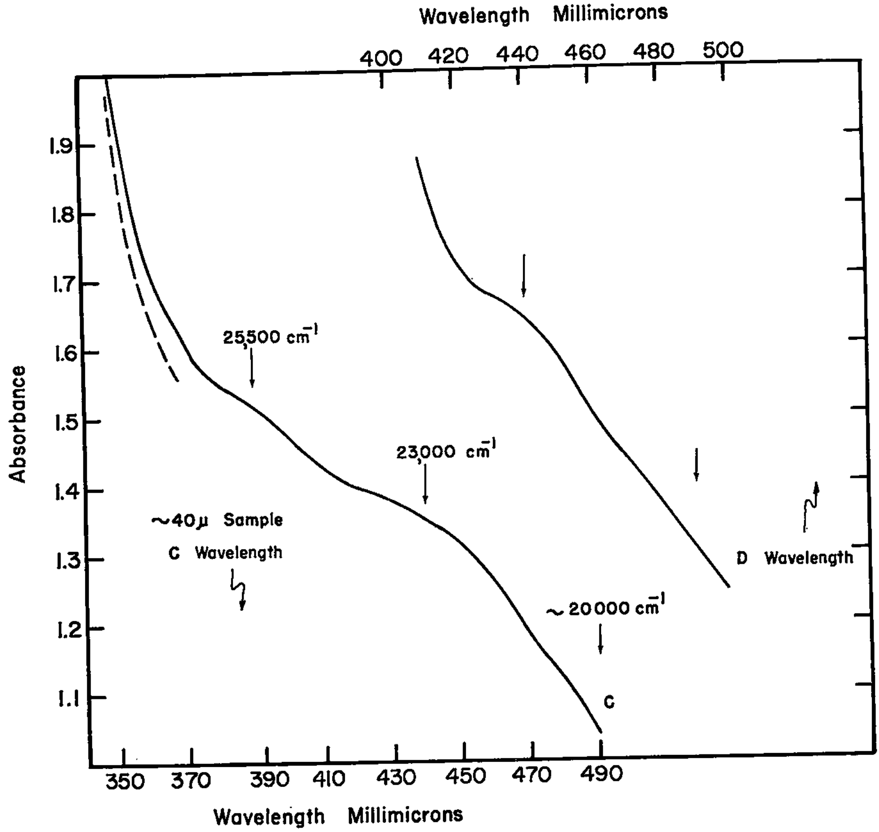

FIG. 2. Absorption spectra of Timmins sphalerite. Energy range 20,000–30,000 cm^{-1}.

absorption bands are those of a single absorbing species. The absorption spectra have been reported in two Figures so that the finer details of the spectra may be more readily observed. An intense absorption in the infrared at 3 microns has not been included in these Figures. The band is characteristically that of Fe(II) in tetrahedral S sites, and its features are similar to those described earlier in detail for tetrahedrally bound Fe in sphalerite (Low & Weger, 1960) and CdS (Pappalardo & Dietz, 1961). The band shows that Fe is present as Fe(II) in the substitutional sites.

Because Fe is the principal transition metal impurity, we are justified in attempting to correlate, initially, the observed spectra (Figs. 1 and 2) with octahedrally or tetrahedrally bound Fe. Other cations isoelectronic with Fe(II) and Fe(III) are Co(III) and Mn(II). Co(III) complexes, with very rare exceptions, are octahedral (Ballhausen, 1962), and diamagnetic $Co(OH_2)_6^{3+}$ has a two-band *d-d* spectrum. For CoF_6^{3-}, a high-spin complex, a broad band split into two distinct peaks is observed (Ballhausen, 1962). Hence, we may conclude that the spectra reproduced in Figs. 1 and 2 are not due to Co(III). Mn(II) in octahedral sites may be eliminated because of both the extreme weakness of Mn bands and the low Mn:Fe ratio of the crystals. The spectra in Figs. 1 and 2 are quite different from a typical spectrum of Mn^{2+} in tetrahedral sites (Cotton & Wilkinson, 1962).

Let us consider the details of the spectra reported in Fig. 1. Three peaks are apparent in both A and B, with energies of 12,000, 14,000 and 15,750 cm^{-1}. These bands are reasonably well resolved at room temperature. Fe(II) in an octahedral cage of six oxygens has a band at ~10,000 cm^{-1}, but no band was observed at this or some slightly smaller energy in our spectra. The absorptions in Figs. 1 and 2 would therefore seem to be due to Fe(III).

Pappalardo & Dietz (1961) and Manning (1966) have demonstrated that the S ligand field is slightly weaker than that of O, and that *d-d* bands for cations in S environments are observed at lower energies. The three bands at 12,000, 14,000 and 15,750 cm^{-1} in our spectra (Fig. 1) correlate well with the three lowest energy bands for octahedrally bound Fe(III) listed in Table 1. It is possible that the energy differences for the two lowest energy bands may be within the experimental error in the determination of the peak maxima. The band at 15,750 cm^{-1} is clearly displaced to a much lower energy.

Figure 2 shows resolved bands at the higher energy end of the spectrum. The fundamental absorption edge of the Timmins sphalerite (dotted line) corresponds reasonably well with that of an ultra-high-purity sphalerite crystal (purchased from Eagle-Picher Inc., Miami, Oklahoma). The observed band gap is ~3.5 ev. This "cut-off" is, of course, the upper limit of our spectral investigation. The three resolved bands at ~20,000, 23,000 and 25,500 cm^{-1}, correlate excellently with the higher energy bands of Ballhausen's tabulation in Table 1, namely, 20,000, 23,000 and 26,500 cm^{-1}. It is readily evident, therefore, that the absorption bands in the spectra of the Fe-containing sphalerites, either in or flanking the visible region, are entirely compatible with the spectra of octahedrally coordinated Fe(III).

It should be noted that Fe(III) spectra contain charge-transfer bands of considerably greater intensity than *d-d* bands. The weaker *d-d* bands will, therefore, be superimposed on the charge-transfer bands. If we assume that all the Fe in the Chihuahua crystal is present as Fe(III), the extinction coefficient (ϵ) of the 12,000 cm^{-1} band is ~1. This ϵ value is, of course, a lower limit, but if 2 per cent of the Fe is Fe(III), $\epsilon \sim 50$.

Both of these ϵ values are reasonable for *d-d* bands. However, all Fe(III) *d-d* bands are theoretically spin-forbidden, because the ground state ^6S is the only sextuplet term. The 12,000 cm^{-1} band is approximately three orders of magnitude less intense than the absorption band at 3μ that is characteristic of tetrahedral Fe(II). The absorption bands in Figs. 1 and 2 are, therefore, most certainly *d-d* bands. The relative intensities of the 12,000 cm^{-1} and 3μ bands are readily comprehensible on the basis of cation symmetry and the spin-forbidden nature of the Fe(III) bands. Because the extinction coefficient is likely to be closer to 1 than 50, it would seem that $\sim$10% of the total Fe is present as interstitial Fe^{3+}. We hope to carry out precise chemical analyses of these sphalerites in the near future.

The absorption spectrum of Fe(III) in tetrahedral sites differs from that of Fe(III) in octahedral fields (Friedman, 1952). The difference is typified by a relatively strong absorption at 19,000 cm^{-1} in tetrahedral systems that is missing in our spectra and also the spectra of octahedral $FeCl_3.aq$ complexes.

The electronic configuration of the ground state of Fe(III) in octahedral O fields is $t_{2g}^3e_g^2$. The electronic configurations of the first two excited states ($^4T_{1g}$ and $^4T_{2g}$) are $t_{2g}^4e_g^1$, so that a Jahn-Teller splitting (Jahn & Teller, 1937) can be expected. The spectral assignments made in Table 1 are based on a Jahn-Teller mechanism being operative. Cotton & Meyers (1960) have investigated the Jahn-Teller splittings of excited states of Fe(II) and Co(III) complexes, and showed that the energy splittings were $\sim$2,000–3,000 cm^{-1}. The difference in energy between the 12,000 and 14,000 cm^{-1} bands falls nicely into the above energy range. For the 15,750 and 20,000 cm^{-1} bands, however, the energy difference ($\sim$4,000 cm^{-1}) seems rather large, but Jahn-Teller splittings of this magnitude are known (Ballhausen, 1962). The 20,000 cm^{-1} band is weak and its precise energy is rather difficult to estimate. The four lowest energy bands in our spectra are associated with the transitions $^6A_1 \rightarrow {}^4T_{1g}$ and $^6A_1 \rightarrow {}^4T_{2g}$, both of the excited states being split. The 23,000 and 25,500 cm^{-1} bands correspond to electron excitation to the $^4E_g/^4A_{1g}$ and $^4T_{1g}$ levels. We also found in our thinner sections a band at $\sim$27,000 cm^{-1}, which could be due to the transition $^6A_{1g} \rightarrow {}^4T_{2g}$. This particular band is difficult to observe because of its proximity to the fundamental absorption edge. The facile manner in which the absorption spectra in Figs. 1 and 2 can be interpreted in terms of Ballhausen's tabulation (Table 1) and an operative Jahn-Teller mechanism leads us to conclude that Fe(III) is located in interstitial octahedral sites in sphalerite. Jahn-Teller splittings are extremely small and usually not observed in tetrahedrally bound cation systems.

In an earlier publication (Manning, 1966) that described the doping of synthetic ultra-high-purity sphalerite with Cu, it was shown that the Cu was located interstitially as Cu(II). We have repeated the doping experiments using Fe, but the rate of diffusion of Fe into sphalerite at 800° C seemed insufficiently great (4 days baking) to allow the resolution of any *d-d* bands characteristic of either substitutional or interstitial Fe. It is of interest to note, nevertheless, that interstitial cations have now been observed in both synthetic (Cu) and natural (Fe) sphalerites.

The colours of thin sections of the Timmins and Chihuahua sphalerites were similar to the brown of the Santander sphalerite. We would suggest, therefore, that the brown colour for the familiar Santander sphalerite and for sphalerites in general may be associated with interstitial Fe^{3+}. The brown colour is due to preferential absorption of light in the blue-green region as is depicted in Fig. 1.

It is conceivable that the presence of interstitial Fe(III) could affect the sphalerite cell dimensions, and the greater the Fe(III) content the greater the cell distortion. If the Fe(III):Fe(II) ratio does not remain constant for all sphalerites, the direct application of the Kullerud (1953) "sphalerite geothermometer" to practical problems could lead to misleading conclusions.

CONCLUSIONS

The absorption spectra of Fe-containing sphalerites suggest that Fe is distributed between the tetrahedral substitutional sites and the octahedral interstitial sites. The valence states of Fe are 2 in the former and 3 in the latter, and the Fe(II):Fe(III) ratio is $\sim$10.

The brown or reddish brown colour of natural sphalerites would seem to be due to interstitial Fe(III).

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