1182. *Electrical and Optical Properties of Crocidolite and Some Other Iron Compounds*

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The variation of the electrical resistance with temperature has been measured for several samples of the mixed-valent iron-containing mineral crocidolite. The conductivity depends on the ratio Fe(II) : Fe(III) and on the treatment of the compound. Conductivity is associated with the Fe(II)–Fe(III) interaction, which also gives rise to a prominent charge-transfer band in the absorption spectrum. Charge-transfer bands are also found in the complex $[Fe(II)(bipyridyl)_3]^{2+}$, but the conductivities of its salts, even with oxidising anions, are very low.

THE mixed-valent oxide Fe_3O_4 is a good semiconductor. Its absorption spectrum is a broad band covering the whole of the visible spectrum. It is of interest to discover how the conductivity, and the colour, in similar mixed-valent compounds depends upon the Fe(II)–Fe(III) distance. Therefore we have examined the properties of minerals related to crocidolite, which has the idealised formula $Na_2Fe(III)_2[Fe(II),Mg]_3Si_8O_{22}(OH)_2$.[1]

In a previous Paper [2] we showed that $Tl_3[Fe(CN)_6]$ is a good semiconductor. We now report the examination of other iron compounds which contain both an oxidising ion, *e.g.*, $Cr_2O_7^{2-}$ and $[IrCl_6]^{2-}$, and a reducing cation, $[Fe(II)(bipyridyl)_3]^{2+}$.

EXPERIMENTAL

Materials.—The crocidolite samples were supplied by Dr. W. E. Addison. Their analyses are given in ref. 1. Table 1 gives the Fe(II) : Fe(III) ratio.

TABLE 1

	R.S. 8	R.S. 10	Bolivian *
% Fe(II)	15·65	15·77	3·05
% Fe(III)	12·38	13·32	10·91
Ratio Fe(III) : Fe(II)	1 : 1·265	1 : 1·182	1 : 0·279

* Notation of J. J. Le R. Cilliers, A. G. Freeman, A. Hodgson, and H. F. W. Taylor, *Econ. Geol.*, 1961, **56**, 1421.

A stock solution of $[Fe(II)(bipyridyl)_3]SO_4$ was made by shaking 2,2′-bipyridyl with aqueous ferrous ammonium sulphate in the correct proportions.[3] Addition of barium chloride precipitated barium sulphate, which was filtered off, and an aqueous solution of $[Fe(II)(bipyridyl)_3]Cl_2$, from which crystals were grown by slow evaporation. The corresponding bromide and iodide were made in a similar way. Addition of concentrated aqueous solutions of K_2PtCl_6, Na_3IrCl_6, $K_2Cr_2O_7$, and $KClO_4$ to the stock solution precipitated the other complex salts which were crystallised from very dilute aqueous solutions.

Spectra.—Reflection spectra were measured with a Unicam S.P. 500 spectrophotometer with reflection attachment. Potassium bromide (1 g.) was ground for 1 hr. with $[Fe(II)(bipyridyl)_3]X$ (see Table 2) (1 mg.) or crocidolite (4 mg.). Potassium bromide, similarly ground, was used as a reference.

Conductivity.—Crocidolite resistances were measured in a heated evacuated glass tube using an E.I.L. 20 million megohmmeter. Samples were attached, using silver paste, to one flexible and one large copper electrode. The latter acted as a heat sink and held a copper–constantan thermocouple. Resistances of the $[Fe(II)(bipyridyl)_3]^{2+}$ salts were measured in an enclosure insulated with Teflon, capable of evacuation, and surrounded by an earthed shield, using an E.I.L. vibrating reed electrometer model 33C.

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[1] C. C. Addison, W. E. Addison, G. H. Neal, and J. H. Sharp, *J.*, 1962, 1468.

[2] P. S. Braterman, B. P. B. Phipps, and R. J. P. Williams, *Proc. Chem. Soc.*, 1963, 12.

[3] P. Blau, *Monatsh.*, 1898, **19**, 647.

RESULTS

The absorption spectra of different samples of the minerals are shown in Figure 1. In addition to the typical charge-transfer band of Fe(III) in an oxide lattice, at 330 mμ, there is a new band at 620 mμ. The intensity of the new band depends on the Fe(II) content at approximately constant Fe(III) content, as shown by the comparison between R.S. 8 and R.S. 10, and the Bolivian crocidolites. On heating in oxygen, which is known to convert Fe(II) into Fe(III) even in the interior of the samples,[1] the blue band disappears (Figure 1). We assign the blue band to the transition Fe(II) $\curvearrowright$ Fe(III). The fibres are dichroic, indigo along the needle axis and blue-green across it.

A typical series of observations on the variation of the conductivity of crocidolites with temperature is shown in Figure 2. The measurements were made along the fibre direction. At high temperatures the data are highly reproducible and the activation energy (16 ± 1 kcal.mol.$^{-1}$ for conduction), which was measured on four separate occasions for each of the three samples, is independent of the sample, and of its treatment. The repeated cycling of the sample from low to high temperatures at a pressure of 3 τ brings about definite changes in the conductivity at low temperatures, and the plot of log(resistance) against $1/T$ finally shows two branches of activation energy, 7·5 ± 1·0 and 16·0 ± 1 kcal. mole^{-1}. The cause of the irreversible change is understandable from observations [1] that the samples become preferentially oxidised on the surface. This is confirmed by the reflection spectra of heated samples which have a brown appearance. The chemical nature of the changes will be disucssed below.

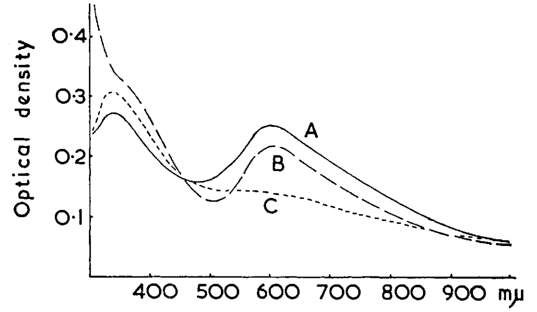

FIGURE 1. The effect of changing Fe(II) content on the crocidolite reflection spectra. A, R.S. 8 and R.S. 10; B, Bolivian; C, R.S. 8 and R.S. 10 after repeated cycling

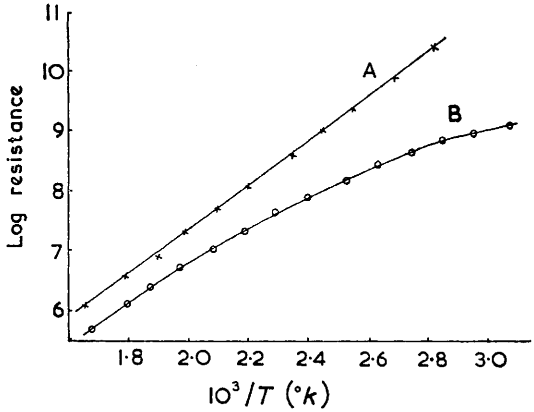

FIGURE 2. Typical plot used for obtaining the activation energy for conduction. A, Initial run; B, final run. The final run is the fifth cycle of the crocidolite over the temperature range

The specific resistances at 500° were R.S. 8 and R.S. 10 10^9 ohm cm.$^{-1}$ and Bolivian 10^{10} ohm cm.$^{-1}$. Conductivity across the fibre direction was very low

The absorption spectrum (Table 2) of $[\text{Fe(II)(bipyridyl)}_3]^{2+}$ is hardly affected by crystallisation with I^-, ClO_4^-, $IrCl_6^{2-}$, SO_4^{2-}, or $Cr_2O_7^{2-}$. There are no bands in the spectra of the compounds which cannot be attributed to the separate ionic species. The conductivity of samples prepared from solvents containing no water was immeasurably small. Hydrated samples were

TABLE 2

Reflection and solution spectra of [Fe(II)(bipyridyl)$_3$]X (mμ)

Reflection					Solution
X = $(I^-)_2$	$(ClO_4^-)_2$	$IrCl_6^{2-}$	SO_4^{2-}	$Cr_2O_7^{2-}$	All anions
520	525	520	520	520	516
490sh	500sh	495sh	497sh	494sh	490sh
355	355	350	355	355	350
315	315	315	315	312	298
290	290	290	290	295	288
253	247	247	250	263	247

better conductors, but this conductivity is likely to be due to water, and the compounds were not studied further.

DISCUSSION

The relative dispositions of the atoms of interest in crocidolite are shown in Figure 3. There are two Fe(II)–Fe(III) distances of 3·11 Å along the axis and 3·25 Å perpendicular to it. Both conductivity and the charge-transfer adsorption are clearly related to the Fe(II)–Fe(III) chains along the fibres. The activation energy for conduction is independent of the Fe(II) content but the specific conductivity falls as Fe(II) is replaced by Mg(II).

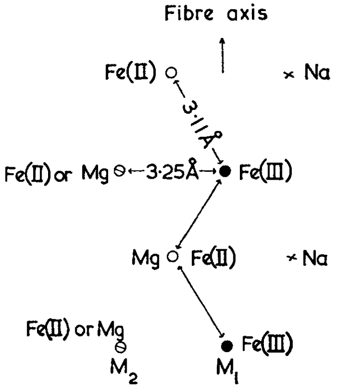

FIGURE 3. Chains of metal ions in crocidolite

When the ratio of Mg(II) to Fe(II) exceeds 5, as in the Bolivian sample it is not possible for any chain of $M_1 \cdots M_2$ or $M_1 \cdots M_3$ to be an unbroken succession of Fe(II) ⋯ Fe(III). Thus, the conduction depends on the presence of Fe(II)–Fe(III) pairs but not on a continuous series of such pairs. The charge carriers are not electrons travelling 3·11 Å from ion to ion but must be able to migrate at least twice this distance. Now the structure contains O^{2-} and OH^- groups. A possible mechanism for conduction is then:

$$Fe^{3+}\ O^{2-}\ H\overset{-}{O}\ Fe^{2+} \longrightarrow Fe^{2+}\ O^-\ H\overset{-}{O}\ Fe^{2+} \longrightarrow Fe^{2+}\ O\overset{-}{H}\ O^-\ Fe^{2+} \longrightarrow Fe^{2+}\ O\overset{-}{H}\ O^{2-}\ Fe^{3+}$$

This mechanism involves the transport of H. Evidence in favour of such a mechanism comes from the similarity of the activation energy of conduction (16 kcal. mole^{-1}) to that of oxidation of crocidolite (21 kcal. mole^{-1}) which is known to involve hydrogen-atom transport.[1] A very similar mechanism for Fe(II)–Fe(III) exchange in water or ice has an activation energy of 8·2 kcal. mole^{-1}. A second possible mechanism involves electron transfer along the silicate chain.

The activation energy for conduction characteristic of the oxidised state (7·5 kcal. mole^{-1}) is too low to be due to a pure surface layer of Fe_2O_3 (12·7 kcal. mole^{-1}) [4] but would be reasonable for a layer of Fe_2O_3 + Fe(II).

The absence of charge-transfer bands and of conductivity in crystals containing

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[4] G. Martinet, *Compt. rend.*, 1952, **234**, 2167.

[Fe(II)(bipyridyl)$_3$]$^{2+}$ and oxidising anions, *e.g.*, [IrCl$_6$]$^{2-}$, is surprising. Electron spin resonance data show that there is considerable spin density on the Cl atoms, and similar measurements on [Fe(bipyridyl)$_3$]$^{3+}$ show the presence of unpaired electrons in the ring. Moreover it has been observed[5] that the oxidation of [Fe(II)(4,7-dimethyl-1,10-phenanthroline)$_3$]$^{2+}$ by IrCl$_6$$^{2-}$ is very fast, being virtually diffusion-controlled. These observations suggest that either electron-transfer takes place by way of the solvent, water, or that a special stereochemical relationship between the two ions must be achieved before reaction will take place. In support of the first mechanism it is known that [Fe(III)(*o*-phenanthroline)$_3$]$^{3+}$ oxidises OH$^-$ rapidly. In either event, activation energies of redox reactions in solution become complex quantities, not open to simple discussion in terms of the stabilisation of the different valence states in their respective complexes.

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[5] J. Halpern, R. J. Legare, and R. Lumny, *J. Amer. Chem. Soc.*, 1963, **85**, 680.