Charge Transfer in Solid Chlorocuprates(I, II)

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INORGANIC ionic solids containing oxidizing anions and reducing cations have absorption bands which have been assigned[1,2] to charge transfer from the cation to the anion. Thermally-activated charge transfer, detectable as semiconductivity, was also recently observed[2] in one such solid, thallous ferricyanide. In ionic solids, both thermal and photochemical electron transfer is likely to take place with the smallest energy expenditure when the same element is present in two valence states, and we have therefore examined the light-absorption and semiconductivity of a series of hexamminecobalt(III) chlorocuprates(I,II) first prepared by Mori.[3] These compounds offer the exceptional advantage of a continuous variation in mole fraction of each valence state, with only minor structural changes.

The cupric salt $Co(NH_3)_6CuCl_5$ is orange–yellow, the colour of the cation, since the ligand-field absorption of $CuCl_5^{3-}$ lies in the near-infrared region.[4] The anion of the cuprous salt $[Co(NH_3)_6]_4Cu_5Cl_{17}$ has no absorption in the visible region, and the crystals are also orange–yellow. In contrast, the mixed-valence chlorocuprates range from orange–brown to black, owing to the presence of a new absorption band at about 17 kK. To estimate the variation of intensity of the new absorption band with the mole fractions of the two valence states, we have measured diffuse reflectance spectra using carefully controlled grinding to obtain equal particle sizes. Figure 1 shows values of the well known Kubelka-Munk function,[5] which is proportional to the absorption constant, plotted at various wavelengths againist the mole fraction of Cu^I. Both in the near-infrared and in the ultraviolet regions, where absorption is due to the Cu^{II} species alone, the plots are monotonic functions of the mole fraction, but in the visible region the absorption is most intense when the two valence states are present in equal amounts. If the intensity were proportional to the product of the mole fractions, the curve would be a parabola, and such a function fits the data quite well (see Figure 1). The absorption therefore involves collective excitation of a chlorocuprate(I) and a chlorocuprate(II) group, and we assign it to an intermolecular charge transfer from the former to the latter. A similar dependence of "interaction absorption" on composition has been found for Cu^I and Cu^{II} [6] and Sb^{III} and Sb_V [7] in HC lsolution, though in neither case was the structure of the interaction complex conclusively established.

The volume resistivities of the salts have been

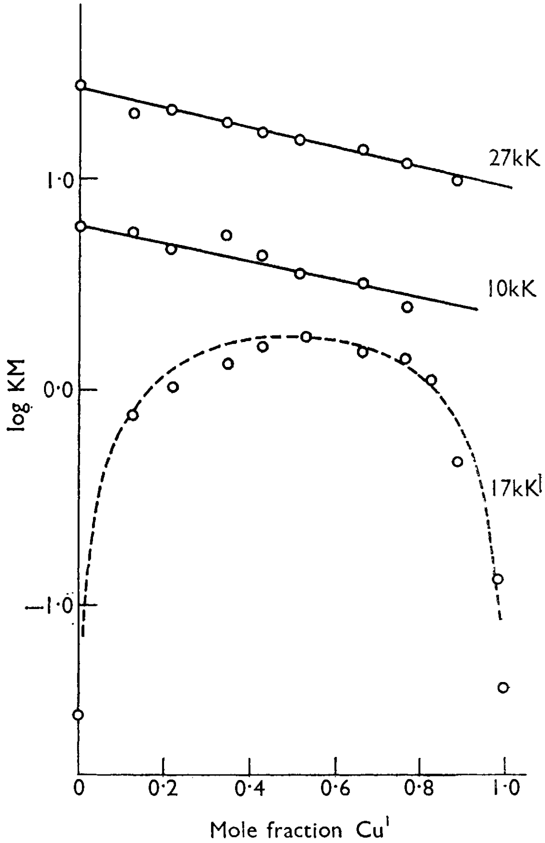

FIGURE 1. *Absorption intensity and composition of mixed-valence chlorocuprates.*

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[5] G. Kortum, *Trans. Faraday Soc.*, 1962, **58**, 1624.
[6] H. M. McConnell and N. Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 3168.
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measured *in vacuo* at room temperature, in the form of compressed pellets and single crystals. Both single-valence salts were extremely non-ohmic and showed polarisation effects characteristic of ionic conductivity, in contrast to the mixed-valence salts, which obeyed Ohm's Law quite accurately. The conductivity (and the light-absorption intensity) varied with composition in a strikingly similar way (Figure 2). All the mixed-valence salts behaved as semiconductors, with activation energies almost independent of composition (6·0—7·5 kK).

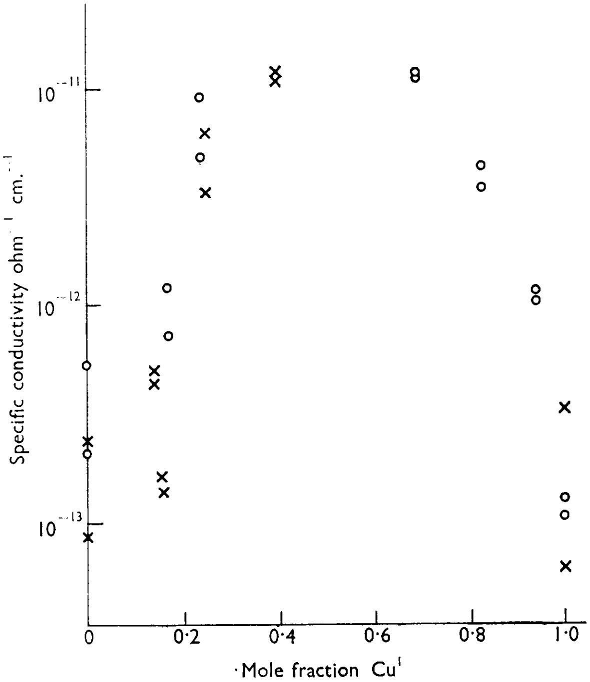

FIGURE 2. *Conductivities of mixed-valence chlorocuprates.* × = *single crystals*; ○ = *pellets.*

It is interesting that the energy required for thermally-activated charge transfer is only about one third of that required for the photochemical process, a situation previously found in thallous ferricyanide and well known in the simplest mixed-valence semiconductor, lithium-doped NiO. This reflects the fact that if two potential-energy surfaces interact above their minima, the adiabatic path from one minimum to the other always requires less energy than a vertical (Franck–Condon) transition followed by a vibrational relaxation. In both of the latter examples quoted, the electron transfer is of the "inner-sphere" type, in that a single group (CN^- or O^{2-}) bridges the metal ions which are oxidized and reduced. The chlorocuprates(I,II) and the hexachloroantimoniates(III,V)[8] provide examples of "outer-sphere" electron transfer in the solid state. As more detailed structural information becomes available, it may be possible to correlate the rates of electron transfer in the solids revealed by conductivity measurements with those found by other methods in solution.[9]

(*Received, August 24th,* 1965; *Com.* 539.)

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