Reactivity and Catalytic Activity of Copper Chlorides

Part 4.—Electrical Properties and Acceptor Levels Produced in CuCl by Cl_2 Gas

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Studies of electrical conductivity, thermoelectric power and transport numbers in CuCl, pure or after exposure to Cl_2 gas, in the range 24-240°C, have shown that all phenomena observed are caused by electronic rather than ionic conduction, except in pure CuCl above about 140°C. Two acceptor levels are identified, at 0.51 and 0.88 eV above the valence band. The former is attributed to cation vacancies; the latter, tentatively, to anion interstitials. For high concentrations of cation vacancies, the conduction below 100°C is predominantly by electrons in a narrow band at the acceptor level, the activation energy of this " hopping " process being 0.36 eV. The difference between the two acceptor levels is briefly discussed in terms of ligand field splitting of the Cu $3d$ orbitals.

The first three parts of this series [1-3] were concerned with some properties of a heterogeneous $CuCl/CuCl_2$ system (" $CuCl_x$ ") produced from CuCl and Cl_2 gas. For most properties, the main interest lay in the highly defective $CuCl_2$ phase. But the electrical conductivity of CuCl is much greater than that of $CuCl_2$. For this property alone of those studied previously, the experimental evidence related mainly to the CuCl phase.

At high extents of reaction with Cl_2, an apparent activation energy of 0.9 eV was tentatively attributed to ionic conduction.[3] In the present paper, this assignment is changed to acceptor-controlled positive hole conduction. At low extents of chlorination, an activation energy of 0.34 eV was found from 24°C to very roughly 100°C. A change above 100°C was not fully characterized in the previous work, which was not pursued above 160°C. In the present paper, a more complete study has been made up to 240°C. Thermoelectric power data have also been obtained, and have proved very significant in arriving at detailed explanations of various values of the apparent activation energy between 0.55 eV and about half that value (all of which had been reported by other workers [4, 5] but neither characterized in relation to sample purity nor explained beyond a general assignment to positive holes).

EXPERIMENTAL

MATERIALS

Copper(I) chloride (Fisher A.C.S.) was dissolved in 6 M HCl, precipitated with water, washed with acetone, dried at 40°C, evacuated for 10 h and sublimed four times *in vacuo*. In the well-studied region of ionic conduction above 200°C, this material reproduced very closely the conductivity behaviour reported for zone-refined CuCl [6] and for CuCl prepared from the elements [7]; see fig. 1.

Chlorine (Matheson, 99.5 %) was dried with two sulphuric acid traps. Non-condensable gases were pumped off, after freezing, before and after drying.

Reaction of CuCl with Cl_2 was conducted at 24°C up to 2 % reaction ($CuCl_{1.02}$) and at 130°C for higher extents of reaction. Extent of reaction was found from the weight increase of the solid.

Pellets, area 1.326 cm², weight 1.5-2 g for conductivity and 4-6 g (length 1-1.5 cm) for thermoelectric power, were pressed (8000 p.s.i., 3 min) from finely ground CuCl or $CuCl_x$. In the latter case, water vapour was excluded and the powder dried at 100°C for several hours. Pellets could be stored in a desiccator for weeks with no change in their electrical properties.
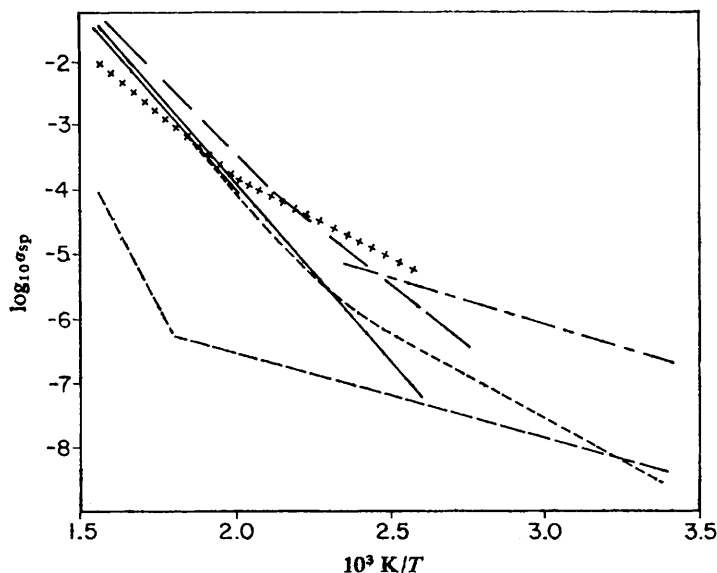

FIG. 1.—Previous and present conductivity data for CuCl. Solid lines: shorter line, Wagner and Wagner[7]; longer line, Hsueh and Christy.[6] Long dashes, Tubandt.[8] Medium dashes, Maidanovskaya, Kirovskaya and Lobanova.[5] Shortest dashes, this work (fig. 2). +++, Bradley, Munro and Spencer.[4] Alternating dashes, Harrison and Ng.[3]

APPARATUS AND PROCEDURES

Conductivity was measured by connecting the sample in series with a standard resistance (Keithley decade shunt, 10^3-10^{12} ohm, or other standards down to 10 ohm), applying a potential difference (d.c. or a.c., usually about 1.2 V) with dry cells or a 200 Hz oscillator, and measuring the p.d. across the standard with a Keithley 200B electrometer (10^{14} ohm at input) or, for a.c., a Hewlett-Packard 403A a.c. voltmeter. The upper limit of a.c. resistance measurements was 10^6 ohm. D.c. conductivities were taken as averages before and after reversing the applied p.d. Electrodes were of bright Pt, mounted in fired lava. Blank resistance of the cell (Teflon sample) was 2×10^{12} ohm. One electrode comprised an inner disc and guard ring, to check surface conductivity. When Ag or Cu electrodes were used, they were inserted between Pt electrodes and pellet. A Pt/10 % Rh thermocouple lead was attached to one electrode. The cell was enclosed in a high vacuum system and the entire circuitry in a grounded copper box.

Thermoelectric power was measured in a Teflon cell with Pt electrodes and a Pt/10 % Rh thermocouple lead on each. The furnace was wound to give a temperature difference along the sample of about 6° at mean 40°C and 30° at mean 240°C.

Transport numbers were found by a gravimetric method, analogous to the Hittorf method for solutions. The conductivity cell was in series with an Ag coulometer, and 0.5 to 22.5 V was applied. For pure CuCl, anion migration was assumed absent [8] and transport numbers t_+(cations) and t_e(electrons) were found by using Cu electrodes and comparing Cu transferred

with electricity passed. For $CuCl_x$ (which is reduced by Cu electrodes), three pellets were stacked between Pt electrodes. From the changes in weight of the pellets, t_+, t_- and t_e can be found.

For pure CuCl, a method due to Wagner [7, 9] was also used. P.d.'s of 0.4 to 0.8 V were applied across a cell Pt|CuCl|Cu so as to drive Cu away from the Pt electrode. Cationic conduction should be suppressed and the electronic component observed by itself, modified to non-ohmic behaviour.

The Hall effect was sought, but found to be absent (sensitivity 0.2 μV for 22.5 V applied) from all samples. Several sample shapes were tried, concluding with a square sample (large-area Pt current electrodes, point Pt Hall probes mounted on screws) for maximum sensitivity. An electromagnet with 11 cm pole pieces (gap 3 cm) gave up to 2000 G, p.d.'s up to 22.5 V were applied from dry cells, currents were measured with Keithley shunt and electrometer and the Hall e.m.f. was sought with a Hewlett–Packard 425A d.c. microvoltmeter.

RESULTS

PURE CuCl

CONDUCTIVITY

A plot of $\log_{10}\sigma_{sp}$ against $1/T$ is shown in fig. 2 for a typical sample out of a total of seven samples studied. (σ_{sp} is specific conductance.) A.c. data are shown down to 130°C, and d.c. data below that temperature. Surface conduction was found to be insignificant throughout. Changing the electrode material (Cu, Ag or Pt) had no effect on any a.c. data or on d.c. data at low temperatures. But above about 190°C, d.c. conductivity with Cu electrodes was about 10 % below a.c. conductivity, and replacement of the electrodes by Ag or Pt caused the d.c. value to fall further by roughly 40 % and 80 % respectively. This may represent a tendency, when inert electrodes are used, for ionic carriers to be suppressed. Such an effect is rendered complete and used to advantage in the Wagner [7, 9] method of determining the electronic transport number.
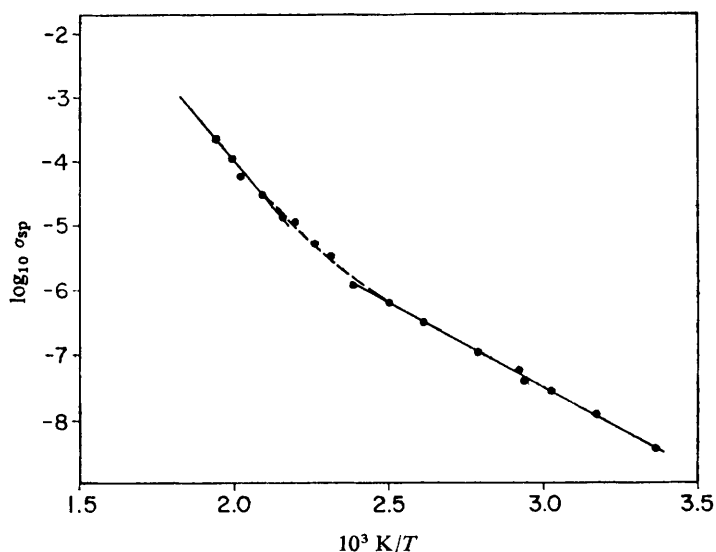

FIG. 2.—Conductivity data for pure CuCl, this work. The broken line is the calculated sum of conductivities from the two linear portions extrapolated.

The results (fig. 2) showed two distinct regions, the one above 180°C with apparent activation energy $E_\sigma = 1.03 \pm 0.01$ eV (range of all seven samples, 1.00-1.08 eV), and the other below 140°C, with $E_\sigma = 0.55 \pm 0.01$ eV (range of all samples, 0.51-0.59 eV). Between these ranges, the data lie distinctly above either straight line, but correspond closely to the sum of the conductivities given by the two straight lines (dotted line in fig. 2). Thus it appears that the mechanisms responsible for the two ranges operate independently in parallel in the intermediate region where their contributions are comparable.

In the upper range, our data agree very well with previous work on highly purified samples [6, 7] (fig. 1). A lower range activation energy comparable to ours has been reported only by Bradley, Munro and Spencer [4]; their material was not highly purified (it was prepared by reducing A.R. cupric chloride with sodium sulphite) and gave an unusually low E_σ in the upper range (0.85 eV; fig. 1). Not all previous studies have covered the lower temperature range. Apart from that of Bradley et al., studies down to 24°C have been made by Maidanovskaya, Kirovskaya and Lobanova [5] and in this laboratory by Harrison and Ng.[3] Both gave a lower range E_σ about one-half of that reported from the present work.
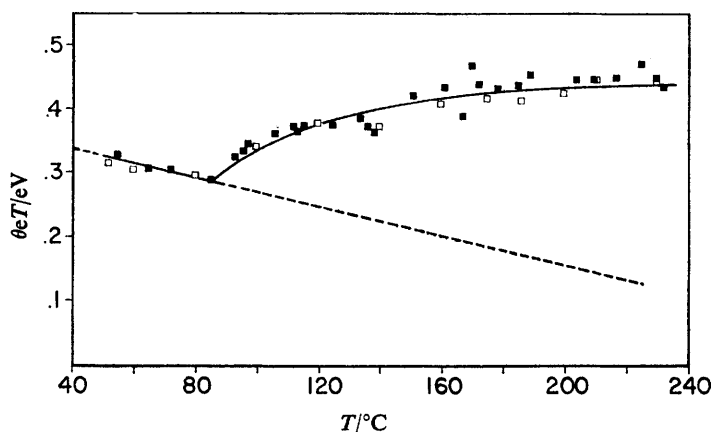

FIG. 3.—Peltier coefficient of pure CuCl, against temperature. ■, Cu electrodes; □, Pt electrodes. All θ values are positive (i.e., $\Delta V/\Delta T$ is negative).

The upper range has generally been attributed to cationic conduction by a Frenkel defect mechanism, and the lower range to positive hole conduction. On this basis, the % ionic conduction at any temperature can be calculated from the conductivity data. This is shown in fig. 4, curve C.

In well-purified material, positive hole conduction is most likely to arise from an intrinsic tendency of the compound to become slightly non-stoichiometric on the side of anion excess. The positive hole concentration should then be controlled by the action of cation vacancies as acceptors. If these greatly outnumber residual impurities capable of acting as donors, E_σ should be $\frac{1}{2}$ of the gap E_a between valence band and acceptor level; but if sufficient donors are present to give " compensated " behaviour, then $E_\sigma = E_a$. In this paper, we develop the interpretation that $E_a = 0.55$ eV. We thus regard " purification " processes, while they undoubtedly remove foreign materials, as having a much greater effect in bringing the material closer to stoichiometry. Thus in " pure " material, the impurity/acceptor ratio has actually increased, to give compensated behaviour and show the full value of E_a as E_σ.

THERMOELECTRIC POWER

Of the thermoelectric effects, the Seebeck coefficient θ is the most easily measured, but the Peltier coefficient θeT is the one most obviously related to mechanisms, because it shows directly the mean energy transported by the charge carriers. Our data for pure CuCl are shown as Peltier coefficient against temperature in fig. 3.

For a compensated positive-hole semiconductor, as described in detail in the discussion section below, the plot of θeT against T should be linear, of negative slope, extrapolating to E_a at $T = 0$. Our data show this behaviour up to 85°C and extrapolate to $E_a = 0.53$ eV, thus supporting the correlation between E_σ and E_a given above. From 85°C upwards, θeT rises, and appears to have reached a constant value at the highest temperature of our study. We attribute this to the changeover from electronic to ionic conduction. Analysis of the data in this way (for equations, see discussion section) yields a variation of % ionic conduction with T shown by curve G of fig. 4.
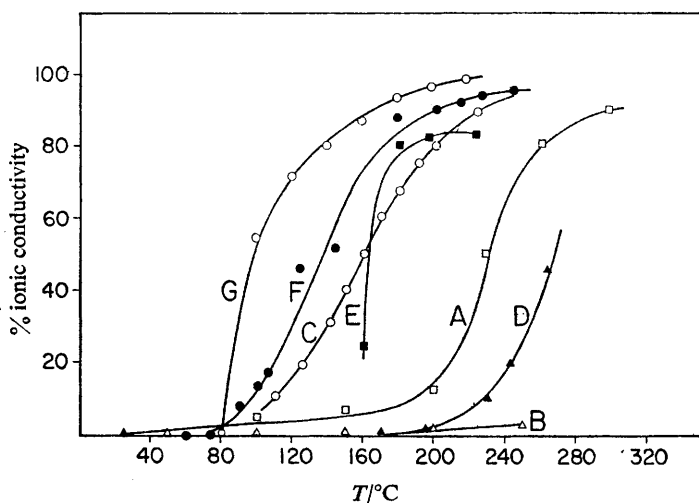

FIG. 4.—% ionic conductivity against temperature for pure CuCl. A—Hittorf-type experiment, Tubandt.[8] B—E.m.f. of cell with transference, Maidanovskaya et al.[5] C—conductivity, this work (fig. 2). D—Hittorf-type experiment, 22.5 V, this work. E—Hittorf-type experiment, 0.5 V, this work. F—Wagner's method, this work. G—Peltier coefficient, this work (fig. 3).

GRAVIMETRIC TRANSPORT NUMBER DETERMINATIONS

The classical transport number study of Tubandt[8] is shown as curve A of fig. 4. It indicates that the conductivity becomes 50 % ionic at 230°C, a temperature much higher than the 160°C indicated by our conductivity data (fig. 2, crossing-point of the two straight lines, and fig. 4, curve C). Tubandt's CuCl was purified by sublimation; we have not been able to find what p.d. he applied across the sample.

We first made transport number measurements with 22.5 V across the sample, with the results shown in fig. 4, curve D; conductivity is 50 % ionic at 265°C. In these experiments, however, the conductivity of the sample, which was initially close to that found in our conductivity work, rose often by a factor > 10 as d.c. was passed through the sample continuously for a long time. (The conductivity reached a maximum after about 10 h in one experiment at 222°C, and thereafter decreased slightly, but remained far above its initial value.)

Consequently, we carried out further experiments with an applied p.d. of 0.5 V, selected to be below any possible decomposition potential of the sample ($2CuCl \rightarrow 2Cu + Cl_2$, 1.22 V; $2CuCl \rightarrow Cu + CuCl_2$, 0.77 V; both at 25°C). Conductivities now remained close to those expected from our conductivity work, and the transport number data (fig. 4, curve E) showed 50 % ionic conductivity at 160°C. The shape of the curve could not be followed accurately to low temperatures, because the time required for an experiment became extremely long.

WAGNER METHOD FOR TRANSPORT NUMBERS

According to Wagner,[7, 9] the steady-state current I across a CuCl sample between an inert anode and copper cathode, with applied p.d. (E) less than any possible decomposition potential, should be

$$I = (ART/LF)[\sigma_n(1 - \exp(-Ee/kT)) + \sigma_p(\exp(Ee/kT) - 1)]. \tag{1}$$

Here L and A are length and cross-section of the sample and σ_n and σ_p are the contributions to the total conductivity of the sample made by electrons and holes when *both* electrodes are copper. For $Ee \gg kT$, eqn (1) approximates to

$$I = (ART/LF)[\sigma_n + \sigma_p \exp(Ee/kT)]. \tag{2}$$

If $\sigma_n = 0$,

$$\log I = \log(\sigma_p ART/LF) + Ee/(2.303 \, kT). \tag{3}$$

In these circumstances, a plot of $\log I$ against E should be linear, with slope $e/(2.303kT)$ and an intercept from which σ_p can be determined.

In our experiments, linear plots of $\log I$ against E were obtained at all temperatures, provided that current was passed in one sense only through the sample. (At low temperatures, where the conductivity is completely electronic without these means to suppress ionic conduction, ohmic behaviour was obtainable by using several values of E in succession cyclically, including negative values.) The slope of the plot was, however, in no case that predicted by eqn (3), but from $\frac{1}{6}$ to $\frac{1}{3}$ of that value. (Roughly, change of E from 0.4 to 0.8 V caused a tenfold increase in I at all T.) Use of the intercept to calculate σ_p assuming that the significance of the intercept is as indicated in eqn (3) gave, for % ionic conductance against temperature, the curve marked F in fig. 4. This is in fair agreement with curve C (from conductivity data), which latter we regard as giving the most reliable account of the variation of % ionic conductance with temperature. Evidently the extrapolation to zero E in the Wagner method is giving a reasonable indication of σ_p, even though we do not fully understand the defect distributions in the sample at finite E.

CHLORINE-TREATED CuCl

CONDUCTIVITY

The data to be described are mainly from a.c. measurements, except for the high-resistance samples obtained by reaction to an extent > 50 %. Pt electrodes were used throughout, because Ag or Cu react with the samples.

For CuCl reacted to the extents of 0.068 % and 0.15 %, ($\log \sigma$, $1/T$) plots were linear from 24 to 240°C, with slope corresponding to $E_\sigma = 0.38$ eV. In all other cases, from 0.29 to 64.5 % reaction, the plots showed two regions of different activation energy as shown in table 1. The temperature of the break between the two regions showed no significant correlation with extent of reaction, and lay always between 90 and 120°C. For samples up to 6.75 % chlorinated, the absolute values of the conductivity were almost independent of extent of reaction and were at all T

from 10^2 to 10^3 times greater than that of pure CuCl. (This increase in conductivity was missed entirely in the earlier studies in this laboratory,[3] in which no measurements were made between 0 and 4.8 % chlorination.)

TABLE 1.—CONDUCTIVITY DATA FOR PURE AND CHLORINE-TREATED CuCl

overall composition	apparent activation energy E_σ/eV		$\log_{10}\sigma_{sp}$	
	upper range	lower range	24°C	200°C
CuCl	1.03	0.55	−8.45	−4.59
	———*	———*		
CuCl$_{1.000678}$		0.38	−4.75	−2.35
CuCl$_{1.0015}$		0.38	−4.78	−2.43
CuCl$_{1.0029}$	0.43	0.38	−4.77	−2.25
CuCl$_{1.0102}$	0.52	0.28	−4.82	−2.50
CuCl$_{1.012}$	0.55	0.37	−4.88	−2.37
CuCl$_{1.0238}$	uncertain	0.47	−5.27	−2.05
CuCl$_{1.0675}$	0.43	0.31	−4.70	−2.47
CuCl$_{1.204}$	0.52	0.30	−5.35	−3.05
		———*		
CuCl$_{1.308}$	0.52	0.13	−5.65	−3.60
CuCl$_{1.461}$	0.47	0.13	−6.25	−4.65
CuCl$_{1.502}$	0.52	0.22	−7.30	−4.85
	———*			
CuCl$_{1.545}$	0.79	0.12	−8.15	−5.85
CuCl$_{1.552}$	0.89	0.17	−8.50	−5.90
CuCl$_{1.604}$	0.93	0.25	−9.60	−6.58
CuCl$_{1.645}$	0.90	0.45	−10.50	−6.50

* the lines indicate the compositions at which E_σ changes abruptly.

The upper range first appeared in the 0.29 % sample, with a rather low activation energy which was excluded from the average. Beyond this point, the upper range has E_σ matching the *lower* range for pure CuCl. The best value (pure CuCl and chlorinated samples 1.02-50.2 %) is $E_\sigma = 0.51 \pm 0.02$ eV. This agrees exactly with the *lower* range in the work of Bradley et al.[4] In absolute conductivity, their " pure " CuCl seems to lie between the " pure " and slightly-chlorinated samples in the present work. A 0.2 mol % CuCl$_2$-doped sample in their work matches the present slightly-chlorinated samples well for the range with $E_\sigma = 0.51$ eV.

Beyond 50.2 %, the upper range E_σ rises abruptly (*not* gradually, as found in the previous work [3]) to 0.88 ± 0.03 eV. Since we now know, from transport number and θ measurements described below, that there is no ionic transport in this region and that θ is positive, we withdraw our previous tentative assignment [3] of this range to Frenkel defects, and propose that this is a range of positive hole conduction controlled by acceptors at $E_a = 0.88$ eV.

The lower range has $E_\sigma = 0.36 \pm 0.02$ eV from 0.068 to 20.4 % chlorinated. A similar value (0.33 eV) appeared in the work of Bradley et al., but only at high pressures (40 kbar, 2 % CuCl$_2$). From 30.8 % to 55.2 % reacted, $E_\sigma = 0.15 \pm 0.02$ eV in the lower range ; thereafter the lower range E_σ again rises.

TRANSPORT NUMBERS

Because the pellets react with Cu, only the gravimetric method with Pt electrodes and a three-pellet assembly could be used for chlorine-treated samples. To perform an experiment in a reasonable time, for highly-chlorinated samples it was necessary to

use 22.5 V; but, in contrast to pure CuCl, this did not cause σ to change appreciably from the standard value. Hence 22.5 V was used in most experiments on chlorine-treated samples.

For samples 1.43 and 64.5 % chlorinated, no ionic conduction was found at any temperature (limit of detection about 1 %).

THERMOELECTRIC POWER

Fig. 5 shows θ plotted against T for eleven samples, ranging from 0.068 to 64.5 % conversion to $CuCl_2$. Up to 20.4 %, all the curves show a conspicuous maximum, but beyond that composition the curves appear to be flatter. (For samples more than 50 % chlorinated, data below 100°C were unobtainable because of the very high sample resistance.) The disappearance of the maximum correlates with the disappearance, in the conductivity studies, of the lower range with $E_\sigma = 0.36$ eV.
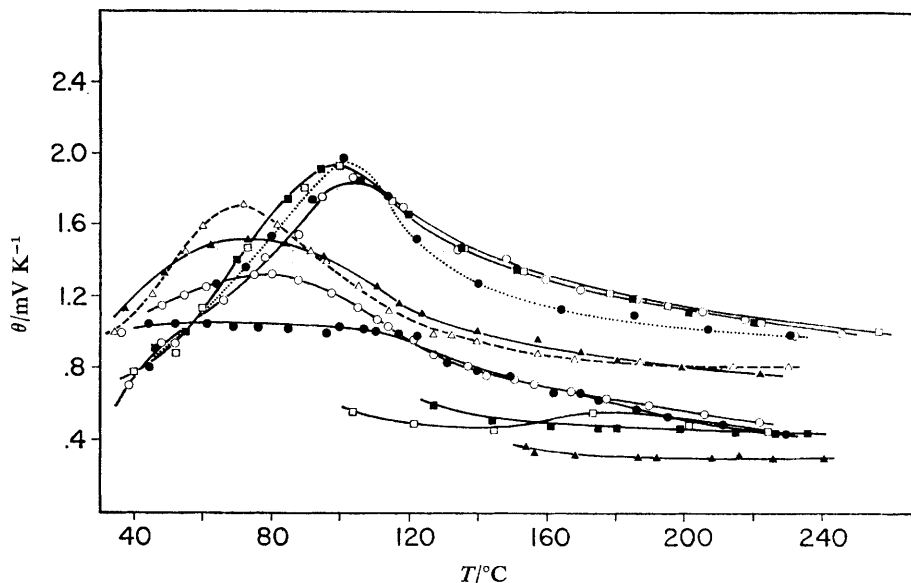

FIG. 5.—Thermoelectric power of chlorine-treated CuCl, against temperature. All θ values are positive ($\Delta V/\Delta T$ negative). N.B. *Where a symbol is repeated in the list, the curve first mentioned is the upper one at high temperature.* $\square$,$CuCl_{1.000678}$; $\blacksquare$, $CuCl_{1.0015}$; $\bigcirc$, $CuCl_{1.0029}$; $\bullet$, $CuCl_{1.0102}$; $\triangle$, $CuCl_{1.0238}$; $\blacktriangle$, $CuCl_{1.0675}$; $\bigcirc$, $CuCl_{1.204}$; $\bullet$, $CuCl_{1.308}$; $\square$, $CuCl_{1.545}$; $\blacksquare$, $CuCl_{1.552}$; $\blacktriangle$, $CuCl_{1.645}$.

As shown below in the discussion section, a marked rise of θ (or, more precisely, of the Peltier coefficient θeT) with T is very difficult to explain on the basis of a single conduction mechanism. A similar effect in NiO was explained by Austin, Spring-thorpe, Smith and Turner [10] in terms of electron conduction by " hopping " at an acceptor level proceeding in parallel with positive hole conduction in the valence band. In fig. 6, our results for samples up to 1.02 % are shown replotted as Peltier coefficient, together with the NiO curve.[10] In the discussion section, we show that, for such a mechanism, the rising portion of the curve should be linearized by an Arrhenius-type plot. Two such plots (one of log θeT, and the other of the same quantity with a " correction " of 4.606 kT, as explained in the discussion section) are shown in fig.7. Both are linear up to a surprisingly high temperature (80°C, only 20° below the

maximum), and their slopes correspond to 0.22 and 0.17 eV. As shown below, this slope should be acceptor level E_a *minus* the true activation energy $E_{\mu n}$ of the electron hopping process. Our assignments of the E_σ values are $E_a = 0.51$ eV and $E_{\mu n} = 0.36$ eV, so that the slopes of the lines in fig. 7 are to be compared with an expected value of 0.15 ± 0.04 eV.
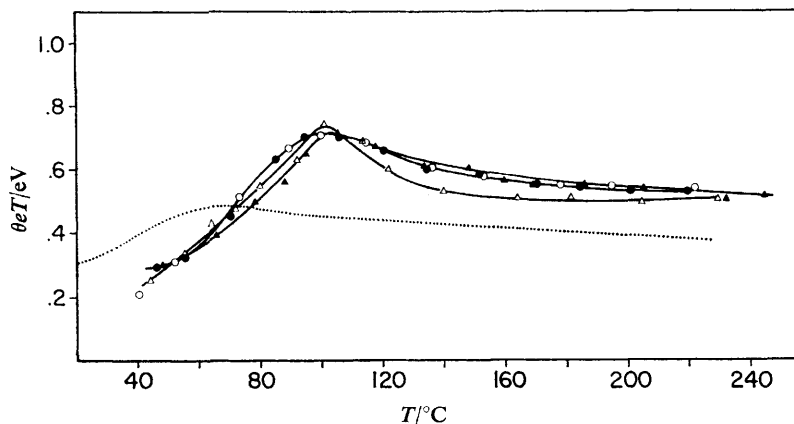

FIG. 6.—Peltier coefficient of chlorine-treated CuCl, and NiO, against temperature. Dotted line, NiO (Austin *et al.*[10]); ○, $CuCl_{1.000678}$; ●, $CuCl_{1.0015}$; ▲, $CuCl_{1.0029}$; △, $CuCl_{1.0102}$.
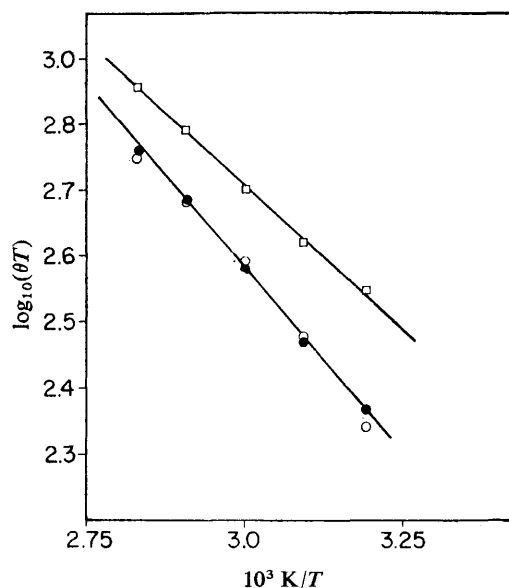

FIG. 7.—Plots of log (θT) against $1/T$. Circles, θT uncorrected; squares, correction $4.606\,kT$. ●, $CuCl_{1.000678}$; ○, mean, $CuCl_{1.000678}$ and $CuCl_{1.0015}$.

THEORY AND DISCUSSION

We consider a semiconductor with a band gap sufficiently wide that electrons in the conduction band cannot be important when the concentration of holes is significant. The hole concentration is controlled by acceptors (concentration N_a, energy

E_a above top of valence band) and partly " compensated " by electrons from donors (N_d, E_d). In all cases arising in the present work, E_a, E_d and the Fermi level E_F are all $\gg kT$, and the low-temperature limiting forms of the equations should be applicable throughout. We use the customary approximation [11] in which the valence band is replaced by a single level ($E = 0$) with density of states

$$N_v = (2\pi m_p^* kT/h^2)^{\frac{3}{2}} = 2.42 \times 10^{15} T^{\frac{3}{2}} \text{ cm}^{-3} \quad \text{if} \quad m_p^* = m_e. \tag{4}$$

In all cases the hole concentration (p) at the top of the valence band is

$$p = 2N_v[1 - 1/(1 + \exp(-E_F/kT))]. \tag{5}$$

When $E_F \gg kT$,

$$p = 2N_v \exp(-E_F/kT). \tag{6}$$

Ionization into the conduction band being negligible, p is determined by ionization of acceptors and compensation by donors according to

$$p = [N_a/(1 + \exp(E_a - E_F)/kT)] - N_d[1 - 1/(1 + \exp(E_d - E_F)/kT)]. \tag{7}$$

If E_F remains well below E_d, the last term in eqn (7) approximates to N_d, i.e., all the donors are ionized to donate electrons downwards to " fill in the holes ". Then eqn (7) becomes

$$p = [N_a/(1 + \exp(E_a - E_F)/kT)] - N_d. \tag{8}$$

From eqn (6) and (8), for the uncompensated case ($N_d = 0$),

$$E_F = (E_a/2) + (kT/2) \ln (2N_v/N_a). \tag{9}$$

$$p = (2N_v)^{\frac{1}{2}} N_a^{\frac{1}{2}} \exp (-E_a/2kT). \tag{10}$$

Thus p is governed by an energy $E_a/2$, which may appear directly as the apparent activation energy of conductivity E_σ.

In the compensated case ($N_d \neq 0$, but values of $N_d \ll N_a$ may suffice to establish the conditions in which the following equations apply)

$$E_F = E_a - kT \ln [(N_a - N_d)/N_d]. \tag{11}$$

$$p = 2N_v[(N_a - N_d)/N_d] \exp (-E_a/kT). \tag{12}$$

We shall wish to discuss a double conduction mechanism in which electrons at the acceptor level (concentration n_a), as well as holes, contribute to conduction. n_a is given by the first term on the right-hand side of eqn (8). Upon substituting for E_F from eqn (11) and assuming $N_a \gg N_d$,

$$n_a = N_d. \tag{13}$$

It is most probable that the positive holes in the valence band migrate without activation energy, while the electrons at the acceptor level migrate with a true activation energy $E_{\mu n}$. The total conductivity should thus be

$$\sigma = pe\mu_p + n_a e\mu_n = 2N_v e\mu_p[(N_a - N_d)/N_d] \exp (-E_a/kT) + N_d e\mu_n^\circ \exp (-E_{\mu n}/kT). \tag{14}$$

where μ_p is the hole mobility and μ_n° the pre-exponential factor in the electron mobility. If $E_a > E_{\mu n}$, conduction may be mainly by electrons at low temperatures and holes at higher temperatures, with apparent activation energy E_σ equal to $E_{\mu n}$ and E_a in lower and upper ranges respectively. As indicated in the results section, we thus explain the data for CuCl from about 1 to 20 % reacted with Cl_2, and we assign the values 0.36 and 0.51 eV to $E_{\mu n}$ and E_a respectively.

Strong support for this interpretation comes from the thermoelectric power data. When conduction is entirely by holes, the Peltier coefficient should be

$$\theta eT = E_F + AkT, \tag{15}$$

where the second term on the right arises from the kinetic energy of the charge carriers and the nature of the scattering processes. Usually, $A \sim 2$; and if $E_F \gg kT$, the second term can often be ignored and θeT regarded as giving the Fermi level directly.

For our chlorine-treated samples, θeT rose rapidly with T in the lower range of temperature. If this is considered to represent the behaviour of E_F, then eqn (6) shows that p must fall as T rises. This is not a reasonable conclusion, in relation to any likely model of defect equilibria. Hence θeT evidently does not give a direct account of the position of the Fermi level. This implies the presence of some other charge carriers, in addition to or in place of valence band holes, for which the heat of transport is not E_F. If these carriers are electrons at the acceptor level, their heat of transport is $(E_F - E_a)$, and if the fractions of the current carried by holes and electrons are f_p and f_n,

$$\theta eT = f_p E_F + f_n(E_F - E_a) = E_F - f_n E_a, \tag{16}$$

the term AkT being neglected. On substituting for E_F from eqn (11),

$$\theta eT = f_p E_a - kT \ln [(N_a - N_d)/N_d]. \tag{17}$$

f_p can be found from the terms on the right of eqn (14); and if $f_p \ll 1$, the expression reduces to

$$f_p = [2N_v(N_a - N_d)/N_d^2](\mu_p/\mu_n^\circ) \exp [-(E_a - E_{\mu n})/kT]. \tag{18}$$

Then

$$\theta eT = [2N_v(N_a - N_d)/N_d^2](\mu_p/\mu_n^\circ)E_a \exp [-(E_a - E_{\mu n})/kT] \ln [(N_a - N_d)/N_d]. \tag{19}$$

Thus if an Arrhenius-type plot is made of the quantity $\theta eT + kT \ln [(N_a - N_d)/N_d]$, it should be linear with slope indicating an energy $(E_a - E_{\mu n})$. This has been tested for the present data by the plots in fig. 7, one of which is of θeT with no correction, while the other shows the effect of assuming $(N_a - N_d)/N_d = 100$. Both plots are linear, but the correction brings the slope closer to prediction.

The above discussion follows the proposal of Austin et al.[10] for NiO; the two instances share the peculiar feature that θ can have a positive sign when the majority carriers are electrons. Those authors, however, although they pointed out qualitatively that a double mechanism is indicated whenever θ rises rapidly with T, did not attempt to analyze quantitatively the rising portion of their curve. While we appear to have a satisfactory explanation of this part of the curve, there remains a discrepancy close to the maximum of the curve. As T rises and the contribution from electrons decreases, θeT should first rise and then, when f_n has become negligible and θeT correctly represents E_F, fall according to eqn (11). But eqn (16) shows that θeT can at no stage exceed E_F, and E_F is expected to stay below E_a throughout the range of our study. Thus the fact that the maxima of the curves in fig. 6 lie above 0.51 eV is anomalous. This may indicate that, as proposed by Tsuji,[12] the heat of transport of " hopping " electrons should include $E_{\mu n}$. Addition of $f_n E_{\mu n}$ to eqn (17) yields

$$\theta eT = f_p(E_a - E_{\mu n}) - kT \ln [(N_a - N_d)/N_d] + E_{\mu n}. \tag{20}$$

In this case, the temperature dependence of θeT in the rising portion could still be essentially that of f_p, but the maximum could be raised.

With pure CuCl, we are concerned with a different dual conduction mechanism: holes and Cu^+ interstitials (subscripts p and i respectively in the equations below). The Peltier coefficient should be

$$\theta eT = f_p \theta_p eT + f_i \theta_i eT. \tag{21}$$

At low temperatures, $f_p = 1$ and θeT should decrease linearly with T according to

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eqn (17). At high temperatures, $f_i = 1$ and θ should attain a constant value such that $\theta e T$ is the heat of transport of an interstitial plus half the energy of formation of a Frenkel defect.[13] From eqn (21), with $f_p + f_i = 1$,

$$f_i = (\theta e T - \theta_p e T)/(\theta_i e T - \theta_p e T). \tag{22}$$

Here, $\theta_p e T$ is read off at any temperature from the extrapolation of the linear low-temperature portion (fig. 3, broken line) and $\theta_i e T$ is the limiting value of $\theta e T$ at high temperatures. Calculation from the data of fig. 3 according to eqn (22) gives curve G of fig. 4. This curve appears, in comparison with curves C and F (from conductivity data and the Wagner method) to indicate correctly that the transition from electronic to ionic conductivity occupies the temperature range 80 to 240°C; but between those limits, curve G overestimates the ionic contribution. The deficiency in this method is the assumption that θ_i is temperature-independent; AgCl, for example, shows rather complicated temperature dependence of θ_i in the same temperature range.[13]

PROPOSED DEFECT STRUCTURES

" Pure " CuCl is slightly non-stoichiometric, containing holes and cation vacancies which act as hole traps (depth $E_a = 0.51$ eV). Their concentrations are low, and they are " compensated " by donor impurities; $E_\sigma = E_a$. Less highly purified samples are more non-stoichiometric. Hole and vacancy concentrations are too large to be compensated by the chance presence of donors; $E_\sigma = E_a/2$ (Harrison and Ng,[3] Maidanovskaya et al.[5]). Reaction with Cl_2 (0.07 to 20 %) produces high concentrations of holes and traps, but also produces donors; $E_\sigma = E_a$ (at higher T than for pure CuCl). The donors are probably Cu^+ at the reaction interface, in favourable locations for Cu^{2+} to reside. But the acceptors are now so close together that " hopping " conduction of electrons at the acceptor level predominates below 100°C; $E_\sigma = E_{\mu n} = 0.36$ eV. This correlates with the observation of Bradley et al.[4] that the appearance of $E_\sigma = 0.33$ eV in $CuCl_2$-doped CuCl is assisted by high pressure (which should assist incipient band formation at the acceptor level). On the basis of this interpretation, $E_\sigma = 0.36$ eV and (θ, T) curves with a maximum should always appear in the same samples. That is observed in our work; both phenomena disappear together at about 20 % conversion to $CuCl_2$. At about that extent of reaction, the mechanism of the $CuCl/Cl_2$ reaction changes: $CuCl_2$, which previously formed separate crystals, now builds up over the entire surface of each CuCl particle.[1] Evidently an important structural change takes place at that surface. We have suggested that the donor centres reside at that surface; perhaps they are now suppressed, leading to a corresponding suppression of electrons at the acceptor level and electrical phenomena associated with those electrons. The suppression probably occurs because a more direct transfer of Cu from the CuCl to the $CuCl_2$ lattice is now possible. But the donors are not completely removed; compensated behaviour, $E_\sigma = E_a$, persists in the high-temperature range.

The origin of $E_\sigma = 0.15$ eV, which now appears at low T, is obscure. It may arise from electron withdrawal from the CuCl producing holes without enough traps for them.

Beyond about 50 % reaction, $E_\sigma = 0.88$ eV appears, and we have suggested that this represents another acceptor level for which the traps are anion interstitials. Such a site is in a sense a more " natural " trapping site than a cation vacancy, because its immediate environment provides valence band orbitals, which that of the cation vacancy does not. The valence bands of CuCl are believed to be predominantly Cu 3d (at the top, 79 % Cu 3d, 21 % Cl 3p, according to the calculations of Song [14,15]). The large trapping energies which we are considering must correspond to localization

of the hole essentially on the nearest neighbours of the trap. For an anion interstitial, these neighbours are cations and provide valence band orbitals. But for a cation vacancy, the neighbours are anions, and trapping involves promotion of the holes. The Cl $3p$ band lies about 3 eV away from the Cu $3d$ band (*below* for electrons, *above* for holes). If so much promotion were needed, the cation vacancy could not act as a trap. The five Cu $3d$ bands are, however, split (zinc blende lattice, tetrahedral site symmetry) into three bands corresponding to atomic t_2 orbitals and two corresponding to the e orbitals. The highest energy levels of the three t_2 bands are degenerate, likewise the e bands, and they are separated by 0.53 eV, according to Song.[14, 15] The t_2 orbitals (d_{xy}, d_{yz} and d_{zx}) are so oriented that overlap between corresponding orbitals on adjacent atoms is large, but the e orbitals (d_{z^2}, $d_{x^2-y^2}$) are oriented to favour interaction with neighbouring Cl $3p_{x,y,z}$. One may anticipate that the e bands will have much more Cl $3p$ character than the t_2 bands. This mixture may adequately represent the orbitals in the near environs of a cation vacancy. On this basis, a crude approximation to the promotion energy of a hole on being trapped at a cation vacancy is the ligand field splitting, 0.53 eV, to be compared, therefore, with the difference of the two acceptor levels, $0.88 - 0.51$ eV $= 0.37$ eV. Theoretical work on the trapping energies would clearly be useful.

Without Hall Effect data, no precise estimates can be made of the concentrations of defects in the samples. For acceptors in slightly-chlorinated samples, a rough estimate can be made from the observation that the absolute conductivities had reached their maximum values even at the lowest extent of chlorination studied, 0.0678 %. This figure evidently is equal to or greater than the maximum % of defects which can be produced in CuCl by chlorination. On this basis, the maximum concentration of cation vacancies is about 2×10^{19} cm^{-3}, and their average distance apart is at least 11 spacings of the cation lattice, i.e. 4.35 nm. This is clearly too far for the " hopping " process, and indicates that the distribution of vacancies in the sample must be non-uniform. Probably they are concentrated at grain boundaries and dislocations.

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