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The systems CuCl-$M^{II}Cl_2$ (M = Mn, Cd) – crystal structures of Cu_2MnCl_4 and γ-CuCl

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Neutron diffraction – Cu_2MnCl_4, $Mn_{0.84}Cu_{0.32}Cl$, *and* γ-CuCl / *Fast copper ion conductors* / α-CuI-*type copper chlorides* / *Systems* CuCl-$MnCl_2$ *and* CuCl-$CdCl_2$

Abstract. The phase relationships of the quasibinary systems CuCl-$M^{II}Cl_2$ (M^{II} = Mn, Cd) were studied by high-temperature X-ray methods and difference thermal analyses (DTA). Four phases have been established: $CdCl_2$-type $M^{II}_{1-x}Cu_{2x}Cl_2$ and α-CuI-type $Cu^{I}_{1-y}M^{II}_{0.5y}Cl$ solid solutions (above 361 and 321°C, respectively), and β- and γ-CuCl with negligible solubility for M^{II}. The phase widths of the Cd containing compounds are $0 < x < 0.35$ at 25°C, $0 < x < 0.6$ at 315°C, and $0 < y < 0.4$ at 420°C; those of the manganese compounds are similar. The crystal structures of α-CuI-type Cu_2MnCl_4 at 400°C and of $Mn_{0.84}Cu_{0.32}Cl_2$ and γ-CuCl both at 60°C were determined by means of neutron powder diffraction. The structures were refined by Rietveld's method to final R_I = 1.7, 6.0, and 2.5%, respectively. The hitherto unknown high-temperature α-polymorph of CuCl can be stabilized by Mn^{II} and Cd^{II}. The α-CuI-type solid solutions are fast Cu^+ ion conductors with conductivities of $\sigma > 10^{-1}\ \Omega^{-1}\ cm^{-1}$ above 350°C.

Introduction

By substitution of the lithium ions of spinel-type fast ionic conductors $Li_2M^{II}Cl_4$ (M^{II} = Mg, Mn, Cd) by copper(I) it has been revealed that the tetrahedrally coordinated lithium ions are most important in the conduction

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process (Lutz, Kuske and Wussow, 1988; Lutz, Pfitzner and Wickel, 1991). Furthermore, it has been shown that there are complete series of solid solutions at least at elevated temperatures. Since ternary $Cu^I_2M^{II}Cl_4$ (M^{II} = Mn, Cd) hitherto have been not reported in the literature we investigated these compounds with respect to structure, phase relationships, and ionic conductivity.

In the system CuCl-$CdCl_2$ two ternary compounds are reported, viz. Cu_4CdCl_6 (Hermann, 1911; Matsui and Wagner, 1977) and $CuCdCl_3$ (Kuku, 1987). Investigations on the system CuCl-$MnCl_2$ are not known so far. The binary chlorides are well established. $MnCl_2$ and $CdCl_2$ crystallize in a $CdCl_2$-type structure. CuCl is dimorphic, i.e. γ-CuCl has sphalerite structure, β -CuCl wurtzite structure (see, for example, Graneli, Dahlborg and Fischer, 1988).

Experimental

Starting materials were CuCl (2N, Merck), $MnCl_2$ (2N, Fluka) and $CdCl_2$ (for synthesis, Merck). $MnCl_2$ and $CdCl_2$ were dried at 450 and 300° C, respectively, in a stream of HCl and Ar. CuCl was recrystallized from aqueous hydrochloric acid. Ternary manganese and cadmium containing chlorides were prepared by fusing stoichiometric amounts of the binary chlorides in glass ampoules and annealing at 350 and 370° C, respectively.

The samples obtained were characterized by X-ray (high-temperature X-ray photographs) and thermoanalytical methods (difference thermal analysis (DTA)) using both a Huber Guinier 600 system and an Enraf-Nonius Guinier Simon FR 553 camera, and a Linseis thermoanalyser L62. The heating rates were 10 K h^{-1} and 10 K min^{-1}, respectively. The unit-cell dimensions were computed by least-squares refinements (LSUCR) from data corrected by the reflections of α-SiO_2 used as an internal standard. The electrical conductivity was determined by impedance measurements. For further details of these techniques see, for example, Lutz, Pfitzner and Wickel (1991) and Pfitzner (1991).

Neutron diffraction studies were performed on the powder diffractometer D2B at the Institut Laue Langevin (ILL) in Grenoble. Quartz ampoules were used as sample container because vanadium cans are corroded by copper chlorides at elevated temperatures. The background of the diffraction patterns, which show some broad peaks due to the quartz ampoule, was determined graphically. The neutron wavelength used was 159.4 pm. The structure refinement was performed by means of the modified Rietveld program PROFIL (Cockcroft, 1990). The scattering lengths used were b(Cu) = 7.718, b(Mn) = -3.73, and b(Cl) = 9.5792 fm (Koester and Rauch, 1983).

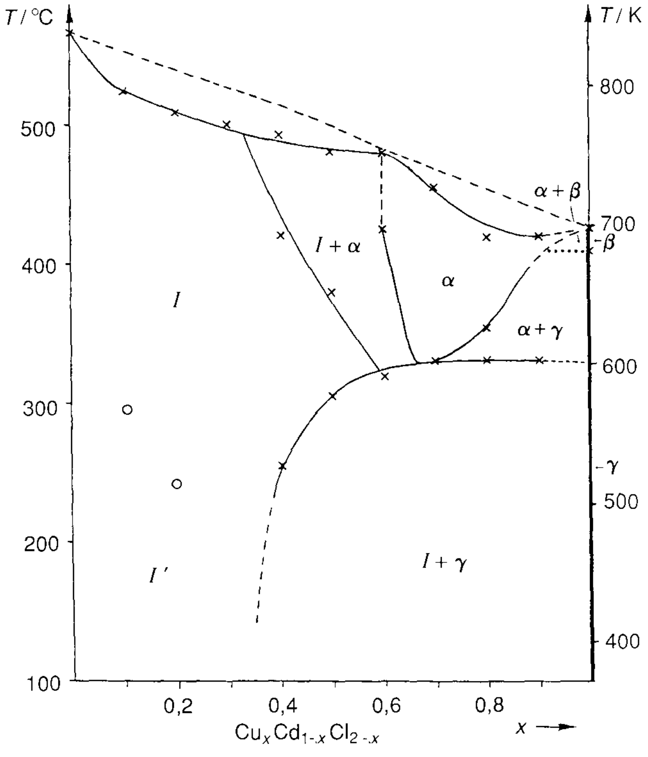

Fig. 1. Phase diagram of the system CuCl-$CdCl_2$ (high-temperature X-ray data); *I*, $CdCl_2$-type solid solutions; *I'*, distorted $CdCl_2$-type mixed crystals; γ, γ-CuCl; β, β-CuCl; α, α-type $Cu_{1-y}Cd_{0.5y}Cl$ solid solutions; ○, transition *I* ⟷ *I'*. The phase diagram of the system CuCl-$MnCl_2$ (not shown) is very similar.

Results

Phase relationships

In both systems studied, ternary chlorides with large homogeneity regions are formed at elevated temperatures (see Fig. 1), which obviously correspond to the compound Cu_4CdCl_6 already described by Hermann (1911). Ternary $Cu^I_{1-y}M^{II}_{0.5y}Cl$ (M^{II} = Mn, Cd) cannot be quenched to ambient temperature. The relatively large mutual solubilities at elevated temperatures decrease on cooling down to ambient temperature (see Fig. 1). The solubility limits of copper(I) in $CdCl_2$-type $M^{II}Cl_2$ of samples slowly cooled to room temperature are 35 mol % for both systems (see Fig. 2). The solubility of $M^{II}Cl_2$ in β- and γ-CuCl is negligible.

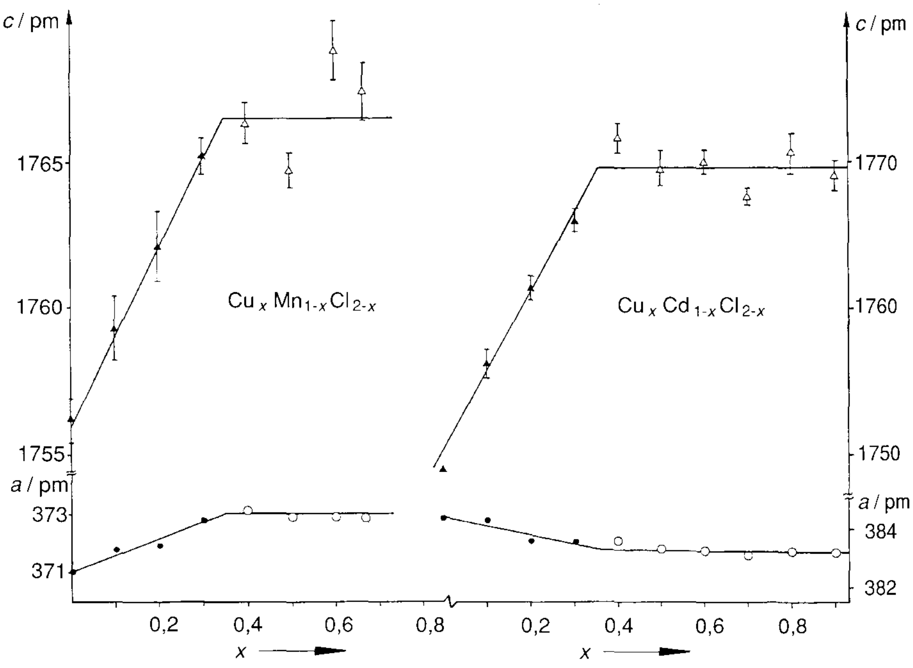

Fig. 2. Unit-cell dimensions of $CdCl_2$-type $M^{II}_{1-x}Cu^{I}_{2x}Cl_2$ solid solutions (M^{II} = Mn, Cd) slowly cooled to ambient temperature.

The lattice constants c of $M^{II}Cl_2$-type mixed crystals increase strongly with increase in copper content; the changes of a are relatively small (see Fig. 2). The crystal structure of the $CdCl_2$-type $Cd_{1-x}Cu_{2x}Cl_2$ solid solutions is somewhat distorted compared to the ideal $CdCl_2$ structure (space group $R\bar{3}m$) as shown from splitting of the 009 and 0012 reflections in the Guinier photographs. This splitting, which is not observed in the case of the $Mn_{1-x}Cu_{2x}Cl_2$ mixed crystals, disappears at temperatures above 230–300°C. The distorted samples are called $CdCl'_2$ in Figure 1.

Ionic conductivity of $Cu_2M^{II}Cl_4$ (M^{II} = Mn, Cd)

The ionic conductivity of monophase "$Cu_2M^{II}Cl_4$" is $> 10^{-1}\ \Omega^{-1}\ cm^{-1}$. Therefore, these compounds are fast Cu^+ ion conductors. The decomposition of the ternary copper chlorides to CuCl and $M^{II}_{1-x}Cu_{2x}Cl_2$ solid solutions below 361°C and 321°C, respectively, is also revealed by a strong decrease in conductivity (see Fig. 3).

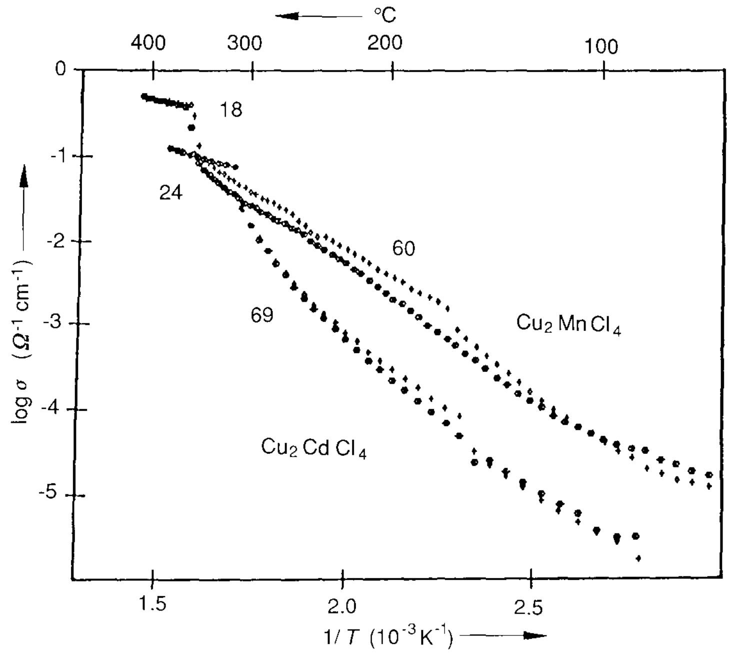

Fig. 3. Specific electric conductivity (log σ versus 1/*T*, Arrhenius plots) and activation energies for conduction (kJ mol^{-1}) of α-CuI-type Cu$_2$MnCl$_4$ and Cu$_2$CdCl$_4$ (○, heating; +, cooling).

Neutron diffraction studies

"Cu$_2$MnCl$_4$"

Neutron diffraction data of "Cu$_2$MnCl$_4$" were collected at 400°C. The refinement converged to a final $R_I = 1.7\%$ based on 145 observations containing 12 reflections and 133 degrees of freedom. The final profile and structural parameters are given in Table 1.

"Cu$_2$MnCl$_4$" crystallizes in space group $Fm\bar{3}m$ with $Z = 1$. Cl$^-$ and Mn^{2+} occupy the 4*a* and 4*b* positions, respectively, i.e. the Mn^{2+} ions are randomly distributed in octahedral voids of the cubic close packed arrangement of the Cl$^-$ ions. The site occupancy of the Mn position is 25%.

The positions of the Cu$^+$ ions can be described by different models. Best results are obtained assuming a 32*f* split position (see Table 1). If the Cu$^+$ ions are located in both 8*c* ($^1/_4$, $^1/_4$, $^1/_4$) and 32*f* (*x*, *x*, *x*) positions only isotropic temperature factors can be refined. Distribution of Cu$^+$ between these positions is listed in Table 1. The high disorder as well as the conspicuous anisotropic temperature factors reveal the high mobility of the

Table 1. Profile and structural parameters of α-CuI-type "Cu_2MnCl_4" at 400°C.

Lattice constant:	$a = 536.75(2)$ pm
Space group:	$Fm\bar{3}m$, $Z = 1$
2θ range:	10–140°
Number of observations:	145
Number of reflection with $I > 0$:	12
Number of degrees of freedom:	133
Halfwidth parameters (°^{2}):	$U = 0.70(3)$
	$V = -0.20(5)$
	$W = 0.27(1)$

Structure model I, Cu in 8*c* and 32*f*, isotropic

Atom	Position	Occupation	u	$B/10^4$ pm^2
Cu(1)	32*f*	0.9(1)	0.385(3)	9(3)
Cu(2)	8*c*	1.1(1)	0.25	13(4)
Mn	4*b*	1	0.5	7(1)
Cl	4*a*	4	0	6.4(1)

Number of structural parameters: 7
$R_{wp} = 8.9\%$ (expected 3.1%)
$R_I = 2.2\%$

Structure model II, Cu in 32*f*, anisotropic

Atom	Position	Occupation	u	$B/10^4$ pm^2
Cu	32*f*	2	0.340(1)	–
Mn	4*b*	1	0.5	5.9(9)
Cl	4*a*	4	0	6.4(1)

Anisotropic thermal parameters of Cu ($U_{ij}/100$ pm^2)
$U_{11} = U_{22} = U_{33} = 21.4(12)$, $U_{12} = U_{13} = U_{23} = 10.2(9)$
Number of structural parameters: 6
$R_{wp} = 8.8\%$ (expected 3.1%)
$R_I = 1.7\%$

$u = x = y = z$
Temperature term has the form $\exp(-2\pi^2 \sum_{i,j} U_{ij}\mathbf{h}_i\mathbf{h}_j a_i^* a_j^*)$.

copper ions at 400°C (see Fig. 4). Altogether, the crystal structure of "Cu_2MnCl_4" closely resembles that of α-CuI (Yude, Boysen, and Schulz, 1990).

$Cu_{0.32}Mn_{0.84}Cl_2$ and γ-CuCl

The observed and fitted neutron powder diffraction patterns of a heterogeneous mixture of γ-CuCl and copper rich $CdCl_2$-type $Mn_{1-x}Cu_{2x}Cl_2$ mixed crystals (obtained by decomposition of "Cu_2MnCl_4" on cooling to 60°C) are shown in Figure 5. The respective profile and structural parameters are given in Tables 2–4.

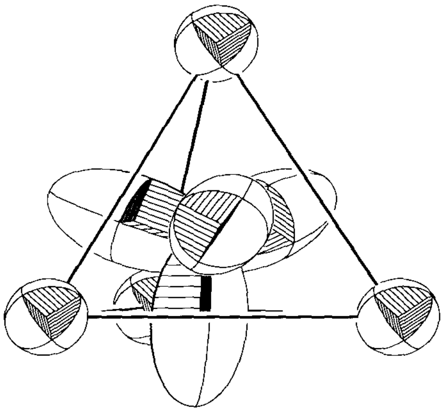

Fig. 4. Part of the crystal structure of strongly disordered α-CuI-type "Cu$_2$MnCl$_4$" (model II), probability (after Johnson, 1976) 50%.

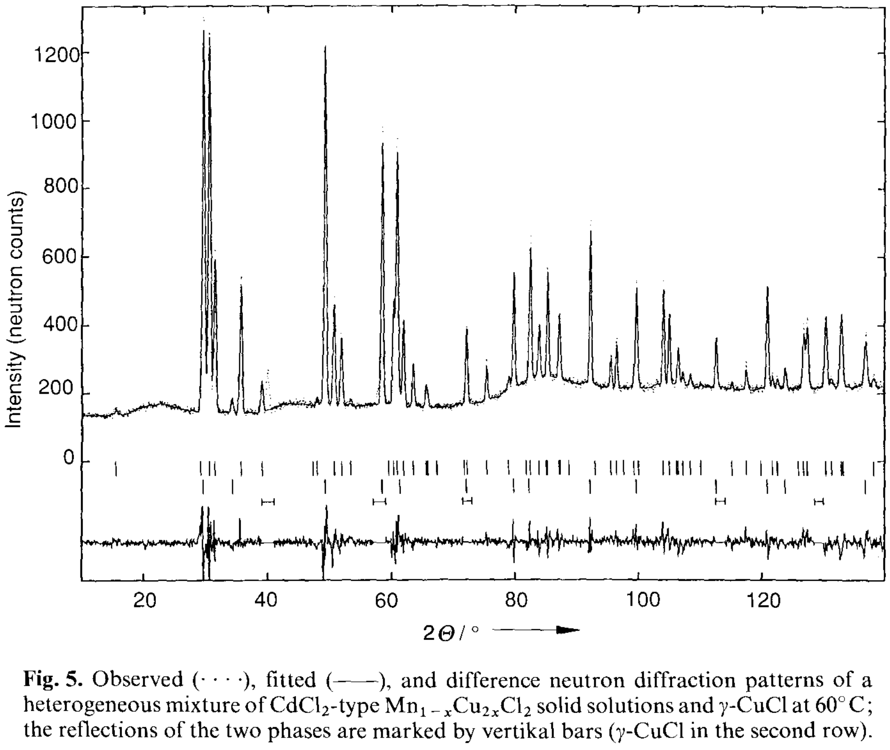

Fig. 5. Observed (· · · ·), fitted (——), and difference neutron diffraction patterns of a heterogeneous mixture of CdCl$_2$-type Mn$_{1-x}$Cu$_{2x}$Cl$_2$ solid solutions and γ-CuCl at 60° C; the reflections of the two phases are marked by vertikal bars (γ-CuCl in the second row).

Table 2. Profile parameters of a heterogeneous mixture of $CdCl_2$-type $Mn_{0.84}Cu_{0.32}Cl_2$ solid solution and γ-CuCl at 60°C.

2θ range:	10–140°
Number of observations:	529
Number of reflections with $I > 0$:	65
Number of degrees of freedom:	510
Halfwidth parameters (°²):	$U = 0.103(7)$
	$V = -0.23(1)$
	$W = 0.265(6)$

Table 3. Structural parameters of $CdCl_2$-type $Mn_{0.84}Cu_{0.32}Cl_2$ at 60°C.

Lattice constants: $a = 372.99(1)$, $c = 1769.1(1)$ pm
Space group: $R\bar{3}m$, $Z = 3$

Atom	Position	Occupation	x	y	z	$B/10^4$ pm^2
Cu	6*c*	0.96(3)	0	0	0.090(1)	3.9(7)
Mn	3*a*	2.52(1)	0	0	0	1.4(2)
Cl	6*c*	6	0	0	0.2542(3)	1.73(5)

$R_{wp} = 10.9\%$ (expected 4.9%)
$R_I = 6.0\%$

Table 4. Structural parameters of γ-CuCl at 60°C.

Lattice constant: 542.03(1) pm
Space group: $F\bar{4}3m$, $Z = 4$

Structure model I, Cu in 4a, isotropic

Atom	Position	Occupation	u	$B/10^4$ pm^2
Cu	4*a*	4	0	5.5(1)
Cl	4*b*	4	0.25	2.12(1)

$R_{wp} = 11.0\%$ (expected 4.9%)
$R_I = 4.1\%$

Structure model II, Cu in 16*e*, isotropic

Atom	Position	Occupation	u	$B/10^4$ pm^2
Cu	16*e*	4	−0.028(1)	3.4(5)
Cl	4*b*	4	0.25	2.15(5)

$R_{wp} = 10.9\%$ (expected 4.9%)
$R_I = 3.4\%$

Structure model III, Cu in 16*e*, anisotropic

Atom	Position	Occupation	u	$B/10^4$ pm^2
Cu	16*e*	4	−0.017(1)	–
Cl	4*b*	4	0.25	2.27(7)

anisotropic thermal parameters of Cu ($U_{ij}/100$ pm^2)
$U_{11} = U_{22} = U_{33} = 0.081(3)$, $U_{12} = U_{13} = U_{23} = 0.052(5)$
$R_{wp} = 10.7\%$ (expected 4.9%)
$R_I = 2.5\%$

Table 5. Selected interatomic distances (pm) and angles (°) of $CdCl_2$-type $Mn_{0.84}Cu_{0.32}Cl_2$ and γ-CuCl at 60°.

$Mn_{0.84}Cu_{0.32}Cl$		
Cu – Cl	3 × 216.2(2),	1 × 290.5(18)
Cl – Cu – Cl	95.1(5),	119.2(2)
Mn – Cl	6 × 256.8(3)	
Cl – Mn – Cl	93.1(1),	86.9(1), 180
γ-CuCl		
Cu – Cl	3 × 229.9(3),	1 × 250.7(9)
Cl – Cu – Cl	105.7(2),	112.95(19)

The $Mn_{1-x}Cu_{2x}Cl_2$ solid solution crystallizes in space group $R\bar{3}m$ ($Z = 3$). The refinement (final $R_I = 6.0\%$, for details see Pfitzner, 1991) results in a composition of $Mn_{0.84}Cu_{0.32}Cl_2$ for the $CdCl_2$-type mixed crystals. The Cu^+ ions are incorporated in tetrahedral voids 6*c* (0, 0, *z*) whereas Mn^{2+} ions are located in position 3*a* (0, 0, 0). The coordination of the Cu^+ ions, however, is distorted with one elongated Cu – Cl distance, i.e. 290.49 pm compared to 3 × 216.20 pm. Thus, the Van der Waals gap of the layered structure is mainly unoccupied. The site occupancy factors of the 3*a* (Mn^{2+}) and 6*c* sites (Cu^+) are 84 and 16%, respectively.

Refinement of the neutron scattering data of γ-CuCl (space group $F\bar{4}3m$, $Z = 4$, final $R_I = 2.5\%$) confirms deviation from an ideal sphalerite structure owing to an anharmonic displacement of the Cu^+ ions towards to the basal plane of the $CuCl_4$ tetrahedra (see Table 5). The anharmonic displacement parameters, i.e. $\delta = -0.028$ and -0.017 at 60° C for isotropic and anisotropic refinement, respectively, (see Table 4) corresponds to the literature data ($\delta = -0.024$ and -0.021) obtained at ambient temperature (Sakata, Hoshino, and Harada, 1974; Graneli, Dahlborg, and Fischer, 1988).

Discussion

The phase transitions of copper(I)halides (CuX (X = Cl, Br, I) are well known. All form a low temperature modification (γ-CuX) with a sphalerite-type structure and a β-form of the wurtzite-type. CuCl, however, does not show a transition to a high-temperature α-polymorph before melting. The α-CuX-type structure can obviously be stabilized with divalent metal ions, e.g. Mn^{2+} and Cd^{2+}. Thus, solid solutions $Cu_{1-y}M^{II}_{0.5y}Cl$ (M^{II} = Mn, Cd) with a high copper ion conductivity are formed.

The electrical conductivity and activation energy for conduction obtained for "Cu_2CdCl_2" ($1 \cdot 10^{-1}\ \Omega^{-1}\ cm^{-1}$ at 350° C, 24 kJ mol^{-1} above

321°C) confirm the data reported by Matsui and Wagner (1977) (22 kJ mol^{-1}). However, the structure of "Cu_2CdCl_2" is not of β-CuCl type and the phase transition β- to γ-type structures claimed (e.g. 330°C for Cu_2CdCl_2, Matsui and Wagner, 1977) is in fact the decomposition to CuCl and $CdCl_2$-type $Cd_{1-x}Cu_{2x}Cl_2$ solid solutions. Tetragonal $CuCdCl_3$ reported by Kuku (1987) does not exist at any temperature (see Fig. 1).

$Cu_{1-y}M^{II}_{0.5y}Cl$ solid solutions are not formed in the case of M^{II} = Mg, Fe, Co, and Ni. These findings are possibly due to the relatively high melting points of the corresponding chlorides compared to those of manganese and cadmium (see Pfitzner (1991)). Furthermore, the solubilities of CuCl in $M^{II}Cl_2$ with M^{II} = Mg, Fe, Co, and Ni are much smaller than in those of M^{II} = Mn and Cd.

The Cu–Cl distances of both γ-CuCl and $CdCl_2$-type $Mn_{1-x}Cu_{2x}Cl_2$ mixed crystals are unusually small, viz. 229.9 and 216.2 pm, respectively, compared to the respective ionic radii (Cu^+: 74, Cl^-: 167 pm, Shannon (1976)). This is obviously due to the more trigonal planary coordination of the copper ions (instead of a regular tetrahedron).

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