Electrical Conductivity and Phase Transitions of the Solid Electrolyte System $(Cs_{1-y}Rb_y)Cu_4Cl_3(I_{2-x}Cl_x)$

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Results of electrical conductivity measurements, thermal analysis, and X-ray diffraction studies indicate the existence of four phases, between 295 K and the melting points, in the system $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$. These phases are designated α, α', β, γ in order of decreasing temperature. The α phase is isostructural with α-$RbAg_4I_5$; the α' phase is also cubic and very likely belongs to space group $P2_13$, a subgroup of $P4_132$ and $P4_332$ to which the α phase belongs. There is a high probability that the $\alpha' \rightarrow \alpha$ transition is continuous. The $\alpha' \rightarrow \alpha$ transition is not discernible in the conductivity measurements or thermal analysis; therefore the line of α'–α transitions is presently unknown. The β phase transforms to the α', and the γ phase transforms to the β phase when $y \leq 0.36$; the γ phase transforms to the α phase when $y \geq 0.36$. That is, there is a triple point at $y = 0.36$, $T = 399$ K. The γ–β, β–α', and γ–α transitions are all hysteretic and are therefore first order. The conductivities of the β phases are relatively low and the enthalpies of activation relatively high. The conductivity of the β phase decreases with increasing y. The β phase probably belongs to space group $R3$, in which the Cu^+ ions can be ordered. The α and α' phases are the true solid electrolytes; the conductivities are high, >0.73 Ω^{-1}-cm^{-1} at 419 K, and the enthalpies of activation of motion of the Cu^+ ions low, 0.11 eV.

In the system $CsCu_4Cl_3(I_{2-x}Cl_x)$, $0 \leq x \leq 0.25$, the Cl^- for I^- substitutions affect the transitions to only a small extent relative to the stoichiometric compound. The β phase occurs for all x and transforms to α'.

1. Introduction

This is the sixth of a series of papers (*1–5*) from this laboratory on solid electrolytes which are Cu^+-ion conductors and have crystal structures related to that of α-$RbAg_4I_5$ (*6*). The first, third, and fourth deal with the crystal structure, stability, and conductivity of the $RbCu_4Cl_3(I_{2-x}Cl_x)$ system, and the second with the crystal structure, stability, and conductivity of NH_4-$Cu_4Cl_3(I_{1.9}Cl_{0.1})$. The fifth (*5*) is a preliminary report on the new solid electrolyte $CsCu_4Cl_3I_2$. In that paper, it was first reported that the conductivity-vs-temperature results indicated that two phase transitions occurred above room temperature. Subsequently, a third transition was found by differential thermal analysis (DTA) and a note concerning this result was added in proof.

Attempts to define these four phases

crystallographically with experiments on the polycrystalline specimens were not completely successful. The two highest temperature phases both appeared to be cubic in X-ray powder diffraction photography. As already indicated (5), the lower temperature phase of these two might be rhombohedral; as in the $RbAg_4I_5$ case (7), the distortion from cubic dimensions might be so small as to render it unmeasurable from X-ray diffraction powder *photographs*. The dilemma has been resolved; it appears that the endotherm observed in the DTA must be associated with *slight* decomposition of every sample when it transforms from the cubic to the lowest temperature phase.

In further experiments designed to define the individual phases, particularly with the view toward eventually determining their crystal structures, attempts have been made to obtain single crystals. In the course of this work, a fourth phase has been found. It would be erroneous to conclude that this newly found phase accounts for the additional endotherms discussed earlier, because they occur for all specimens including those in the composition region in which the new phase no longer exists.

The new phase, which we label α', is cubic and most likely belongs to space group $P2_13$, which is a subgroup of $P4_332$ and $P4_132$, to which the α phase belongs. There is strong evidence that the $\alpha' \rightarrow \alpha$ transition is continuous.

Crystals quenched in the α' phase slowly change to the β phase at room temperature. In single crystal form, the β phase is relatively stable at room temperature. The crystals of both the α' and β phases are twinned. X-ray powder photographs of the β phase clearly show a small distortion from cubic dimensions. The $\beta \rightarrow \alpha'$ transition appears to be an order–disorder transition; if so, the β phase probably belongs to space group $R3$. This is in contrast with the

behavior of $RbAg_4I_5$ in which case the $\alpha–\beta$ transition is continuous (6–9) and involves a "disorder–disorder" transition (7).

When $0 \leq y \leq 0.36$, the γ phase, which is orthorhombic (5), transforms to the β phase; when $0.36 \leq x \leq 1.0$, the γ transforms to the α phase. Both transformations are first order.

The sluggishness of the transitions in these materials containing Cu^+ ions is in contrast with the rapidity of the transitions that occur in the other halogenide solid electrolytes. The greatest contrast is with $RbAg_4I_5$ for which even the first-order $\beta–\gamma$ transition which occurs at 122 K is instantaneous (7, 8).

Our main purpose in this paper is to report, as closely as possible, the effects of substitutions, as given by the formula $(Cs_{1-y}Rb_y)Cu_4Cl_3(I_{2-x}Cl_x)$, on conductivities and transition temperatures. It is important for this purpose to give the conclusions, even if at present somewhat tentative, obtained thus far, from the single crystal work.

2. Experimental

2.1. Specimen Preparation

CuCl was prepared by the method of Keller and Wycoff (10) and CuI by the method of Kauffman and Pinnell (11) with modification (3) to remove occluded $Na_2S_2O_3$. CsCl and RbCl (both Cerac 99.9%) were used after drying in vacuo at 100–110°C for 16 h.

To prepare the (substituted) pseudo-ternary salts, appropriate amounts of CsCl, RbCl, CuCl, and CuI, for a 2.1–2.4 g specimen, were ground together in an agate mortar, inside a nitrogen-recirculating glove box. The mixture was then pelletized (3), put into a Pyrex test tube which was evacuated, flushed with dry nitrogen, evacuated, and again flushed with dry nitrogen. The pressure was then reduced to 0.5 atm, the tube sealed off, and heated for 2 h at a temperature depending on the specimen com-

TABLE I

LATTICE CONSTANTS AT 298 K AND PREPARATION ANNEALING TEMPERATURES FOR THE CUBIC PHASES IN THE SYSTEM $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$

	y	a (Å)	Annealing temp. (°C)
α'	0.00	10.158	210 ± 5
	0.05	10.152[a]	
	0.10	10.145	
	0.20	10.133	
	0.32	10.117	205 ± 5
α	0.40	10.109	
	0.50	10.096	
	0.60	10.083	
	0.70	10.070	
	0.75	10.063	190 ± 5
	0.85	10.049	

[a] By interpolation.

position (3) (see Tables I–III). The tube was removed from the furnace and opened in the glove box; the specimen was reground, repelletized, put into a Pyrex tube, again sealed off, and heated as before. Usually six cycles sufficed to produce a single-phase specimen as ascertained by X-ray powder diffraction photography.

Particularly at higher Cs^+ contents, grinding of the quenched α'- or α-phase specimens converts them partially to the γ phase. Therefore, to obtain pure single α'- or α-phase specimens for X-ray powder diffraction photographs, the *powdered* specimens were annealed at the temperatures of Tables I–III for at least 5 h. It should be

TABLE II

LATTICE CONSTANTS AT 298 K AND PREPARATION ANNEALING TEMPERATURES FOR THE CUBIC PHASES IN THE SYSTEM $(Cs_{1-y}Rb_y)Cu_4Cl_3(I_{1.833}Cl_{0.167})$

	y	a (Å)	Annealing temp. (°C)
α'	0	10.150	205 ± 5
	0.05	10.143	205 ± 5
	0.20	10.125	220 ± 5
α	0.50	10.084	220 ± 5
	1.00	10.016	205 ± 5

TABLE III

LATTICE CONSTANTS AT 298 K AND PREPARATION ANNEALING TEMPERATURES FOR THE α' PHASES IN THE SYSTEM $CsCu_4Cl_3(I_{2-x}Cl_x)$

x	a (Å)	Annealing temp. (°C)
0.05	10.156	205 ± 5
0.10	10.153	
0.167	10.150	
0.25	10.148	185 ± 5

remarked that before grinding, these specimens must be entirely α' or α phase, and that after grinding, they are still largely α' or α phase. This is emphasized here because we have observed that once the specimen is completely converted to the γ phase, its powder may not reconvert entirely to the α' or α phase even when heated for two days at the original preparation temperature. On the other hand, if a dense pill of the pure γ-phase specimen is heated at the preparation temperature for two days, it is completely converted to the α' or α phase.

To obtain the γ phase, the specimens were annealed at temperatures below the $\gamma \rightarrow \beta$ or $\gamma \rightarrow \alpha$ transition temperatures in 0.5 atm N_2 in sealed tubes. (Approximate transition temperatures were known from many preliminary measurements.) Specimens with larger y require longer annealing periods; conversion of the specimens in pill form is much faster than in powder form.

If allowed to stand at room temperature in pill form, in time, all the specimens containing Cs^+ convert completely to the γ phase.

2.1.1. Single crystals. Small crystals were obtained by melting polycrystalline specimens in nitrogen-flushed, evacuated, sealed-off fused silica tubes. Each tube was suspended in a vertical tube furnace having a temperature gradient. The specimen was kept at 300°C for one h; then the tube was pulled at a rate of 6.3 cm per day to a speci-

men temperature of 255°C, after which the tube was rapidly removed from the furnace and quenched in water at room temperature. All the materials melt incongruently; thus the crystals generally have compositions differing from those of the starting materials. Nevertheless, it is possible to estimate their compositions by measuring the lattice constants of the cubic phases, in the case of the β phase, obtained by appropriate annealing and quenching.

Precession photographs (Mo$K\alpha$ radiation), X-ray powder photographs (Cu$K\alpha$ and Cr$K\alpha$ radiation), and flat plate oscillation photographs (Cu$K\alpha$ radiation) with 6.80-cm film to crystal distance indicate the occurrence of two different phases when $y \leq 0.36$. Both show the presence of $h00$ reflections only when $h = 2n$. One phase is cubic and because it appears to be related to the α phase by a second-order transition, probably belongs to space group $P2_13$. If so, it should have Laue symmetry $m3$; it actually has Laue symmetry $m3m$ and is therefore twinned. Aside from the presence of reflections with $h = 2n$, n odd, the sums of overlapping reflection intensities are such as to indicate a very close relation of the structure of this phase (which we call α') to that of the α phase. Because of the low intensities and multiplicity of the $h00$ reflections, powder photographs do not distinguish the α and α' phases.

In the precession photographs, there is no obvious deviation of the other phase, β, from $m3m$ Laue symmetry. However, the noncubicity is clearly seen in powder photographs taken with Cu$K\alpha$ and especially with Cr$K\alpha$ radiation. The oscillation photographs show some "splitting" of reflections indicative of twinning. In particular, the hhh reflections are doubled. This implies that the phase cannot be tetragonal or orthorhombic. It is most likely rhombohedral; crystals with composition CsCu$_4$Cl$_3$(I$_{1.9}$Cl$_{0.1}$) have $a = 10.15$ Å, $\alpha = 89.7°$.

Periodic X-ray photography of a pow-

dered α'-phase crystal shows that the α' phase changes slowly to the β phase at room temperature.

Some crystals of the β phase of composition CsCu$_4$Cl$_3$(I$_{1.9}$Cl$_{0.1}$) were ground into a powder and an X-ray powder diffraction photograph taken within the β region with a Bond (12) high temperature camera and Cu$K\alpha$ radiation. Unfortunately, high angle lines are not observable and the low angle lines do not show any deviation from cubicity. This implies only that the rhombohedral angle decreases with increasing temperature.

2.2. Conductivity Measurements

The method of preparation of the cell for conductivity measurement is described in detail in Ref. (4) with modifications given in Ref. (5), except that in the latter, the pressure applied to the electrode material first placed into the die should have been 600 kg cm^{-2} (instead of 60 kg cm^{-2}) and the pressure applied finally should have been 5700 kg cm^{-2} (instead of 770 kg cm^{-2}). For specimens other than CsCu$_4$Cl$_3$I$_2$, reported here, the final pressure applied was 5000 kg cm^{-2}.

The equipment used to control and measure the temperatures of the cells is described elsewhere (13). Some of the resistances were measured with the vector impedance meter (1). Most were measured with a Hewlett–Packard 4274A multifrequency LCR meter. The frequency was 1 kHz; in the α-phase region, the results were independent of frequency to the frequency limit, 100 kHz, of the instrument.

2.3. Thermal Analysis

Differential thermal analysis (DTA) was performed with a Deltatherm apparatus, Model D2000 (ca. 1965). Heating rate was 10°C/min. The inert reference material was RbAg$_4$I$_5$. Transition temperatures were corrected by comparison with the AgI $\beta \rightarrow \alpha$ transition at 419 K.
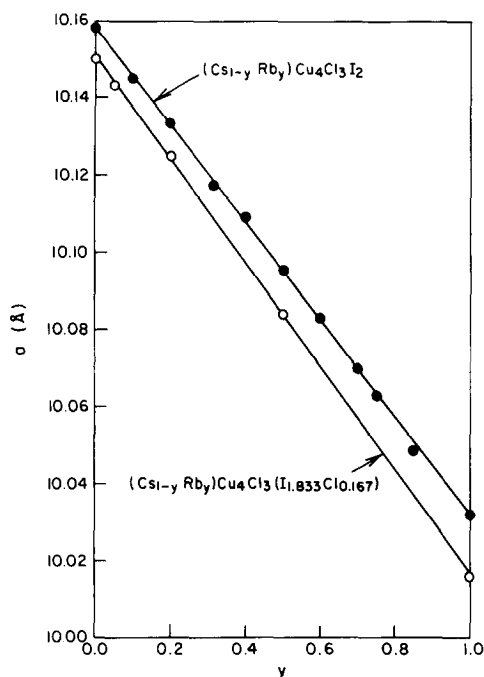
Differential scanning calorimetry (DSC)

FIG. 1. Lattice constant a vs y.

was performed (in Calcutta) with a Perkin-Elmer DSC II. The heating rate was 10°C/min; gold was the reference material.

3. Results and Discussion

3.1. Lattice Constants and Composition

Lattice constants of the quenched cubic phases for the systems $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ and $(Cs_{1-y}Rb_y)Cu_4Cl_3(I_{1.833}Cl_{0.167})$ are listed in Tables I and II, respectively, and plotted vs y in Fig. 1. In both cases, the relation of lattice constant to y is linear; the two lines are not parallel, however, because the substitution of Cl^- for I^- ions has a much larger effect in the $RbCu_4Cl_3(I_{2-x}Cl_x)$ system (3) than in the $CsCu_4Cl_3(I_{2-x}Cl_x)$ system[1] (Table III and Fig. 2). In all cases (Figs. 1 and 2),

[1] It has been found by experiment that maximum x for the system $CsCu_4Cl_3(I_{2-x}Cl_x)$ is close to 0.25, whereas in the system $RbCu_4Cl_3((_{2-x}Cl_x)$, maximum x is 0.40 (3). Maximum x should increase toward 0.40 as y is increased toward 1.00 in $(Cs_{1-y}Rb_y)Cu_4Cl_3(I_{2-x}Cl_x)$.

the deviation of a measured point from the line is less than 0.002 Å; this attests to the high quality of the specimens.

Lattice constants, obtained by indexing of data collected with an X-ray powder diffractometer, have been reported (5) for the orthorhombic γ phase of stoichiometric $CsCu_4Cl_3I_2$; they are $a = 14.242$, $b = 24.984$, $c = 11.712$ Å, all ±0.005 Å, and also for the isostructural phase (3) of $RbCu_4$-$Cl_3(I_{1.96}Cl_{0.04})$: $a = 13.908$, $b = 24.752$, $c = 11.664$ Å, all ±0.005 Å. The γ phase is orthorhombic, but pseudo-hexagonal; a measure of the distortion from hexagonality is the b/a ratio, which would be exactly equal to $\sqrt{3}$ if the crystals were truly hexagonal. That is to say, the cell is a distorted orthohexagonal cell. The values of b/a for the above specimens are 1.754 and 1.800, respectively. Thus the stoichiometric γ-Cs-$Cu_4Cl_3I_2$ crystal is less distorted from hexagonal than the γ-$RbCu_4Cl_3(I_{1.96}Cl_{0.04})$ crystal.

The matrix which transforms the cubic to orthohexagonal axes (or indices) is $(\bar{1}10/\bar{1}12/\frac{2}{3}\frac{2}{3}\frac{2}{3})$. The numerical relation of the lattice constants is $a_o = a_c\sqrt{2}$, $b_o = a_c\sqrt{6}$, $c_o = 2a_c\sqrt{3}/3$, where the subscripts o and c refer to the orthohexagonal and the cubic cell, respectively. For $CsCu_4Cl_3I_2$ with $a_c = 10.158$ Å, the orthohexagonal cell has lattice constants $a_o = 14.366$, $b_o = 24.882$, $c_o = 11.729$ Å. The ratios of these to the actual

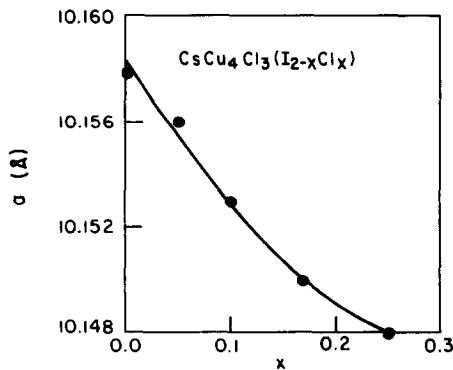FIG. 2. Lattice constant a vs x.

values of the γ phase are, respectively, 1.0087, 0.9979, and 1.0015. For $RbCu_4$-$Cl_3(I_{1.96}Cl_{0.04})$ with $a_c = 10.028$ Å, the ortho-hexagonal cell has lattice constants $a_o = 14.182$, $b_o = 24.563$, $c_o = 11.579$ Å. The ratios of these to the actual values are, respectively, 1.0197, 0.9924, 0.9927. Thus the γ-phase unit cell of $RbCu_4Cl_3(I_{1.96}Cl_{0.04})$ is considerably more distorted from the cubic cell than that of $CsCu_4Cl_3I_2$.

The lattice constants of the γ phases for other compositions have not been determined. However, the powder photographs of specimens in the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system show the progressive increase of the deviation from the cubic cell with increasing Rb^+ content. Increasing the Cl^- replacement of I^- does not have a marked effect.

3.2. The $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ System

3.2.1. Conductivity.
The $\gamma \to \beta$, $\gamma \to \alpha$, and $\beta \to \alpha'$ phase transitions are very sluggish. The temperature region in which the β phase exists is small; the temperature region decreases and the activation enthalpy increases substantially with increasing y. To delineate the β-phase temperature composition region required very careful measurements, long time periods and "step-retracing."

A plot of $\log_{10}(\sigma T)$ vs T^{-1} for stoichiometric $CsCu_4Cl_3I_2$ is given in Ref. (5); the $\gamma \to \beta$ and $\beta \to \alpha'$ crystallographic transitions are manifested most clearly in this plot. They are also observable in the plot of $\log_{10}(\sigma T)$ vs T^{-1} for $(Cs_{0.95}Rb_{0.05})Cu_4Cl_3I_2$ given in Fig. 3. The data for the conductivities of the γ phase to 409.5 K were taken over a period of 11 h. Then the temperature was held at 409.5 K for 11 h, at the end of which the conductivity was 0.025 Ω^{-1} cm^{-1}. The temperature was increased very slowly to 413.3 K (i.e., into the β-phase region) over a period of 10 h, and then held at 413.3 K for another 14 h; at this point the conductivity was 0.048 Ω^{-1} cm^{-1}. The temperature
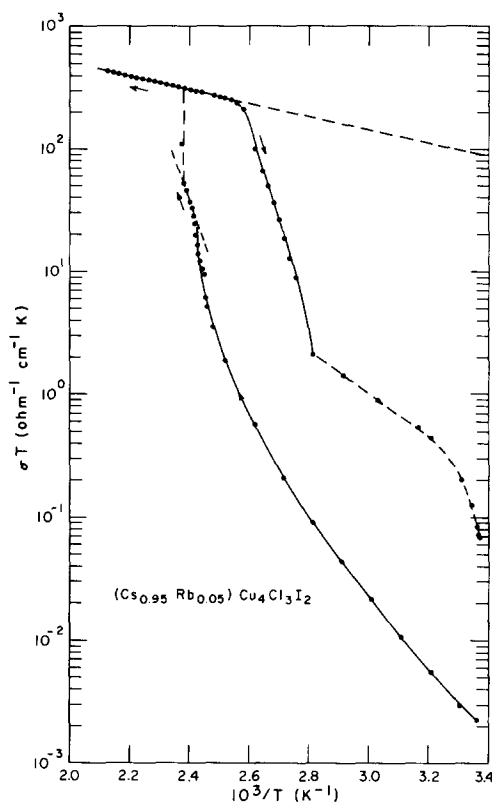

FIG. 3. $\log_{10}$ (conductivity × temperature) vs (temperature)$^{-1}$ (see text for detailed description).

was increased to 421.6 K over a period of 6.5 h, at the end of which the conductivity was 0.14 Ω^{-1} cm^{-1}. Then the temperature was brought back to 419.6 K and held for 11 h at which point the conductivity was 0.24 Ω^{-1} cm^{-1}. The temperature was then held at 420.6 K for 13 h after which the conductivity increased to 0.64 Ω^{-1} cm^{-1}, indicating complete conversion to the α' phase. Data were then taken to 438.3 K over a period of 2 h. The cell was cooled to 427.0 K, without taking data, and data were then taken down to 406.3 K, after which the cell was reheated to 438.3 K without taking data, and data taken to 471.3 K. At this point, the conductivity was 0.92 Ω^{-1} cm^{-1}. All these data were taken in a period of 1.3 h; when the complete conversion to the α' or α
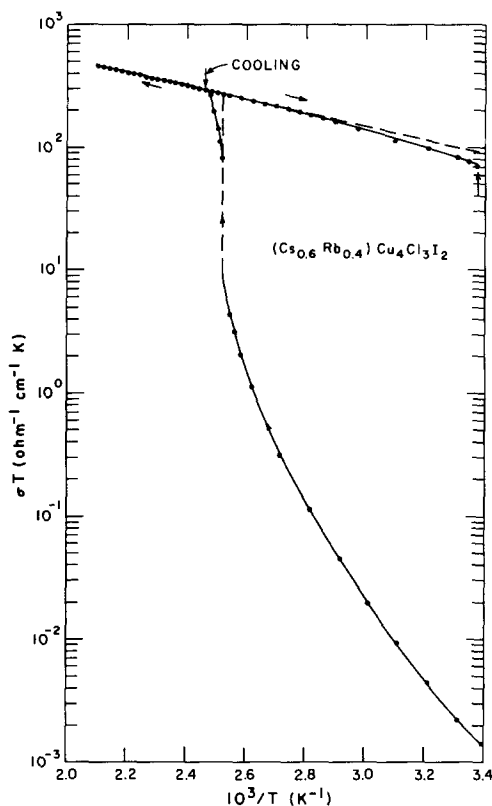
FIG. 4. $\log_{10}$ (conductivity × temperature) vs (temperature)$^{-1}$ (see text for detailed description).

phase is attained, the conductivities change rapidly with temperature.

The cell was then cooled to 430 K without taking data, and held overnight (16 h) at this temperature. Then data were taken over a period of 9 h as the cell was cooled to room temperature, at which the conductivity was $2.4 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$, indicative of the presence of a small amount of the β and/or α' phase. The total time elapsed for the measurements was 105 h. The $\gamma \rightarrow \beta$ transition occurred at 411 K and the $\beta \rightarrow \alpha'$ transition occurred at 420 K.

In Ref. (5), it was pointed out that the $\alpha \rightarrow \beta$ (now $\alpha' \rightarrow \beta$ always) transition was infinitely sluggish. This is correct in the β-phase region. However, it is now known that the transformation to the β phase does occur at temperatures below the γ–β transi-

tion temperature, and it is probable that some β phase is present along the cooling curve (Fig. 3).

A typical plot in which the β phase no longer appears is that for $(Cs_{0.6}Rb_{0.4})Cu_4Cl_3I_2$ shown in Fig. 4. Because there is no β phase, the measurements did not require the same time. The total heating time was 56 h, 41 of which were used for the region 392.5–409.8 K. The temperature was increased to above that of the transition (see Fig. 4) to hasten the $\gamma \rightarrow \alpha$ conversion. Measurements during cooling from 406.3 K ($\downarrow$, Fig. 4) to 298.8 K ($10^3\ T^{-1} = 3.347\ K^{-1}$) took 8 h; the conductivity at 298.8 K was $0.26\ \Omega^{-1}\ cm^{-1}$. Sixteen hours later, the conductivity at 296.6 K ($\uparrow$, Fig. 4) was still $0.23\ \Omega^{-1}\ cm^{-1}$ and 24 h after that it had changed by 2% (based on the third decimal place). This shows that increased Rb$^+$ content markedly decreases the reconversion rate especially at room temperature.

Some specific results of the conductivity measurements made in the solid electrolyte regions of the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system are given in Table IV. The α'- and α-phase conductivities are indistinguishable. The bulk densities of the pills, which were all γ phase, were usually 93–95% of the corresponding X-ray densities of the γ phases. Because the lattice constants of all the γ phases were not determined, their X-ray densities were estimated by multiplying the densities of the cubic phases at room temperature by the factor 1.006 which is the ratio of the γ to (room-temperature) α'- or α-phase densities of both α'-CsCu$_4$Cl$_3$I$_2$ (5) and α-RbCu$_4$Cl$_3$(I$_{1.96}$Cl$_{0.04}$) (3).

The temperature ranges over which the measurements were made differ somewhat. At the high temperature end, some difficulty was encountered as manifested by decreases in conductivity with increases in temperature. Although these changes occurred at different temperatures in different specimens, they did not show a correlation with composition. Usually grain growth

TABLE IV

CONDUCTIVITY RESULTS FOR THE CUBIC PHASES OF THE $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ SYSTEM

y	Bulk density[a]	Temp. range (K)	h_m (eV)	$\sigma(\Omega^{-1}\,cm^{-1})$ at 298 K[b]	$\sigma(\Omega^{-1}\,cm^{-1})$ at 419 K
0.00	94	397–459	0.110	0.30	0.73
0.05	93	388–476	0.110	0.31	0.75
0.10	93	407–476	0.111	0.30	0.75
0.20	93	394–455	0.107	0.31	0.74
0.32	94	406–443	0.104	0.32	0.75
0.40	93	368–481	0.109	0.31	0.76
0.50	95	368–463	0.106	0.33	0.77
0.70	94	370–463	0.101	0.34	0.76

[a] Of pellet as percent of X-ray density of γ phase. See text.

[b] Extrapolated.

and microscopic cracks were found in the specimens after completion of the measurements.

There is no systematic variation in h_m, the enthalpy of activation of motion of the Cu^+ ions, with respect to y. Probably the largest error in h_m occurs for the specimen with $y = 0.70$, because h_m for the stoichiometric $RbCu_4Cl_3I_2$ is 0.112 eV (4). There was more experimental difficulty with the measurement of conductivities of the cesium than with the purely rubidium compounds (4). There is no a priori reason to expect replacement of Cs^+ by Rb^+ to change h_m or the conductivities significantly from those of $RbCu_4Cl_3I_2$ although the conductivities of the latter were found to be significantly higher.

There are no systematic differences in the conductivity values for specimens in the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system; the average of the values at 298 K, extrapolated from the ranges given in Table IV, is 0.32 ± 0.02 $\Omega^{-1}\,cm^{-1}$ and at 419 K, the $\beta \rightarrow \alpha$ transition temperature of AgI, 0.75 ± 0.02 $\Omega^{-1}\,cm^{-1}$. The analogous values for $RbCu_4Cl_3I_2$ are 0.39 and 0.97 $\Omega^{-1}\,cm^{-1}$. For $RbCu_4Cl_3I_2$ (4), $\log_{10}(\sigma T) = -565\ T^{-1} + 3.96$; for the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system, the average for the eight specimens of Table V is $\log_{10}(\sigma T) = -540\ T^{-1} + 3.79$. Thus there is a dis-

placement of the two lines indicating 20–25% lower conductivities for the specimens containing Cs^+. However, at the very least, the conductivity results for the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system should extrapolate to the values obtained for $RbCu_4Cl_3I_2$. They do not, and within experimental error, for all specimens in the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system, they are the same for the same temperature.

TABLE V

TRANSITION TEMPERATURES OF THE $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ SYSTEM

y	$T_{\gamma \rightarrow \beta}$ (K)	$T_{\beta \rightarrow \alpha'}$ or	$T_{\gamma \rightarrow \alpha}$ (K)
0.00	414[a]	427[a]	
0.05	411	420	
0.10	409	416	
0.20	402	407	
0.32	400[b]	401	
0.40	—	—	397
0.50	—	—	387
0.70	—	—	371
1.00	—	—	350[c]

[a] In Ref. (5), 418 and 431 K were reported for these transitions, respectively. Errors in the temperature scale of the temperature controller have since been discovered and corrected.

[b] By interpolation.

[c] Ref. (3).

We believe that the results obtained for both the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ and $RbCu_4Cl_3(I_{2-x}Cl_x)$ systems indicate reasonably high *precision*. However, it is likely that the results for the latter are considerably more *accurate* than for the former. In the case of the $RbCu_4Cl_3(I_{2-x}Cl_x)$ system (4), all specimens measured were in the cubic, solid electrolyte phase at the start. In each case, the electrode material was a mixture of 2-μm silver powder and the particular solid electrolyte (4). The measurements were made between room temperature, 298 K, and 415 to 460 K, depending on the specimen (see Table I of Ref. (4)). There *was* some difficulty in obtaining good results for the stoichiometric compound and it was necessary to make the measurements on freshly prepared cells in all cases.

For the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$, freshly prepared cells were also always used. However, we could not obtain good results by using each particular compound to prepare the electrode material for each run as we had for the $RbCu_4Cl_3(I_{2-x}Cl_x)$ system (4). It is for this reason that we settled on the use of $RbCu_4Cl_3(I_{1.9}Cl_{0.1})$ for measurements on all the specimens containing Cs^+. Furthermore, all specimens were in the γ phase at the beginning of the measurements. To reach the temperature region in which the cubic, solid electrolyte phase exists, at least one first-order transition must be traversed. It will be shown eventually that a subtle chemical reaction must also take place. Probably of considerable importance is the long duration of the measurements, which, we know from inspection, causes grain growth and microscopic cracks. The systematic error giving the lower conductivity results for the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system, and for the other Cs^+-containing specimens as well, is probably connected with one or more of the above.

It should be noted that the conductivity of the β phase decreases markedly with increasing y. At the centers of the β-phase

regions 421, 415, 413, and 405 K, for $y = 0$, 0.05, 0.10, and 0.20, respectively, the conductivities are 0.13, 0.09, 0.05, 0.02 Ω^{-1} cm^{-1}, respectively. The activation enthalpies are very high and increase markedly with increasing y: 0.77, 1.4, 2.5, and 1.9 eV, respectively. With such large activation enthalpies, the β phases cannot be true solid electrolytes and it is probable that the Cu^+ ions are ordered in the β-phase crystal structure. If so, the most probable space group is $R3$.

It was shown in Ref. (5) that the $\log_{10}(\sigma T)$-vs-T^{-1} curve for the γ phase of $CsCu_4Cl_3I_2$ can be approximated rather closely by two intersecting straight lines represented by

$$\sigma T = 8.77 \times 10^6 \exp(-0.577/kT)$$
$$+ 2.43 \times 10^{19} \exp(-1.538/kT).$$

This equation indicates that in the lower temperature region in which the γ phase exists there are some ions that are relatively mobile, while in the higher temperature region, additional ions are being thermally excited into mobile states. Further, if the enthalpy in the lower temperature region is considered to be entirely enthalpy of motion h_m, then the formation enthalpy (14) h_f in the higher temperature region is 1.92 eV because $1/2\, h_f + h_m = 1.54$ eV.

The behavior of $\log_{10}(\sigma T)$ vs T^{-1} of the γ phase of all the other specimens is similar to that of γ-$CsCu_4Cl_3I_2$. It does not seem necessary to calculate the relations for any more of them.

For completeness, it is worth pointing out (as in Ref. (5)) that the $\log_{10}(\sigma T)$-vs-T^{-1} behavior of the γ phase is similar to that of β-$PyAg_5I_6$ (15), implying that in the γ-phase crystal structure, there are "built-in" sites into which Cu^+ ions can move.

3.2.2. Temperature-composition phase diagram. Figure 5 is a temperature-composition solid-state phase diagram of the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system. The transition
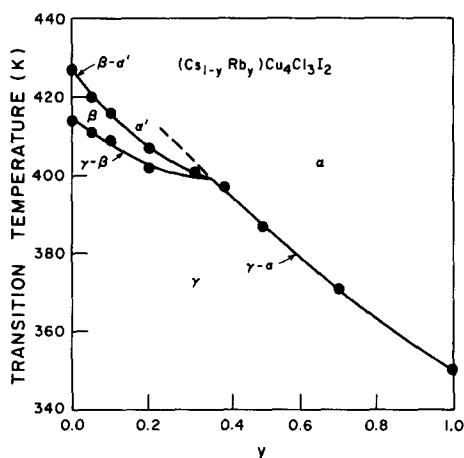
FIG. 5. Temperature-composition solid-state phase diagram. The broken line which is supposed to represent the $\alpha'-\alpha$ phase transition line is an extension of the $\gamma-\alpha$ phase coexistence line and is included to emphasize its existence. The correct $\alpha'-\alpha$ line is yet to be determined (see text).

temperatures, also listed in Table V, were obtained from the conductivity measurements.

The β phase exists in very narrow temperature ranges: 13 K for $CsCu_4Cl_3I_2$, decreasing to zero for $y = 0.36$. The broken line (Fig. 5) representing the second-order $\alpha'-\alpha$ transitions is drawn simply as an extension of the $\gamma-\alpha$ coexistence line. It is included to emphasize its existence. We hope to establish the correct line by monitoring the decrease in intensity of the (200) reflections with increasing temperature and perhaps by collaboration with someone who has more sensitive DSC equipment.

The triple point at $y = 0.36$, $T = 399$ K "forces" the $\alpha'-\alpha$ transition to be continuous. (Fisher (16) has suggested that the term "continuous" be used for all transitions other than first order.) At such transitions, the states of both phases are considered to be the same (17).

The β-phase temperature region for the specimen with $y = 0.32$ is about 1 K. The $\gamma \rightarrow \beta$ transition could not be detected in the conductivity measurements.

We now have further information on the $\alpha \rightarrow \gamma$ transformation of $RbCu_4Cl_3I_2$. Originally we did believe that this transformation was attained only by cold work for reasons described in detail in Ref. (3). However, among the specimens prepared for Ref. (4) which are now approximately two years old, those with $x \leq 0.03$ have transformed partially to the γ phase. None of the specimen with $x = 0.04$ remained, so that we do not how it behaves. Specimens with $x \geq 0.05$ are still α phase.

We do not know why the old samples investigated for Ref. (3) that should have changed did not or why specimens with $0 < x \leq 0.03$ would not transform when subjected to the cold work. Suffice it to say now that the new observations must imply that for $x \leq 0.03$ (possibly $x \leq 0.04$), the α phases are unstable with respect to the γ phase at room temperature. The transformation always involves a decomposition, in which two of the products are CuI and γ-$RbCu_4Cl_3(I_{1.96}Cl_{0.04})$. When the old specimens with $x \leq 0.03$ were reannealed at 200°C, they converted to the cubic phase with $x = 0.04$; the presence of CuI was detected in the X-ray powder photographs, just as in the case of the results on stoichiometric $RbCu_4Cl_3I_2$ reported earlier (3).

3.2.3. Thermal analyses. Shown in Fig. 6 are the results of a DSC run on $CsCu_4Cl_3I_2$; three distinct endotherms occur but heat is still being absorbed between ~428 and 460 K. It is difficult to establish a baseline, and almost impossible to resolve the two effects that occur around 420 K for the purpose of determining transition temperatures. In the DTA run (not shown), there is no resolution of the two peaks at all.

The two peaks about 420 K must be associated with the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha'$ transitions. Even when the $\gamma \rightarrow \beta$ transition no longer occurs, results obtained from the DSC or DTA for transition temperatures do not agree well with those obtained from the conductivity measurements. The thermal
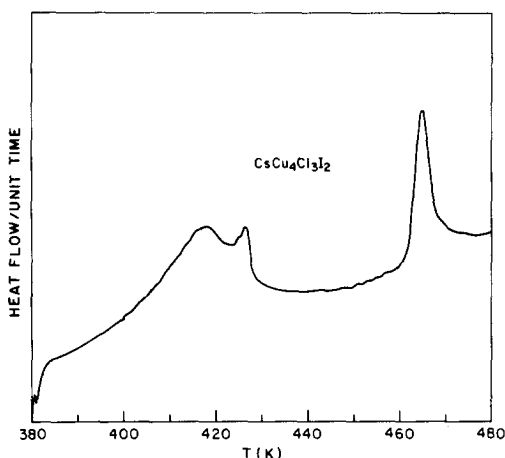
FIG. 6. Differential scanning calorimeter trace. The first and second peaks are related to the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha'$ transitions, respectively. The third peak is associated with a chemical reaction (see text).

analyses give higher values, e.g., for $(Cs_{0.3}Rb_{0.7})Cu_4Cl_3I_2$, the DTA gives a $T_{\gamma \rightarrow \alpha}$ of 395 K as opposed to 371 K from conductivity measurements. From the earlier discussion of the two examples, it is readily seen, that the error in transition temperatures from conductivity measurements could only be on the high side. Thus the sluggishness of the transitions is probably the cause of the discrepancy with DTA results. DSC results are similarly high and in general, agree with the DTA results.

In Fig. 6, there is also a peak at ~465 K. A similar peak is seen in both the DSC and DTA runs on every specimen containing Cs^+ on which they have been made in the systems $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ and $CsCu_4Cl_3(I_{2-x}Cl_x)$. The temperature at which this peak occurs appears to depend on composition, the highest being for $CsCu_4Cl_3I_2$. As indicated earlier, it was at first believed that this peak indicated another phase transition. However, there is no systematic indication of such a transition in the conductivity-vs-temperature measurements. Furthermore, these endotherms also occur for specimens with $y > 0.36$. Thus, it

seemed that these peaks must represent a chemical reaction.

To determine the order of this "transition," the following experiment was carried out with the DTA equipment. A sample of $CsCu_4Cl_3I_2$ was heated through the temperature of this (endothermic) heat effect; on *cooling*, the highest temperature peak, which would be exothermic, did not appear. This proved that this heat effect is associated with a first-order process.

We then carried out the following experiments on specimens of $(Cs_{0.3}Rb_{0.7})Cu_4Cl_3I_2$ and $(Cs_{0.8}Rb_{0.2})Cu_4Cl_3I_2$. Each specimen was heated to about 5° above its temperature of transition (Fig. 5 and Table V) to its (first) cubic phase. The block was quickly removed from the furnace and the specimen cooled under a continuous flow of dry nitrogen. When the furnace and block cooled sufficiently, the block was replaced in the furnace and the specimen again heated to just above its $T_{\gamma \rightarrow \alpha}$ and $T_{\beta \rightarrow \alpha'}$, respectively, the block quickly removed and the specimen cooled under a continuous flow of nitrogen. After about 10 such treatments, these transitions no longer appeared.[2] Then, in both cases, a DTA run to well above the temperature of the highest temperature peak, 417 and 446 K, respectively, showed that this peak was no longer present. This *proves* that this peak is not associated with what one would normally consider to be a crystallographic transition.

Although the important conclusion is that the highest temperature peak observed by DTA and DSC is not a normal crystallographic transition, it is of interest to know what does occur. This is not easily done experimentally, but we can suggest a plausible explanation. When *all* the β or γ phase is removed, there is only the cubic phase (α, α', respectively) left and it is a pure sta-

[2] It would have been much better to heat the specimen to just above the transition and keep the temperature constant there. This cannot be done with the DTA equipment that is available to us.

TABLE VI

CONDUCTIVITY RESULTS FOR THE CUBIC PHASES OF THE $CsCu_4Cl_3(I_{2-x}Cl_x)$ SYSTEM
AND TRANSITION TEMPERATURES

x	Bulk density[a]	Temp. range (K)	h_m (eV)	$\sigma(\Omega^{-1}\,cm^{-1})$ at 298 K[b]	$\sigma(\Omega^{-1}\,cm^{-1})$ at 419 K	Transition temp. (K)	
						$T_{\gamma\to\beta}$	$T_{\beta\to\alpha}$
0.10	93	413–480	0.104	0.30	0.69	413	426
0.167	94	413–485	0.103	0.30	0.69	413	422
0.25	92	413–458	0.101	0.29	0.64	412	421

[a] As a percentage of the X-ray density of the γ phase (see text).
[b] Extrapolated.

ble phase. With a heating rate of 10°C/min as was required to see even the peaks as shown (Fig. 6), some of the β and/or γ phase remained with the cubic phase, possibly not yet having the composition of the pure cubic phase, to a higher temperature and reacted with minute amounts of decomposition products still present to form more of the cubic phase. The question is: What decomposition products?

It is disconcerting to be forced to suggest that in *every* case when the cubic phase is annealed entirely to the γ phase, the latter is not phase pure! This cannot be discerned in the X-ray powder diffraction photographs for specimens in the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system when $y \le 0.75$. However, a minute amount, estimated at $\le\sim0.5\%$ by weight, of CuI is detected in a diffractometer pattern of γ-$CsCu_4Cl_3I_2$. Almost surely, there must also be present some other intermediate phase. Such phases $CsCu_2Cl_3$, Cs-Cu_2ICl_2, $CsCu_2I_2Cl$, $CsCu_2I_3$ do exist, but we have not seen any of them in the diffractometer pattern, probably because of the presence of much smaller amounts than CuI and overlap with the lines of the γ phase. A similar problem occurred in the study of $RbCu_4Cl_3I_2$ (3); in that case, it was proved that this explanation *is* correct. Moreover, in the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system, we do see the CuI in the X-ray powder diffraction photographs of the low-tempera-

ture-annealed specimens for $y \ge 0.75$, but unlike the $RbCu_4Cl_3I_2$ case, when heated for about 10 h at 200°C, the γ phase, CuI, and other phases present recombine to form the single α or α' phase.

It should be emphasized that for the specimens in the $(Cs_{1-y}Rb_y)Cu_4Cl_3I_2$ system, the decomposition cannot be significant with respect to the electrical properties of the γ phase. In any case, because of the time taken to attain the α or α' phase in the measurements of conductivity, there is no doubt that these represent the pure cubic solid electrolytes with the formulas as given, e.g., in Tables I–III.

3.3. Conductivity and Phase Transitions in the System $CsCu_4Cl_3(I_{2-x}Cl_x)$

Conductivity measurements and thermal analyses have been made on three specimens in the $CsCu_4Cl_3(I_{2-x}Cl_x)$ system, i.e., for $x = 0.10$, 0.167, and 0.25. Results of conductivity measurements on the solid electrolyte phases are given in Table VI. Also given are the $\beta \to \alpha'$ transition temperatures. Substitution of Cl$^-$ for I$^-$ has a relatively small effect on the transition temperatures.

The enthalpies of activation of motion h_m are probably low, and should probably increase with increasing x (4). The low values of h_m are a result of some drop-off of conductivity with increasing temperature be-

cause of grain growth and/or development of microscopic cracks in the cells.

Acknowledgments

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