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Crystal structure and conductivity of the solid electrolyte α-$RbCu_4Cl_3I_2$

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Crystals of the solid electrolyte $RbCu_4Cl_3I_2$ are isostructural with $RbAg_4I_5$. The crystal of $RbCu_4Cl_3I_2$ on which the structure analysis was done belongs to space group $P4_332$ (O^6) with lattice constant 10.032 ± 0.003 Å. As in $RbAg_4I_5$, there are three sets of tetrahedral sites for the charge carriers with a total of 56 sites. In $RbCu_4Cl_3I_2$, all the tetrahedra have both Cl^- and I^- ions at apices, but the coordination polyhedron about the Rb^+ ions contain only Cl^- ions. The room-temperature distribution of charge carriers differs from that in $RbAg_4I_5$. Although the occupancies of the two sets of 24-fold sites are almost equal, that of the eightfold sites is still very low and thus overall the distribution is nonuniform. Room-temperature conductivities as high as $0.44\ \Omega^{-1}cm^{-1}$ have been measured directly on a specimen having only 94% of theoretical density. Thus it is probable that the true electrolytic conductivity exceeds at least $0.47\ \Omega^{-1}cm^{-1}$. At the temperature of the transition of AgI to α-AgI, 419 K, the minimum value of the conductivity of $RbCu_4Cl_3I_2$ is 1.53 $\Omega^{-1}cm^{-1}$, about 17% higher than that of α-AgI at the transition. Thus $RbCu_4Cl_3I_2$ has the highest conductivity of any solid electrolyte over a wide temperature range in the lower-temperature regions. Conductivity measurements between 130 and 383 K indicate that the α-β transition occurs at 221 K and a β-γ transition at 170 K; the nature of the latter differs from that of the $RbAg_4I_5$ β-γ transition. There is evidence that the average mobility of the Cu^+ ion is higher than that of the Ag^+ ion.

INTRODUCTION

Until recently, the solid electrolyte with the highest room-temperature electrolytic conductivity was $RbAg_4I_5$.[1] $RbAg_4I_5$ is cubic and belongs to space groups $P4_132$ (O^7) or $P4_332$ (O^6)[2]; crystals of both have been grown.[3] There are 20 iodide ions per unit cell divided between a 12-fold and an 8-fold set. Only the former are bonded to the Rb^+ ions. Consequently, when the title of a paper by Takahashi *et al.* appeared in the list of papers to be given at the Second International Meeting on Solid Electrolytes on a new solid electrolyte in the system RbCl-CuCl-CuI, it was immediately apparent what the formula must be, namely, $RbCu_4Cl_3I_2$. Just as a matter of fit, it was most probable that it would be the chloride ions that would be bonded to the Rb^+ ions. Our very first specimen with the stoichiometry given above gave a sharp x-ray powder diffraction photograph that showed clearly that the material was single phase.

The extended abstract of the Takahashi *et al.* paper[4] contains a much different formula from that given above. Takahashi pointed out in his talk that the formula given in this abstract is incorrect, and gave the correct formula to be $Rb_4Cu_{16}Cl_{13}I_7$. This is to be compared with the formula for the total unit-cell content derived from our formula, namely, $Rb_4Cu_{16}Cl_{12}I_8$. As will be seen, all our results and especially the single-crystal structure analysis confirm our proposed composition.

Note added in proof. However, as a result of continued investigation, it appears that there is a solid solution range in the cubic phase from $RbCu_4Cl_3I_2$ to $RbCu_4Cl_3(I_{1.6}Cl_{0.4})$. This range includes the composition reported by Takahashi *et al.*[4]

CONDUCTIVITY

Sample preparation

CuCl was purified by boiling an HCl acidified solution with 99.99% pure copper metal shot for 3 h. Upon dilution, white CuCl was precipitated. The CuCl was washed twice with 2*N* HCl and 20 times with distilled water and then three times with reagent-grade acetone. The resulting material was dried with continuous pumping, utilizing a liquid-N_2 trap, for several hours.

CuI was prepared by mixing solutions of reagent-grade $CuSO_4$ and KI. The precipitate was filtered and washed ten times with 1*N* KI and 70 times with distilled water until no I_2 was detected. The CuI was off-white in color and was dried in the same manner as the CuCl.

The RbCl was used as received from the Cerac Chemical Company.

Stoichiometric amounts of RbCl, CuCl, and CuI sufficient to prepare about 5 g of $RbCu_4Cl_3I_2$ were weighed into a Pyrex test tube. The tube was evacuated continuously while the contents were melted. The melt was quenched to room temperature and the tube transferred to a nitrogen filled dry box. The contents were removed from the tube and ground with an agate mortar and pestle.

Pellets of about 1 g each were made with a $\frac{3}{8}$-in. i.d. die and application of approximately 1 kbar uniaxial pressure with a laboratory press. The pellets were individually sealed in Pyrex tubes under vacuum, placed in a furnace, and annealed at 200 °C for 4 h. The tubes were then removed from the furnace, broken open, and the pellets reground in the dry box. After repelletizing and sealing, an additional 4 h anneal was performed. X-ray powder diffraction photography showed the presence of only $RbCu_4Cl_3I_2$ following the second anneal.

Various attempts were made to optimize electrode contact to carefully dried $RbCu_4Cl_3I_2$. This, in fact, was the most formidable problem in the present investigation. The other was to obtain a dense specimen from the polycrystalline material. This contrasted with the ease in obtaining very close to theoretical densities of silver compounds by compressing them in a pill press at 2800 $kg\,cm^{-2}$.

The best bulk density obtainable by uniaxial compression of an approximately 1-cm diam pill with 2800 $kg\,cm^{-2}$ was ~90%. Exceeding this pressure caused pellet lamination. An attempt to improve this situation was carried out as follows: The specimen first compressed in a pill press was inserted into a latex rubber "finger" so that no oil could get to it, then into a teflon capsule containing Dow Corning No. 704 diffusion pump oil, and utilizing a Kennedy press, subjected to a pressure of 10–11 kbar. This gave 94% of theoretical density, which is low relative to silver compounds, but apparently the best that could be done without making a career of it. X-ray powder photographs were taken of one of these specimens to ascertain that the high-pressure treatment had not caused decomposition. We propose eventually to make conductivity measurements on single crystals of the material. Work on the crystal growth has already begun.

Our attempts to optimize electrode-specimen contact included the use of copper powder mixed with electrolyte as electrodes. It turned out that although the x-ray photograph of the copper powder showed very little Cu_2O present, the surface oxidation was sufficient to render the powder essentially nonconducting.

We tried pressing solid copper discs (0.05 mm thick) onto the specimen when we first compressed it, as apparently done by Takahashi *et al.*[4] We also tried well amalgamated copper electrodes. All these gave very poor results.

Our best results and those to be reported herein were obtained by using a mixture of 25-wt% 1-μm silver powder and 75 wt.% of the electrolyte as electrodes first compressed with the specimen in a pill press followed by the treatment at 11 kbar.

Conductivity measurement

Conductivities were measured by the complex plane technique first applied to solid electrolytes by Bauerle[5] and which is now widely used by others. The vector impedance measuring device was built in this laboratory. It presently has a frequency range of 0.5 Hz to 350 kHz, but we are planning to extend this range at the high end. The device comprises two major sections, a reference section which generates both an inphase square wave and a quadrature square wave, and an analog section. The analog circuit applies a sine wave of digitally selectable amplitude to the sample pellet and produces an output signal proportional to the current passing through the pellet. This output signal is further processed by synchronous rectification into its real and imaginary parts. These outputs and the voltage amplitude applied to the pellets are read out on a digital voltmeter and used to calculate the total impedance, resistance, reactance, and phase angle.

Results

As indicated earlier, there was difficulty with electrode contact. However, we have obtained a room-temperature conductivity as high as 0.44 $\Omega^{-1}\,cm^{-1}$ for a specimen of 94% of theoretical density. This must imply that the actual room-temperature conductivity is higher than this, probably substantially.

Figure 1 is a plot of the ($\log_{10}$) conductivity multiplied by temperature versus reciprocal temperature. The data were used to calculate the best straight lines in the three temperature regions that are obvious in the figure. The equations of the lines are as follows:

High, $\log_{10}\sigma T = -0.741\ (1000/T) + 4.557$

Intermediate, $\log_{10}\sigma T = -0.923\ (1000/T) + 5.380$

Low, $\log_{10}\sigma T = -1.540\ (1000/T) + 9.000\,.$

The activation enthalpies of motion calculated from the slopes are 0.15, 0.18, and 0.31 eV, respectively. The high- and intermediate-temperature region lines intersect at $T = 221$ K; the intermediate- and low-temperature region lines, at 170 K. These are very likely transition temperatures which we name α-β and β-γ, respectively. The β and γ phases may be isostructural with the analogous $RbAg_4I_5$ phases, but the character of the β-γ transition differs for the two compounds.

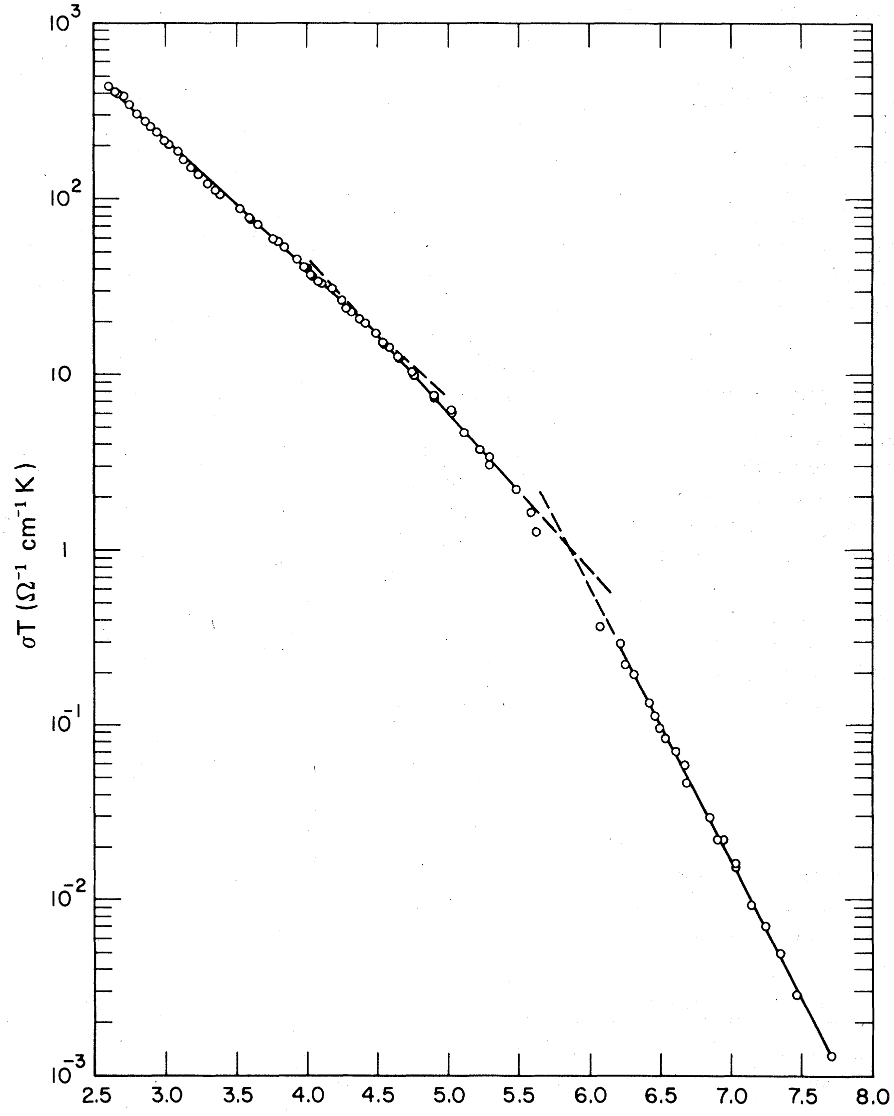

FIG. 1. $\log_{10}$ of the conductivity multiplied by temperature vs reciprocal temperature for $RbCu_4Cl_3I_2$.

X-RAY DIFFRACTION DATA

An x-ray powder photograph of the $RbCu_4Cl_3I_2$ taken with Cu *Kα* radiation gave a lattice constant of 10.032 ± 0.003 Å. Subsequent experiments indicated that no significant solid solution range exists, giving additional support to the formula proposed here.

Description of the growth of single crystals of $RbCu_4Cl_3I_2$ will be given elsewhere. Buerger precession photographs were taken of a small single crystal, confirming what the powder photograph indicated—that the crystals of $RbCu_4Cl_3I_2$ are isostructural with $RbAg_4I_5$. The crystal had diffraction symmetry $m3m$; the only systematically absent reflections are those with indices $h00$ $(0k0,\ 00l)$ with $h\ (k, l) \neq 4n$. This implies that the most probable space group to which these crystals belong is either $P4_332$ (O^6) or $P4_132$ (O^7).

Small single-crystal pieces of $RbCu_4Cl_3I_2$ were placed in a sphere grinder.[6] Dry nitrogen was used to propel the crystals. A spherical crystal of 0.12-mm diameter was mounted on a goniometer head and coated with methylcellulose dissolved in xylene. After the xylene had evaporated from the coating, the crystal was aligned so that the fourfold crystal axis was the rotation axis.

The data were collected with a Buerger-Supper diffractometer automated by a NOVA 1200 computer. Zr-filtered Mo *Kα* radiation was used in the range $10° \leq 2\theta \leq 60°$. The scan rate was 1°/min; the scan width was $(1.5 + 0.5Lp)$, where L is the Lorentz and p the polarization correction. Background was counted at $\frac{1}{4}$ the scan time, before and after the scan.

The x-ray density of $RbCu_4Cl_3I_2$ is 4.604 g/cm^3. For Mo $K\alpha$ radiation, the linear absorption coefficient is 19.24 mm^{-1}, giving 1.15 for μR. Absorption corrections were applied to the data. A total of 334 independent reflections was included in the 2θ range used. Of these, 250 were above the threshold count of 50. The 330 reflection was particularly affected by a contribution from a "dirty" radiation streak and was omitted from the calculations.

REFINEMENT OF THE CRYSTAL STRUCTURE

The refinement of the structure was carried out by least-squares calculations for which the NUCLS5 program[7] was used. Starting parameter values were close to those of $RbAg_4I_5$; some adjustment was made in the chloride ion parameter to give a reasonable Rb–Cl distance.

The final R value, $R = (\sum ||F_0| - |F_c||)/\sum |F_0|$, is 0.072; the standard error of an observation of unit weight is 0.97 based on the following weighting scheme:

$$\sigma = 0.03\,F, \quad F \geq 100\,,$$

$$\sigma = 3 + 0.03(100 - F), \quad F < 100\,,$$

$$w = 1/\sigma^2\,.$$

The scale factors (one for each layer of reflections) had clearly converged before the final cycles and these were not varied in the final two cycles. Also not varied was the x parameter of the eightfold Cu^+ ion sites. In previous cycles this parameter was showing a standard error of 0.008 and was moving in a direction so as to give unlikely Cu–Cl and Cu–I distances. This probably resulted from the low occupancy of these sites. The value of this Cu^+-ion-site parameter was fixed at 0.161. All other parameters *were* varied and *no* constraint was put on the total Cu^+ ion content of the unit cell.

The sum of the Cu^+ ion multipliers is 0.677 with a standard error of 0.15. The deviation of 0.010 from the true value of 0.667 is less than one standard error. The combined results give high reliability to the correctness of the structure and of the formula proposed here.

The least-squares calculations were carried out in space group $P4_132$. In the course of these calculations, the imaginary parts of the anomalous-dispersion[8] contributions were introduced. It was found that the enantiomorph was favored. Thus the crystal on which our work was done belongs to space group $P4_332$. However, we shall give the parameters in the $P4_132$ space group (see Table I) so as to facilitate a direct comparison with the earlier paper[2] on $RbAg_4I_5$. It is probable, as in the case of $RbAg_4I_5$ (Ref. 3), that both enantiomorphs of $RbCu_4Cl_3I_2$ will be shown to exist.

Interionic distances

A list of interionic distances calculated with the ORFFEC program[11] is given in Table II. For con-

TABLE I. Positional and thermal parameters.

Ion position	Rubidium	Iodide	Chloride	Copper (cuprous)		
	4a	*8c*	*12d*	*24e*	*24e*	*8c*
Multiplier	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	0.339	0.294	0.044
σ				0.020	0.017	0.008
x	$\frac{3}{8}$	0.0103	$\frac{3}{8}$	0.5214	0.0026	0.161
$\sigma(x)$		0.0001		0.0015	0.0013	
y	$\frac{3}{8}$	$=x$	−0.1504	0.2919	0.8341	$=x$
$\sigma(y)$			0.0005	0.0018	0.0017	
z	$\frac{3}{8}$	$=x$	$=(\frac{3}{4}-y)$	0.7977	0.2132	$=x$
$\sigma(z)$				0.0016	0.0018	
β_{11}	0.0110	0.0068	0.0082	0.0146	0.0063	0.0111
$\sigma(\beta_{11})$	0.0004	0.0001	0.0009	0.0019	0.0013	0.0034
β_{22}	$=\beta_{11}$	$=\beta_{11}$	0.0072	0.0218	0.0207	$=\beta_{11}$
$\sigma(\beta_{22})$			0.0005	0.0030	0.0032	
β_{33}	$=\beta_{11}$	$=\beta_{11}$	$=\beta_{22}$	0.0153	0.0211	$=\beta_{11}$
$\sigma(\beta_{33})$				0.0024	0.0032	
β_{12}	0	0.0001	−0.0015	0.0006	−0.0009	−0.0011
$\sigma(\beta_{12})$		0.0001	0.0004	0.0018	0.0014	0.0021
β_{13}	0	$=\beta_{12}$	$=\beta_{12}$	0.0037	0.0017	$=\beta_{12}$
$\sigma(\beta_{13})$				0.0015	0.0015	
β_{23}	0	$=\beta_{12}$	−0.0023	0.0022	−0.0001	$=\beta_{12}$
$\sigma(\beta_{23})$			0.0007	0.0016	0.0020	

TABLE II. Interionic distances and standard errors.

Atom types and symmetry	No. of distances	Distance (Å)	Analogous distance in $RbAg_4I_5$
I–I	3	4.228(2)	4.505(4)
I–Cl	3	3.960(7)	4.358(4)
I–Cl	3	4.147(1)	4.670(3)
I–Cl	3	4.315(7)	4.880(5)
Cl–I	2	3.960(7)	4.358(4)
Cl–I	2	4.147(1)	4.670(3)
Cl–I	2	4.315(7)	4.880(5)
Cl–Cl	4	3.740(4)	4.455(3)
Cl–Cl	2	5.520(13)	5.425(6)
Chloride octahedron about $Rb^+(a)$			
Rb–Cl	6	3.381(3)	3.627(2)
Cl–Cl	6	3.740(4)	4.455(3)
Cl–Cl	3	5.520(13)	5.425(6)
Cl–Cl	3	5.758(8)	6.069(4)
Tetrahedron about $Cu^+(c)$			
Cu–I	1	2.62	2.79(6)
Cu–Cl	3	2.43	2.91(3)
I–Cl	3	4.315(7)	4.880(5)
Cl–Cl	3	3.740(4)	4.455(3)
Tetrahedron about $Cu^+(e)$ (0.521, 0.292, 0.798) II			
Cu–I	1	2.77(2)	2.94(1)
Cu–Cl	1	2.32(2)	2.81(1)
Cu–I	1	2.70(2)	2.87(1)
Cu–Cl	1	2.45(2)	2.92(1)
I–I	1	4.228(2)	4.505(4)
Cl–Cl	1	3.740(4)	4.455(3)
Cl–I	3	4.315(7)	4.880(5)
Cl–I	1	4.147(1)	4.670(3)
Tetrahedron about $Cu^+(e)$ (0.003, 0.834, 0.213) III			
Cu–Cl	1	2.52(2)	2.87(2)
Cu–I	1	2.70(2)	2.92(2)
Cu–I	1	2.54(1)	2.73(1)
Cu–Cl	1	2.33(2)	2.80(1)
I–I	1	4.228(2)	4.505(4)
Cl–I	1	3.960(7)	4.358(4)
Cl–I	2	4.147(1)	4.670(3)
Cl–Cl	1	3.740(4)	4.455(3)
Cl–I	1	4.315(7)	4.880(5)
Nearest-neighbor Cu^+ tetrahedral sites			
Cu(*c*)–Cu(II)	3	1.54	1.76(2)
Cu(II)–Cu(*c*)	1	1.54	1.76(2)
Cu(II)–Cu(III)	1	1.54(2)	1.68(2)
Cu(II)–Cu(III)	1	1.45(2)	1.71(2)
Cu(II)–Cu(II)	1	1.79(3)	1.91(2)
Cu(III)–Cu(II)	1	1.54(2)	1.68(2)
Cu(III)–Cu(II)	1	1.45(2)	1.71(2)

venience, the analogous distances in $RbAg_4I_5$ (Ref. 2) are also given. In CuI, the Cu–I distance[12] is 2.624 Å; the x parameter of Cu(c) was adjusted to give this distance in analogy with the Ag–I distance in $RbAg_4I_5$. The average of the Cu(II)–I distances is 2.74(2) Å and of Cu(III)–I distances, 2.62(2) Å, the former being significantly longer than that in CuI. In CuCl, the Cu–Cl distance[12] is 2.346 Å; the (adjusted) longer Cu(c)–Cl distance is analogous to the longer Ag–I distance (Table II) in $RbAg_4I_5$. The average Cu(II)-Cl distance is 2.39(2) Å, and the average Cu(III)–Cl distance is 2.43(2) Å, the latter significantly longer than the Cu–Cl distance in CuCl. The trend of these distances is similar to that of the Ag–I distances in $RbAg_4I_5$, but the overall analogy is imperfect. There is no good reason to expect that it should be perfect.

In RbCl, the Rb–Cl distance[12] is 3.274 Å, to be compared with 3.381(3) Å in $RbCu_4Cl_3I_2$. The Rb–I distance in α-$RbAg_4I_5$ is somewhat shorter than in RbI. The chloride octahedron about the Rb^+ ions in $RbCu_4Cl_3I_2$ is considerably distorted as can be seen (Table II) from the Cl–Cl distances. The iodide octahedron about the Rb^+ ions in α-$RbAg_4I_5$ is also highly distorted.

The icosahedron surrounding a chloride ion now comprises six iodide and six chloride ions at apices, with two Cl–Cl distance *considerably* longer than even the longest Cl–I distance. Thus the distortion of this icosahedron is considerably greater than that of the analogous iodide icosahedron in α-$RbAg_4I_5$. It may well be that the chlorides at 5.519 Å (Table II) should not be considered to be within the coordination sphere of the chloride ion.

DISCUSSION

The structures of α-$RbCu_4Cl_3I_2$ and α-$RbAg_4I_5$ are so similar as not to require reiteration of the discussion of the conduction network. This has been given originally by Geller[2] in the first paper on the structure of α-$RbAg_4I_5$ and subsequently elaborated by him in several papers.[13,14]

The distribution of the Cu^+ ions in α-$RbCu_4Cl_3I_2$ is somewhat different from the distribution of Ag^+ ions in α-$RbAg_4I_5$, but it should be emphasized that in both, the distribution of the charge carriers is markedly nonuniform. However, if we take 3σ limits of error, the occupancies of the Cu(II) and Cu(III) sites must be considered not to be significantly different in this case. Occupancy of the c sites is low as in the case of α-$RbAg_4I_5$. There are, on the average, 1.06, 8.14, and 7.06 Cu^+ ions distributed over the Cu(c), Cu(II), and Cu(III) sites, respectively, with standard errors of 0.19, 0.48, and 0.41 atoms, respectively. In $RbAg_4I_5$, the analogous numbers are 0.88, 9.38, and 5.50 for the occupancies (in number of ions) and 0.10, 0.29, and 0.29 for the standard errors. The fractional occupancies of the sites in α-$RbCu_4Cl_3I_2$ are 0.339, 0.294, and 0.132. For a uniform distribution, the fractional occupancy is 0.286. It may be said that the distribution of charge carriers in α-$RbCu_4Cl_3I_2$ is closer to uniform than are those in α-$RbAg_4I_5$. It does seem that the occupancy of the c sites has a tendency to be low and that this tendency will continue at higher temperatures. This can still mean that the residence time is low rather than that these sites are not used. On the other hand, they are not in the channels and are not required for Cu^+ ion diffusion through the crystal.

The conductivity of α-$RbCu_4Cl_3I_2$ is substantially higher than that of $RbAg_4I_5$. The number of carriers per unit cell is the same in both, but the carrier concentration is higher in the former because the volume of the unit cell is lower. The values are 1.585×10^{22} and 1.127×10^{22} cm^{-3} for α-$RbCu_4Cl_3I_2$ and α-$RbAg_4I_5$, respectively. The ratio is 1.41; if the conductivity were simply related to the carrier concentration as, for example, in $\sigma = qn\mu$, where q is the charge, n the carrier concentration, and μ the mobility, the room-temperature conductivity of α-$RbCu_4Cl_3I_2$ should be 0.38 Ω^{-1}cm^{-1}.

The higher value, (at least) 0.44 Ω^{-1}cm^{-1}, obtained by us implies that the average Cu^+ ion mobility is higher than that of the Ag^+ ion at room temperature. It is noteworthy that the line relating the conductivity to temperature predicts a value of at least 1.53 Ω^{-1}cm^{-1} for the conductivity at 419 K, the β-α transition temperature of AgI. At this temperature α-AgI has a conductivity[15] of 1.3 Ω^{-1}cm^{-1}. α-AgI has a charge carrier concentration of 1.57×10^{22} cm^{-3} at 419 K; neglecting density change of the $RbCu_4Cl_3I_2$ resulting from thermal expansion, we see (above) that the charge carrier concentration of $RbCu_4Cl_3I_2$ is the same as that of α-AgI. The available site concentration[13,16] in α-AgI is 1.7 times that of $RbCu_4Cl_3I_2$. This implies that the Cu^+ ion may in general be expected to have higher mobility than the Ag^+ ion.

The α-β and β-γ transitions occur at reasonable temperatures relative to those of the analogous silver compounds. These, of course, are worthy of further study, as is our intention.

Finally, it seems necessary to recognize a recent paper[17] which claims that the Rb^+ sites in $RbAg_4I_5$ have lower symmetry than 3. It appears that it would be very difficult indeed to argue that α-$RbAg_4I_5$ is *not* cubic. It would, for example, be necessary to establish that the birefringence is too small to be observed! Thus we must look for other possibilities.

One possibility is that for some reason, not obvious, the Rb^+ ions are disordered, i.e., moved off the precise space-group positions, but are, *on-the-average*, at these positions. This could be manifested by an especially large thermal parameter for Rb^+. This does not really appear to be the case in either α-$RbAg_4I_5$ or α-$RbCu_4Cl_3I_2$.

The other possibility is an increase in the size of the unit cell. In both α-$RbAg_4I_5$ and in α-$RbCu_4Cl_3I_2$, there is no x-ray diffraction evidence for this; thus it would be necessary to assume that there is a very large number of Bragg reflections with intensities too low to be observed. Because the crystals are optically active they *must* belong to point group 432 or 23. This limits the possible space groups to eight in 432 plus five in 23. If the cell edge were doubled, which is the smallest increase that could occur, there would be 32 Rb^+ ions in the unit cell. Because the agreement of calculated and observed intensities is so good, these must be in positions which are close to the body diagonals, but according to Brinkmann *et al.*,[17] *not on them.* Now it is interesting that in all space groups belonging to point groups 432 or 23, at least some of the 32 Rb^+ ions *must* lie on threefold axes. The minimum is 2 and the maximum is all 32. This is on a basis *not* considering that the Rb^+ ions *must* be near the threefold axes. We are forced to the conclusion that although it is possible that Brinkmann *et al.*[17] are right (see, e.g., Ref. 18), there is still some work for them to do to be convincing, as, for example, to study the eightfold iodide resonances.

This paper[17] also reports that the α-β transition is first order, but what should be emphasized is that the deviation from second order is miniscule.

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[11] ORRFEC is a modified version by J. A. Ibers of the Oak Ridge ORFFE3 program version of January 1971.

[12] Obtained from the lattice constant given by J. D. H. Donnay and H. Ondik [*Crystal Data, Determinative Tables*, 3rd ed. (U.S. Dept. of Commerce and Joint Committee on Powder Diffraction Standards, Washington, D.C., 1973), Vol. 2].

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