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Crystal Structure and Electrical Conductivity of $Rb_{18}Cu_{31}Cl_{49}$

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Crystals of $Rb_{18}Cu_{31}Cl_{49}$ belong to the cubic space group $I\bar{4}3d(T_d^6)$ with $a = 21.220 \pm 0.008$ Å, $Z = 4$. One of the two crystallographically nonequivalent Rb^+ ions clearly has nine-coordination to Cl^- ions; the other has what might be called (7 + 2)-coordination to Cl^- ions. All Cu^+ ions are tetrahedrally coordinated to Cl^- ions; each of two of the four crystallographically nonequivalent Cu^+ ions has a very long Cu^+–Cl^- distance. The arrangement of the $[CuCl_4]$ tetrahedra is complex with mostly corner and some edge sharing. The Cu^+ ions in at least one set of positions are disordered, i.e., there are 12 Cu^+ ions in a set of 16 c positions. At 298 K, the specific electrical conductivity measured at 1 kHz is $3.2 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, while at 420 K, it is $1.1 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$. A straight line is obtained for $\log_{10}(\sigma T)$ vs T^{-1}, with an enthalpy of activation of motion of 0.35 eV. Two octahedra and two five-cornered pyramids of Cl^- ions connect the $[CuCl_4]$ tetrahedra through face sharing throughout the crystal structure. It is probable that $Rb_{18}Cu_{31}Cl_{49}$ is a true solid electrolyte, albeit a poor one, with considerable correlation in the motions of the Cu^+ charge carriers. © 1986 Academic Press, Inc.

1. Introduction

There have been two reports (*1, 2*) implying the existence of one or more solid electrolytes in the system RbCl–CuCl. There is also substantial indecision regarding the nature and even the formulas of the phases in this system (*3*). We have undertaken, therefore, to define these phases, in particular those that appear to be stable at room temperature. All formulas heretofore reported for phases in this system are incorrect.

The simplest phase in the system has the formula Rb_2CuCl_3, and appears to be isostructural with K_2CuCl_3 (*4*). Aside from the Rb_2CuCl_3, the remaining phases are complex, not only structurally, but their formulas are unusual for such double salts. There are three more phases in the system. Here we report on $Rb_{18}Cu_{31}Cl_{49}$, which, with some qualification, appears to be a true solid electrolyte.

The phase that is *clearly* a true solid electrolyte has the formula $Rb_4Cu_9Cl_{13}$ (*5*). The remaining phase has the formula $Rb_4Cu_5Cl_9$, the structure of which is now being completed (*6*).

2. Experimental

Starting materials were as described elsewhere (*3*). Initial specimens were prepared by melting appropriate mixtures of reactants, RbCl and CuCl, in sealed Pyrex tubes containing 0.5 atm N_2, stirring while in the molten state, followed by annealing at

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TABLE I

Preparation Conditions for Different Formulations

Nominal formula	Molar ratio, $\frac{CuCl}{RbCl}$	Melting temp.[a] (°C)	Annealing temp. (°C)	Annealing time (hr)
$Rb_3Cu_5Cl_8$	1.667	?	150	22
$Rb_{17}Cu_{29}Cl_{46}$	1.706	220	160	96
$Rb_{18}Cu_{31}Cl_{49}$	1.722	200	160	36
$Rb_9Cu_{16}Cl_{25}$	1.778	180	165	120

[a] Not to be confused with melting *point*.

lower temperatures. Four specimens with different ratios of reactants were made (Table I). Examination of X-ray diffraction powder photographs indicated that the most probable formula of the particular compound, in which we were interested, was $Rb_{18}Cu_{31}Cl_{49}$. The crystal structure determination confirmed this formula.

Small crystals were obtained by the Bridgman technique. A spherical crystal of 0.20 mm diam. was obtained from one of these crystals with a sphere grinder (*7*).

Powder photographs had indicated that crystals of $Rb_{18}Cu_{31}Cl_{49}$ were body-centered cubic with $a = 21.23(2)$ Å. Buerger precession camera photographs taken with Mo$K\alpha$ radiation confirmed that the crystal is body-centered cubic with diffraction symmetry $m3m$. Reflections hkl are present only when $h + k + l = 2n$; reflections hhl are present only when $2h + l = 4n$; hhl permutable. This implies that the most probable space group is $I\bar{4}3d(T_d^6)$.

The data used for the structure determination and refinement were collected with a Nicolet P3/F autodiffractometer using the $\theta - 2\theta$ scanning technique with scan rates ranging from 1.0 to 29.3° per min and Mo$K\alpha$ radiation monochromatized by a graphite crystal in the incident beam. The scanning range was 0.8° below α_1 to 0.9° above α_2. The cell constant was obtained by least-squares refinement of measured spacings of 15 reflections. The value obtained is 21.220(3) Å.

The volume of the unit cell is 9555(4) Å^3. The formula weight of $Rb_{18}Cu_{31}Cl_{49}$ is 5245.4; there are four $Rb_{18}Cu_{31}Cl_{49}$ per unit cell, giving an X-ray density of 3.646 g cm^{-3}. The density, measured pycnometrically, using ethylene dibromide as the heavy liquid, was 3.59 g cm^{-3}. Generally, all reasonable errors in such a measurement lead to a low result, as in the case here. However, unfortunately, this low result *could* imply that the formula should contain one less CuCl; as will be seen later the probability that this is so must be extremely low. The measured density *does* rule out a higher CuCl content.

The linear absorption coefficient for Mo$K\alpha$ radiation is 170 cm^{-1} giving for μR, 1.70. Lorentz-polarization and absorption corrections were applied to the data.

The total number of independent reflections measured in the range $2.0° \leq 2\theta \leq 50.0°$ was 1109; of these 282 were accepted as observed, based on the criterion:

$$F^2_{\text{obs}} > 3\sigma(I)$$

where

$$\sigma(I) = 2 \cdot F_{\text{obs}} \cdot \sigma(F)$$

Of the 282, nine were admitted to the list of observed reflections even though subsequent calculations showed continuously that they were very likely unobserved. These were therefore rejected, leaving a total of 273 F_{obs} for structure refinement.

The method of preparation of the cell for conductivity measurement was similar to that described in Ref. (*8*). The device used for the conductivity measurements is shown in Fig. 1 of Ref. (*9*). Resistances were measured with a Hewlett–Packard 4274A multifrequency LCR meter. The frequency used was 1 kHz, at and below which (to 100 Hz) the results were almost independent of frequency. The capacitance was negligible in this range of frequency and over the temperature range, 298–420 K, in which the measurements were made.

3. Determination and Refinement of the Structure

The structure was solved by a combination of the direct methods (MULTAN), a three-dimensional Patterson map and trial and error. The peaks obtained from MULTAN contained almost the whole structure, but the peak heights must be ignored in this particular case.

The general positions of space group $I\bar{4}3d$ are 48-fold. $I\bar{4}3d$ also contains one 24-fold set with site symmetry 2, a 16-fold set with site symmetry 3 and two 12-fold sets with site symmetry $\bar{4}$. This distribution itself puts strong restrictions on the formula that the compound could have. For example, the formula $Rb_{18}Cu_{32}Cl_{50}$ (or $Rb_9Cu_{16}Cl_{25}$) cannot be accommodated by this space group, because too many ions, 8 Cu^+ and 8 Cl^-, must be located on each threefold axis. In the case of $Rb_{18}Cu_{30}Cl_{48}$ (or $Rb_3Cu_5Cl_8$), either there could be *no* ions on the threefold axes, which would be very unlikely, or if *any* are on threefold axes, there would be a minimum of 12 of *one kind* on each, again, *very* improbable. The remaining formula of Table I, $Rb_{17}Cu_{29}Cl_{46}$, is also easily excluded by the space group. The above arguments depend on *ordered* structures. Disorder, of the Cu^+ ions, for example, could change the restrictions. However, even consideration of the particular case of Cu^+-ion disorder, which is the only one that could be expected, would still rule out the formulas ruled out by the ordered structures because of the required distributions of the Cl^- ions.

The formula $Rb_{18}Cu_{31}Cl_{49}$ is not trouble-free either. Each unit cell contains 72 Rb^+, 124 Cu^+, and 196 Cl^-. If the largest possible number of general positions are occupied, there would be the following distribution: 48 + 24 for Rb^+; 2 × 48 + 16 + 12 for Cu^+ and 3 × 48 + 24 +16 + 12 for Cl^-. The distribution of ions in the correct structure is close to this, the only difference being for Cu^+. The 12 Cu^+ ions are not in a 12-fold set, but are disordered in a 16-fold set.

TABLE II

POSITIONAL PARAMETERS AND THEIR STANDARD ERRORS

Ion	Position	x	y	z
Rb1	48e	0.8781(2)	0.0031(2)	0.0944(1)
Rb2	24d	0.0281(2)	0	$\frac{1}{4}$
Cu1	48e	0.0530(2)	0.1895(2)	0.3319(2)
Cu2	48e	0.1764(3)	0.0617(3)	0.1725(3)
Cu3	16c	0.0677(2)	$=x$	$=x$
Cu4[a]	16c	0.1891(3)	$=x$	$=x$
Cl1	16c	−0.0010(6)	$=x$	$=x$
Cl2	48e	0.2516(4)	0.1260(3)	0.1195(3)
Cl3	48e	0.3645(4)	−0.0167(4)	0.1175(4)
Cl4	48e	−0.0096(3)	0.1081(4)	0.1343(4)
Cl5	24d	0.2516(5)	0	$\frac{1}{4}$
Cl6	12b	$\frac{7}{8}$	0	$\frac{1}{4}$

[a] There are only 12 Cu^+ ions distributed over the 16 sites.

The Patterson map indicated that all positional parameters were close to multiples of one-sixteenth.

Eventually the above considerations led to the correct structure which was refined by the least-squares technique. In all, there are 74 positional and thermal parameters plus the scale factor to be refined. In the final cycles, all positional and thermal parameters were permitted to vary to 0.00000 shift. For the 273 observed reflections $R = \Sigma||F_{\text{obs}}| - |F_{\text{calc}}||/\Sigma|F_{\text{obs}}| = 0.035$. The final estimated standard deviation of an observation of unit weight is 1.00. The final values of the positional parameters are given in Table II. Table III gives the final values of the $U_{ij} = a^2\beta_{ij}/2\pi^2$ and $U_{\text{iso}} = \frac{1}{3}\Sigma_i U_{ii}$, and Table IV, the axial lengths of the root-mean square vibration ellipsoids.

In the course of the least-squares calculations, occupancies of the Cu sites were varied. It was thought that especially the Cu2 sites, with their associated high thermal parameter values, would prefer lower occupancy. All trials indicated that the disorder

TABLE III

THERMAL PARAMETERS U_{ij}, ($Å^2$) AND THEIR STANDARD ERRORS

Ion	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}
Rb1	0.039(1)	0.040(2)	0.036(1)	0.001(2)	−0.009(2)	−0.006(2)	0.038(1)
Rb2	0.034(2)	0.038(3)	0.072(3)	0	0	0.016(3)	0.048(3)
Cu1	0.060(3)	0.083(3)	0.068(3)	−0.042(3)	−0.012(3)	0.012(3)	0.070(3)
Cu2	0.095(4)	0.099(4)	0.061(3)	−0.043(3)	0.010(3)	−0.030(3)	0.085(4)
Cu3	0.063(3)	$=U_{11}$	$=U_{11}$	0.008(3)	$=U_{12}$	$=U_{12}$	0.063(3)
Cu4	0.067(3)	$=U_{11}$	$=U_{11}$	−0.024(3)	$=U_{12}$	$=U_{12}$	0.067(3)
Cl1	0.077(4)	$=U_{11}$	$=U_{11}$	0.035(7)	$=U_{12}$	$=U_{12}$	0.077(4)
Cl2	0.019(3)	0.029(3)	0.047(3)	−0.014(5)	0.006(4)	0.013(4)	0.032(3)
Cl3	0.040(5)	0.056(5)	0.034(4)	0.033(4)	0.010(4)	0.005(4)	0.043(5)
Cl4	0.021(4)	0.037(4)	0.040(4)	0.000(4)	0.014(4)	−0.001(4)	0.033(4)
Cl5	0.029(5)	0.029(5)	0.034(5)	0	0	0.008(6)	0.031(5)
Cl6	0.059(9)	0.049(9)	0.000(6)	0	0	0	0.036(8)

was confined mainly to the Cu4 sites. However, there is the possibility that there is *some* disorder over all the Cu sites. This is implied especially by the results of the conductivity measurements (see below).

Calculations were also done on the enantiomorph including the varying of the Cu-site occupancies. Again the indication was that the disorder is mainly in the Cu4 sites. The results indicated that the two enantiomorphs were indistinguishable.

The calculations were carried out with the Structure Determination Package on the PDP11/23 supplied by Molecular Structure Corporation, modified for ions. Atomic scattering factors were taken from Volume 4 of the International Tables for Crystallography.

TABLE IV

ROOT MEAN SQUARE AMPLITUDES OF THERMAL VIBRATION (Å)

Ion	Min.	Intermed.	Max.
Rb1	0.165	0.197	0.223
Rb2	0.177	0.184	0.280
Cu1	0.166	0.250	0.348
Cu2	0.200	0.257	0.386
Cu3	0.235	0.235	0.280
Cu4	0.135	0.303	0.303
Cl1	0.205	0.205	0.382
Cl2	0.092	0.167	0.241
Cl3	0.113	0.181	0.290
Cl4	0.177	0.193	0.218
Cl5	0.152	0.171	0.200
Cl6	0.002	0.222	0.244

4. Discussion of the Cation Coordination

The structure has two sets of crystallographically nonequivalent Rb^+ ions, one in general positions, the other with point symmetry 2. Both Rb^+ ions are surrounded by a distorted trigonal prism of Cl^- ions, and three additional Cl^- ions through the lateral faces of the prism (Figs. 1 and 2). There is a principal difference between the two. Although the Rb1–Cl distances (Fig. 1) have the range 3.27–3.70 Å, their average is 3.44 Å, which as will be shown later, is reasonable for a nine-coordination Rb–Cl distance. The Rb2–Cl distances have the range 3.28–3.77 Å (Fig. 2) with an average of 3.50 Å, somewhat too long for a nine-coordination Rb–Cl distance. If the two 3.77-Å distances are excluded, the average of the seven remaining distances is 3.42 Å, which is somewhat too long for a seven-coordination Rb–Cl distance.

The coordination polyhedron for Rb1 may be drawn in a different way, that is, to

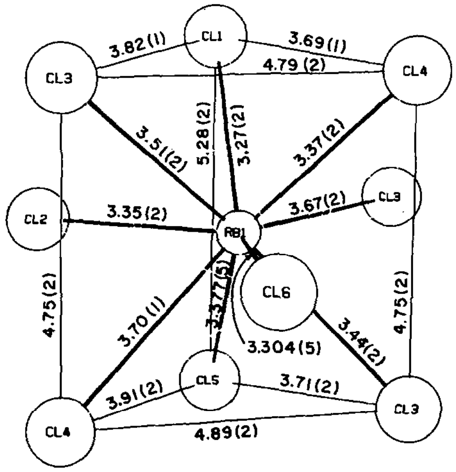

FIG. 1. RbI coordination to Cl$^-$ ions. Distances are in Ångstroms.

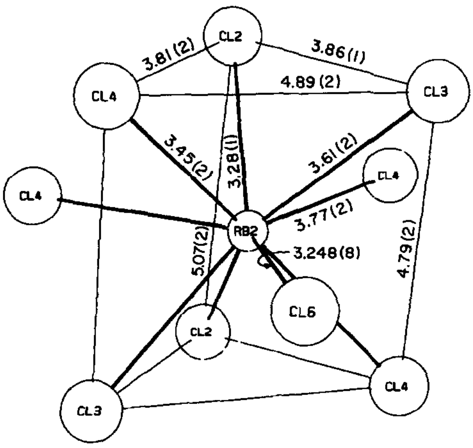

FIG. 2. Rb2 coordination to Cl$^-$ ions. Distances are in Ångstroms.

include eight Cl$^-$ ions in a distorted antiprism, and a ninth Cl$^-$ through a face (this can be readily seen at the top of Fig. 3). As seen in Fig. 3, one could also consider the Rb2 coordination to be represented this way, but it seems less reasonable to do so because of the two long Rb2–Cl distances. In any case, it may be appropriate to con-

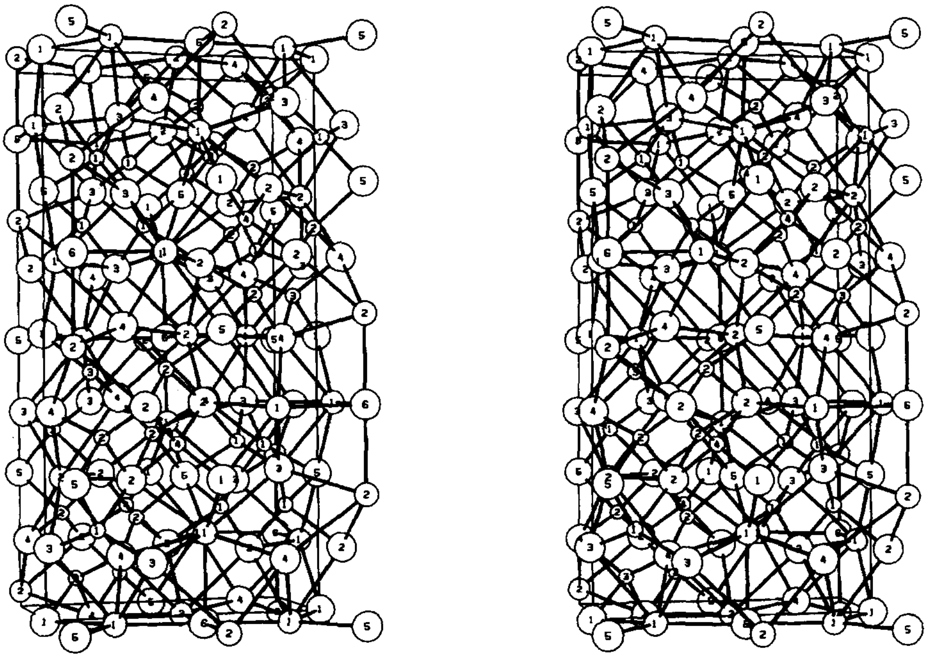

FIG. 3. Stereoscopic view of the structure roughly down the *b*-axis. The box represents *a*/2 to the right; *b*/4 to the rear; *c*, up. Thus, $0 < x < \frac{1}{2}$, $-\frac{1}{4} < y < +\frac{1}{4}$, $0 < z < 1$. The smallest circles represent Cu$^+$ ions, the intermediate circles, Rb$^+$ ions, and the largest, Cl$^-$ ions.

TABLE V

INTERIONIC DISTANCES AND STANDARD ERRORS (Å)

Rb1 polyhedron		
Rb–Cl distances (see Fig. 1)		Average 3.44(2)
Cl–Cl distances in trigonal prism, see Fig. 1.		
External Cl to Cl of trigonal prism		
Cl2–Cl1	3.79(1)	
–Cl3	3.73(2)	
–Cl4	3.79(1)	
–Cl5	3.68(2)	
Cl3–Cl1	3.82(2)	
–Cl3	4.03(3)	
–Cl4	3.98(2)	
–Cl5	4.01(2)	
Cl6–Cl3	(2)4.17(2)	
–Cl4	(2)4.16(2)	
Rb2 polyhedron		
Rb–Cl distances (see Fig. 2)		Average 3.50(2)
Cl–Cl distances in trigonal prism, see Fig. 2.		
External Cl to Cl of trigonal prism		
2Cl4–Cl2	3.79(1), 4.10(2)	
–Cl3	3.99(2)	
–Cl4	3.99(2)	
Cl6–Cl3	(2)4.17(2)	
–Cl4	(2)4.16(2)	
Cu1 tetrahedron		
Cu1–Cl2	2.74(2)	
–Cl3	2.24(2), 2.24(2)	
–Cl5	2.41(2)	Average 2.41(2)
Cl2–Cl3	3.73(2), 3.86(1)	
–Cl5	3.68(2)	
Cl3–Cl3	4.03(3)	
Cl5–Cl3	3.71(2), 4.01(2)	Average 3.84(2)
Cu2 tetrahedron		
Cu2–Cl2	2.38(2), 2.34(2)	
–Cl4	2.23(2)	
–Cl5	2.64(1)	Average 2.40(2)
Cl2–Cl2	3.87(2)	
Cl4–Cl2	3.81(2), 4.10(2)	
–Cl4	3.91(2)	
Cl5–Cl2	3.68(2), 3.85(1)	Average 3.87(2)
Cu3 tetrahedron		
Cu3–Cl1	2.52(1)	
–Cl4	(3)2.33(1)	Average 2.38(1)
Cl1–Cl4	(3)3.69(2)	
Cl4–Cl4	(3)3.99(2)	Average 3.84(2)
Cu4 tetrahedron		
Cu4–Cl1	2.20(1)	
–Cl2	(3)2.40(1)	Average 2.35(1)
Cl1–Cl2	(3)3.79(2)	
Cl2–Cl2	(3)3.87(2)	Average 3.83(2)
Cu^+–Cu^+ distances		
Cu1–Cu1	(2)3.03(1), 3.41(1)	
–Cu2	3.325(9)	
–Cu4	4.19(1)	
Cu2–Cu1	3.325(9)	
–Cu2	(2)3.39(1), 4.20(2)	
–Cu3	3.21(1)	
–Cu4	2.74(1)	
Cu3–Cu2	(3)3.21(1)	
Cu3–Cu4	4.464(5), 4.725(5)	

sider the Rb1–Cl coordination, nine, and designate the Rb2–Cl coordination as (7 + 2) to indicate the difference between the two.

There is a precedent for this designation. Messer (*10*) referred to the coordination of Rb^+ to Cl^- in $RbGeCl_3$ as 7 + 2, because in that case, there are seven Rb–Cl distances in the range 3.39–3.42 Å and two equal to 3.72 Å. The coordination *geometry* is quite different from those of Rb1 and Rb2 in $Rb_{18}Cu_{31}Cl_{39}$, however. In $RbGeCl_3$, there is a trigonal prism of Cl^- ions but the Rb^+ is not inside it; it is just outside one of the lateral faces. The remaining three Cl^- ions, two of which give the 3.72 Å Rb–Cl distances, are outside just one of the lateral faces. Furthermore, the vertical Cl–Cl distances, 3.38 and 3.56 Å, are shorter than the shortest Cl–Cl distance in $Rb_{18}Cu_{31}Cl_{49}$, namely 3.68 Å (Table V). The accepted diameter of the Cl^- ion is 3.62 Å (*11*).

It appears that nine- (or 7 + 2) coordination of Rb^+ to Cl^- ions has so far been reported only in $RbGeCl_3$. In $RbGeCl_3$, the average Rb–Cl distance is 3.47 Å; when the two 3.72 Å distances are excluded, the average Rb–Cl distance for the seven is 3.40 Å.

At least three points are available for estimating the Rb–Cl distances for various coordinations. In the NaCl-type RbCl, the lattice constant is 6.5820 Å (*12*), giving 3.291 Å for the C.N. 6 distance. The estimated lattice constant for NaCl-type CsCl is 6.941 Å (*12*), a factor of 1.0545 times that of RbCl. Assuming that the ratio is the same for the CsCl types gives 3.903 Å for the lattice constant of CsCl-type RbCl or 3.380 Å for the C.N. 8 distance. In the structures of $RbNiCl_3$ (*13*) and $RbCoCl_3$ (*14*) the Rb^+ ion is coordinated to 12 Cl^- ions, with average Rb–Cl distances 3.560(6) and 3.58(1) Å, respectively. We assume then that the C.N. 12 distance is 3.57 Å. The three points fall on a straight line, from which one obtains 3.43 Å for the C.N. 9 Rb–Cl distance.

The average Rb1–Cl value, 3.44 Å, including all nine ligands, is in excellent agreement with the derived value, 3.43 Å. The average Rb2–Cl value, 3.50 Å, is close to a value expected for C.N. 11, but exclusion of the two 3.77 Å distances gives an average value for the remaining seven Rb2–Cl distances of 3.42 Å. The values are close to those of the (7 + 2)-coordination in $RbGeCl_3$.

The Cu^+-ion-coordination geometry in this structure also appears to be unusual. There are four sets of crystallographically nonequivalent Cu^+ ions of which two are in special positions, namely on the threefold axes. One of these sets, Cu4 (Table II), is three-fourths occupied.

In cubic CuCl, the Cu–Cl distance is 2.345 Å and the Cl–Cl distance is 3.830 Å. In $Rb_{18}Cu_{31}Cl_{49}$, the Cu^+ ions are in tetrahedra as expected, but there are some anomalies. The average Cl–Cl distances (Table V) in the four crystallographically nonequivalent tetrahedra are all close to the value, 3.83 Å, in CuCl. The average Cu1–Cl and Cu2–Cl distances (Table V) are greater than the Cu–Cl distance in CuCl, though the difference is not *statistically* significant. Nevertheless, such greater average Cu–Cl distances also occur in $RbCu_4Cl_3I_2$ (*15*) and $NH_4Cu_4Cl_3(I_{1.9}Cl_{0.1})$ (*16*).

The main anomalies occur in the individual Cu–Cl distances (Table V). For Cu1, there is one *very* long distance and two relatively short ones; for Cu2, there is one very long and one relatively short distance. For Cu3, there is one rather long distance, and for Cu4, one rather short distance.

5. Description of the Structure

Figure 3 is invaluable for visualizing the structure of $Rb_{18}Cu_{31}Cl_{49}$. Each unit cell contains 12 tetrahedral groups of Cu1 ions surrounded by Cl^- ion tetrahedra. One such group may be seen in the lower right of Fig. 3. Each of these groups contains an empty Cl octahedron formed from 4Cl3 and 2Cl5 ions. Each Cu1 tetrahedron shares a corner with each of the three other Cu1 tetrahedra; this sharing involves the one Cl5 and two Cl3 ions in each tetrahedron. Each Cu1 tetrahedron also shares a Cl2–Cl5 edge with a Cu2 tetrahedron; each of the Cl's in this edge is also shared with another Cu2 tetrahedron. The Cl2 ion is also shared with a Cu4 tetrahedron.

The Cu1 tetrahedron shares a Cl3–Cl5 edge with a trigonal prism surrounding the Rb1 ion and a Cl2–Cl3 edge with the trigonal prism surrounding the Rb2 ion. It also shares three edges that the "external" Cl ions make with lateral faces of the trigonal prism of Rb1.

There are four equilateral triangular groups of Cu2 ions on each threefold axis. The Cu2 ions in these triangles are at a distance of 3.38 Å from each other (Table V). However, these groups of Cu2 ions are arranged such that (almost) linear strings of four are arranged along ⟨110⟩ directions (see lower right of Fig. 3). These linear strings intersect with each other throughout the structure.

Each Cu2 tetrahedron shares a Cl2–Cl5 edge with a Cu1 tetrahedron, a Cl2–Cl2 edge with a Cu4 tetrahedron, a Cl2 corner with another Cu2 tetrahedron, and a Cl4 corner with a Cu3 tetrahedron. The Cu2 tetrahedron also shares a Cl4–Cl5 edge with the trigonal prism of Rb1 and an edge (Cl2–Cl5) that the external Cl ions make with a lateral face of the Rb1 trigonal prism. The Cl4–Cl2 (3.81 Å) edge of the Cu2 tetrahedron is also shared by the Rb2 trigonal prism and the other Cl4–Cl2 (4.10 Å) edge is also one of the edges made by the external Cl4 ion to a Cl2 ion of the Rb2 trigonal prism.

The Cu3 tetrahedron shares three Cl4 corners with three Cu2 tetrahedra and a Cl1 corner with a Cu4 tetrahedron. Each of the three Cl1–Cl4 edges of the Cu3 tetrahedron is shared with an edge of the Rb1 trigonal prism and each Cl4–Cl4 edge is also an edge that an external Cl4 makes with a Cl4 belonging to the Rb2 trigonal prism.

Each of the Cl2–Cl2 edges of the Cu4 tetrahedron is shared with a Cu2 tetrahedron. Each Cl2 corner is shared with a Cu1 tetrahedron and the Cl1 corner is shared with a Cu3 tetrahedron. The Cl2–Cl1 edge is also an edge that an external Cl2 makes with a Cl1 of the Rb1 trigonal prism.

Four Rb1 and 2 Rb2 ions form octahedra at the center of which is a Cl6 ion. There are 12 such octahedra in each unit cell. Such octahedra also occur in $Rb_4Cu_9Cl_{13}$ (*5*).

For the Cu1 ion with coordinates given in Table II, the Cu1–Cl2 bond is close to the $[\bar{1}11]$ direction. Using the U_{ij} values of Table III, the rms amplitude of the Cu1 ion in this direction is 0.34 Å, essentially equal to the maximum rms vibration amplitude (Table IV). This is the direction of the longest Cu–Cl distance in this tetrahedron, and the Cu1 ions actually move in and out of the empty octahedron mentioned above.

Three Cu2 and 1 Cu3 ions form a tetrahedron of Cu^+ ions (Fig. 3), similar to that formed by the Cu1 ions. This tetrahedron also "includes" an empty octahedron of Cl^- ions formed from 3 Cl2 and 3 Cl1 ions. Along the $[1\bar{1}1]$ direction, the rms vibration amplitude of the Cu2 ion with the coordinates given in Table II, is 0.37 Å, very close to the maximum rms vibration amplitude (Table IV). The Cu2–Cl5 bond is close to the $[1\bar{1}1]$ direction. Again the Cu2 ion vibrates into the empty octahedron. Similarly, the maximum rms vibration amplitude of the Cu3 ion is along the [111] direction, and this largest amplitude is in the case, precisely along the longest bond distance (Table V), Cu3–Cl4.

As to Cu4, the *lowest* rms vibration amplitude (Table IV) is along the [111] direction. This is precisely along the Cu4–Cl1 bond which has the shortest distance, 2.21 Å (Table V) in the structure. The highest rms vibration amplitudes are along the $[\bar{1}10]$ and $[11\bar{2}]$ directions. These are not along Cu4–Cl2 bonds, which are closer to $\langle 111 \rangle$ directions.

The octahedron formed by four Cl3 and two Cl5 ions (Fig. 3) shares faces with four Cl1 tetrahedra. The octahedron formed by three Cl2 and three Cl4 (Fig. 3) shares faces with three Cu2 tetrahedra and one Cu3 and one Cu4 tetrahedron. There are also two five-cornered ("square") pyramids (Fig. 3): one formed by two Cl2, one Cl1, one Cl3, and one Cl5, shares one face with a Cu1 tetrahedron, one face with a Cu2 tetrahedron, and one face with a Cu4 tetrahedron; the second, formed by two Cl2, two Cl4, and one Cl5, shares two faces with Cu2 tetrahedra. These four polyhedra connect the tetrahedra by face sharing throughout the structure, thereby providing channels for motion, *if possible*, of Cu^+ ions. Such connections occur in the $Rb_4Cu_9Cl_{13}$ structure (*5*), and Gaines, examining our structure model, found them in ours.

The centers of the first octahedron are in 12a: $\frac{3}{8}$, 0, $\frac{1}{4}$; of the second octahedron in 16c: $x = 0.122$, of the first pyramid in 18c: 0.253, 0.125, 0.221, and of the second pyramid in 24d: $x = 0.152$. The distance of the center of the first octahedron to the Cu1 ions is 1.93 Å, of the center of the second octahedron to the Cu2, Cu3, and Cu4 ions, 2.01, 1.98, and 2.46 Å, respectively: of the center of the first pyramid to the Cu1, Cu2, and Cu4 ions, 2.36, 2.35, and 2.04 Å, respectively, and of the center of the second pyramid to the Cu2 ions, 2.17 Å.

There is a rather short Cu2–Cu4 distance, 2.74 Å, across a shared Cl2–Cl2 edge. This is by far the shortest Cu^+–Cu^+ distance (Table V) in the structure. In $CsCu_2Cl_2I$ (*17*) the shortest Cu^+–Cu^+ distance, which is across a Cl^-–I^- edge, is 2.90 Å; $CsCu_2ClI_2$ (*17*), the shortest Cu^+–Cu^+ distance across an edge is 2.84 Å; and in $CsCu_2Cl_3$ (*18*), it is 2.81 Å. Although in the Cs compounds, the shortest Cu^+–Cu^+ distance is significantly longer than the shortest Cu^+–Cu^+ distance in $Rb_{18}Cu_{31}Cl_{49}$, such short cation–cation distances do occur in double-salt halogenides. An example is the shortest Ag^+–Ag^+ distance, 2.78 Å,

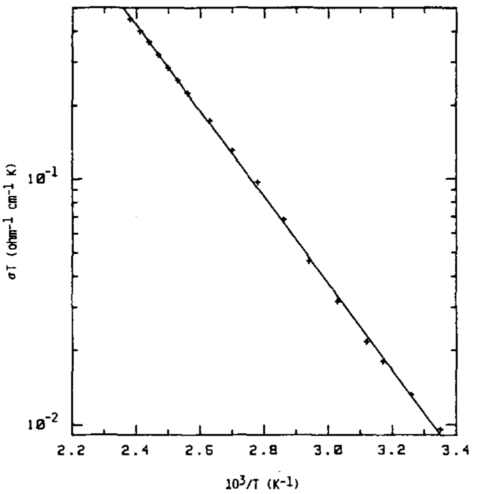

FIG. 4. Log_{10} (conductivity × temperature) versus (temperature)$^{-1}$.

across an I^-–I^- edge in $SrAg_2I_4 \cdot 8\ H_2O$ (*19*).

6. Electrical Conductivity

The plot of $\log_{10}(\sigma T)$ vs T^{-1} (Fig. 4) is, within experimental error, a straight line, giving an enthalpy of activation of motion, h_m, of 0.35 eV. This value is in contrast to 0.10 eV, for the best solid electrolytes such as $RbAg_4I_5$, and up to about 0.20 for good ones. The h_m for $Rb_{18}Cu_{31}Cl_{49}$ is comparable with that of Ag_2HgI_4 which has an h_m of 0.33 eV (*20*), and which is not a good solid electrolyte.

At 298 K, the specific electrical conductivity is $3.2 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and at 420 K, it is $1.1 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. These are rather low conductivities, but are, nevertheless, substantially larger than for defect-type ionic conductors like sodium chloride. Further, the $\log_{10}(\sigma T)$ vs T^{-1} behavior is *not* that of the latter (*8*), but rather more like that of a true solid electrolyte.

It appears that the channels described in the preceding section do provide the means for some Cu^+ ion drift when an electric field is imposed on the crystals of $Rb_{18}Cu_{31}Cl_{49}$. The least-squares calculations indicated that the octahedra and "square" pyramids were empty, implying that the residence times of the Cu^+ ions in these sites are very low. The calculations also did not rule out the possibility of some vacancies in the Cu1 and Cu2 sites. However, there are only 228 sites for the 124 Cu^+ ions per unit cell and it would appear that the movements of the Cu^+ ions should be strongly correlated.

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