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The Crystal Structure of K_2CuCl_3 and Isomorphous Substances

By Clara Brink

Laboratory of Inorganic Chemistry of the University, Leiden, Holland

and Carolina H. MacGillavry

Laboratory of General and Inorganic Chemistry of the University, Amsterdam, Holland

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The crystal structure of K_2CuCl_3 and isomorphous substances has been determined. The crystals are orthorhombic with cell dimensions: $a=12\cdot00$, $b=12\cdot55$, $c=4\cdot20$ A. There are four molecules in the cell and the space group is *Pnam*. Weissenberg diagrams have been taken along the c axis with Cu $K\alpha$ and Mo $K\alpha$ radiation and the positions of the atoms have been fixed by means of an approximate three-dimensional Patterson analysis and a Fourier projection along the c axis.

All atoms are situated in the symmetry planes perpendicular to the c axis. There are chains of the composition $CuCl_3$ in the direction of the c axis (needle axis) consisting of $CuCl_4$ tetrahedra sharing corners; they are more compact than the SiO_3 chains in the pyroxenes. The K atoms are situated between these chains, surrounded by seven Cl atoms.

The direction of the chains is in agreement with the optical behaviour: largest refractive index in the needle direction.

Introduction

Compounds of the general composition $M^{\mathrm{I}}_2\,M^{\mathrm{I}}(\mathrm{Hal})_3$ have been known for a long time. Boullay (1827) prepared K_2AgI_3, Mitscherlich (1842) K_2CuCl_3. Wells & Wheeler (1892) described the preparation of Cs_2AgCl_3, Rb_2AgI_3 and K_2AgI_3, with crystallographic measurements of Penfield. The crystals were found to be isomorphous and to crystallize in the orthorhombic system with axial ratios:

Cs_2AgCl_3 $a:b:c=0\cdot971:1:0\cdot244$
Rb_2AgI_3 $a:b:c=0\cdot977:1:0\cdot236$
K_2AgI_3 $a:b:c=0\cdot977:1:0\cdot234$

Mitscherlich reports only that K_2CuCl_3 crystallizes in '*Rectanguläroktaëdern*' and Groth (1906–19, pt. 1, p. 316) supposes that it is isomorphous with the compounds mentioned above.

As in these compounds we have an example of complexes formed from monovalent ions only it seemed interesting to determine their crystal structure. From Weissenberg photographs it was deduced that K_2CuCl_3 is isomorphous with the silver compounds and this compound was used for the structure determination; for comparison photographs were also taken of Cs_2AgCl_3 and Cs_2AgI_3.

Preparation

K_2CuCl_3 was prepared by adding to a warm, saturated solution of KCl (air driven out with CO_2) an equivalent amount of CuCl and heating till CuCl was quite dissolved. On cooling the solution, colourless needles of K_2CuCl_3 were formed, which on exposure to the air immediately turned opaque and took on a green colour. The diffraction photographs were taken with a crystal sealed in a Lindemann capillary.

Cs_2AgCl_3 was obtained by saturating a concentrated hot solution of CsCl with AgCl and evaporating at room temperature. It forms colourless needles, which become opaque in the air. For the exposure the Cs_2AgCl_3 crystals had to be enclosed in Lindemann tubes.

Cs_2AgI_3 was formed by dissolving calculated amounts of AgI and CsI in a hot concentrated solution of KI. It precipitates in colourless needles, which are relatively stable. It was therefore not necessary to take special precautions in handling the Cs_2AgI_3 crystals.

The unit cell and space group

The a and b periods were determined from oscillation diagrams along the needle axis [001] with Cu $K\alpha$ radiation. As it was impossible to obtain crystals extended in any direction other than the c axis, the c period was determined from measurements of the layer-line separations. The cell dimensions and axial ratios thus obtained are given in Table 1. As we see, there is a considerable difference between these values and the values derived from the crystallographic measurements of Penfield. Apparently Penfield chose the diagonals of the basal plane as a and b axis. (He reports that his measurements are not very accurate.)

Table 1. *Cell dimensions and axial ratios*

	a (A.)	b (A.)	c (A.)	$a:b:c$
K_2CuCl_3	$12\cdot00\pm0\cdot02$	$12\cdot55\pm0\cdot02$	$4\cdot20\pm0\cdot02$	$0\cdot956:1:0\cdot334$
Cs_2AgCl_3	$13\cdot19\pm0\cdot02$	$13\cdot74\pm0\cdot02$	$4\cdot57\pm0\cdot02$	$0\cdot960:1:0\cdot333$
Cs_2AgI_3	$14\cdot39\pm0\cdot02$	$15\cdot16\pm0\cdot02$	$5\cdot02\pm0\cdot02$	$0\cdot949:1:0\cdot331$

The density found for Cs_2AgI_3 is 4·1 g.cm.$^{-3}$, so there are four molecules in the cell.

From the zero-, first- and second-layer-line Weissenberg diagrams with Cu $K\alpha$ radiation the following reflexions were found: hkl all orders, $hk0$ all orders, $h0l$ only for $h=2n$, $0kl$ only for $k+l=2n$. The space group is therefore *Pnam* (in the *Internationale Tabellen Pnma*) or *Pna*. As the needles have no distinct terminal faces, it cannot be deduced from the habitus whether the c axis is polar or not. Now it is seen from a rotation diagram along [001] with Mo $K\alpha$ radiation that the intensities in the second and fourth layer lines are practically identical with the intensities in the zero layer line (though weaker) and similarly the intensities in the third layer line are practically identical with the intensities in the first layer line. This means that the atoms all lie in two planes (001) at a mutual distance of $\frac{1}{2}c$. Such an arrangement fulfils the symmetry requirements of the space group *Pnam*, as will be shown presently.

Atomic positions

The space group *Pnam* has two symmetry planes perpendicular to the c axis at $c=\frac{1}{4}$ and $c=\frac{3}{4}$. There are four molecules in the cell, so there are to be placed: 4 Cu, 8 K and 12 Cl. The atomic positions are:

$$\left.\begin{array}{l}(4a)\colon 0,0,0;\ 0,0,\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}\\ (4b)\colon 0,\tfrac{1}{2},0;\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},0,0;\ \tfrac{1}{2},0,\tfrac{1}{2}\end{array}\right\}\ \text{at the centre of symmetry, between the symmetry planes.}$$

(4c): $x, y, \frac{1}{4}$; $\bar{x}, \bar{y}, \frac{3}{4}$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{4}$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4}$ in the symmetry planes.

(8d): x, y, z; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; $\bar{x}, \bar{y}, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $x, y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$ general atomic positions between the symmetry planes.

The K and Cl atoms cannot be located between the symmetry planes as the distance between these planes is only 2·10 A. (K^+ radius = 1·33 A., Cl^- radius = 1·81 A. for co-ordination number six), so these atoms can be placed only in the symmetry planes (4c). Since the $hk2$ intensities are practically identical with those of $hk0$, as stated above, Cu has also to lie in the symmetry planes.

For every four atoms in equivalent positions there are two parameters, so there are twelve parameters to be determined.

Three-dimensional Patterson analysis

All maxima of the Patterson function $P(u, v, w)$ will be situated in the sections in $w=0$ and $w=\frac{1}{2}$ (u, v and w are the co-ordinates in the vector space).

$$P(u,v,0)=\sum_{\substack{-\infty\\ hkl(l=2n)}}^{+\infty} F^2(hkl)\cos 2\pi(hu+kv) + \sum_{\substack{-\infty\\ hkl(l=2n+1)}}^{+\infty} F^2(hkl)\cos 2\pi(hu+kv),$$

$$P(u,v,\tfrac{1}{2})=\sum_{\substack{-\infty\\ hkl(l=2n)}}^{+\infty} F^2(hkl)\cos 2\pi(hu+kv) - \sum_{\substack{-\infty\\ hkl(l=2n+1)}}^{+\infty} F^2(hkl)\cos 2\pi(hu+kv)$$

(suppressing the constant factor).

Now, with all atoms in positions (4c), the geometric structure factors $S(h.k.l+2n)$, with n any integer, are identical. If we assume that the ratios of the atomic scattering factors are approximately the same for all these reflexions, then we may replace

$$\sum_{\substack{l=-\infty\\ l=2n}}^{+\infty} F^2(hkl) \text{ by } A_0F^2(hk0),$$

and

$$\sum_{\substack{l=-\infty\\ l=2n+1}}^{+\infty} F^2(hkl) \text{ by } A_1F^2(hk1).$$

Moreover, if we assume that A_0 is equal to A_1, the Patterson functions become (omitting the proportionality constant A):

$$P(u,v,0)=\sum_{\substack{-\infty\\ hk}}^{+\infty} F^2(hk0)\cos 2\pi(hu+kv) + \sum_{\substack{-\infty\\ hk}}^{+\infty} F^2(hk1)\cos 2\pi(hu+kv),$$

$$P(u,v,\tfrac{1}{2})=\sum_{\substack{-\infty\\ hk}}^{+\infty} F^2(hk0)\cos 2\pi(hu+kv) - \sum_{\substack{-\infty\\ hk}}^{+\infty} F^2(hk1)\cos 2\pi(hu+kv).$$

That is, in such a case with all atoms lying in two mirror planes, say parallel to (001), approximate Fourier transforms can be made with data $hk0$ and $hk1$ only.

The procedure of assuming A_0 and A_1 to be indepent of hk, and of taking A_0 equal to A_1, was later tested by calculation, using $F(hkl)$ values computed from the final atomic co-ordinates. The results for some reflexions are given here:

hk	32	42	34	35	53	75	3,11
A_0	2·2	2·8	3·2	3·0	3·1	3·6	4·2
A_1	3·5	3·4	3·4	3·8	3·8	3·5	3·7

In the determination of the structure of NH_4CdCl_3 (same space group and all atoms in positions (4c)) Brasseur & Pauling (1938) applied a better approximation, as they multiplied the intensities of the reflexions $hk0$ and $hk1$ with factors obtained by summing over l an averaged function of f^2/Z^2 (f being the atomic scattering factor and Z the atomic number), with l either even or odd.

The intensities of the reflexions of the zero- and first-layer-line Weissenberg photographs along [001] with Cu $K\alpha$ radiation were estimated visually, using an intensity scale prepared from the crystal, and corrected for Lorentz, polarization and absorption factors. The absorption correction was very rough, for it was assumed that the crystal was a cylinder with radius $2{\cdot}3\times10^{-2}$ cm., whereas the true dimensions were in perpendicular directions: 5·4 and $3{\cdot}6\times10^{-2}$ cm. (The crystal was too soft to be ground to cylindrical shape.)

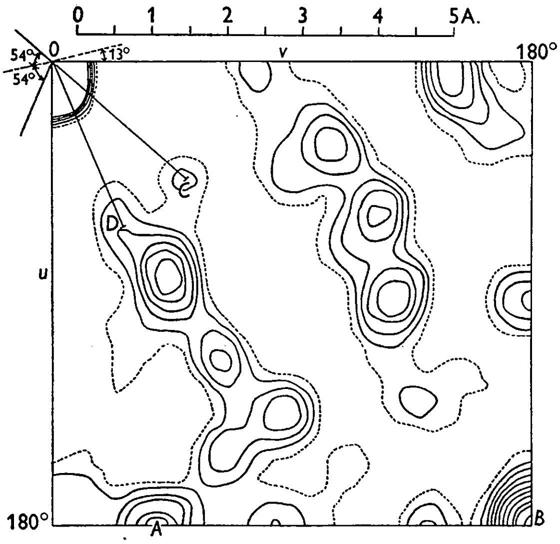


Fig. 1. Patterson function $P(u, v, 0)$ for K_2CuCl_3. Contour lines at equal height differences on arbitrary scale. Zero line dotted.

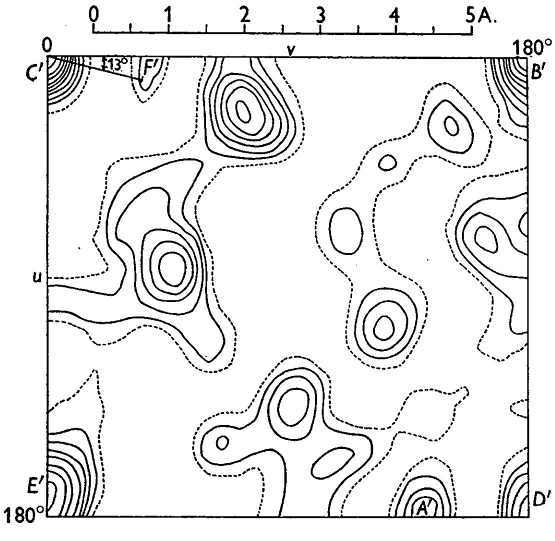


Fig. 2. Patterson function $P(u, v, \frac{1}{2})$ for K_2CuCl_3. Contour lines as in Fig. 1.

The Patterson functions $P(u, v, 0)$ and $P(u, v, \frac{1}{2})$ are shown in Fig. 1 and Fig. 2. $P(u, v, 0)$ must have a peak giving the Cu–Cu vector distance in a symmetry plane with $u=180°$ and $v=180°-2y$. There are two peaks which may correspond to this vector:

(*a*) $v=180-2y=40°$, $y=70°$ (peak *A* in Fig. 1);

(*b*) $v=180-2y=180°$, $y=0°$ (peak *B* in Fig. 1).

From $P(u, v, \frac{1}{2})$ both the x and y co-ordinates of the Cu atom can be deduced, for the vector distance of two Cu atoms in successive symmetry planes gives a peak in $P(u, v, \frac{1}{2})$ with co-ordinates $u=2x$, $v=2y$. The different possibilities are:

(*a*) $u=180°$, $v=140°$ (peak A' in Fig. 2), giving Cu co-ordinates: $x=90°$, $y=70°$. The corresponding peak, with $u=180-2x=0$, $v=180°$ is also present (peak B').

Possibility (*b*) must correspond to a peak in $P(u, v, \frac{1}{2})$ at $v=0$. There are two peaks which come in question:

(b_1) $u=0$, $v=0$ (peak C'), giving $x=0$ and $y=0$, with another peak D' at $u=180°$, $v=180°$;

(b_2) $u=170°$, $v=0$ (peak E'), giving $x=85$ and $y=0$, with another peak (elongation of peak B') at $u=10°$, $v=180°$.

In order to decide between these possibilities we assume that in our crystal the surrounding of the Cu atom by the Cl atoms is the same as in CuCl. CuCl has the zincblende structure, so the Cu atom is tetrahedrally surrounded by the Cl atoms (Cu–Cl distance 2·34 A.). In our structure we can fit in a $CuCl_4$ tetrahedron by placing the Cu atom and two Cl atoms in a symmetry plane, say $c=\frac{1}{4}$, and the other two Cl atoms of the tetrahedron in the symmetry planes $c=\frac{3}{4}$ and $c=-\frac{1}{4}$ respectively. A chain of tetrahedra, sharing corners, is thus formed in the direction of the c axis. For such a structure the distance between the symmetry planes ($\frac{1}{2}c$) is calculated to be

in $K_2CuCl_3 \simeq 2{\cdot}34 \sin 55° = 1{\cdot}92$,

in $Cs_2AgCl_3 \simeq 2{\cdot}77 \sin 55° = 2{\cdot}27$,

and in $Cs_2AgJ_3 \simeq 2{\cdot}81 \sin 55° = 2{\cdot}30$,

and these values are in rough agreement with the observed c periods.

Assuming these tetrahedra, configuration (b_1) is impossible, as in this structure the Cu atom is placed in $0, 0, \frac{3}{4}$ and $0, 0, \frac{1}{4}$ and so the distance between Cu ($c=\frac{3}{4}$), and Cl ($c=\frac{3}{4}$), belonging to the tetrahedron of Cu ($c=\frac{1}{4}$), would be much too short (1·34 A.).

In agreement with the assumption of the tetrahedra is the fact that we can deduce from our Patterson function $P(u, v, 0)$ two vector distances of about 2·35 A., including a tetrahedral angle, which may correspond with Cu–Cl distances. The peaks *C* and *D* define vector distances of approximately the required length, and on reflecting *D* across the x axis and *C* about the origin we obtain two vectors including a tetrahedral angle. In $P(u, v, \frac{1}{2})$ we can find a vector of length corresponding with the distance between Cu ($c=\frac{1}{4}$) and Cl ($c=\frac{3}{4}$) in the assumed tetrahedra, and with a direction which can be deduced by reflexion across the x axis of the bisector of the tetrahedral angle in $P(u, v, 0)$.

The two possibilities left are the configurations (*a*) and (b_2). Knowing the Cu position and the direction of the Cu–Cl vectors it is possible to locate all Cu and Cl atoms, to insert the K atoms and to calculate the co-ordinates. On calculating the intensities of some low reflexions it was seen that configuration (*a*) gives a much better agreement with the observed intensities than configuration (b_2).

Almost all peaks in the Patterson functions $P(u, v, 0)$ and $P(u, v, \frac{1}{2})$ can be accounted for with configuration (a). The peak C' (in $(0, 0)$) of $P(u, v, \frac{1}{2})$ is unaccounted for and the height of the peaks is not in agreement with the scattering factors. This is probably due to the fact that the even layer lines are given too high a weight in our approximation.

Two-dimensional Fourier synthesis

Assuming configuration (a) with Cu in $x=90°$, $y=70°$ and Cu–Cl vectors as found from $P(u, v, 0)$, the structure factors of all observed reflexions of the zero layer line along [001] were calculated, and the signs were used for a Fourier synthesis. In order to reduce the influence of the absorption, zero-layer-line Weissenberg diagrams were taken along [001] with Mo $K\alpha$ radiation. The intensities were estimated visually by comparison with an intensity scale and corrected for Lorentz and polarization factors. The intensities of the lower reflexions, which do not appear on the molybdenum diagram were taken from the copper photograph and were correlated with the molybdenum intensities. In the preliminary Fourier summation about twenty F's were omitted because the signs were uncertain. In the second and definitive summation all F's were used with the now calculated signs.

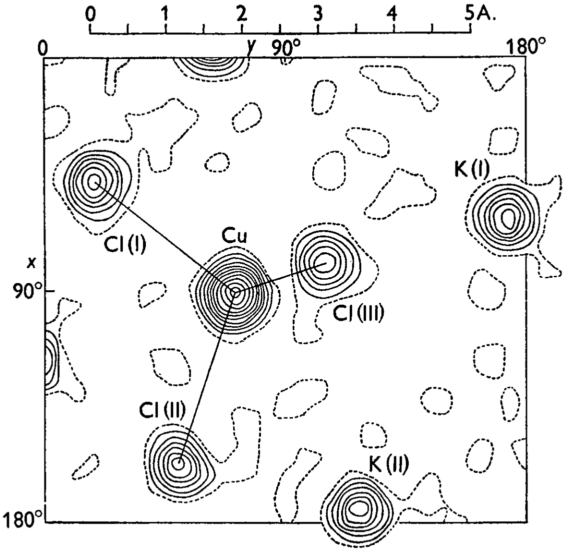


Fig. 3. Fourier projection of K_2CuCl_3 along [001]. Contour lines as in Fig. 1.

Fig. 3 shows the Fourier projection along the c axis. The peaks are well resolved from each other, and the co-ordinates may be determined accurately. The electron-density map shows false maxima, all very low, which must be due to experimental errors and to the fact that many reflexions with low intensity were apparently submerged in the general background and so were not included in the series.

The final co-ordinates are listed in Table 2 and differ only by a few degrees from the co-ordinates deduced from the Patterson analysis (only the x co-ordinate of K (II) has been shifted over 8 degrees of the cell dimension).

Table 2. *Parameter values found for* K_2CuCl_3

(Values in fractions of the cell dimensions.)

	x	y
Cu	0·252	0·197
Cl (I)	0·133	0·052
Cl (II)	0·435	0·138
Cl (III)	0·277	0·791
K (I)	0·172	0·480
K (II)	−0·488	−0·327

In order to estimate the accuracy of the co-ordinates obtained, a Fourier synthesis was made as suggested

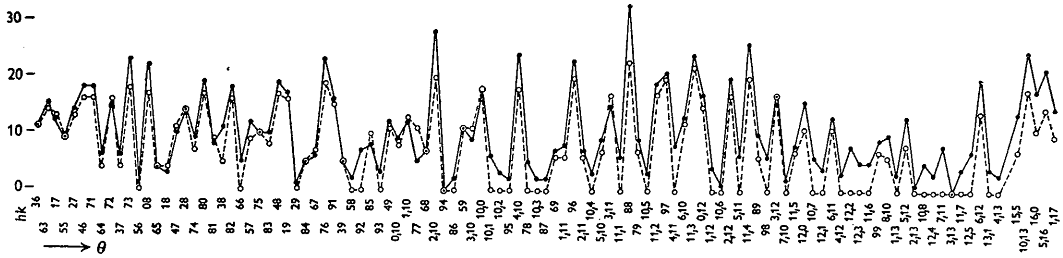


Fig. 4. Comparison of calculated (full line) and observed (dotted line) structure factors $F(hk0)$ for K_2CuCl_3. Mo $K\alpha$ radiation.

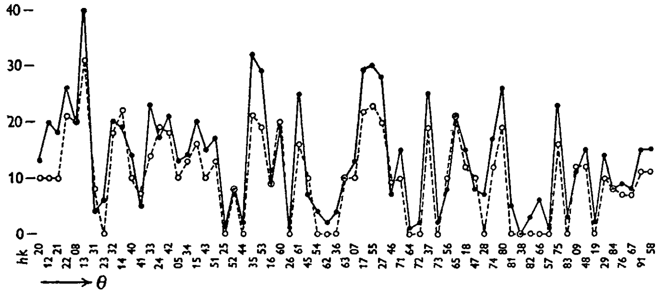


Fig. 5. Comparison of calculated (full line) and observed (dotted line) structure factors $F(hkl)$ for K_2CuCl_3. Cu $K\alpha$ radiation.

by Booth (1947), using the structure factors calculated from the final co-ordinates and omitting the structure factors of reflexions not observed. The co-ordinates derived from this synthesis have a deviation from the final co-ordinates within the accuracy of the graphical determination of the co-ordinates of the maxima. The maximum error in the final co-ordinates, due to finite termination, is thus about ½°, that is 0·02 A.

In Figs. 4 and 5 are illustrated graphically the observed structure factors and the structure factors calculated (without temperature factor), using the atomic scattering factors listed in the *Internationale Tabellen*, for part of the *hk*0 and for the lower *hk*l reflexions. The agreement for the latter reflexions is less good, probably owing to the much stronger absorption of the copper radiation.

Table 3. *Observed intensities and calculated structure factors*, *F*(*hk*0), *for* Cs_2AgCl_3 *and* Cs_2AgI_3 *computed with the parameters found for* K_2CuCl_3

	Cs_2AgI_3				Cs_2AgCl_3	
hkl	$10^3 . \sin^2 \theta_{Cu}$	I_{Cu}	I_{Mo}	$F_{calc.}$	I_{Cu}	$F_{calc.}$
130	26				*m*	−52
310	28				*m*	+60
230	34	*w*		+27	*vw*	+19
320	36	*w*		+65	—	+7
040	41	—		+25	*w*	+32
140	44	—		+10	*w*	−36
400	46	*m*		+58	*ss*	+65
410	48	*ms*		−81	*w*	−33
330	49	*vw*		−26	—	−10
240	52	*s*		−102	*ms*	−63
420	56	*s*		−139	*s*	−90
150	67	*vw*		+15	—	+11
340	67	*w*		+8	*w*	+24
430	69	*vw*		−25	—	−18
510	73	*w*		−27	*vw*	−15
250	75	*s*		+102	*m*	+47
520	81	*vw*		+20	*vw*	+19
440	87	—	*vw*	−14	*vw*	−19
350	90	*s*	*ss*	+94	*ms*	+72
060	93	*m*	*ss*	+95	*ms*	+90
530	94	*m*	*s*	−68	*m*	−64
160	96	—	*vw*	−20	—	0
600	103	—	—	+7	*ms*	+35
260	104	—	*vw*	+25	*vvw*	+13
610	105	*vw*	*vw*	−18	*w*	−18
450	110	—	—	+10	—	−7
540	112	*w*	*w*	−31	—	−12
620	113	*m*	*ss*	+81	*ms*	+54
360	119	—	—	−3	*vw*	−21
630	126	*m*	*s*	−64	—	−11
170	129	*w*	*m*	−49	—	−12
550	135	*w*	*m*	−34	—	−9
270	137	*w*	*m*	+57	*vw*	+28
460	139	*m*	*m*	+57	*w*	+44
710	142	*m*	*ss*	+74	*w*	+24
640	144	*w*	*w*	+34	—	+18
720	150	—	*vw*	−36	*m*	−42
370	152	—	—	+25	*w*	+32
730	163	*m*	*s*	−87	*ms*	−56
560	164	*m*	*m*	−37	*vw*	+25
080	165	*vw*	*m*	−59	*w*	−40
650	167	*w*	*vw*	+14	—	+17
180	168	—	*vw*	+9	*vw*	−31
470	172	*w*	*w*	−42	*w*	−37
280	176	—	*vw*	+30	—	−1
740	181	—	—	+1	—	+22
800	183	*vw*	*w*	+40	*m*	+37
810	185	*w*	*m*	−39	*vw*	−18
380	191	—	—	+27	—	+23
820	193	*vw*	*w*	−43	*s*	−61
660	196	*w*	*w*	+31	*w*	+43
570	197	*w*	*w*	+51	—	+9

s = strong, *m* = medium, *w* = weak, *vw* = very weak, *ss* = very strong.

Isomorphous substances

For comparison, zero-layer-line photographs along the needle axis were also taken of Cs_2AgCl_3 and Cs_2AgI_3. Taking for these substances the same parameter values as for K_2CuCl_3, we find for the distance Ag–I in the mirror plane 2·78 A. (in AgI this distance is 2·81 A.); for the distance Cs–I 3·86 A. (sum Cs^+ and I^- radii for co-ordination number six = 3·85 A.); for the distance Ag–Cl 2·54 A. (in AgCl with rocksalt structure 2·77 A.); and for the distance Cs–Cl about 3·54 A. (sum Cs^+ and Cl^- radii for co-ordination number six = 3·48 A.). The parameter values in these substances therefore cannot be very different and so the *F*(*hk*0) values (only the lower reflexions) for Cs_2AgCl_3 and Cs_2AgI_3 were calculated with the parameter values found for K_2CuCl_3.

Table 3 shows that there is already a fairly good agreement with the estimated intensities. (In both substances the absorption is still stronger than in K_2CuCl_3.) We may therefore conclude that Cs_2AgCl_3 and Cs_2AgI_3 have the same structure as K_2CuCl_3.

Discussion of the structure

Fig. 6 gives the structure projected along the *c* axis. The Cl atoms form tetrahedra about the Cu atom and these tetrahedra form chains in the direction of the *c* axis, as successive tetrahedra share corners. The two

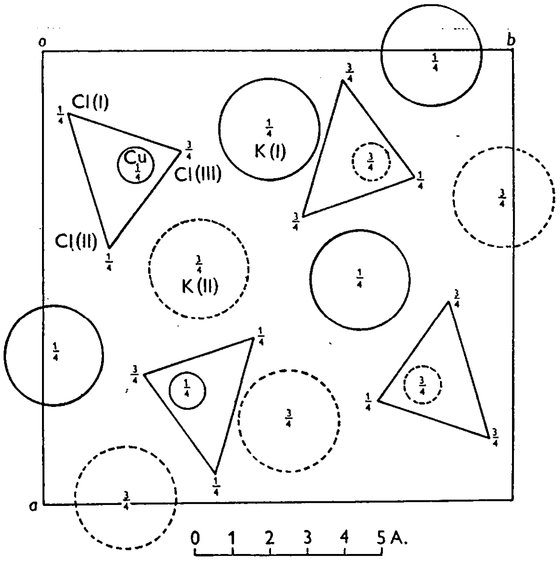


Fig. 6. Projection of the structure of K_2CuCl_3 along [001]. There are in the unit cell four chains of tetrahedra in the direction of the *c* axis. These chains appear in this projection as triangles with Cl at the corners and Cu in the centre. The large circles are K. K (I) at $c=\frac{1}{4}$ is surrounded by 1 Cl at $c=\frac{1}{4}$, 3 Cl at $c=\frac{3}{4}$, and 3 Cl at $c=-\frac{1}{4}$. K (II) at $c=\frac{1}{4}$ is surrounded by 3 Cl at $c=\frac{1}{4}$, 2 Cl at $c=\frac{3}{4}$, and 2 Cl at $c=-\frac{1}{4}$.

K atoms are located between the chains in positions which are not equivalent, but both K atoms are surrounded by seven Cl atoms, six in the corners of a distorted trigonal prism and one on a lateral face. The c axis of the structure is parallel to the trigonal axis of the prism around K(I) and to one of the base edges of the trigonal prism around K(II). The calculated distances are listed in Table 4.

Table 4. *Calculated distances in* K_2CuCl_3

(Values in A. Maximum error about 0·04 A.)

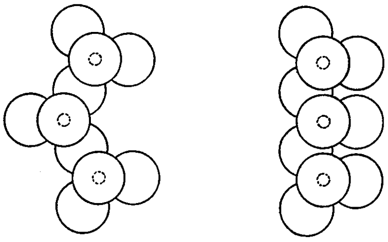
Cu–Cl (I) in the same symmetry plane	2·31
Cu–Cl (II) in the same symmetry plane	2·32
Cu–Cl (III) in different symmetry planes	2·43
K (I)–Cl (II) in the same symmetry plane	3·20
K (I)–Cl (II) in different symmetry planes	3·18
K (I)–Cl (III) in different symmetry planes	3·22
K (I)–Cl (I) in different symmetry planes	3·27
K (II)–Cl (III) in the same symmetry plane	3·23
K (II)–Cl (III) in the same symmetry plane	3·18
K (II)–Cl (I) in the same symmetry plane	3·18
K (II)–Cl (II) in different symmetry planes	3·22
K (II)–Cl (I) in different symmetry planes	3·12
Cu–Cl distance in CuCl	2·34
K–Cl distance in KCl	3·14

The chains have some analogy with the SiO_3 chains in the pyroxenes, but still there is a typical difference, resulting in greater compactness of the $CuCl_3$ chain (Fig. 7). In a $CuCl_3$ chain of the type of the SiO_3 chain in the pyroxenes the Cu–Cu distance would be larger.

The structure satisfies the electrostatic valence rule (Pauling, 1939, p. 364): the sum of the strength of the electrostatic bonds to Cl I and to Cl II is: $\frac{5}{7}+\frac{1}{4}=0·96$, and to Cl III: $\frac{4}{7}+\frac{2}{4}=1·07$.

The chains are in agreement with the observed optical behaviour (largest refractive index in the needle direction).

It is a great pleasure to us to thank Prof. Dr A. E. van Arkel, Leiden, for suggesting and stimulating this investigation and for reading the manuscript.



(*a*) (*b*)

Fig. 7. (*a*) Chain in pyroxenes (idealized). Small circles are Si, large circles O. (*b*) Chain in K_2CuCl_3 (idealized). Small circles are Cu, large circles Cl.

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Relation between Residual Strain Energy and Elastic Moduli*

By Clarence Zener

Institute for the Study of Metals, The University of Chicago, Ill., U.S.A.

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It is shown that the presence of residual strain energy necessarily results in a lowering of the overall tensile and shear moduli, and a quantitative relation is derived between the density of residual strain energy and the decrease in tensile and shear moduli. An interpretation is thereby given to the recent observations of Köster that solute atoms of only a small solubility lower the tensile modulus when they are atomically dispersed.

Introduction

The inspiration for the present paper has been derived from the recent study of Köster & Rauscher (1948) regarding the influence of solute atoms in solid solution upon the tensile elastic modulus of metals. Köster has found that alloying elements always reduce the tensile elastic moduli of Cu, Ag, and Au provided the maximum solubility of the alloying elements is less than 20 atomic %. He further found a rough correlation between the maximum solubility and the rate at which the elastic modulus decreases with increasing concentration, the lower the solubility the greater the rate at which the elastic modulus decreases. The general trends are indicated in Fig. 1 for alloying elements in copper.

It would appear at first sight as if no correlation whatsoever should exist between the limit of solubility and the decrease in elastic modulus. Closer examina-

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