References and Notes

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4 May 1967 ■

Crystal Structure of the Solid Electrolyte, RbAg$_4$I$_5$

Abstract. *The crystal structure of the solid electrolyte* RbAg$_4$I$_5$ *has been determined from single-crystal x-ray diffraction counter data. There are four* RbAg$_4$I$_5$ *in a cubic unit cell with* $a = 11.24$ Å. *The structure refinement, by least squares, is based on space group* $P4_13$ (O^7). *The arrangement of the iodide ions is similar to that of the manganese atoms in β-manganese, and provides 56 iodide tetrahedra per unit cell, which share faces in such manner as to provide diffusion paths for the silver ions. The occurrence of the two low-temperature phases of* RbAg$_4$I$_5$ *has been established by x-ray diffraction and optical examination.*

The unusual family of isostructural solid electrolytes with formula MAg$_4$I$_5$ in which M is K$^+$, Rb$^+$, or NH$_4$$^+$ was discovered at the Atomics International laboratories by B. B. Owens (*1*). Inasmuch as it appeared that the material would have considerable application, publication was delayed. However, two papers have now been published by Bradley and Greene (*2*) on their independent discovery of the compounds.

No clue to the structure of the compounds has as yet been given. I have determined it, however, and my purpose here is to describe it and show how it accounts for the conductivity.

The compound which appeared to be the best suited for this work is that in which M is Rb, because it is the most stable against moisture (*1*). The x-ray data, on which the structure reported here was based, were obtained from a single crystal ground to a sphere of 0.22-mm diameter with a Bond (*3*) sphere grinder. The single crystal was grown by Hiller and Owens (*4*), under conditions based on a phase diagram worked out by Topol (*5*).

Crystals of RbAg$_4$I$_5$ are optically isotropic, therefore cubic, with *a* equal to 11.24 ± 0.02 Å and cell content of four RbAg$_4$I$_5$. The x-ray density is 5.384 g/cm^3, in good agreement with the density, 5.30 g/cm^3, measured by Owens (*1*). The crystals have diffraction symmetry *m*3*m*; the only systematic absences are those for $h00$ with $h \neq 4n$. On the assumption that intensities of such reflections are identically zero, the crystal belongs to one of the enantiomorphous space groups $P4_33(O^6)$ or $P4_13(O^7)$. No attempt has been made to determine the absolute configuration; the imaginary contributions of the anomalous dispersion for MoKα radiation are small, and no deviation from *m*3*m* symmetry was observed on a set of Buerger precession camera photographs. (When larger single crystals are available, polarimetric examination will be made.) The determination and refinement of the structure was based on space group $P4_13$.

With the knowledge of the properties of the crystal (*1*), it was apparent that the Ag$^+$ ions would not be ordered. Disorder of the I$^-$ and Rb$^+$ ions appeared to be precluded by their sizes. Thus the iodide ions were probably in sets 8(*c*) and 12(*d*) of the space group. The combination of these two sets allows only moderate variation on one logical arrangement of these ions in the unit cell: the arrangement is that of the Mn atoms in β-Mn (*6*). (β-Manganese and some isostructural intermetallic compounds are the only other crystals known to belong to the space group.) The Rb$^+$ ions are in the 4(*a*) sites, which are surrounded by distorted octahedra of iodide ions. It remained to determine the parameters of the iodide ions and to find the sites for the Ag$^+$ ions and their occupation numbers.

The intensity data were collected manually with a Buerger-Supper goniometer and North American Philips cir-

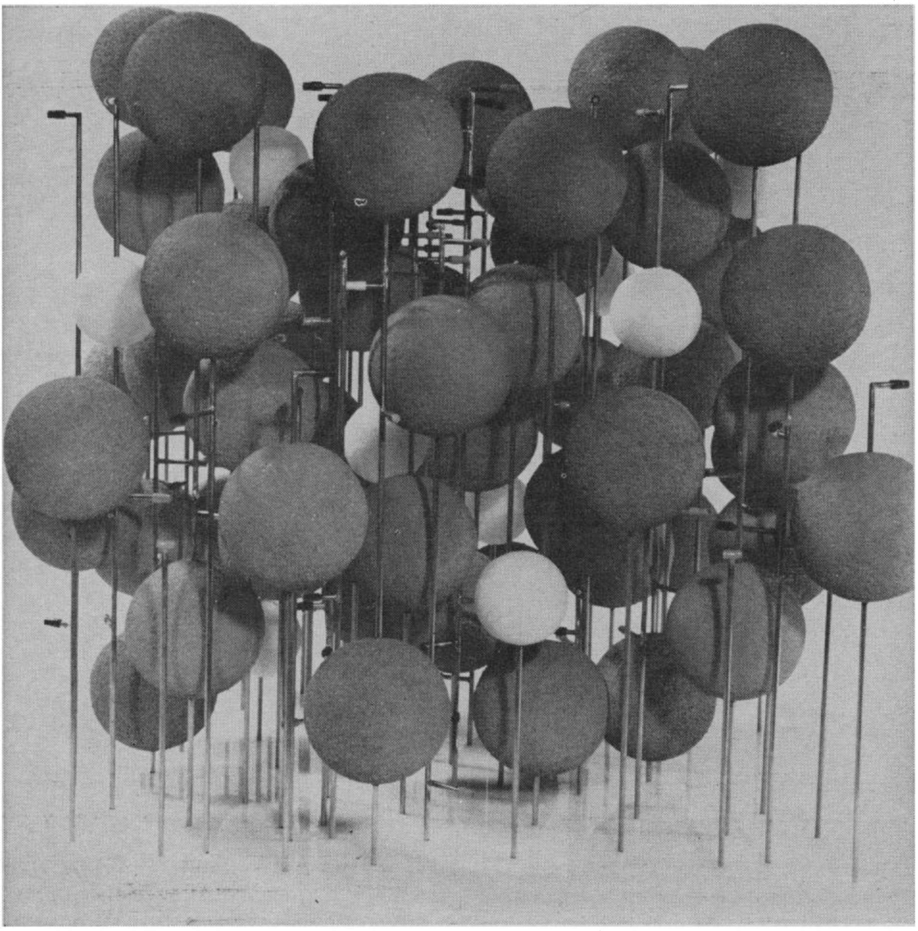

Fig. 1. Model of the structure of RbAg$_4$I$_5$. Large spheres represent iodide ions, small white spheres, Rb$^+$ ions. Centers of sleeves on short horizontal arms designate possible positions of Ag$^+$ ion. The three shades represent the three crystallographically nonequivalent sites. Note the channels in the upper middle and lower left parts of the model.

cuitry and scintillation counter. Zirconium-filtered MoK$_\alpha$ radiation was used. Crystal and counter settings were calculated on the IBM-360 computer. Each reflection was scanned for 100 seconds (50 seconds to peak center). Background was counted for 100 seconds before and after the scan of the reflection for lower angle peaks, but for most reflections it was found unnecessary to do both background counts. Intensities of all independent reflections for 2θ less than or equal to 56° were measured; at room temperature there were very few observable ones at higher angles. Structure amplitudes were obtained by applying the Lorentz-polarization-Tunell (*7*) and absorption (*8*) corrections.

A three-dimensional Patterson function was helpful in establishing the initial values of the iodide parameters; the sites for Ag$^+$ ions were found mainly by examining models of the "skeleton" formed by the iodide ions. Refinement was carried out with the Busing-Martin-Levy (*9*) least-squares program on the IBM 7094 and 360 computers. Atomic scattering factors used were those of Cromer and Waber (*10*), corrected for the real part of the anomalous dispersion with values calculated by Cromer (*11*).

The final parameters and their standard errors are listed in Table 1. The discrepancy factor

$$R = \frac{\Sigma \| F_o | - | F_c \|}{\Sigma | F_o |}$$

is 0.083. Some of this residual is probably caused by the inadequate description of the motion of the Ag$^+$ ions by the usual six (or less) parameter matrix.

The important interionic distances and their standard errors (*12*) are given in Table 2. The limits of error of the I-I distances are between ± 0.01 and ± 0.02 Å and of Rb-I, ± 0.006 Å. The limits of error for Ag-I distances are much larger, as one would expect.

The limits of error (± 0.015) on the multiplier of the Ag$^+$ ion in the 4 (*b*) sites do not differ significantly from zero. (These sites are at centers of trigonal bipyramids, and if any Ag$^+$ ions are in these sites, they are trapped because they have no access routes to the tetrahedral sites.) Further, the thermal parameter is also very large with a very large standard error.

Thus, there are essentially three sets of crystallographically nonequivalent sites for the Ag$^+$ ions, one 8-fold set and two 24-fold sets, making a total of 56 sites for 16 Ag$^+$ ions per unit cell.

Table 1. Positional and thermal parameters.

Ion position	Rubidium 4(*a*)	Iodide		Silver			
		8(*c*)	12(*d*)	24(*e*)	24(*e*)	8(*c*)	4(*b*)
Multiplier	1/6	1/3	1/2	0.391	0.229	0.037	0.014
σ				.012	.012	.004	.005
x	3/8	0.0306	3/8	.5299	.9964	.1739	1/8
$\sigma(x)$		.0002		.0009	.0012	.0029	
y	3/8	$= x$	−0.1780	.2713	.8506	$= x$	3/8
$\sigma(y)$			.0002	.0010	.0017		
z	3/8	$= x$	$= (3/4)$-y	.7980	.2154	$= x$	5/8
$\sigma(z)$				.0009	.0013		
β_{11}	0.0142	0.0076	0.0100	.0113	.0081	0.0163	0.054
$\sigma(\beta_{11})$	.0005	.0001	.0003	.0011	.0013	.0028	.022
β_{22}	$= \beta_{11}$	$= \beta_{11}$	.0083	.0200	.0227	$= \beta_{11}$	$= \beta_{11}$
$\sigma(\beta_{22})$			.0002	.0010	.0028		
β_{33}	$= \beta_{11}$	$= \beta_{11}$	$= \beta_{22}$	.0146	.0118	$= \beta_{11}$	$= \beta_{11}$
$\sigma(\beta_{33})$			−0.0006	.0017	.0017		
β_{12}	0	−0.0002		.0013	.0020	−0.0015	0
$\sigma(\beta_{12})$		.0002	0.0002	.0009	.0014	0.0029	
β_{13}	0	$= \beta_{12}$	$= \beta_{12}$	.0025	.0028	$= \beta_{12}$	0
$\sigma(\beta_{13})$				.0008	.0012		
β_{23}	0	$= \beta_{12}$	−0.0006	−0.0021	−0.0033	$= \beta_{12}$	0
$\sigma(\beta_{23})$			0.0002	0.0010	0.0016		

As shown in Table 1, the ions are not distributed at random over these sites. There are, on the average, 0.88 ± 0.30 Ag$^+$ions in the 8 (*c*) sites and 9.38 ± 0.87 and 5.50 ± 0.83 Ag$^+$ ions in the two sets of 24-fold sites, respectively (Table 1). (The limits of error on these as well as on the thermal parameters of the Ag$^+$ ions are large because, as might be expected, there are sizable interactions (*13*) between the multipliers and the thermal parameters.) If the distribution of Ag$^+$ ions were random, the values would be 2.29, 6.86, and 6.86 Ag$^+$ ions in the respective sites.

In Table 2, I have designated the three important sets of silver ion sites as Ag(*c*), Ag(II), and Ag(III). A silver ion in an Ag(*c*) site may move to one of three Ag(II) sites in neighboring tetrahedra which share faces with the tetrahedron about the Ag(*c*) site. The fourth face of the Ag(*c*) tetrahedron is shared with the Rb$^+$ octahedron; it is, therefore, highly unlikely that an Ag$^+$ ion in the *c*-site would move out through that face. It should be kept in mind that, with all the Ag(II) sites being only 1.76 Å away (see Table 2) from an Ag(*c*) site, such sites about an occupied Ag(*c*) site must be empty, or else ions in one or more of these tetrahedra must be on their way to other available sites.

A silver ion in an Ag(II) site may move through faces shared by tetrahedra to four neighboring sites: namely, to an Ag(*c*) site, to another Ag(II) site, or to one of two Ag(III) sites. Of course, again, all four of these sites about a particular occupied Ag(II) site should be available because of the short "inter-site" distances, 1.68 to 1.91 Å (see Table 2).

A silver ion in an Ag(III) site may move only to two Ag(II) sites through shared tetrahedron faces. The remaining two tetrahedron faces give access only to the Rb$^+$ ion which would repel the Ag$^+$ ion.

Figure 1 is a photograph of a model of the structure. Possible sites for Ag$^+$ ions are indicated by the centers of white, black, and gray plastic pieces at

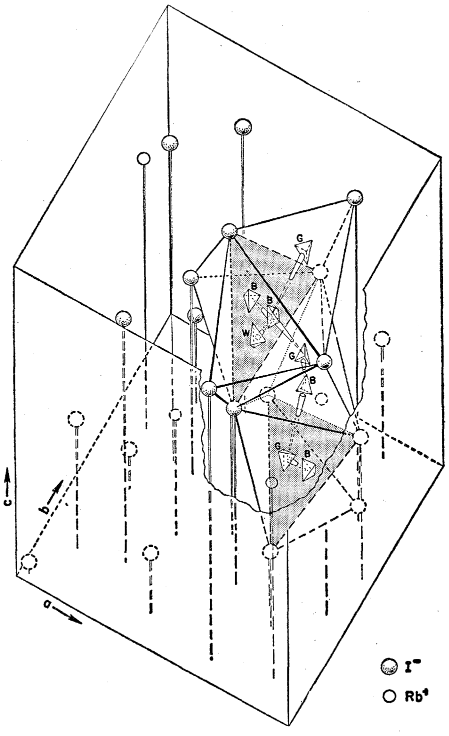

Fig. 2. Perspective drawing of iodide and Rb$^+$ ion arrangement. Some of the shared tetrahedron faces and diffusion steps are shown. The small tetrahedra designate the Ag$^+$ sites associated with the larger tetrahedra. W, B, and G are the white (*c*), black (II), and grey (III) sites of Fig. 1 (Table 2).

ends of small arms. The sleeves—white, black, and grey—indicate Ag(*c*), Ag(II), and Ag(III) sites, respectively. Figure 2 is an isometric drawing of the I^- and Rb^+ ion arrangement in a single unit cell. Eight of the tetrahedra showing the face-sharing are drawn in.

The Ag(II) sites must be involved in every diffusion step, but at least one of the other sets of sites is *required* if diffusion is to take place. Alternating Ag(II) and Ag(III) sites form channels parallel to the three unit cell axes. Two of these channels can be seen in Fig. 1. There are two such channels perpendicular to each unit cell face. The Ag(*c*) sites help to connect these channels. It should be emphasized that the Ag^+ ions are not expected to move straight through the channels, but rather through the shared tetrahedron faces, as indicated in Fig. 2.

Table 2. Interionic distances and standard errors.

Atom types and symmetry	No. of distances	Distance (Å)	± SE (Å)
Nearest I^- neighbors of I^- (c)			
I(*c*)—I(*c*)	3	4.505	0.004
I(*c*)—I(*d*)	3	4.358	.004
I(*c*)—I(*d*)	3	4.670	.003
I(*c*)—I(*d*)	3	4.880	.005
Nearest I^- neighbors of I^-(d)			
I(*d*)—I(*c*)	2	4.358	0.004
I(*d*)—I(*c*)	2	4.670	.003
I(*d*)—I(*c*)	2	4.880	.005
I(*d*)—I(*d*)	4	4.455	.003
I(*d*)—I(*d*)	2	5.425	.006
Iodide octahedron about Rb^+ (a)			
Rb —I(*d*)	6	3.627	0.002
I(*d*)—I(*d*)	6	4.455	.003
I(*d*)—I(*d*)	3	5.425	.006
I(*d*)—I(*d*)	3	6.069	.004
Iodide tetrahedron about Ag^+ (c)			
Ag —I(*c*)	1	2.79	0.06
Ag —I(*d*)	3	2.91	.03
I(*c*)—I(*d*)	3	4.880	.005
I(*d*)—I(*d*)	3	4.455	.003
Iodide tetrahedron about Ag^+(e) (0.530, 0.271, 0.798), II			
Ag —I(*c*)	1	2.94	0.01
Ag —I(*d*)	1	2.81	.01
Ag —I(*d*)	1	2.87	.01
Ag —I(*d*)	1	2.92	.01
I(*c*)—I(*c*)	1	4.505	.004
I(*d*)—I(*d*)	1	4.455	.003
I(*c*)—I(*d*)	4	4.880	.005
Iodide tetrahedron about Ag^+ (e) (0.996, 0.851, 0.215), III			
Ag —I(*c*)	1	2.87	0.02
Ag —I(*c*)	1	2.92	.02
Ag —I(*d*)	1	2.73	.01
Ag —I(*d*)	1	2.80	.01
I(*c*)—I(*c*)	1	4.505	.004
I(*c*)—I(*d*)	1	4.358	.004
I(*c*)—I(*d*)	1	4.670	.003
I(*d*)—I(*d*)	1	4.455	.003
I(*c*)—I(*d*)	2	4.880	.005
Nearest neighbor Ag^+ tetrahedral sites			
Ag(*c*)—Ag(II)	3	1.76	0.02
Ag(II)—Ag(*c*)	1	1.76	.02
Ag(II)—Ag(III)	1	1.68	.02
Ag(II)—Ag(III)	1	1.71	.02
Ag(II)—Ag(II)	1	1.91	.02
Ag(III)—Ag(II)	1	1.68	.02
Ag(III)—Ag(II)	1	1.71	.02

Thus the arrangement of the I^- ions provides 56 iodide tetrahedra, per unit cell, which share faces in such manner as to provide diffusion paths for the Ag^+ ions and therefore account for the ionic conductivity of the crystal. The nearness and numbers of neighboring sites put restrictions on the site occupancy as well as on the diffusion rate.

The average positions of Ag^+ ions in the three crystallographically nonequivalent sites are such that the average Ag-I distances in them are, respectively (in the order listed in Table 2): 2.86 ± 0.12, 2.88 ± 0.03, and 2.83 ± 0.04 Å. Only the average Ag(II)-I distance appears to be significantly longer than the Ag-I distance, 2.80 Å, in zinc blende type AgI (*14*). The nearest neighbor I-I distance in AgI is 4.59 Å. The average I-I distances in $RbAg_4I_5$ are 4.60 Å for I(*c*) and 4.56 Å for I(*d*) (when the 5.425 Å distances are omitted). But the average I-I distances of the tetrahedra are somewhat larger: 4.67, 4.74, and 4.62 Å for Ag(*c*), Ag(II), Ag(III) tetrahedra, respectively. The Rb-I distance, 3.627 ± 0.006 Å, is close to that, 3.670 Å, in RbI (NaCl-type structure). The octahedron about the Rb^+ ion is highly distorted, but the average I-I distance, 5.10 Å, is close to the I-I distance, 5.19 Å, in RbI.

It is of interest to compare the Mn-Mn distances in β-Mn (*6,15*) with the I-I distances in $RbAg_4I_5$. About Mn(*c*), the distances, analogous to those of I(*c*) in Table 2, are respectively, 2.37, 2.54, 2.68, and 2.69 Å, while about Mn(*d*) they are 2.54, 2.68, 2.69, and 2.62 Å. The distortion of the iodide icosahedra is greater than that of the Mn icosahedra. In fact, it appears that the I(*d*) ion has only 10-coordination to iodide ions.

There are two low-temperature modifications of $RbAg_4I_5$. The first indication of a transition at −154°C appeared in the plot of conductivity versus temperature, obtained by Owens and Argue (*1*). An x-ray powder diffraction pattern taken at −180°C with a Norelco diffractometer and low-temperature adaptor, similar to that described by Calhoun and Abrahams (*16*), shows many additional weak lines. It appeared that the pattern could be indexed on a cubic unit cell with *a* equal to 33.4 Å, but this phase is definitely not cubic (see below).

A small, thin crystal of $RbAg_4I_5$ was mounted under a microscope between crossed polaroids. A copper-constantan thermocouple was arranged so that it just touched the crystal. On cooling, the crystal became birefringent at −25°C (*17*); this transition was reversible without hysteresis. The crystal remained birefringent between −25° and −180°C. At the lowest temperatures a definite domain structure was observed; when allowed to warm to room temperature, the crystal was single again.

At −100°C the x-ray powder pattern showed only line broadening and at least one "split" line; at −180°C, where the many extra lines were observed, the lines were quite sharp.

Single-crystal Buerger precession-camera and Laue-transmission photographs have also been taken at −100° and −180°C; as expected, the occurrence of twinning makes interpretation difficult.

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