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Low-temperature phases of the solid electrolyte $RbAg_4I_5$†

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Important structural features of the two low-temperature phases of $RbAg_4I_5$, designated β,γ in order of decreasing temperature, have been determined, even though the precise structure of the γ phase is unattainable because of the large number of structural parameters and the limitations on available data. At 130 K, the β phase is rhombohedral, space group $R32(D_3^7)$, with $a = 11.17 \pm 0.01$ Å, $\alpha = 90.1° \pm 0.05°$. Most of the displacements of ions and equilibrium Ag^+ ion sites, relative to the α phase, are small, the largest, 0.3 Å, being those for two Ag^+ ion sites. The largest displacement of an I^- ion is 0.1 Å. The most significant difference between the α and β phases is the *preferential* distribution of Ag^+ ions, in the latter, over sets of sites formerly crystallographically equivalent. However, the distribution does not change very much over *analogous* sites: In α-$RbAg_4I_5$ the distribution is 0.9, 9.4, and 5.5 Ag^+ ions in the Ag–*c*, Ag–II, and Ag–III sites, respectively, while the analogous values in β-$RbAg_4I_5$ are 1.3, 10.5, and 4.2. (The limits of error are probably about the same as in the α phase.) Neither α- nor β-$RbAg_4I_5$ can be ordered and therefore the 209-K transition is a "disorder-disorder" transition. The γ-$RbAg_4I_5$ is trigonal, most probable space group $P321$ (D_3^2), with $a = 15.776 \pm 0.005$ Å and $c = 19.320 \pm 0.005$ Å at 90 K. The unit cell has three times the volume of the rhombohedral cell and therefore contains 12 $RbAg_4I_5$. The structure of the γ phase is closely related to that of the β phase and can be derived from it by first transforming the rhombohedral structure to a triply primitive hexagonal cell and then permitting further displacement of ions and Ag^+ ion sites with respect to their positions in the β phase, **thus resulting in a primitive cell.** It is shown that there are 146 possible ordering schemes (under the assumption that 30 Ag^+ ions fill Ag–II *type* sites) and that a study of these leads to the probable Ag^+ ion distribution schemes in the β phase. This was actually instrumental in attaining the distributions in the β phase. The γ phase does not appear to be ordered at 90 K, but the single most probable arrangement for an ordered γ phase is deduced from the Ag^+ ion distribution in the β phase.

INTRODUCTION

The solid electrolyte $RbAg_4I_5$ has the highest room-temperature specific conductivity, $0.27\,(\Omega\,\mathrm{cm})^{-1}$, of any ionic crystal.[1,2] At temperatures above 208 K, crystals of $RbAg_4I_5$ belong to space group $P4_332$ (O^6) or $P4_132$ (O^7).[3] Crystals belonging to both space groups have been grown.[4] Originally, the structure was defined in space group $P4_132$ and this description will be used throughout this paper. (Of course, because $P4_332$ is the enantiomorph of $P4_132$, it is a simple matter to follow through all the reasoning in the former, given what follows for the latter.)

There are two low-temperature transitions of $RbAg_4I_5$, a first-order one at 121.8 K,[1,5] and a second-order one at 209 K.[3,5] In both cases the iodide substructure persists, so that all the $RbAg_4I_5$ phases (i.e., including the high-temperature cubic ones) are closely related. In this paper the phases will be designated α, β, γ in order of *decreasing* temperature.

Each unit cell of α-$RbAg_4I_5$ contains four $RbAg_4I_5$. The twenty iodide ions form 56 tetrahedra which share faces in such manner that they produce a network of passageways through which the Ag^+ ions can diffuse. There are three crystallographically nonequivalent sets of sites for the Ag^+ ions: one eightfold and two 24-fold sets. These were called[2] Ag–*c*, Ag–II, and Ag–III sites, respectively.

The iodide face-sharing tetrahedra involving alternate Ag–II and Ag–III sites form channels parallel to the three cubic axes. Within each unit cell, there are two such channels parallel to each of the axes, and each channel increment within the unit cell contains four each of Ag–II and Ag–III sites. The channels are joined by Ag–II sites. Each Ag–*c* site has three near-neighbor Ag–II sites. The Ag–*c* sites give an alternate way of joining channels, but are not required for Ag^+ ion diffusion.

Inasmuch as there are 16 Ag^+ ions per unit cell and one set of eight-fold and two sets of 24-fold sites for the Ag^+ ions, there is *no way* in which the Ag^+ ions can be ordered in this (highest temperature) phase of $RbAg_4I_5$. Under no circumstance can there be more than 12 Ag^+ ions in the Ag–II sites because each Ag–II site has a near-neighbor Ag–II site at 1.91 Å. If an Ag–II site is occupied, its two near-neighbor Ag–III sites cannot be occupied and, of course, if an Ag–III site is occupied, its two neighboring Ag–II sites cannot be occupied. This puts additional constraints on the site occupancy. It is noteworthy that if there were 12 Ag^+ ions in Ag–II sites (at room temperature, there are 9.38 ± 0.87 atoms in Ag–II sites), there could be at *most* 12 Ag–III and 4 Ag–*c* sites available to the remaining Ag^+ ions.

CRYSTALLOGRAPHY OF THE LOW-TEMPERATURE PHASES

Intermediate phase, β-$RbAg_4I_5$

An x-ray powder diffraction pattern taken (about ten years ago[3]) at 170 K with Cu $K\alpha$ radiation showed line broadening indicative of line splitting but no lines not corresponding to those of the cubic structure. This intermediate phase of $RbAg_4I_5$ therefore has a crystal structure, the unit cell of which is a small distortion of that of the cubic phase. Inasmuch as the transition is of the λ type,[5] the structure must belong to a subgroup of $P4_132$ (or $P4_332$).

The powder pattern definitely indicates that the $\{hhh\}$ reflections are split. Of the reflections equivalent to the cubic $\{h00\}$ reflections, only the $\{400\}$ appears in the pattern and, on careful comparison with the pattern taken at room temperature, this reflection is not split. It is therefore concluded that the distortion is rhombohedral.

Early inspections of the powder diffraction pattern taken at 170 K indicated that the rhombohedral distortion of the unit cell is no greater than 0.1°. At first, the severe overlapping of nonequivalent peaks seemed to preclude a determination of the direction of this distortion. Subsequently, the results of the structure determination (see below) led to the conclusion that the angle $\alpha = 90.1°$ to within better than 0.05°. This angle is almost surely not significantly different at 130 K. At 170 K, $a = 11.19$ Å; at 130 K, $a = 11.17$ Å.

The most probable space group to which the intermediate phase belongs is $R32\ (D_3^7)$, as is also confirmed by the results of the "single-crystal" investigation (see also Table I).

Low-temperature phase, γ-$RbAg_4I_5$

As reported earlier,[3] a powder diffractometer pattern taken at 90 K showed many new lines in addition to those of the substructure. All the lines are quite sharp, the substructure lines being much sharper than the corresponding lines at room temperature. It was pointed out[3] that this pattern could be indexed on a cubic cell with lattice constant 33.4 Å. It has now been found that the pattern may be indexed even more accurately on a cubic cell with lattice constant 33.465. Å. However, the phase cannot be cubic because it is birefringent.[3]

In the cubic indexing of the pattern, the sum of the squares of indices (that is, $h^2 + k^2 + l^2$) of each reflection is divisible by 3, which we might call a "magic" number. This number implies that the phase is hexagonal. If there were *no* extra lines we would find that the indices of the reflections based on a hexagonal cell would obey the relation $-h + k + l = 3n$. That is to say, we would be referring the cubic cell of $RbAg_4I_5$ to hexagonal axes, considering the cubic cell to be rhombohedral with a rhombohedral angle of 90°. This hexagonal cell would be triply primitive.

We divide 33.465 Å by 3, giving 11.155 Å for the substructure cell, which must also have cubic dimensions. The hexagonal cell then has dimensions $a = 11.155\sqrt{2} = 15.776$ Å, $c = 11.155\sqrt{3} = 19.321$ Å. *Every* line on the pattern taken at 90 K is accounted for by a cell with $a = 15.776$ Å, $c = 19.320$ Å. There is much overlapping of nonequivalent reflections, but there are no systematic absences. Thus this hexagonal cell is primitive and has three times the volume of the substructure cell; it therefore contains 12 $RbAg_4I_5$.

We must now deduce the space group to which this phase belongs. Because the substructure dominates the pattern, we know that the arrangement of Rb^+ and I^- ions is very similar to that in the high-temperature cubic modification. Laue transmission photographs (to which reference was made earlier[3]) suffered from slight misalignment, but there is no doubt that the phase is not truly hexagonal; it must be trigonal. Even without the Laue photographs, this can readily be deduced by reasoning from the substructure. The trigonal structure is related to the triply primitive one derived from the rhombohedral one. Following through, the most probable space group to which this phase belongs is $P321\ (D_3^2)$ (see Table I).

TABLE I. Space groups and equipoint transformations of $RbAg_4I_5$ phases. Numbers in parentheses designate point symmetries.

$T > 209$ K $P4_132$	$209\text{ K} > T > 122$ K $R32$	$T < 122$ K $P321$
Rb in 4*a* (32)	1*a*(32)	1*a*(32) 2*d*(3)
	3*e*(2)	3*f*(2) 6*g*(1)
I, Ag–*c* in 8*c* (3)	2*c*(3)	2*c*(3) 2 sets 2*d*(3)
	6*f*(1)	3 sets 6*g*(1)
I in 12*d* (2)	3*d*(2)	3*e*(2) 6*g*(1)
	3*e*(2)	3*f*(2) 6*g*(1)
	6*f*(1)	3 sets 6*g*(1)
Ag–II, Ag–III in 24*e*	4 sets of 6*f* each; 8 sets of 6*f*, total	3 sets 6*g* each; 24 sets of 6*g*, total

For completeness, we summarize the important transformations between the rhombohedral and triply primitive hexagonal cells: For rhombohedral to hexagonal (trigonal) indices, $(1\bar{1}0/011/111)$ (the notation represents a 3×3 matrix, first, second, and third rows) and for the reverse $\frac{1}{3}(211/\bar{1}11/\bar{1}\bar{2}1)$; for rhombohedral to trigonal coordinates, $\frac{1}{3}(2\bar{1}\bar{1}/11\bar{2}/111)$, and for the reverse, $(101/\bar{1}11/0\bar{1}1)$.

We go on to discuss the detailed determination of the structure of β-$RbAg_4I_5$.

CRYSTAL STRUCTURE OF β-$RbAg_4I_5$

Experimental

Crystals of $RbAg_4I_5$ used in this work were obtained by slowly cooling a nonstoichiometric melt containing 75 mole% AgI, kept in argon atmosphere.[4,6] Only a very small crystal was required and there was no problem in finding material in the cooled mass more than adequate to the task. Several spheres were made with a Bond sphere grinder[7]; the air used was filtered and then passed through Drierite and a glass-wool filter before it entered the sphere grinder.

The spherical crystal chosen for this work had a radius of 0.11 mm. For Mo $K\alpha$ radiation and for the crystal density at 130 K of $5.488\,g/cm^3$, the linear absorption coefficient is $21.63\,mm^{-1}$. The crystal was oriented with the use of a Buerger precession camera and transferred by means of a Supper crystal transfer device to another goniometer head so that a fourfold axis was the rotation axis. The crystal was carefully coated with a very small amount of ethyl cellulose in toluene (suggested by G. F. Ruse). After allowing this coating to dry, an additional coating of light mineral oil was added. The coatings were used to avoid the devastating effect of moisture on the crystal.

The temperature of the crystal was held at 130 K by means of the technique first reported by Post, Schwartz, and Fankuchen.[8] The single-crystal data were collected with a Buerger-Supper diffractometer automated by a Nova 1200 computer. Zirconium-filtered Mo $K\alpha$ radiation and a scan rate of 1°/min were used. Background counts were taken at $\frac{1}{6}$ the scan time on both sides of each peak. The scan width for each peak was $1.7+0.3\,Lp$, where L is the Lorentz and p the polarization factor. Lorentz-polarization-Tunell and absorption[9] factors were applied; relative $|F_0|^2$ are put out by the Nova computer on paper tape as well as printed online by the teletype; the intensities are also plotted on a strip-chart recorder.

Data in the range $10° < 2\theta < 55°$ were collected. Within this range, 363 independent intensities occur, of which only 16 were below threshold (100 count net). (This is in contrast to 99 below threshold out of a possible 384 in the range $0° < 2\theta < 56°$ for α-$RbAg_4I_5$, the measurements having been made at 25°C.) The total number of data used to determine the structure was 333, 14 being excluded because of unreliability for such reasons as "dirty" radiation streaks, secondary extinction, nearness of the diffracted beam to the edge of the beam trap.

Determination of the structure

When a single crystal of $RbAg_4I_5$ is cooled below the 209-K transition, it becomes multiply twinned. There is no obvious way of avoiding this if the crystal is to be small, spherical, and give the required data. The cubic fourfold axis becomes a pseudofourfold axis. That is to say, reflections formerly equivalent because of the cubic fourfold axis, still give equal measured intensities. This implies that the overall twin volumes are equal. Each Bragg intensity for a general set of h, k, l indices, $h, k, l > 0$, $h > k > l$ as in the cubic case, is actually composed of contributions from four Bragg reflections. If two indices are equal, the contributions from two of the reflections are equal. If one of the indices is equal to zero, the contributions from two pairs are equal; if two of the indices are equal to zero, all contributions are equal.

A version of the Busing-Martin-Levy[10] least-squares program, modified (by L. Y. Y. Chan) to include the specific twinning, was used to refine the parameters. This modification was the replacement in the calculation of $|F_{hkl}|$ by

$$\tfrac{1}{2}(|F_{hkl}|^2+|F_{\bar{k}kl}|^2+|F_{h\bar{k}l}|^2+|F_{\bar{h}\bar{k}l}|^2)^{1/2}.$$

The general positions in the calculation were, of course, those of space group $R32$. The observed structure amplitudes F_0 were weighted in accordance with:

$$1/w = 1.89e^{F_0/100} \quad \text{for } F_0 \geqslant 200,$$

$$1/w = 0.07F_0 \quad \text{for } 50 < F_0 < 200,$$

$$1/w = (157/F_0)e^{5.5/F_0} \quad \text{for } F_0 \leqslant 50.$$

Because the rhombohedral structure belongs to a subgroup of the cubic ones, the positions of the atoms in the latter go continuously into those of the former through the transition—a necessary condition for a second-order transition. The specifically related sets of positions are given in Table I.

In Table I, it is shown that the three crystallographically nonequivalent sets of sites for the Ag^+ ions in the cubic crystal transform into a total of ten crystallographically nonequivalent sets of sites in the rhombohedral crystal. The task of determining the distribution of the Ag^+ ions was arduous mainly as a result of the twinning, which reduced, considerably, the sensitivity of the data to the Ag^+ ion distribution. Three reflections *are* particularly sensitive to this distribution, namely, the 320, 321, and 322, and especially the last. The 322 intensity increases monotonically and substantially as the temperature is decreased toward that of the lower transition. The 209-K transition is marked by the onset of the increase of the intensity of the 322 reflection. Thus, regardless of how good the overall agreement between calculated and observed structure amplitudes might be, it is especially necessary for the agreement of the 320, 321, and 322 cases to be very good.

The 24-fold general set of positions in $P4_132$ may be divided into four sixfold groups which are related by the 4_1 axis (↻ denotes a cyclic permutation):

1 (a) $x, y, z,$; ↻

(b) $\frac{3}{4}-y, \frac{3}{4}-x, \frac{3}{4}-z$; ↻

2 (a) $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; ↻

(b) $\frac{1}{4}+y, \frac{1}{4}-x, \frac{3}{4}+z$; ↻

3 (a) $\frac{1}{2}+z, \frac{1}{2}-x, \bar{y}$; ↻

(b) $\frac{1}{4}+x, \frac{1}{4}-z, \frac{3}{4}+y$; ↻

4 (a) $\frac{1}{2}+y, \frac{1}{2}-z, \bar{x}$; ↻

(b) $\frac{1}{4}+z, \frac{1}{4}-y, \frac{3}{4}+x$; ↻

As mentioned earlier, the positions of the Ag^+ ions of the Ag–II type are such that only half these can be occupied. The nearest neighbor sets are as follows: 1(a)-1(b), 2(a)-4(b), 2(b)-4(a), 3(a)-3(b). The transformation of these positions to the rhombohedral structure simply involves a shift of origin $-(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$, to be in accord with the *International Tables for X-Ray Crystallography*.[11] *Within* each numbered set above, those in (a) and those in (b) are then related by the unique threefold axis, while those in (a) *and* (b) are related by twofold axes.

Along a particular channel in which Ag–II and Ag–III sites alternate in the α-$RbAg_4I_5$ structure, each channel increment within the cubic unit cell contains eight sites, four of each type related by the 4_1 axis. The 4_1 axis is no longer part of the rhombohedral β-$RbAg_4I_5$; therefore, neither the Ag–II nor the Ag–III sites in a single channel are any longer equivalent. Each site belongs to one of the set of six related by the threefold and twofold axes. Each of these is in one of the six channels in each unit cell.

It is to be expected that in the transition, the equilibrium positions of the Ag^+ ions will remain inside the tetrahedra. However, their distribution over the *ten* sets of sites now available in the β phase could be quite different. In fact, calculations of the contributions from the Ag^+ ions in the now ten nonequivalent sets of sites to the *composite* 320, 321, and 322 structure factors showed that this must be so. The displacements of the I^- and Ag^+ ions themselves could not account for the increases in the values of these composite structure factors. Further, while all 16 Ag^+ ions *could* reside in the (transformed) (Ag–III)-type positions (which is possible in the cubic structure), the calculations showed that they did not. There is no *a priori* reason to expect that they should and, in fact, it will be shown later that the distribution over the cubic equivalent (Ag–*c*)-, (Ag–II)-, and (Ag–III)-*type* sites does not change significantly.

In the cubic structure, there are nine positional, 21 anisotropic thermal, and three occupancy parameters to be refined, a total of 33. If all ten sets of nonequivalent sites for the Ag^+ ions are included, the analogous numbers for the rhombohedral case are respectively 38, 84, 10, a total of 132, a factor of 4 larger than for the cubic case. Even if the crystal were not twinned and the structure were not so close to the cubic one, this is a large number of parameters for the data available. But these two factors make the situation worse. Not to be overlooked also, is the expense of such calculations; it should be kept in mind that four structure factors and their derivatives are calculated for each observed one (see above).

Another point is this: Even when the data for solid electrolyte crystals are not complicated by twinning, it is usually a tedious matter to obtain convergence of the least-squares calculations for the site occupancies, especially when the number of crystallographically nonequivalent sets of sites is large. Thus, a somewhat intuitive approach is required to attain convergence.

As indicated earlier, the structure of γ-$RbAg_4I_5$ is also closely related to the cubic one, and more so to the β phase, even though it does not belong to a subgroup of either. While it is impossible for the Ag^+ ions to be ordered in the β structure, it *is* possible for them to be ordered in the γ structure. Admittedly, at first it appeared that ordering of the Ag^+ ions *would* occur in the γ phase. In any case, a knowledge of the possible ordered arrangements in that structure did aid in bringing the work on the β structure to a successful conclusion.

In the rhombohedral case, we have designated the (Ag–II)-type sets Ag(n), $n = 1, 2, 3, 4,$; the (Ag–III)-type sets Ag(n), $n = 5, 6, 7, 8$; and the (Ag–*c*)-type sets Ag(cn), $n = 1, 2$, where $n = 2$ denotes the twofold special positions. For the (Ag–II)-

type, $n=1-4$ correspond to the numbers given earlier for the four cubic sets related by 4_1; for the (Ag–III)-type, $n=5-8$ are derived from the cubic sets numbered 1–4, respectively. The Ag($c2$) set derives from x, x, x and $\frac{3}{4}-x, \frac{3}{4}-x, \frac{3}{4}-x$ of the $8c$ set of $P4_132$, and the Ag($c1$) set from the remaining six positions. The triply primitive trigonal cell positions are obtained by first transforming the rhombohedral cell positions using the transformation given earlier and then adding $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ to each position (obverse setting[12] to be in accord with the latest *International Tables for X-Ray Crystallography*). This first step is only a geometric construction; it does not represent the actual physical transformation. The physical transformation consists in discontinuous displacements of the atoms from their positions in the rhombohedral cell such as to make the hexagonal cell primitive. This description shows how the γ phase has a cell with three times the volume of the rhombohedral cell.

In the γ structure we denote by Ag–II(n), $n=1,2,3$, the three sets derived from Ag(1) in the β structure; by Ag–II(n), $n=4,5,6$, the three sets derived from Ag(2), etc. We denote by Ag–III(n), $n=1,2,3$, the three sets derived from Ag(5), by $n=4,5,6$ those derived from Ag(6), etc. We denote by Ag–$C(n)$, $n=1,2,3$, those derived from Ag($c1$) and by Ag–$C(n)$, $n=4,5,6$, those derived from Ag($c2$).

It turns out that if there is ordering in the γ structure under the circumstance that there are 30 Ag^+ ions in (Ag–II)-type sites, then the Ag–II(1) and Ag–II(9) sites must be empty because half of the sites are too close to the other half in each of these sets. Furthermore, there are five pairs of sets which cannot be simultaneously occupied for the same reason. That is to say, there are exactly five sets of (Ag–II)-*type* sites that *can* be simultaneously occupied in the γ structure. However, there are 2^5 such combinations. For each of these 32 combinations, there are restrictions on the occupancy of the Ag–III(n) and Ag–$C(n)$ sets, again because of the nearness of certain of these sites to those of the particular combination of (Ag–II)-type sites. All possible ordered arrangements with 30 Ag^+ ions in type-II sites are contained in Table II. Some Ag–$C(n)$ and Ag–III(n) sets are eliminated more than once because of their close approaches to more than one set of the (Ag–II)-type sites.

The total number of possibilities for an ordered γ structure with 30 Ag^+ ions in the (Ag–II)-type sites is 146. Cases 1–4, 9, 10, 13, 14, 17–20, 23, 26–29 each give four possibilities; cases 5, 6, 11, 12, 21, 22, 25, 31 each give one possibility; and cases 7, 8, 15, 16, 24, 30, 32 each give ten possibilities.

If the γ phase is to be ordered, then one might expect that at 130 K the β-phase structure would be indicative of this by having a distribution of Ag^+ ions in accord with that in the ordered phase. The number of possible distributions in the β phase analogous to those in the ordered phase is much smaller than in the latter, of course. We note in Table II that if ordered, the γ phase can have no Ag^+ ions in the Ag–III(4), (5), (6) sites. Analogously, it should be expected that the β phase will have very few or no Ag^+ ions in the Ag(6) sites. Each set of six equivalent sites in the γ structure transforms to two equivalent sites in the β structure. Thus, for example, if the sites Ag–II(2) are filled in the γ structure, this would transform to the occupancy of one-third of the Ag(1) sites of the β structure. It follows that case 1 for the γ structure transforms into the following for the β-structure: one-third of the Ag(1), all Ag(2), one-third of the Ag(4), and no Ag(3) sites occupied, and an appropriate combination of three (thirds total) of the following: one- or two-thirds of the Ag(5), one-third of Ag(7), and one-third of Ag($c1$) sites occupied. Case 2 of the trigonal structure transforms into exactly the same as case 1. The possible cases all reduce to those shown in Table III.

There is a total of 33 possibilities of Ag^+ ion distribution if the rhombohedral structure is to be a precursor of the trigonal one [recalling that in the latter, 30 Ag^+ ions are to be in (Ag–II)-type sites].

Table III predicts that of the (Ag–II)-type sites in the β structure, the largest contributions, two- or three-thirds, are from either Ag(2) or Ag(4). Experimentally, this was independently indicated to be the actual case from the increase in the intensity of the 322 reflection ascertained by calculation. The problem still remained, however, as to which of the four type-II possibilities was the correct one.

All the possibilities in Table III were tested either by least-squares calculations or by calculation of the structure factors contributing to the 320, 321, and 322 composite observed data. The result was that none of these possibilities was *precisely* suited to the data. However, this analysis gave considerable insight into the nature of the two low-temperature structures. It already indicated that there was a good chance that the γ phase is actually not ordered (see later discussion of this phase).

If none of the Ag^+ ion distributions given in Table III fits, then what is the case? One thing was certain: Either the Ag(2) or Ag(4) sites must have a high occupancy to give good agreement

TABLE II. Key to all possible ordered arrangements of Ag^+ ions in γ- $RbAg_4I_5$ with 30 Ag^+ ions in (Ag–II)-type sites.

Case	Ag-II(n) sites filled										Ag-C(n) sites eliminated						Ag-III(n) sites eliminated											
	2	3	4	10	5	12	6	11	7	8	1	2	3	4	5	6	1	2	3	4	5	6	7	8	9	10	11	12
1	✓		✓		✓		✓		✓			✓	✓	✓	✓	✓	✓			✓	✓	✓	✓	✓		✓	✓	✓✓
2		✓	✓		✓		✓		✓		✓	✓		✓	✓	✓	✓			✓	✓	✓	✓		✓	✓	✓✓	✓
3	✓		✓			✓	✓		✓			✓✓	✓	✓		✓	✓	✓		✓	✓	✓	✓	✓			✓	✓✓
4		✓	✓			✓	✓		✓		✓	✓✓		✓	✓	✓	✓	✓		✓	✓	✓	✓		✓		✓✓	✓
5	✓		✓		✓			✓	✓		✓	✓	✓	✓	✓		✓		✓	✓	✓	✓	✓	✓		✓		✓✓
6		✓	✓		✓			✓	✓		✓✓	✓		✓	✓		✓		✓	✓	✓	✓	✓		✓	✓	✓	✓
7	✓		✓		✓		✓			✓			✓✓	✓	✓	✓		✓		✓	✓	✓		✓	✓	✓	✓	✓✓
8		✓	✓		✓		✓			✓	✓		✓	✓	✓	✓		✓		✓	✓	✓			✓✓	✓	✓✓	✓
9	✓		✓		✓			✓		✓	✓		✓✓	✓	✓			✓	✓	✓	✓	✓		✓	✓	✓		✓✓
10		✓	✓		✓			✓		✓	✓✓		✓	✓				✓	✓	✓	✓	✓			✓✓	✓	✓	✓
11	✓		✓			✓		✓	✓		✓	✓✓	✓	✓			✓	✓	✓	✓	✓	✓	✓	✓				✓✓
12		✓	✓			✓		✓	✓		✓✓	✓✓		✓			✓	✓	✓	✓	✓	✓	✓		✓		✓	✓
13	✓		✓			✓		✓		✓	✓	✓	✓✓	✓				✓✓	✓	✓	✓	✓		✓	✓			✓✓
14		✓	✓			✓		✓		✓	✓✓	✓	✓	✓				✓✓	✓	✓	✓	✓			✓✓		✓	✓
15	✓		✓			✓	✓			✓		✓	✓✓	✓		✓		✓✓		✓	✓	✓		✓	✓		✓	✓✓
16		✓	✓			✓	✓			✓	✓	✓	✓	✓		✓		✓✓		✓	✓	✓			✓✓		✓✓	✓
17	✓			✓	✓		✓		✓			✓	✓✓		✓	✓	✓✓			✓	✓	✓	✓	✓		✓	✓	✓
18		✓		✓	✓		✓		✓		✓	✓	✓		✓	✓	✓✓			✓	✓	✓	✓		✓	✓	✓✓	
19	✓			✓		✓	✓		✓			✓✓	✓✓			✓	✓✓	✓		✓	✓	✓	✓	✓			✓	✓
20		✓		✓		✓	✓		✓		✓	✓✓	✓			✓	✓✓	✓		✓	✓	✓	✓		✓		✓✓	
21	✓			✓	✓			✓	✓		✓	✓	✓✓		✓		✓✓		✓	✓	✓	✓	✓	✓		✓		✓
22		✓		✓	✓			✓	✓		✓✓	✓	✓		✓		✓✓		✓	✓	✓	✓	✓		✓	✓	✓	
23	✓			✓	✓		✓			✓			✓✓✓		✓	✓	✓	✓		✓	✓	✓		✓	✓	✓	✓	✓
24		✓		✓	✓		✓			✓	✓		✓✓		✓	✓	✓	✓		✓	✓	✓			✓✓	✓	✓✓	
25	✓			✓	✓			✓		✓	✓		✓✓✓		✓		✓	✓	✓	✓	✓	✓		✓	✓	✓		✓
26		✓		✓	✓			✓		✓	✓✓		✓✓		✓		✓	✓	✓	✓	✓	✓			✓✓	✓	✓	
27	✓			✓		✓		✓	✓		✓	✓✓	✓✓				✓✓	✓	✓	✓	✓	✓	✓	✓				✓
28		✓		✓		✓		✓	✓		✓✓	✓✓	✓				✓✓	✓	✓	✓	✓	✓	✓		✓		✓	
29	✓			✓		✓		✓		✓	✓	✓	✓✓✓				✓	✓✓	✓	✓	✓	✓		✓	✓			✓
30		✓		✓		✓		✓		✓	✓✓	✓	✓✓				✓	✓✓	✓	✓	✓	✓			✓✓		✓	
31	✓			✓		✓	✓			✓		✓	✓✓✓			✓	✓	✓✓		✓	✓	✓		✓	✓		✓	✓
32		✓		✓		✓	✓			✓	✓	✓	✓✓			✓	✓	✓✓		✓	✓	✓			✓✓		✓✓	

TABLE III. Key to possible Ag^+ ion arrangements in β-$RbAg_4I_5$. Numbers in columns under types of sites represent multiples of $\frac{1}{3}$ (see text).

Case \ n	Type II(n) sites					Type III(n) sites		Type (cn) sites		Total number of possible arrangements
	1	2	3	4	5	7	8	1	2	
1	1	3	0	1	1 or 2	1 or 2	0	1 or 2	0	7
2	1	2	1	1	1 or 2	1 or 2	1	1	0	10
3	1	2	1	1	1	1	0	2	0	2
4	1	1	1	2	1	1 or 2	1 or 2	0	0	5
5	1	1	1	2	1	1	0	1	0	1
6	1	1	1	2	0	1	1	1	0	1
7	1	1	1	2	1	0	1	1	0	1
8	1	1	1	2	0	2	0	1	0	1
9	1	0	1	3	0	1 or 2	1 or 2	0	1	5

for the 320, 321, and 322 observed data. A number of least-squares cycles were carried out, mostly using isotropic thermal parameters, thereby reducing the total number of parameters by about a factor of 3. Finally after a substantial number of calculations, the results of Table IV were obtained. In the last calculations, the distribution of the Ag^+ ions and the isotropic thermal parameters of the Ag^+ ions were held constant. The remaining parameters converged to the values shown. The agreement index $R=\sum||F_0|-|F_c||/\sum|F_c|$ for the 333 structure factors[13] is 0.082. The agreement for the 320, 321, and 322 reflection is almost perfect (perhaps too good). The observed and calculated values for these are, respectively, 108.7, 108.3; 98.2, 97.9; 140.6, 139.2.

In the calculations, the atomic scattering factors used were those of Cromer and Waber,[14] corrected for the real part of the anomalous dispersion.[15]

Discussion

Under the circumstances outlined earlier the values shown in Table IV are the best obtainable. Numerous calculations indicated, for example, that the Ag(2) sites have very low occupancy and these were therefore completely removed from the calculation. Exclusion of the Ag(6) ions appeared to worsen the agreement as did inclusion of Ag^+ ions in Ag(8) or Ag(5) sites. This is particularly significant because any ordered γ phase would not have any Ag^+ ions in the Ag–III(4), (5), (6) sites which derive from the Ag(6) sites of the β phase (see Table II). Also, the calculations indicated that the Ag(c1) sites have very low occupancy and therefore these were not included in the calculations. The necessity of including the Ag(6) sites was quite troublesome in the work because of the bias against such inclusion caused by

TABLE IV. Final parameter values for β-$RbAg_4I_5$, analogous positional parameters of α-$RbAg_4I_5$ (Ref. 3), and relative displacements of ions in the two structures. Numbers in parentheses are standard errors applied to right-most digits. Those parameters not having numbers in parentheses were held constant in the final least-squares cycle.

Ion	Site symmetry	Multiplier[a]	x	y	z	Displacement (Å)	B (Å^2)	α-structure analog
Ag(1)	1	0.50	0.1600(18)	0.8862(17)	0.4277(20)	0.14(4)	2.25	
			0.1549(9)	0.8963(10)	0.4230(9)			Ag–II
Ag(3)	1	0.45	0.9209(28)	0.6013(35)	0.3440(32)	0.13(6)	4.10	
			0.9230(9)	0.5951(10)	0.3537(9)			Ag–II
Ag(4)	1	0.80	0.3968(14)	0.3272(18)	0.0956(18)	0.01(4)	3.97	
			0.3963(9)	0.3270(10)	0.0951(9)			Ag–II
Ag(7)	1	0.50	0.3135(26)	0.1266(23)	0.7856(20)	0.33(5)	3.76	
			0.3404(12)	0.1286(17)	0.7744(13)			Ag–III
Ag(6)	1	0.20	0.0959(46)	0.2636(44)	0.4091(47)	0.31(9)	2.30	
			0.1214(12)	0.2744(17)	0.4096(13)			Ag–III
Ag(c2)	3	0.217	−0.1983(15)	$=x$	$=x$	0.05(6)	3.00	
			−0.2011(29)	$=x$	$=x$			Ag–c
I1	1	1	0.2491(9)	0.9523(8)	0.1964(9)	0.06(2)	1.97(12)	
			$\frac{1}{4}$	0.9470(2)	0.1970(2)			I(d)
I2	1	1	0.1499(8)	0.0948(9)	0.5875(8)	0.10(2)	2.03(11)	
			0.1556(2)	0.0944(2)	0.5944(2)			I(c)
I3	2	$\frac{1}{2}$	0	−0.5607(10)	$=-y$	0.12(2)	3.54(41)	
			0	−0.5530(2)	$=-y$			I(d)
I4	2	$\frac{1}{2}$	$\frac{1}{2}$	0.3038(11)	$=-y$	0.01(1)	2.94(28)	
			$\frac{1}{2}$	0.3030(2)	$=-y$			I(d)
I5	3	$\frac{1}{3}$	−0.3421(36)	$=x$	$=x$	0.04(7)	3.45(35)	
			−0.3444(2)	$=x$	$=x$			I(c)
Rb1	2	$\frac{1}{2}$	$\frac{1}{2}$	−0.2524(24)	$=-y$	0.04(4)	3.79(36)	
			$\frac{1}{2}$	$\frac{1}{4}$	$=-y$			
Rb2	32	$\frac{1}{6}$	0	0	0	0	4.85(13)	
			0	0	0			

[a] Site occupancy, 6 times multiplier.

the analysis of ordering in the γ phase.

The final calculated structure factors[13] show that there are considerable differences in the magnitudes of many of the individual structure factors of each composite reflection. But, there is not nearly the sensitivity of the composite structure factors to the parameters that there would be if the data had been obtainable from an untwinned crystal; obtaining such data must be relegated to the very-low-probability realm. Mainly because of the twinning, the standard errors even of the iodide parameters are considerably larger than those obtained for the α phase[3] or, for that matter, for any of the reported[16-19] AgI-based solid electrolyte structures, in which cases the standard errors for the iodide positional parameters are very low.

In α-$RbAg_4I_5$, the distribution of the Ag^+ ions is as follows: Ag–c, 0.88; Ag–II, 9.38; Ag–III, 5.50. Table IV shows that in the β phase, the analogous numbers are 1.3, 10.5, and 4.2, respectively. This result indicates that the distribution over the *types* of sites is not very different in the two phases.

The transition from the α to the β phase does, however, involve a *preferential* redistribution of the Ag^+ ions over the sets of crystallographically nonequivalent sites derived from those of the cubic structure. This is to be expected. To some extent, the distribution is explainable. At the very least, there must be a *tendency* toward ordering in the γ structure, and this is seen in the β structure despite some occupancy of the Ag(6) sites. The Ag(2) sites are essentially empty, implying that there is a tendency toward one of the arrangements of case 9 of Table III for the β phase, which, in turn, implies a tendency toward one of the arrangements of cases 27–30 inclusive of Table II for the γ phase.

It seems that it can justifiably be argued that the β phase is "less disordered" (in preference to "more ordered") than the α phase. The lower symmetry results in a partial lifting of the site degeneracy, which implies site energy differences among formerly equivalent sites. The site energy differences are further corroborated by occupancy differences which did not exist before. This translates into a nonuniform replacing a uniform distribution of Ag^+ ions over formerly equivalent sites. This then leads logically to the conclusion of less disorder in the lower-symmetry structure. Nevertheless, this argument should not be taken as a contradiction to the statement made earlier: The 209-K transition is a disorder-disorder transition because it is not possible for either phase to be completely ordered.

For comparison, analogous transformed (by origin shift) α-$RbAg_4I_5$ parameters are given in Table IV. Calculated relative displacements of the ions are also given. The largest displacements are for the Ag(7) and Ag(6) sites. The others are rather small and some are not statistically significant in the $\pm 3\sigma$ confidence limits.

The interionic distances calculated[20] from the parameters shown in Table IV are given in Table V. They are listed in a manner analogous to the interionic distances in cubic $RbAg_4I_5$ given in Table 2 of Ref. 3. [There are a few mistakes in that table: In the iodide tetrahedron about Ag–II, the third Ag-I is Ag-I(c) instead of Ag-I(d); instead of four I(c)-I(d) at 4.880 Å, there should only be three and one I(c)-I(d) at 4.670 Å should be added. In the tetrahedron about Ag–III, the first Ag-I should be Ag-I(d) and the third Ag-I(c); there are two I(c)-I(d) 4.670-Å and one 4.880-Å distances instead of the reverse.]

Among the I^- ions, I(c) of the α structure transform to I2 and I5, and I(d) to I1, I3, and I4 of the β structure. It will be noticed that for the most part the averages of I-I distances analogous to those in the cubic structure are very close to the latter when reduced by the ratio of the lattice constants 11.17/11.24 of the two phases. The same is true for the Rb-I distances. There are some rather large discrepancies among Ag-I distances, for Ag(c2)-I1, Ag(3)-I3, Ag(7)-I1, Ag(7)-I2, Ag(7)-I4, Ag(6)-I1, but the average Ag-I distances are not significantly different in the two structures.

Table V shows the nearest-neighbor Ag-Ag distances analogous to those of the cubic structures. Most of these are approximate (those with footnote b) because one of the sets of sites is empty. This is particularly interesting because it shows that the redistribution of the Ag^+ ions is such as to tend to minimize the number of Ag^+ ions occupying the sites in sets that have these very short intersite distances. In fact, of 15 possible short intersite distances, only five are between sets of sites that contain Ag^+ ions in the β phase.

Let us see by an example how significant this is. Suppose instead of partial occupancy of the Ag(6) sites, there were partial occupancy of Ag(8) sites. We would then have a total of seven short Ag-Ag distances between sets that *contain* Ag^+ ions. At the same time, the reader should be reminded that the sites containing Ag^+ ions must not contain too many. For example, the Ag(1) sites contain three as do the Ag(7), Ag(3) contain 2.7, Ag(4) contain 4.8, and Ag(6), 1.2. The Ag(1) and Ag(3) sites cannot contain more than three each because half of the sites of each are too close to the other half.

Prior to the structure determination it was not

TABLE V. Interatomic distances and their standard errors, Å, in β-$RbAg_4I_5$. (n) distance (m): n denotes number of distances of this length; m denotes standard error applied to last digit.

1. Nearest neighbors of I^- ions

I2 Neighbor	I2 Distance	Average	I5 Neighbor	I5 Distance	α-equiv.[a] Distance
I2	4.32(2)	4.47(2)	I2	(3)4.45(2)	(3)4.476(4)
I2	4.66(2)				
I5	4.45(2)				
I1	4.31(1)	4.32(1)	I4	(3)4.35(5)	(3)4.331(4)
I1	4.45(1)				
I3	4.21(1)				
I1	4.52(1)	4.64(1)	I3	(3)4.67(1)	(3)4.641(3)
I1	4.68(2)				
I4	4.71(1)				
I1	4.78(1)	4.88(1)	I1	(3)4.76(6)	(3)4.850(5)
I3	5.00(1)				
I4	4.87(2)				

I1 Neighbor	I1 Distance	Average	I3 Neighbor	I3 Distance	I4 Neighbor	I4 Distance	α-equiv.[a] Distance
I2	4.31(1)	4.38(1)	I2	(2)4.21(1)	I5	(2)4.35(5)	(2)4.331(4)
I2	4.45(1)						
I2	4.52(1)	4.60(2)	I5	(2)4.67(1)	I2	(2)4.71(1)	(2)4.641(3)
I2	4.68(2)						
I2	4.78(1)	4.77(4)	I2	(2)5.00(1)	I2	(2)4.87(2)	(2)4.850(5)
I5	4.76(6)						
I1	4.34(2)	4.40(2)	I1	(2)4.44(1)	I1	(2)4.48(1)	(4)4.427(3)
I1	4.34(2)		I4	(2)4.49(1)	I3	(2)4.49(1)	
I3	4.44(1)						
I4	4.48(1)						
I3	5.34(2)	5.38(2)	I1	(2)5.34(2)	I4	(2)5.37(3)	(2)5.391(6)
I1	5.41(2)						

2. Octahedra about Rb^+ ions

Rb1 Neighbors	Rb1 Distance	Average	Rb2 Neighbors	Rb2 Distance	α-equiv.[a] Distance
Rb1-I1	(2)3.67(3)	3.61(2)	Rb2-I1	(6)3.58(1)	(6)3.604(2)
-I3	(2)3.57(1)				
-I4	(2)3.58(3)				
I1-I3	(2)4.44(1)	4.47(1)	I1-I1	(6)4.34(2)	(6)4.427(3)
I1-I4	(2)4.48(1)				
I3-I4	(2)4.49(1)				
I1-I3	(2)5.34(2)	5.35(2)	I1-I1	(3)5.41(2)	(3)5.391(6)
I4-I4	5.37(3)				
I3-I4	(2)5.98(1)	6.00(1)	I1-I1	(3)6.03(2)	(3)6.031(4)
I1-I1	6.03(2)				

4. Nearest-neighbor tetrahedral sites

Neighbors	Distance	Neighbors	Distance
Ag(c2)-Ag(2)	(3)1.76[b]	Ag(3)-Ag(5)	1.74[b]
Ag(c1)-Ag(1)	1.73[b]	-Ag(7)	1.81(4)
-Ag(3)	1.75[b]	Ag(4)-Ag(8)	1.69[b]
-Ag(4)	1.75[b]	-Ag(6)	1.75(5)
Ag(1) -Ag(7)	1.74(4)	Ag(1)-Ag(1)	1.77(4)
-Ag(8)	1.84[b]	Ag(2)-Ag(4)	1.90[b]
Ag(2) -Ag(8)	1.67[b]	Ag(3)-Ag(3)	1.97(7)
-Ag(6)	1.72[b]		

3. Tetrahedra about Ag^+ ions

Ag(c2) Neighbors	Ag(c2) Distance	α-equiv.[a] Distance
Ag(c2)-I5	2.78(8)	2.77(6)
-I1	(3)2.81(2)	(3)2.89(3)
I5-I1	(3)4.76(6)	(3)4.850(5)
I1-I1	(3)4.34(2)	(3)4.476(3)

Ag(1) Neighbors	Ag(1) Distance	Ag(3) Neighbors	Ag(3) Distance	Ag(4) Neighbors	Ag(4) Distance	α-equiv.[a] Distance
Ag(1)-I2	2.93(2)	Ag(3)-I2	2.92(4)	Ag(4)-I2	2.91(2)	2.92(1)
-I4	2.78(3)	-I3	3.15(4)	-I5	2.83(4)	2.79(1)
-I2	2.88(2)	-I2	2.89(4)	-I1	2.88(2)	2.85(1)
-I1	2.87(3)	-I4	2.79(4)	-I3	2.86(2)	2.90(1)
I2-I2	4.32(2)	I2-I2	4.66(2)	I2-I5	4.45(2)	4.476(4)
I1-I4	4.48(1)	I3-I4	4.49(1)	I1-I3	4.44(1)	4.331(4)
I2-I1	4.78(1)	I2-I3	(2)5.00(1)	I2-I1	4.78(1)	4.850(5)
I2-I4	4.87(2)			I2-I3	5.00(1)	
	4.71(1)	I2-I4	4.87(2)	I5-I1	4.76(6)	
I2-I1	4.68(2)	I2-I4	4.71(1)	I5-I3	4.67(1)	4.641(3)

Ag(7) Neighbors	Ag(7) Distance	Ag(6) Neighbors	Ag(6) Distance	α-equiv.[a] Distance
Ag(7)-I4	3.04(3)	Ag(6)-I3	2.81(5)	2.85(2)
-I2	2.89(3)	-I5	2.98(6)	2.90(2)
-I2	2.80(3)	-I2	2.81(5)	2.71(1)
-I1	2.66(3)	-I1	2.51(5)	2.78(1)
I2-I2	4.32(2)	I5-I2	4.45(2)	4.476(4)
I2-I1	4.45(1)	I2-I3	4.21(1)	4.331(4)
I2-I1	4.68(2)	I5-I3	4.67(1)	4.641(3)
I2-I4	4.71(1)	I2-I1	4.52(1)	
I1-I4	4.48(1)	I3-I1	4.44(1)	4.427(3)
I2-I4	4.87(2)	I5-I1	4.76(6)	4.850(5)

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[a] α-equivalent denotes the analogous distance in the α phase multiplied by 11.17/11.24.

[b] These are approximate distances because one of the Ag(n) sites is empty.

possible to determine whether the rhombohedral angle α was greater or less than 90°. However, after the completion of the structure work, it was possible to interpret the powder diffractometer pattern taken at 170 K in a more detailed fashion. For example, the contributions to an $\{hhh\}$ composite peak are from the rhombohedral $\pm(hhh, \bar{h}hh, h\bar{h}h, \bar{h}\bar{h}h)$, the last three of which are equivalent. In the $\{222\}$ case, the combined intensity contribution of the three is greater than that of the one, while the reverse is true of the $\{333\}$. This is clearly seen in the peak profiles in such manner as to imply that $\alpha > 90°$. The other peaks also give agreement with this conclusion and lead to $\alpha = 90.1°$, with probable limits of error of $\pm 0.05°$. This angle does not change much at lower temperatures.

Calculations based on other distributions did not show this agreement with the peak profiles and this gives additional confidence in the results put forward here.

Thus, for types of measurements in which larger crystals can be used and for which only a few directional measurements need to be made, a uniaxial compression along the cubic [111] direction could eliminate the twinning. Such compression would allow measurements, respectively, along and perpendicular to the unique axis, the only ones required to define completely the optical and conductivity properties. (It does not seem to be a simple matter to measure the elastic properties, however.) The crystals will no longer be optically active; the space group has a *pair* of parallel 3_1 and 3_2 axes.

STRUCTURE OF THE γ PHASE

Given in Table VI are the hexagonal indices, the calculated interplanar spacings, the relative intensities (obtained by measuring the peak areas), and the analogous β-phase indices. Those reflections for which $-h+k+l \neq 3n$ and no analogous β-phase indices can be given are the "superstructure" reflections. The observed interplanar spacings are generally in good agreement with the calculated spacings and are omitted to conserve space.

TABLE VI. Powder diffraction data for γ- $RbAg_4I_5$ at 90 K, the range $10° \leq 2\theta \leq 40.4°$, Cu $K\alpha$ radiation.

hkℓ	d(Å)	Rel. I_{obs}	β-phase hkℓ	hkℓ	d(Å)	Rel. I_{obs}	β-phase hkℓ	hkℓ	d(Å)	Rel. I_{obs}	β-phase hkℓ	hkℓ	d(Å)	Rel. I_{obs}	β-phase hkℓ
110	7.888		$10\bar{1}$	115	3.470	1	—	225	2.760	1	—	511	2.434		$4\bar{1}\bar{2}$
102	7.888	53	—	401	3.363		$3\bar{1}\bar{1}$	007	2.760		—	151	2.434		—
012	7.888		110	041	3.363		—	500	2.732		—	333	2.434		$41\bar{2}$
201	6.440		—	223	3.363	100	$31\bar{1}$	216	2.732	3	—	325	2.434	10	—
021	6.440	3	$11\bar{1}$	205	3.363		311	126	2.732		—	235	2.434		$42\bar{1}$
003	6.440		111	025	3.363		—	501	2.706		—	217	2.434		421
112	6.110	2	—	304	3.314	6	—	051	2.706		$22\bar{3}$	127	2.434		—
210	5.164	3	—	034	3.314		—	413	2.706		$40\bar{2}$	423	2.397	1	—
211	4.989		$20\bar{1}$	313	3.266	4	—	143	2.706	4	$32\bar{2}$	243	2.397		—
121	4.989	3	—	133	3.266		—	315	2.705		420	512	2.378		—
113	4.989		210	402	3.220		—	135	2.705		—	152	2.378		$32\bar{3}$
203	4.686	2	—	042	3.220	22	$22\bar{2}$	107	2.705		322	504	2.378	20	—
023	4.686		—	006	3.220		222	017	2.705		—	054	2.378		$33\bar{2}$
300	4.554		$2\bar{1}\bar{1}$	320	3.134		—	330	2.629		$30\bar{3}$	108	2.378		—
212	4.554		—	106	3.134	3	—	502	2.629		$4\bar{1}\bar{1}$	018	2.378		332
122	4.554	1	$21\bar{1}$	016	3.134		—	052	2.629		—	415	2.360		—
104	4.554		211	321	3.094		$30\bar{2}$	324	2.629	27	$41\bar{1}$	145	2.360	3	—
014	4.554		—	231	3.094	10	—	234	2.629		—	307	2.360		—
302	4.119		—	215	3.094		—	306	2.629		411	037	2.360		—
032	4.119	3	—	125	3.094		320	036	2.629		330	406	2.343	1	—
114	4.119		—	410	2.981		$3\bar{1}\bar{2}$	421	2.559		—	046	2.343		—
213	4.029	2	—	322	2.981		—	241	2.559		$31\bar{3}$	600	2.277		$4\bar{2}\bar{2}$
123	4.029		—	232	2.981	7	$31\bar{2}$	405	2.559	3	—	424	2.277		—
220	3.944		$20\bar{2}$	314	2.981		—	045	2.559		$33\bar{1}$	244	2.277	17	$42\bar{2}$
204	3.944	1	—	134	2.981		$32\bar{1}$	207	2.559		—	208	2.277		422
024	3.944		220	116	2.981		321	027	2.559		331	028	2.277		—
311	3.718		—	411	2.947		—	332	2.537		—	601	2.261		—
131	3.718		$21\bar{2}$	141	2.947	3	—	414	2.537	3	—	061	2.261	1	—
303	3.718	50	300	305	2.946		—	144	2.537		—	227	2.261		—
033	3.718		$22\bar{1}$	035	2.946		—	503	2.515	1	—	430	2.246		—
105	3.718		—	206	2.913	9	—	053	2.515		—	326	2.246	6	—
015	3.718		221	026	2.913		—	422	2.494		$40\bar{2}$	236	2.246		—
222	3.651	7	—	412	2.849	5	—	242	2.494	5	—	431	2.231		$40\bar{3}$
312	3.528		$30\bar{1}$	142	2.849		—	226	2.494		420	341	2.231		—
132	3.528	14	—	323	2.818	5	—	510	2.454		—	505	2.231	33	500
214	3.527		310	233	2.818		—	316	2.454	3	—	055	2.231		—
124	3.527		—	404	2.789	3	—	136	2.454		—	317	2.231		—
				044	2.789		—					137	2.231		430

The γ phase has a much larger number of parameters than the β phase and though considerable work has been done on it, a definitive result has not been attained. To fit the present powder data, the only approach is trial and error and this has not proved successful because of the large number of parameters.

On the basis of the work done, only three more or less intuitive conclusions can be drawn: (i) It is quite unlikely that the phase is ordered at 90 K. Numerous calculations appear to lead to this conclusion. Furthermore, the results of the structure determination of the β phase at 130 K indicate the unlikelihood of ordering in the first-order transition at 121.8 K. If it is true that there is still disorder of the Ag^+ ion distribution in the γ phase, it too may be a solid electrolyte as predicted earlier.[5,21] (ii) It is probable that at 90 K, the *main* contributions to the intensities of those reflections with $-h+k+l\neq 3n$, i.e., the superstructure reflections, are from displacements of the iodide ions and, therefore, the equilibrium Ag^+ ion sites, from the triply primitive cell arrangement, rather than *mainly* from the further redistribution of the Ag^+ ions. This conclusion is more tentative than the first. (iii) As indicated earlier, if the Ag^+ ions do finally become ordered in the γ phase, the arrangement will be one of a total of 22 possibilities contained in cases 27–30, inclusive, of Table III. Of these the *most* likely is the one in case 30 with the Ag^+ ions filling sites Ag–II(3), (10), (12), (11), (8), Ag–*C*(4), (5), (6), and Ag–III(7), (8). This is implied by the Ag^+ ion distribution in β-$RbAg_4I_5$.

It was stated earlier that the dimensions of the γ phase are essentially cubic. Still a compressional stress along the threefold axis quite precisely parallel to the cubic [111] axis might eliminate the twinning of this phase. (Of course, any stress will produce some change in structure, but it can be minimized.) Such stress might then allow the complete description of the optical and conductivity properties. The space group *P*321 has no screw axes at all and, of course, the γ phase is not expected to be optically active.

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