absorption of hydrocarbons from a mixture by III, followed by regeneration of the substrate and recovery of the separated organic component. The spirocyclophosphazene is deposited from xylene solution on to ground firebrick or diatomaceous earth, and this substrate is used for the absorption and purging cycles of the separation process. Specifically, processes have been described for the separation of saturated from unsaturated hydrocarbons, monoolefins from diolefins, and hydrocarbons with different chain lengths and different degrees of branching. The xylene isomers, ethylbenzene, styrene, and the C_8 and C_9 alkenyl aromatic hydrocarbons can be separated. The process

is exceedingly efficient. For example, m-xylene of 96% purity can be isolated in one step from a mixture of 25% of p-xylene, 25% ethylbenzene, and 50% m-xylene. It would seem feasible that the clathration phenomenon could also be used in analytical solid–vapor or solid–liquid chromatography separations.

The subject of cyclophosphazene inclusion adducts has grown from a chance observation to an intriguing new field with ramifications in synthesis, x-ray crystallography, solid-state phenomena, and analytical or commercial organic separation processes. We are currently working to further broaden the scope of this field and to delve deeper into the mechanism and uses of the phenomenon.

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Silver Iodide Based Solid Electrolytes

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In many papers in the literature, the term "solid electrolyte" has been used to describe the nature of a salt such as AgBr which has electrolytic conductivity because of its equilibrium concentration of point defects. That is, the conductivity results from annihilation and creation of defects that would not be present if the crystal were ideally perfect. One may say that, in a sense, such crystals have electrolytic conductivity "by accident", because, if they were ideally perfect and no defects were induced in them by an applied electric field, they would have no electrolytic conductivity. At room temperature such salts have specific conductivities in the range $\sim 10^{-6}$–10^{-12} $(\Omega \text{ cm})^{-1}$.

Electrolytic conductivity in a *true* solid electrolyte is an inherent property of the crystal and is directly associated with the crystal structure. The main structural characteristics of a true solid electrolyte are: (1) a large ratio (in the case of the AgI-based solid electrolytes, between 3 and 6) of sites available to the mobile cations (in some cases, such as the fluorites, the anions are the charge carriers) to the available number of mobile cations; (2) networks of passageways resulting from the face-sharing of anion polyhedra (in some cases, such as the fluorites, both anion and cation polyhedra are involved). These are the most important re-

quirements, but there are others that will emerge in subsequent parts of this Account.

The specific conductivities of these (true) solid electrolytes are several orders of magnitude higher than those that have their origin in point defects. The solid electrolyte with the highest room temperature conductivity is $RbAg_4I_5$, with $\sigma = 0.27$ $(\Omega \text{ cm})^{-1}$. This may be compared with the conductivity, 0.8 $(\Omega \text{ cm})^{-1}$, of 35% aqueous H_2SO_4.

This Account will deal mainly with the research carried out by the author and co-workers in the solid electrolyte field. Until very recently all this work has involved the structure and conductivity determination of AgI-based solid electrolytes and the relation between the two. A structure determination of the Cu^+ ion conductor, $(C_5H_5NH)_2Cu_5Br_7$, first reported by Sammells et al.[1] has recently been completed; the structure is related to those of the AgI-based solid electrolytes.

It will be noticed that the term "solid electrolyte" is used to describe the materials discussed in this paper. The use of the terms "super ionic conductor" or "superionic conductor" has become rather widespread. To say the least, such terms are unnecessary. The first is not even *structurally* correct from a linguistic point of view. Neither conveys a correct meaning to the uninitiated and perhaps even to those who are—as some of the literature attests. In fact, there are at least two cases in the literature[2,3] in which the term is reversed;

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that is, "ionic superconductor" is used. It need hardly be said that the phenomenon of electrolytic conductivity in solids has not the *remotest* connection with superconductivity. It is also fair to say that no "superion entity exists. Other terms which have invaded the field are "liquid sublattice" and "molten sublattice". Again these are misleading and unnecessary. As will be shown, the disorder of the cations in the solid electrolytes is *not* "liquid-like".

The Crystal Structure Problem

There are two special aspects of the solid electrolyte structure problem. One is the determination of the distribution of the current carriers over crystallographically nonequivalent sets of sites, and the other, the anharmonic motions of the current carriers.

In the case of anharmonic motion not much has been done, because it is a particularly difficult problem. The current carriers undoubtedly jump from site to site even when there is no electric field applied to the material. Although this is recognized, it has been customary to use the ordinary description of harmonic motion in the fitting of the calculated to the observed data. To some extent, the agreement factors $\sum ||F_o| - |F_c||/\sum |F_o|$, where F_o and F_c are the observed and calculated structure amplitudes, respectively, are, for this reason, somewhat larger than for the best crystal structure determinations.

As to the distributions of the current carriers, these are usually obtained by allowing the site occupancies to vary in the least-squares calculations. Usually the positional and thermal parameters of the ions that comprise the "rigid" framework tend to converge well, while the occupancy, thermal, and positional parameters of the mobile ions converge more slowly. Subjective decisions are required to obtain final convergence. Partly, the difficulties involve high correlations among occupancy parameters themselves and between occupancy and thermal parameters, and sometimes complete convergence is unattainable.

There are some other interesting features of the structure problem. In the cases of the AgI-based solid electrolytes, the linear absorption coefficients even for short wavelength radiation are rather large. Therefore, even for very small crystals, a large percentage of the radiation is absorbed. Usually the intensities drop off rather rapidly with increasing Bragg angle, so that even when short wavelengths are used, the data obtainable are usually confined to those contained in the Cu Kα Ewald sphere. Nevertheless, the results are sufficient for an understanding of the nature of the phenomenon of electrolytic conductivity in the solid electrolyte.

There are various aids upon which one may draw in attempting to solve crystal structures. In the case of the AgI-based solid electrolytes, an important key was obtained from the solution of the structure of RbAg$_4$I$_5$.[4] In every subsequent structure determination, similar connexity was sought. That is, the "rigid" framework of iodides must be composed of polyhedra that share faces, thus forming a network of pathways[5] through which the current carriers can move. This is a salient feature which therefore aids substantially in the solution of the structures, even though the actual networks

might be surprisingly different.

Conductivity

Investigations of transport properties of solid electrolytes are more widespread than structure determination, and there are many descriptions of techniques in the literature. The technique that we use for measurements on polycrystalline materials has been described in a previous paper;[6] it is essentially a small modification of the technique described earlier by Raleigh.[7]

Single-crystal conductivities have been measured on only two noncubic AgI-based solid electrolytes[8] and (as far as this writer knows) on only one other, namely Na-β-alumina.[9,10]

The conductivity of a solid electrolyte has two components: electronic and electrolytic (or ionic), i.e., $\sigma = \sigma_e + \sigma_i$. (In general, σ is a second-rank tensor, and therefore σ_e and σ_i are also second-rank tensors. Further, for crystal symmetries lower than cubic, it does not seem that these need be simply related.) However, in the AgI-based solid electrolytes, the electronic component is expected to be negligibly small. Simply stated, the ions involved are all in their most stable states, and significant nonstoichiometry is highly improbable. In the case of RbAg$_4$I$_5$, the electronic conductivity at room temperature is[11] less than 10^{-11} (Ω cm)$^{-1}$. In our work thus far on the AgI-based solid electrolytes, we have measured only the total conductivity of polycrystalline specimens. As indicated, the results are expected to be not significantly different from those for electrolytic conductivity. In fact, measurement error is apt to be several orders of magnitude higher than the electronic conductivity of this type of solid electrolyte.

Structures of AgI-Based Solid Electrolytes

Perhaps the most well-known of the AgI-based solid electrolytes is α-AgI itself. The transition of AgI to the solid electrolyte state occurs at 146 °C, as first reported by Tubandt and Lorenz[12] in 1914. About 20 years later, Strock[13] reported that the Ag$^+$ ions were distributed uniformly over 42 sites in the crystals of α-AgI. These results were based on an x-ray investigation of polycrystalline material.

The α-AgI phase is cubic (space group *Im3m*); the unit cell contains two AgI, with the I$^-$ ions at the corners and body-center. There are 12 sites surrounded by tetrahedra of I$^-$ ions which share faces. In view of the structural results subsequently obtained on other AgI-based solid electrolytes, we predicted[5] that the equilibrium distribution of the Ag$^+$ ions in α-AgI would confine them to these tetrahedral sites, contrary to the earlier conclusions. This prediction has now been affirmed.[14,15]

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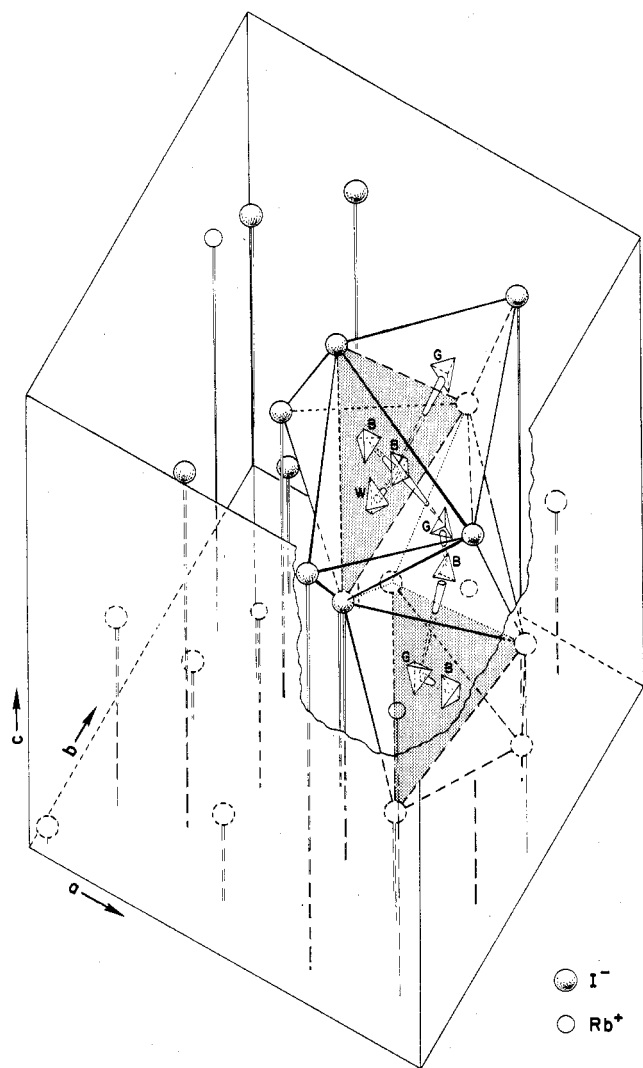
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AgI-Based Solid Electrolytes

Figure 1. Perspective drawing of I^- and Rb^+ ion arrangement in the unit cell of $RbAg_4I_5$. Some of the shared tetrahedron faces and diffusion steps are shown. The small tetrahedra designate the Ag^+ ion sites associated with the larger tetrahedra. Those labeled B and G are two types of 24-fold sites; W refers to the 8-fold sites. (Reprinted with permission from ref 4. Copyright 1967 American Association for the Advancement of Science.)

At least from a scientific point of view, one of the most interesting solid electrolytes is $RbAg_4I_5$. There are several compounds isostructural with it, namely KAg_4I_5, $NH_4Ag_4I_5$, and $(K_{0.5}Cs_{0.5})Ag_4I_5$.[16] Most attention has been given to $RbAg_4I_5$, because it is least affected by the presence of moisture which causes decomposition to AgI and M_2AgI_3. $RbAg_4I_5$ is thermodynamically unstable below 27 °C,[17] but may be easily retained in the metastable state, down to low temperatures, provided that water is absent.[18]

The solid electrolyte $RbAg_4I_5$ has the highest temperature specific electrolytic conductivity, 0.27 $(\Omega\ cm)^{-1}$, of any ionic solid measured to date.[7,19,20] Because it is cubic, the conductivity is isotropic.

What is the origin of this high conductivity? This, like other questions, must have answers on more than

Table I
Space Groups and Equipoint Transformations
of $RbAg_4I_5$ Phases[a]

$T > 209$ K $P4_132$	209 K $> T > 122$ K $R32$	$T < 122$ K $P321$
Rb in 4a (32)	$\begin{cases}$ 1a(32)	$\begin{cases}$ 1a(32) 2d(3)
	3e(2)	3f(2) 6g(1)
I, Agc in 8c (3)	2c(3)	2c(3) 2 sets 2d(3)
	6f(1)	3 sets 6g (1)
I in 12d (2)	3d(2)	3e(2) 6g(1)
	3e(2)	3f(2) 6g(1)
	6f(1)	3 sets 6g(1)
AgII, AgIII in 24e	4 sets of 6f each; 8 sets of 6f, total	3 sets 6g each. 24 sets of 6g, total

[a] Numbers in parentheses designate point symmetries.

one level. As already indicated, electrolytic conductivity in solids is a strongly structure-related property and at least at room temperature, the most effective structure is that of $RbAg_4I_5$.

At temperatures above 209 K, $RbAg_4I_5$ belongs to space group $P4_132(O^7)$ or $P4_332(O^6)$, with lattice constant $a = 11.24$ Å and four $RbAg_4I_5$ in the unit cell. The 20 iodide ions form 56 tetrahedra which share faces, thereby forming a network of pathways for the Ag^+ ion diffusion. There are two zigzag channels perpendicular to each face of the unit cell that would extend between opposite faces of a perfect crystal. These channels are also cross-linked, so that diffusion takes place in three dimensions. The arrangement is partially depicted in Figure 1 (see also Figure 1 of ref 4).

The 16 Ag^+ ions are distributed over the 56 sites in a *markedly* nonuniform manner. The 56 sites comprise three crystallographically nonequivalent sets: two 24-fold and one 8-fold. (*Within* each of these sets, the distribution must be uniform because the sites *are* crystallographically equivalent.) The nonuniform distribution is to be expected, of course, because it follows that crystallographically nonequivalent sites are usually energetically nonequivalent. Further, such nonuniformity of distribution should persist right to the melting point. This hardly requires proof; however this has been shown[21] experimentally for the solid electrolyte $PyAg_5I_6$ (see below).

There are two low-temperature phase transformations in $RbAg_4I_5$: second order at 209 K[4,22,23] and first order at 122 K.[16,22] The transition at 209 K is to the subgroup $R32(D_3^7)$.[18] At 130 K the lattice constants of the rhombohedral cell are $a = 11.17 \pm 0.01$ Å, $\alpha = 90.1 \pm 0.05°$. The unit cell content is the same as that of the cubic cell. Displacements of I^-, Rb^+ ions, and Ag^+ ion sites relative to their positions in the cubic space group are small. The *main* difference is a redistribution of the Ag^+ ions.

The space groups and equipoint transformations of the $RbAg_4I_5$ phases are shown in Table I. The three

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Table II
Predicted[24] Contrasted with Actual[18] Occupancies of Sites
Available to Ag^+ Ions in β-RbAg$_4$I$_5$

Site designation	Occupancies, number of Ag⁺ ions	
	Actual	Predicted
Ag(1)	3.0	....
Ag(2)	0	6 or 0
Ag(3)	2.7	....
Ag(4)	4.8	0 or 6
Ag(5)	0	
Ag(6)	1.2	
Ag(7)	3.0	
Ag(8)	0	
Ag(c1)	0	
Ag(c2)	1.3	

crystallographically nonequivalent sets of sites in space group $P4_132$ go into 10 sets in space group $R32$. The structure analysis[18] shows that four of these sets are empty (Table II). The sites that are occupied *tend* to be as far from each other as possible.

A recent paper[24] claims to predict theoretically the Ag^+ ion occupancies of the available sites in the rhombohedral phase of RbAg$_4$I$_5$. The predicted site occupancies and those found from the structure determination are shown in Table II.

It should be emphasized that it is *impossible* for the Ag^+ ions to be ordered in either the cubic or the rhombohedral structures. Thus the transformation is a disorder–disorder transformation.[18] Such transformations are unusual; nevertheless to refer to them as order–disorder transformations[25] is incorrect. Regardless of the results of any other measurements, the structures ultimately settle the question.

The transition at 121 K is to the space group $P321$.[18] At 90 K the trigonal cell has lattice constants $a = 15.776 \pm 0.005$ Å, $c = 19.320 \pm 0.005$ Å and contains 12 RbAg$_4$I$_5$. Table I shows that the 10 crystallographically nonequivalent sets of sites for the Ag^+ ions in $R32$ transform into 30 sets in $P321$. While the latter space group is not a subgroup of $R32$, it is closely related to it. Because of the very large number of parameters and the sparsity of diffraction data for this phase, it was not possible to determine the structure accurately. In this structure it *is* possible for the Ag^+ ions to be ordered. Calculations indicate that it is unlikely that ordering does take place near the transition. However, the most likely ordering scheme has been deduced.[18] The conductivity data, the results of specific heat measurements, and the structure analyses all indicate that even the phase that exists below 122 K may still be a solid electrolyte.[5,18,22]

Another very interesting solid electrolyte is (C$_5$H$_5$-NH)Ag$_5$I$_6$ ((C$_5$H$_5$NH)$^+$ is the pyridinium ion, written hereafter as Py). A plan review of the structure at –30 °C[26] is shown in Figure 2. At this temperature, the structure is ordered. The structure belongs to space group $P6/mcc$ (D_{6h}^2). At –30 °C, the lattice constants of the hexagonal cell are $a = 11.97 \pm 0.02$ Å, $c = 7.41 \pm 0.01$ Å, and there are two PyAg$_5$I$_6$ in the unit cell. The ten Ag^+ ions are in two sets of crystallographically nonequivalent sites; the space group designations are 4c and 6f. The former are octahedrally coordinated, the
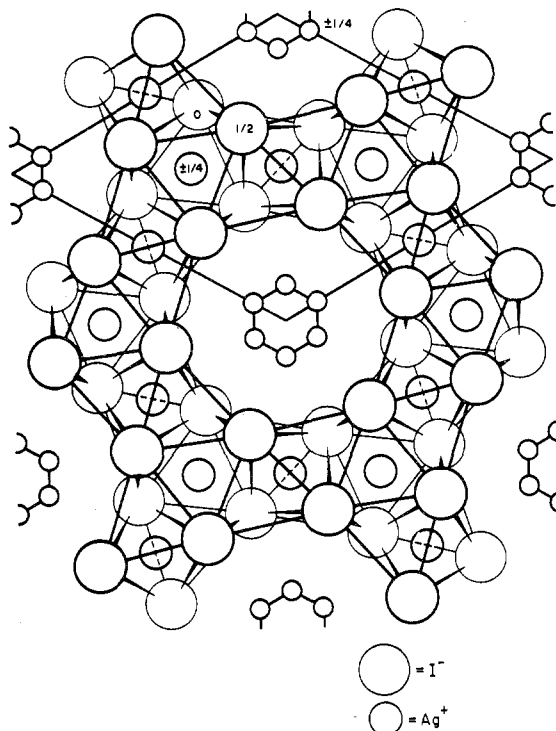
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Figure 2. Plan view of the structure of the crystal structure of (C$_5$H$_5$NH)Ag$_5$I$_6$ at –30 °C. The m sites are in the empty tetrahedra. (Reprinted with permission from ref 26. Copyright 1972 American Association for the Advancement of Science).

latter tetrahedrally coordinated. There are 24 tetrahedral sites (space group designation m) that are empty. Every iodide ion is at the corner of one of these "m-type" tetrahedra.

The octahedra share faces that are parallel to the hexagonal (001) plane, thus making straight channels along the c axis. The remaining six faces of each octahedron are shared with the m-tetrahedra. An m-type tetrahedron shares one face with an octahedron, one face with an f-type tetrahedron, and one face (parallel to (001)) with another m-type tetrahedron; the fourth face opens to the Py$^+$ ion and therefore is not involved in the diffusion of Ag^+ ions in the crystal. The f-type tetrahedra share only two edges with other f-type tetrahedra and four faces with m-type tetrahedra.

Short intersite distances prevent the occupancy of an f site and an immediately neighboring m site, or two immediately neighboring m sites, but both m and c sites may be occupied simultaneously. As the temperature is increased from –30 °C, Ag^+ ions in the c and f sites are excited into m sites.[21] However, the process cannot begin with Ag^+ ions moving from c to m sites; it must begin with Ag^+ ions moving from f to m sites. When an Ag^+ ion moves from an f site to an m site, one other m-type tetrahedron is freed for occupancy by Ag^+ ions from the octahedra.

The plot of log (σT) vs. $1/T$ for polycrystalline PyAg$_5$I$_6$ (see Figure 2 of ref 21) shows a transition at ~325 K. The transition has been confirmed by Hibma.[8] The interpretation suggested by Geller and Owens[21] is that the transition is of the disorder–disorder type. In the lower temperature phase not all the Ag^+ ions are mobile, while in the higher temperature phase all are mobile. The distribution of the Ag^+ ions over the c, f, and m sites is, however, nonuniform, although the occupancies of the c and f sites do tend to remain

nearly equal. Hibma[8] has recently indicated that this transition is neither first nor second order because of the broadness of the peak in the specific heat vs. temperature plot. Another view is presented by Pardee and Mahan,[25] namely that the transition is of the order–disorder type.

Based on the criterion[27] that in a second-order phase change one space group must be a subgroup of the other, this transition cannot be called second order because the space group is the same in both temperature regions. In fact, from an atomistic point of view, there seem to be three phases belonging to the same space group. One phase is that in which the Ag^+ ions are ordered. When the Ag^+ ions move into the m sites, there is really a new crystal structure because sites which were originally empty are now partially occupied, and sites that were originally filled are no longer so. The physical properties in the two temperature regions in which there is disorder of the Ag^+ ions are different because of structural constraints as indicated earlier. Therefore, one may say that there is an ordered (except for the Py^+ ion) phase between 220 and 240 K (see below), a phase of "low" disorder between 240 and 325 K, and one of "high" disorder above 325 K. Tentatively, I have referred to these phases as β', β, and α, respectively.[28]

In the hexagonal phases, the centers of the Py^+ ions lie on sixfold symmetry axes, but it is clear that the Py^+ ion cannot have sixfold symmetry. The Py^+ ions are therefore disordered in these phases. They do have, however, an "average" sixfold symmetry as opposed to cylindrical symmetry. (It is noteworthy that in a recent structure determination of PyI itself[29] similar disorder of the Py^+ ions was found; however, in that case threefold axes are perpendicular to the planes of the ions at their centers.) Hibma[8] first reported another transition at about 230 K in $PyAg_5I_6$. Subsequently Hibma and I investigated[30] the crystallographic behavior below 240 K and found this transition to occur more nearly at 220 K and yet another transition at approximately 180 K. These transitions must involve ordering of the Py^+ ions. (Again a similar transition appears to occur in PyI itself.[8])

These low-temperature transitions in $PyAg_5I_6$ are quite interesting for several reasons. The β–γ transition was shown to be second order by the specific heat results,[8] but the specific heat measurements did not show the γ–δ transition which *must* be first order. The behavior of the lattice constants (Figure 3) of the γ phase corroborates the second-order nature of the transition, while that of the δ phase indicates a strange first-order transition.

Both low-temperature phases are monoclinic, and both have structures closely related to that of the ordered hexagonal one. In both cases, the monoclinic c axis corresponds to the hexagonal c axis. In the γ phase, the monoclinic a and b axes correspond to the orthohexagonal B and A axes, respectively; in the δ phase the correspondence is reversed. The cell content in both cases is 4 $PyAg_5I_6$, but in both cases the unit
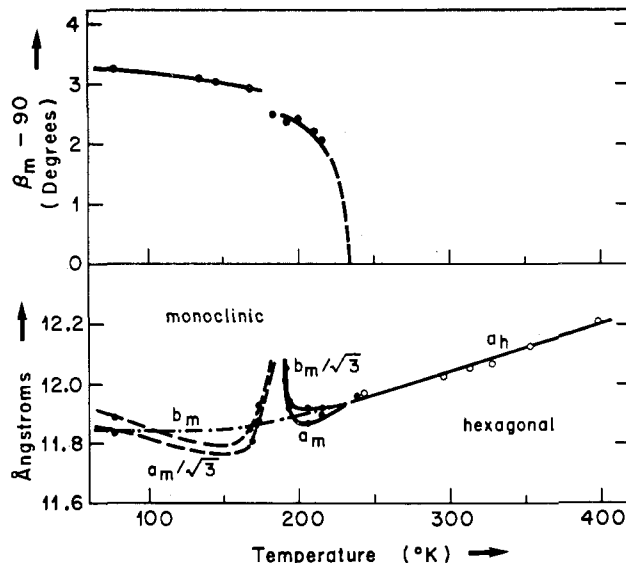

Figure 3. The lattice parameters of $PyAg_5I_6$ as a function of temperature. The data for the hexagonal phases are taken from ref 21. The long monoclinic axes were divided by $3^{1/2}$ to compare them with the hexagonal a axis. The c_m parameters are constant and equal to 7.38 ± 0.02 Å. The figure demonstrates that the phase transition at about 230 K is second order and the transition at about 180 K is first order. (Reprinted with permission from ref 30. Copyright 1977 Academic Press.)

cell is C-face-centered. The most probable space group for the γ phase is $Cc(C_s^4)$ *if* the Py^+ ions order. (This space group is, of course, a subgroup of $P6/mcc$.) If the Py^+ ions are ordered in the δ phase, the N atoms must lie on twofold axes in $C2/c$ (C_{2h}^6); however, the space group Cc is also possible for this phase. The bases for these conclusions are given in detail elsewhere.[30]

Another solid electrolyte in the PyI–AgI system has the formula $Py_5Ag_{18}I_{22}$,[6,31] belongs to space group $P\bar{6}2m$ (D_{3h}^3) with lattice constants $a = 13.62 \pm 0.02$ Å, $c = 12.58 \pm 0.02$ Å, and the trigonal cell contains one formula unit. Twenty-two of the 23 I^- ions form 55 tetrahedra which share faces in such manner as to provide pathways for the diffusion of the Ag^+ ions (Figure 4). These pathways are confined to slabs separated by three Py^+ and one I^- ions per unit cell (Figure 4); that is, there are no pathways for the Ag^+ ion diffusion through these layers that are perpendicular to the c axis, implying that the electrolytic conductivity in the c-axis direction should be zero. Our conductivity measurements were made on polycrystalline material;[6] from these results we deduced the value of σ_1, 0.012 $(\Omega\ cm)^{-1}$, the conductivity in the basal plane (equal to $^3/_2$ the average conductivity). Measurements on single crystals have confirmed our conclusions; that is, Hibma[8] reports $\sigma_1 = 0.017$ $(\Omega\ cm)^{-1}$, $\sigma_3 = 10^{-5}$–10^{-6} $(\Omega\ cm)^{-1}$.

A substantial number of tetraalkylammonium iodide solid electrolytes have been reported by Owens.[20,32] We have determined[33] the structure of the compound $[(CH_3)_4N]_2Ag_{13}I_{15}$, which has one of the higher room-temperature conductivities in this group. The structure belongs to space group $R32$ (D_3^7), contains one $[(CH_3)_4N]_2Ag_{13}I_{15}$ per unit cell, and has $a = 11.52 \pm 0.02$ Å, $\alpha = 67.35 \pm 0.15°$.

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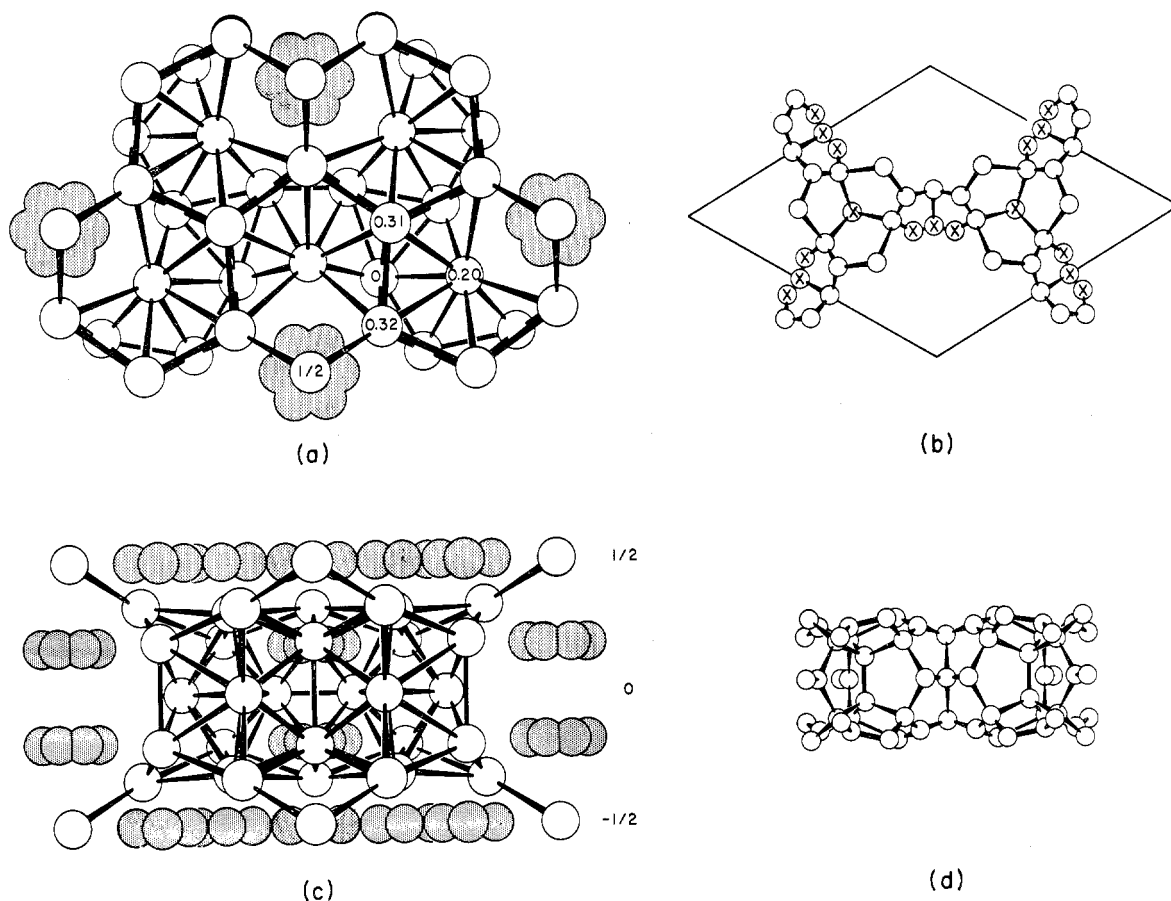(33) S. Geller and M. D. Lind, *J. Chem. Phys.*, **52**, 5854 (1970).

(a)

(b)

(c)

(d)

Figure 4. $Py_5Ag_{18}I_{23}$. (a) Top view of iodide arrangement; the pyridinium ions (stippled) on the hexagonal axes are shown, but those in the planes $z = {}^1/_2$ are omitted. (b) Top view of Ag^+ ion paths; the equilibrium Ag^+ ion sites are shown; X indicates connection between upper and lower halves of the Ag^+ path network within the conducting layer; see also (d). (c) Side view of the iodide arrangement; the pyridinium ions in the $\pm^1/_2c$ levels of the unit cell are now included; these together with the I^- ions at $\pm(0,0,^1/_2)$ block movement of Ag^+ ions in the c-axis direction. (d) Side view of the Ag^+ ion paths. (Reprinted with permission from ref 6. Copyright 1975 The Electrochemical Society Inc.)

All the iodide ions in the structure are at the corners of tetrahedra which share faces forming two kinds of channels (see Figure 2 of ref 33). One type ends at opposite surfaces of the crystal; the other consisting of ten tetrahedra each begins and ends at a tetramethylammonium ion. The channels are interconnected, and the material is a three-dimensional solid electrolyte. There are eight crystallographically nonequivalent sets of sites for Ag^+ ions; the sites in one of these sets are not directly in channels but do link channels. Again the 13 Ag^+ ions are distributed in a markedly nonuniform manner over the total of 41 tetrahedral sites in the unit cell. Further, there is no way in which the Ag^+ ions can be ordered in this crystal. No transition has been observed in conductivity measurements made above 220 K,[20,32] but, of course, there may be one (or more) below this temperature. Strictly from a numbers point of view, the Ag^+ ions could order in any of the subgroups of $R32$, but there is really no *requirement* that such a transition occur.

All the solid electrolytes discussed above are "double salts" in which the anion is common. Takahashi and co-workers[34,35] have reported some in which the cation is common. The compound reported[34] to be $Ag_6I_4WO_4$

appeared to be a likely candidate for structure determination, because small single crystals were rather readily obtainable. Early x-ray diffraction photography and density measurements indicated that the reported formula could not be correct; these led to the formula $Ag_{13}I_9W_2O_8$. Because the x-ray diffraction data indicated that the structure of this solid electrolyte was complex, it appeared worthwhile to investigate the crystal structure of silver tungstate itself.

Considerable structural work has been done on various tungstate crystals. (For a brief review, see ref 36.) Most often these involve continuous structures, that is, in which there is no real tungstate entity. Crystals of "$7Li_2WO_4\cdot4H_2O$" have been shown[37] to contain $(LiW_4O_{16})^{7-}$ entities. In this ion, four tungstate octahedra are arranged tetrahedrally, the Li^+ ion occupying the tetrahedral site at the center of the tetratungstate structure.

There are at least two modifications of silver tungstate. We were able to obtain crystals of the high-temperature modification. The structure determination was quite challenging, at least partially because, relative to the Ag^+ ions and W atoms, the oxygens contribute so little to the structure amplitudes. The solution[36] showed that this modification contains $(W_4O_{16})^{8-}$ entities as shown in Figure 5. The space

(34) T. Takahashi, S. Ikeda, and O. Yamamoto, *J. Electrochem. Soc.*, **120**, 647 (1973).
(35) T. Takahashi, S. Ikeda, and O. Yamamoto, *J. Electrochem. Soc.*, **119**, 477 (1972).

(36) P. M. Skarstad and S. Geller, *Mater. Res. Bull.*, **10**, 791 (1975).
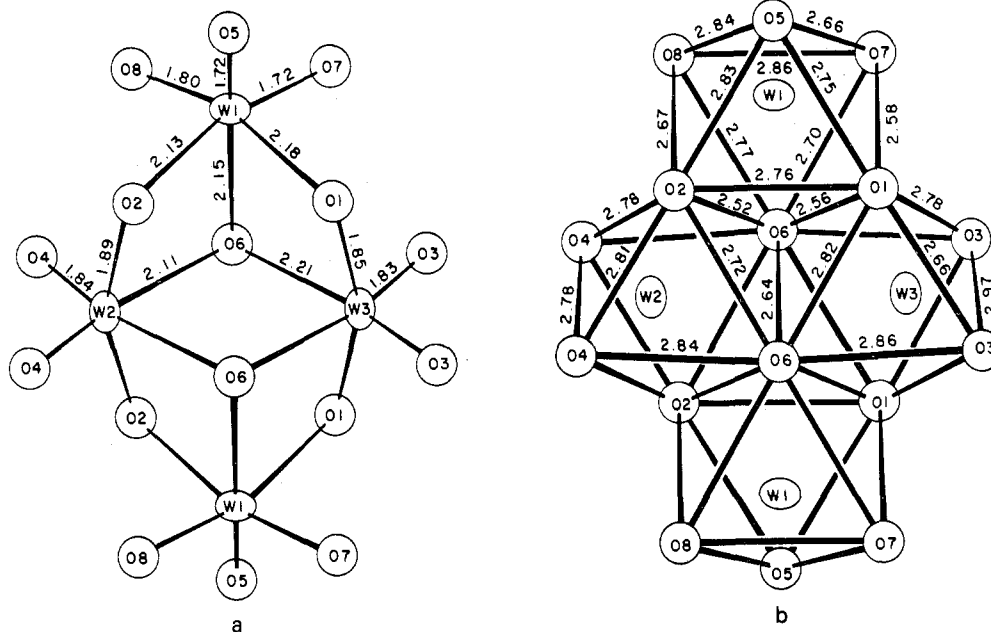(37) A. Hüllen, *Ber. Bunsenges.*, **70**, 598 (1966).

Figure 5. $(W_4O_{16})^{8-}$ ion in $Ag_{26}I_{28}W_4O_{16}$. (a) W–O distances. (b) O–O distances. The $(W_4O_{16})^{8-}$ ion in $Ag_{26}I_{18}W_4O_{16}$ ion is enantiomorphous to that in $Ag_8W_4O_{16}$. (Reprinted with permission from ref 39. Copyright 1977 Academic Press.)

group to which $Ag_8W_4O_{16}$ (the appropriate structural formula) belongs is $Pn2n$ (C_{2v}^{10}), which because of the location of the $(W_4O_{16})^{8-}$ ion in the unit cell requires it to have twofold symmetry. Examination of Figure 5 should show the reader that the ion *might*, under some circumstance, be able to have a mirror plane perpendicular to the twofold axis and, therefore, have a center of symmetry. However, this does not occur in the crystal up to the melting point, and it is probable that this large ion is not centrosymmetric even in the melt.[38]

The $(W_4O_{16})^{8-}$ entities that occur in the high-temperature modification of $Ag_8W_4O_{16}$ occur also in crystals of $Ag_{26}I_{18}W_4O_{16}$ (the appropriate structural formula). These crystals belong to space group $C2$ (C_2^3), with $a = 16.76 \pm 0.03$ Å, $b = 15.52 \pm 0.03$ Å, $c = 11.81 \pm 0.02$ Å, $\beta = 103.9 \pm 0.3°$, and two $Ag_{26}I_{18}W_4O_{16}$ per unit cell. At 25 °C, the average conductivity is 0.059 $(\Omega\ cm)^{-1}$. The symmetry of the crystals is that of the $(W_4O_{16})^{8-}$ ions, the twofold axes of which are coincident with the twofold axes of the unit cell.

A complete description of the structure has been given elsewhere.[39] The conduction passageways in crystals of $Ag_{26}I_{18}W_4O_{16}$ involve 90 iodide polyhedra, two of which are octahedra, and 56 mixed oxygen–iodide polyhedra per unit cell. Again, the passageways are formed by the face-sharing of the polyhedra.

In α-RbAg$_4$I$_5$ (and probably also β-RbAg$_4$I$_5$), α-PyAg$_5$I$_6$, Py$_5$Ag$_{18}$I$_{23}$, and $[(CH_3)_4N]_2Ag_{13}I_{15}$, the Ag$^+$ ions are very likely all mobile. In $Ag_{26}I_{18}W_4O_{16}$, the Ag$^+$ ions are not all mobile. There is a total of 52 Ag$^+$ ions in the unit cell. Of these, 23.2 or 44.5% are in the 146 iodide and mixed oxygen–iodide polyhedra. The occupancies of the latter tend to be higher than those of the former, implying that the mobilities through the latter are lower than those through the former. Ag$^+$ ions fill 12 mixed I–O polyhedral sites (not in the conduction passageways, of course), and 16.8 Ag$^+$ ions per unit cell are in 24 other mixed I–O bypass sites; these 28.8 Ag$^+$

(38) A. Turković, D. L. Fox, J. F. Scott, S. Geller, and G. F. Ruse, *Mater. Res. Bull.*, **12**, 189 (1977).
(39) L. Y. Y. Chan and S. Geller, *J. Solid State Chem.*, **21**, 331 (1977).

ions are probably not mobile.

Relation of Conductivity to Structure

Several points showing how the electrolytic conductivity in solid electrolytes is associated with their structures have already been made. Probably the most important is that they all have networks of passageways formed from the face-sharing of anion polyhedra. (In $Ag_{26}I_{18}W_4O_{16}$, some of the polyhedra are formed from iodides and oxygens bonded to the W atoms of the $(W_4O_{16})^{8-}$ ions.) This feature occurs in almost all solid electrolytes of any kind, as do others to be listed subsequently.

In structures in which the sites available to the current carriers are not crystallographically equivalent, the distribution of carriers over the different sites is markedly nonuniform. This is equivalent to the statement that crystallographically nonequivalent sites have different site energies. Of course, it can happen that two or more different sets of sites have very nearly the same site energy (as indicated by their occupancies), but this does not contradict the general statement of the generally observed nonuniform distribution over all sets of sites. Further, as long as the crystal structure does not change, the distribution, which may change with temperature, will still remain nonuniform.

The conductivity is associated with the nature of the passageways; the simpler they are, the higher will be the conductivity. Three-dimensional networks give higher average conductivities than two-dimensional networks, as particularly illustrated by a comparison of Py$_5$Ag$_{18}$I$_{23}$ with PyAg$_5$I$_6$ and other three-dimensional cases. A larger number of available sites and/or a larger volume of crystal space occupied by the conduction passageways tend to give higher conductivities.

It should be mentioned that there is no simple formula as yet available to fit the parameters to the conductivity. All we can give is tendencies. Bottlenecks could be more serious in some structures than in others; for example, see ref 6. The ratio of available sites to carriers is an important parameter. There is no direct

dependence on this ratio, but it is probable that, if it falls much below three, the conductivity will be low. In fact, if it is two, it is very unlikely that the material will be a solid electrolyte.

Interactions between cations on nearest-neighbor tetrahedral sites must be strong and repulsive because the intersite distances are too short to allow such sites to be simultaneously occupied. The "squeezing" of the Ag^+ ions on passing through a shared triangular face from one polyhedron to another probably determines the activation enthalpy of motion.[5] This is also a very complicated matter for a crystal with crystallographically nonequivalent saddle points, because the activation enthalpies of motion through the different "windows" must also be different. Therefore, even when directional σ vs. T measurements are made, the activation enthalpies derived therefrom are directional averages.

According to Armstrong et al.[40] the stability of the Ag^+ and Cu^+ ions in both four- and three-coordination and their monovalency are responsible for their being the mobile ion in most good solid electrolytes.

Additional discussion of these points will be found in papers already referenced and also in ref 41 and 42.

(40) R. D. Armstrong, R. S. Bulmer, and T. Dickinson, *J. Solid State Chem.*, 8, 219 (1973).
(41) S. Geller in "Fast Ion Transport in Solids", W. Van Gool, Ed., North-Holland, Amsterdam, 1973, pp 607–616.
(42) S. Geller in "Superionic Conductors", G. D. Mahan and W. L. Roth, Ed., Plenum Press, New York, N.Y., 1976, pp 171–181.

Optical and Thermal Electron Transfer in Metal Complexes
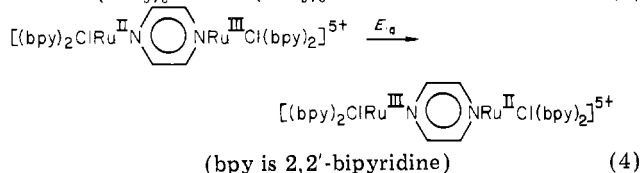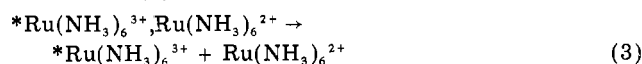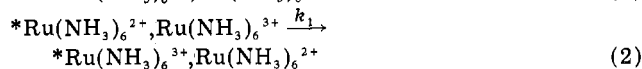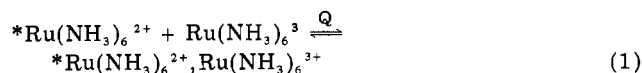
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Received March 9, 1977

There are many cases of transition-metal complexes which retain the same basic structure in different oxidation states. In ions like $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ the gross structures are the same, but the detailed structures are different. Metal–ligand bond strengths and distances usually vary somewhat with oxidation state, and outer-sphere solvation energies and solvent structure vary with ion charge. Simple electron-transfer processes are often facile for such ions because no bonds need be broken, but a sizeable activation barrier to electron transfer can still exist. The barrier arises from the influence of oxidation-state changes on the coordination spheres around the ions.

A reaction coordinate diagram for electron transfer is shown in Figure 1A. The diagram describes the activation barrier for electron transfer within an ion pair of the reactants (eq 2) for an outer-sphere self-exchange reaction (e.g., eq 1–3).[2] It applies equally well to inner-sphere electron transfer in a symmetrical mixed-valence ion like that shown in eq 4, where delocalization is slight.[3] For both reactions, the overall free energy change is 0.

In Figure 1A the curve (2,3) refers to the case where the exchanging electron is localized on one side. It represents a plane drawn through a multidimensional, energy-coordinate surface along a coordinate which is sensitive to changes in oxidation state at both Ru(II) and Ru(III), perhaps the two Ru–Cl distances in re-

$$*Ru(NH_3)_6{}^{2+} + Ru(NH_3)_6{}^{3} \xrightleftharpoons{Q}$$
$$*Ru(NH_3)_6{}^{2+},Ru(NH_3)_6{}^{3+} \qquad (1)$$

$$*Ru(NH_3)_6{}^{2+},Ru(NH_3)_6{}^{3+} \xrightarrow{k_1}$$
$$*Ru(NH_3)_6{}^{3+},Ru(NH_3)_6{}^{2+} \qquad (2)$$

$$*Ru(NH_3)_6{}^{3+},Ru(NH_3)_6{}^{2+} \rightarrow$$
$$*Ru(NH_3)_6{}^{3+} + Ru(NH_3)_6{}^{2+} \qquad (3)$$

$$[(bpy)_2ClRu^{II}N\bigcirc NRu^{III}Cl(bpy)_2]^{5+} \xrightarrow{E_a}$$
$$[(bpy)_2ClRu^{III}N\bigcirc NRu^{II}Cl(bpy)_2]^{5+}$$

(bpy is 2,2'-bipyridine)   (4)

action 4. With regard to the center of the molecule, there are two possible ways of finding the dimer, with Ru(II) on one side or on the other. Curves (2,3) and (3,2) are then identical but displaced along P because the spatial coordinates of the vibrational modes that we are following are different for the two possibilities. Orbital overlap between the electron donor and acceptor sites leads to the splitting in the surface crossing region in Figure 1A and to ground-state electron delocalization from Ru(II) to Ru(III).

Electron transfer can occur by thermal activation and surface crossing, 1 → 2 → 3 → 4 in Figure 1A. Absorption of heat from the surroundings leads to changes in nuclear configurations at the Ru(II) and Ru(III) sites until they are identical at points 2 and 3. Within the limits of the uncertainty principle, the energies at 2 and 3 are also the same, and the only difference between

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