

than the observed apparent velocity. The computed velocities for the high-pressure phase (iv) could match the observed velocities, but the nature of this composition strongly depends on minor constituents (14).

Any of the above petrologic models implies a differentiated lunar mantle whose composition must vary with depth to satisfy the constraints of mean density and moment of inertia. Thermal evolution calculations (15) imply that the crust differentiated from the outer 400 km of the moon mostly within the first 1.5×10^9 years of lunar history. The structure of the mantle and the extent of differentiation and layering cannot be determined until additional seismic data extending to greater distances (Δ) become available from future missions.

Note added in proof: Seismic signals from the Apollo 16 S-IV B impact were recently recorded at Apollo lunar stations 12, 14, and 15. The time and location of this impact were uncertain due to a loss of tracking capability. These parameters can be estimated, however, from the arrival times of P and S waves at the Apollo 12 and Apollo 14 stations. The first detectable motion at the Apollo 15 seismometer (at a distance of 1095) indicates an average velocity in the lunar mantle of at least 8 km/sec near a depth of 130 km. Whether the high-velocity (9 km/sec) zone in the uppermost portion of the mantle (reported above) is a universal feature or not cannot be determined from the new data.

The high frequencies (0.5 to 3.0 hz) of compressional and shear waves observed at station 15 from the latest impact and also from deep moonquakes indicate the absence of high attenuation, precluding widespread melting in the outer several hundred kilometers of the lunar mantle.

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Crystal Structure of the Solid Electrolyte

(C₅H₅NH)Ag₅I₆ at -30°C

Abstract. The crystal structure of pyridinium hexaiodopentaargentate, (C₅H₅NH)Ag₅I₆, is unique among those of the halide and chalcogenide solid electrolytes in that face-sharing iodide octahedra as well as face-sharing tetrahedra and face-sharing between octahedra and tetrahedra provide the paths for silver ion transport. There are two formula units in a hexagonal cell, space group P6₃/mcc (D_{3h}²). At -30°C, the lattice constants are $a = 11.97 \pm 0.02$, $c = 7.41 \pm 0.01$ Å. The structure has three sets of sites for the silver ions. At -30°C two of these sets are apparently filled with the ten silver ions per unit cell, while the third set of tetrahedrally coordinated general positions is empty. Therefore, the conductivity at this temperature is limited by the thermal excitation of the silver ions into the empty tetrahedra.

It has been shown (1) that halide and chalcogenide solid electrolytes with ionic conductivities approaching those of liquid electrolytes have cation-disordered structures and that these structures may be described as having networks of passageways resulting from the face-sharing of anion polyhedra. The number of polyhedra is usually significantly larger than the number of mobile cations.

In solid electrolytes based on a body-centered cubic arrangement of anions (for example, α -AgI) face-sharing tetrahedra only form the passageways for the mobile cations, while in those based

on a face-centered cubic arrangement of anions (for example, α -Ag₂HgI₄) the passageways involve face-sharing between tetrahedra and octahedra (see 1).

In the more complex structure of RbAg₄I₅ (2) and [(CH₃)₄N]₂Ag₁₃I₁₅ (3), the passageways are formed by face-sharing tetrahedra. Each unit cell of the former contains 56 such tetrahedra and an average of only 16 Ag⁺ ions; each unit cell of the latter contains 41 tetrahedra and an average of 13 Ag⁺ ions. In both cases, the passageways are interconnecting and the equilibrium distributions of Ag⁺ ions over

Table 1. Final parameters and estimated standard errors.

Atom	Posi- tions	Positional parameters			Thermal parameters ($10^5 \times$)					
		<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I ⁻	12l	0.44086 (15)	0.14526 (16)	0	680 (14)	765 (15)	2345 (84)	381 (13)	0	0
Ag ⁺	6f	1/2	0	1/4	1479 (31)	2359 (64)	2055 (111)	$= 1/2\beta_{22}$	0	0
Ag ⁺	4c	1/3	2/3	1/4	1460 (35)	$= \beta_{11}$	3063 (151)	$= 1/2\beta_{11}$	0	0
C	12j	0.116*	0	1/4	1500*	1500*	2000*	$= 1/2\beta_{22}$	0*	0

* Assumed.

the tetrahedral sites are significantly non-random.

A structure determination of a crystal of $(C_5H_5NH)Ag_5I_6$ (4) at room temperature (5) showed some disorder of the Ag^+ ions, but the results implied that at lower temperatures there would not be such disorder. For this reason, I determined the structure and the population of Ag^+ ion sites at $-30^\circ C$, where it does appear that there is no disorder of Ag^+ ions, though the arrangement of the iodide and $(C_5H_5NH)^+$ ions appears to be essentially the same as at room temperature (5). The crystal structure of $(C_5H_5NH)Ag_5I_6$ differs markedly from those of all known highly conducting solid electrolytes. The simplest channels for Ag^+ ion transport are formed by face-sharing iodide octahedra.

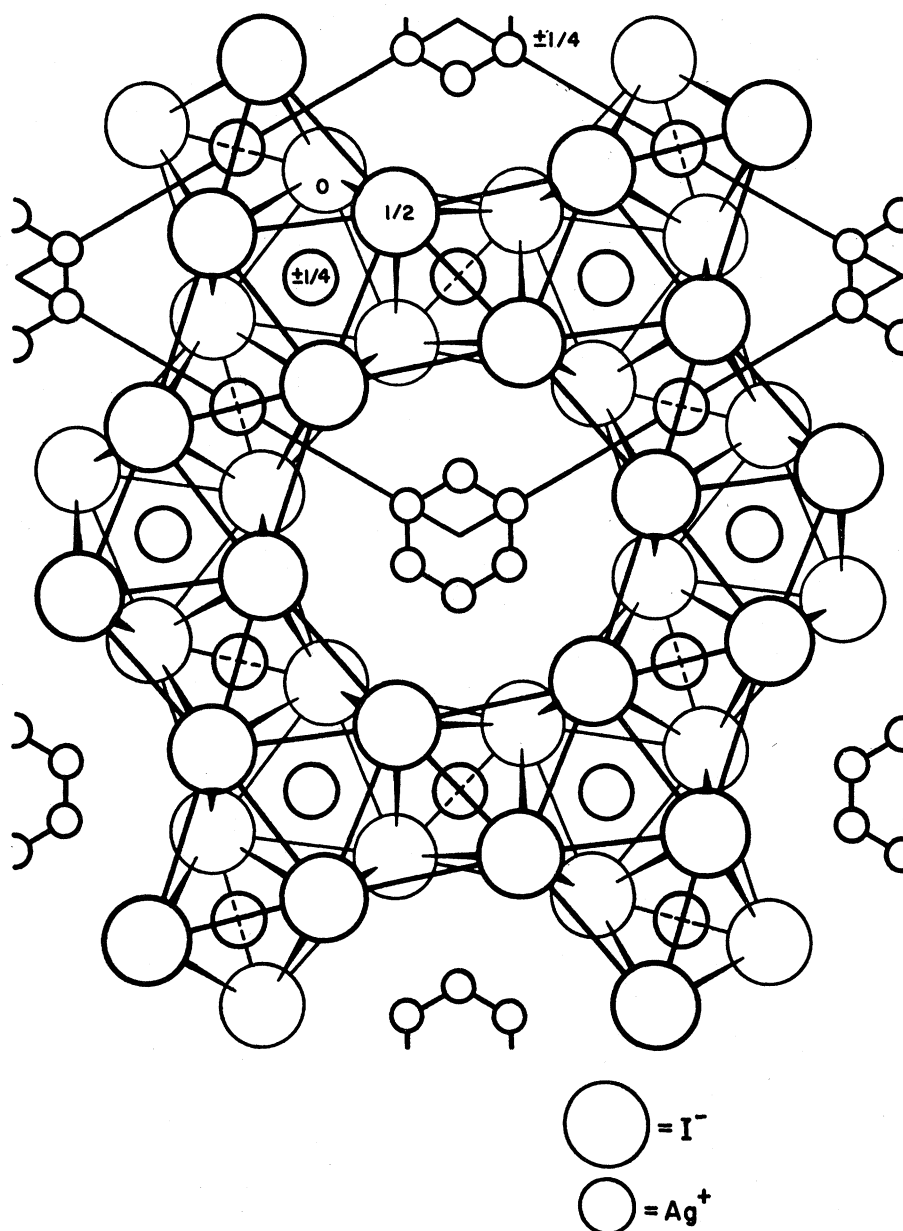
At temperatures between -30° and $100^\circ C$, x-ray photographs taken with a Buerger precession camera show that crystals of $(C_5H_5NH)Ag_5I_6$ have diffraction symmetry $6/mmm$. Systematically absent reflections are those with indices $h0l$ and hhl , $l \neq 2n$. These lead to probable space groups $P6/mcc(D_{6h}^{2h})$ or $P6cc(C_{6v}^{2h})$; the structure analysis establishes the former as most probable. Lattice constants determined from the Buerger precession camera photographs taken at $23^\circ C$ (with $MoK\alpha$, $0.7107 \text{ \AA}$, radiation) are $a = 12.03 \pm 0.02$, $c = 7.43 \pm 0.01 \text{ \AA}$. A cell content of $2(C_5H_5NH)Ag_5I_6$ gives an x-ray density of 4.92 g/cm^3 ; this is in good agreement with the measured (6) value, 4.87 g/cm^3 . Crystals of $(C_5H_5NH)Ag_5I_6$ are optically isotropic when viewed along the c -axis; this corroborates their uniaxiality.

At $-30^\circ C$, the lattice constants determined from Buerger precession camera photographs are $a = 11.97 \pm 0.02$, $c = 7.41 \pm 0.01 \text{ \AA}$; the x-ray density is 4.99 g/cm^3 . The linear absorption coefficient for $MoK\alpha$ radiation at $-30^\circ C$ is 163.8 cm^{-1} .

A crystal was ground into a spherical

shape of radius 0.134 mm with a sphere grinder (7) similar to that described by Schuyff and Hulscher (8). This crystal was aligned along the c -axis. The intensity data were collected with a Buerger-Supper-Pace-Picker diffractometer; $MoK\alpha$ radiation and balanced Zr

and Y filters were used. The data collected were those included within $2\theta = 55^\circ$ to $l=4$, for positive h and k . The continuous scan mode was used with $2^\circ/\text{min}$ scan rate and scan interval 2° or more. Background counts were taken at the beginning and end of the scan

Fig. 1. Plan view of the crystal structure of $(C_5H_5NH)Ag_5I_6$ at $-30^\circ C$.

interval at 1/6 the scan time of each reflection.

The low temperature was attained by blowing dry cooled nitrogen over the specimen in a manner similar to that of Post, Schwartz, and Fankuchen (9). A copper-constantan thermocouple placed less than 1 mm from the specimen and connected to a recorder was used to monitor the temperature. Temperature was adjusted by regulating the gas flow manually.

In the ordered structure, the atoms are in layers of $c/4$; the x-ray data confirm this layering. Thus, as far as positional parameter refinement is concerned, data other than those with $0 \leq l \leq 2$ are redundant. However, for thermal parameter refinement, some data from levels with $l > 2$ are required. Five levels of intensities, that is, with $l = 0$ to 4, were collected.

Relative $|F_o|^2$ were obtained by application of the Lorentz-polarization-Tunell and absorption (10) factors to the intensities. Because $F^2(hkl) = F^2(khl)$, these were averaged. The total number of independent $|F_o|$ was 264, of which 59 were below threshold (less than 100 counts for intensity).

The layering at $c/4$ and the short c -axis require that all the atoms in the ordered structure be in special positions of $P6/mcc$. The arrangement of the iodide ions (12l positions) is such that if the structure is ordered there are only ten positions available to the Ag^+ ions, six tetrahedral and four octahedral sites, positions 6f and 4c, respectively. There is a set of general positions which could be partially occupied by Ag^+ ions in the disordered structure; these are tetrahedrally coordinated sites (see below). The pyridinium ions must be located and "centered" only at the c -axis. The pyridinium ions do not, of course, have hexagonal symmetry, required by the space group; thus, they must be disordered.

The Busing, Martin, Levy least squares program (11) modified by Ibers, Hamilton, Johnson, Ellison, and Levy to include the imaginary part of the anomalous dispersion correction was used in the calculations. The atomic scattering factors were those of Cromer and Waber (12); both the real and imaginary parts of the anomalous dispersion corrections (13) were applied.

The pyridinium ion was approximated by a benzene ring with $C-C = 1.39$ Å. Because of the geometry of this ion, the carbon atoms could not be in the 12l positions. Further, packing con-

siderations eliminated the possibility of their being in a set of 12l positions. There remained the possibility of the static equivalent of free rotation (14) of the pyridinium ions at the $(0,0,\pm 1/4)$ positions, the 12k positions, or the 12j positions. Of these, the last enhanced the agreement between the calculated and observed amplitudes, while the first two detracted from it. It was not possible to refine the single positional parameter and the thermal parameters of the carbon atom, and they were therefore set constant at reasonable values (Table 1).

The final parameter values and their standard errors are given in Table 1. The final discrepancy factor, $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, was 0.059, excluding the five $|F_o|$'s greater than 249. (Inclusion of these actually decreases the value of the discrepancy factor.) In the early cycles of the least square refinement, the possibility that some Ag^+ ions were in the general positions, with approximate coordinates (0.48, 0.10, 0.37), was tested. It was found that, well within one standard error, there were no Ag^+ ions in these sites; that is, the Ag^+ ions fill the 6f and 4c sites. Thus,

Table 2. Interionic distances and estimated standard errors.

Atom types	Number	Distance Å (S.E.)
I-I	2	4.119(2)
	2	4.344(4)
	1	4.361(4)
	2	4.656(3)
	2	4.775(3)
	2	4.866(3)
<i>Tetrahedron about Ag^+ in 6f</i>		
Ag-I	4	2.861(1)
I-I	2	4.361(4)
	2	4.775(3)
	2	4.866(3)
<i>Octahedron about Ag^+ in 4c</i>		
Ag-I	6	3.118(2)
I-I	6	4.344(4)
	3	4.119(2)
	3	4.866(3)
<i>Tetrahedron about general positions*</i>		
I-I	1	4.119(2)
	1	4.344(4)
	1	4.361(4)
	1	4.656(3)
	1	4.775(3)
	1	4.866(3)
<i>Between pairs of possible Ag^+ ion sites†</i>		
Ag(m)-Ag(f)	1	1.60
Ag(m)-Ag(c)	1	2.71
Ag(m)-Ag(m)	1	1.96
Ag(c)-Ag(c)	2	3.71

* (24m) $\sim$ (0.48, 0.10, 0.36). † These are the only possible jump distances for the Ag^+ ions. Even though the intralayer Ag(c)-Ag(f) distance (3.46 Å) is less than the Ag(c)-Ag(c) distance, it is not a jump distance; that is, an edge shared by the octahedron and the tetrahedron intervenes between the c and f sites.

at $-30^\circ C$ the Ag^+ ions appear to be ordered. This is not the case at room temperature and above (5).

Interionic distances and their estimated standard errors (15) are given in Table 2. Each iodide ion has 11 near iodide neighbors at distances ranging from 4.119 ± 0.006 (= 3 S.E. limits of error) to 4.866 ± 0.009 Å; their average is 4.534 ± 0.009 Å. The average I-I distance in the tetrahedron about a 6f position is 4.667 ± 0.009 Å and in the octahedron about a 4c position is 4.418 ± 0.010 Å. The average I-I distance (see Table 2) in the general (empty) tetrahedron is 4.520 ± 0.009 Å. The tetrahedral Ag^+-I^- distance, 2.861 ± 0.003 Å, is substantially longer than that, 2.80 Å, in AgI of the zinc blende type. The octahedral Ag^+-I^- distance, 3.118 ± 0.005 Å, is 9 percent larger than the tetrahedral Ag^+-I^- distance.

Figure 1 is a plan view of the structure. Six of the ten Ag^+ ions are in tetrahedra which share top and bottom edges between them and side edges with the octahedra. They also share all four faces with tetrahedra surrounding general positions; these tetrahedra are essentially empty. The iodide octahedra share top and bottom faces parallel to (001) with each other and the other six faces with the empty tetrahedra. Thus, the latter link the octahedra to the tetrahedra about the 6f positions. A general position tetrahedron also shares a face parallel to (001) with another general position tetrahedron and the fourth opens to the pyridinium ion column.

In $RbAg_4I_5$ (2) and $[(CH_3)_4N]_2Ag_{13}I_{15}$ (3), the Ag^+ ions must "zigzag" through the passageways formed by the face-sharing tetrahedra. In $(C_5H_5NH)-Ag_5I_6$, face-sharing octahedra themselves form straight channels parallel to the c -axis. Motion of Ag^+ ions in the octahedra would be limited by the number of vacancies in these sites. Such vacancies could be created by Ag^+ ions moving into the empty tetrahedra, but because of short intersite distances these must be made available by occurrence of vacant f sites. Silver ions could also move in approximately the c -axis direction in a much more complicated manner, namely by means of the linkages of only the two types of tetrahedra, the general position type providing many vacancies. It would seem, however, that such motions of Ag^+ would not persist for many jumps without soon involving an empty octahedron. Conductivity in approximately

the (001) plane is made possible by the linkage of the octahedra to the tetrahedra of the 6f type by the general position tetrahedra. It should be kept in mind that the distances (see Table 2) between the equilibrium sites for the Ag^+ ions put constraints on the motions of the Ag^+ ions. This is more fully described in (5).

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Environmental Applications of the Weibull Distribution Function: Oil Pollution

Abstract. *The Weibull distribution function appears to be a powerful tool for the statistical analysis and interpretation of environmental pollution data. To illustrate its potential, the method is applied to a variety of oil pollution topics. Other applications are suggested.*

Most forms of environmental pollution cannot be quantified by a single or unique numerical value. Rather, a complicated and interactive set of physical, chemical, biological, and human processes act in concert to yield a spectrum of measured values. In order to establish meaningful and representative concentrations of pollutants, it is thus customary to collect field data from several sampling stations, at different times, and under a variety of sampling conditions. The individual measurements are then combined to yield an average, a median, a mean, a geometric mean, or some other statistical expression of pollutant concentration.

My purpose here is to report some preliminary results of a new method for statistically analyzing environmental pollution data. In this method the Weibull distribution function is used as a correlating model, and the method appears to have considerable potential for interpreting ambient pollutant concentrations. In the following paragraphs, pertinent features of the Weibull distribution function are summarized and then several examples

dealing with oil pollution are given to illustrate the method's versatility and applicability.

The Weibull equation is an empirical three-parameter distribution function which is expressed in linearized form as (1)

$$\ln \ln [1 - F(x)]^{-1} = -\ln \alpha + \beta \ln (x - \gamma) \quad (1)$$

In this equation, $F(x)$ is the cumulative probability that a variable will have a value of x equal to or less than a

given value, α is a scale parameter, β is a shape parameter (which varies with the skewness of the distribution), and γ is a threshold parameter. The parameter of greatest interest in the present application is γ . In its broadest sense, γ may be interpreted as the minimum value that the variable x is likely to attain; that is, the probability of x being less than γ is essentially zero.

The Weibull distribution function (which, in modified form, is known by several other names) has been applied to a wide variety of topics including fatigue (life) testing, quality control, particle size analysis, and odor threshold (1). Although it is basically an empirical model, these applications have suggested that a physical interpretation can be made of its parameters—particularly γ . To my knowledge the Weibull distribution function has not been previously applied to pollution monitoring problems.

The first example deals with beach contamination from natural oil seeps along the southern California coastline (2) (see Fig. 1A). Data used in this analysis were collected at 12 monthly intervals in 1959 and 1960 (3). The ambient amounts of contaminating beach tar deposited at four of the six sampling stations are shown in Fig. 1C (the amounts at stations b and c are very nearly the same as that at station a and are not shown for reasons of clarity). Table 1 summarizes the important Weibull parameters (4).

Although a detailed interpretation of these results is beyond the scope of this report, one observation can be made immediately. The data in Table 1 show that the threshold and median concentration of tar found on beach e is considerably heavier than that on any other sampling station. However, the ratio of the threshold to median values for this beach is essentially the same as for beach f (see Fig. 1A). In the same vein, similar threshold to median ratios exist for beaches a and b in Santa Monica Bay and for beaches c and d in the eastern Santa Barbara Channel. These observations suggest the possibility that the tar deposition process may be governed by several spatially distinct mechanisms of oil transport. Knowledge of the threshold values has thus opened new doors for the interpretation of these data.

The second example deals with the more conventional topic of oil spills. Curve 1 in Fig. 1D shows a Weibull plot for minor and moderate spills, that is, less than 80,000 liters, during the

Table 1. Weibull parameters obtained from the analysis of beach tar deposits along the southern California coastline. Beach locations are shown in Fig. 1A; Table 1 is based on data from (3).

Beach	A Threshold (g/m ²)	B Median (g/m ²)	A/B
a	0.018	0.10	0.18
b	.018	.12	.15
c	.001	.07	.01
d	.001	.03	.03
e	3.6	11.0	.33
f	0.080	0.23	.35