

**The****SPEX**

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**Speaker****THE SECRET LIFE OF SILVER**

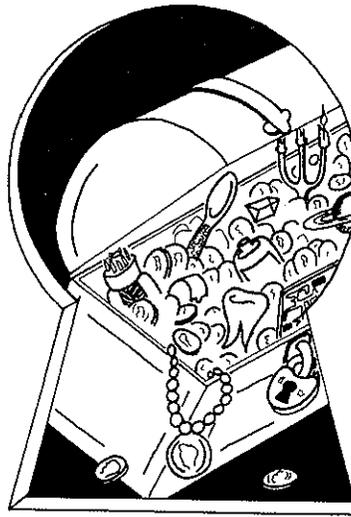
R. Kaminski

**Ag Anniversary time**

With this issue THE SPEX SPEAKER is closing its 24th volume, calling for this brief pause to acknowledge the occasion. Having developed a few silver threads of our own, we're rather pleased to boast that some of our readers have been with us all the way. We know because a goodly number stay in contact, which is great. It's truly gratifying to be able to call long-time customers friends. We're pleased and, well, proud.

But for the young among us (and that's anyone who's had even one less birthday than we have) reminiscing can be a bore. So we'll skip the indulgence in fond memories, say, "Thanks for sticking with us as readers and customers" to the appropriate some of you, "Welcome to the spectroscopies" to the new recruits, and get on with our sterling topic.

Most of us see silver as just a bauble, a bright, shiny metal to wear as jewelry, but hardly something to take seriously, aside from its value as an investment, a hedge against inflation. Mention of the word spawns an image of a filigreed teaspoon, or the jingle of coins in our pockets, even though stainless steel has virtually put an end to the ritual of polishing the silverware, and for the last fifteen years the silver dimes and quarters minted in the United States have been stamped from a copper core clad with an alloy of 75% copper and 25% nickel (turning the jingle



into a clink). Perhaps the only time we really think about this noble metal is when, on the coat tails of gold fever, its price on the commodities market hits a new high and it begins to seem like all the world's supply of bullion will soon be decorating the interior of somebody's wall safe. Yet there's an entire subculture of silver that has escaped the limelight.

Silver has a reputation as gold's poorer cousin, and a visit to the dentist's office, unpleasant as that may be, leaves you walking away with a toothful of an amalgam of one of these precious metals. But when you step outside, those clattering bearings in the engine of your bus can take

the punishment of high temperature and pressure only because a minute amount of silver has been added to the alloy just as pure silver bearings in jet engines are three times more resistant to seizure than traditional babbitt alloys. When you get to the lab, the microprocessor chips inside your data system may be encapsulated or bonded with a silver epoxy whose low-temperature curing does away with potentially destructive solder. Look around your working area and you'll find silver electrodes, batteries, mirrors, solder joints — all hidden facets of silver's secret life. And where would spectroscopy be today were it not for those fragile photographic plates whose suspended crystals of silver halides so accurately recorded the positions of all those spectral lines?

We still haven't reached the bottom of this treasure chest. Silver is a germicide and, though few of us were born with silver spoons in our mouths, a drop of  $\text{AgNO}_3$  in each eye while we were in the delivery room, helped preserve our sight. Astronauts and woodsmen purify their water with silver-lined systems. Submarines and satellites draw their power from compact, silver-zinc batteries which may pave the way to the even more efficient storage devices and fuel cells so sorely needed today. And in the infant science of weather control, significant research has centered on AgI.

No, Pliny was wrong. Silver is not the next folly of mankind after gold. The prodigal has come home, settled down, and gone to work.

Fig 1 Silver caught looking at itself. In this spectrogram of HiPure silver nitrate (TMI of 5 ppm max.) the silver in the photographic plate has frozen the image of its own emission lines.

328.1 nm

338.3 nm

## The Silver Lining

Everybody talks about the weather and at the end of World War II somebody started doing something about it. Research into weather control has been keenest in the Midwest where a drought or a hailstorm (that can strike in the middle of a summer day) means the difference between a boom or an economic bust. And when the farmer suffers, the entire country groans.

Clouds are the key. A nimbostratus, heavy with rain, may pass over a parched corn field without giving up a drop. Or a cumulonimbus may thunder over the horizon to pelt the countryside with ice. The trick is to induce these clouds to drop their loads as rain where they will do the most good (or the least harm).

A cloud condenses when air cools to a temperature where the vapor pressure of water equals the partial pressure of water vapor suspended in the atmosphere. At this dew point, the number of water molecules leaving a suspended droplet equals the number returning to it, so the air is saturated and it can hold no more water. When the temperature drops below the freezing point, the cloud is supercooled to an unstable state that is subject to sudden precipitation if particles are present to form a core for water molecules to cling to. These nuclei are absolutely essential: pollution-free air can reach four times supersaturation before condensation occurs.

If the temperature in the cloud falls below  $-20^{\circ}\text{C}$ , the molecules are their own nucleating agents. Ice crystals form spontaneously and rapidly grow until, too heavy to stay suspended in the air, they fall as rain or snow. With these facts at his fingertips, V.J. Schaefer conceived the notion that clouds could be cleared away simply by chilling them, and early experiments produced micro crystal nuclei after seeding with dry ice. However the real credit for cloud seeding lies with B. Vonnegut [1] who, in 1947, wondered whether artificial nuclei might be found to stimulate precipitation at elevated temperatures. Vonnegut searched through x-ray crystallographic data for substances with cell dimensions and symmetries similar to ice and came across a promising candidate.

Fig 2 is a sketch of the hexagonal lattice of normal ice. Each oxygen atom is surrounded tetrahedrally by four other oxygen atoms with the hydrogen bondings situated essentially at random within the confines of the assembly. Vonnegut found that AgI shares this wurtzite structure and the lattice dimensions were identical to within a few percent. In diffusion cloud chambers [2] AgI induced nucleation at temperatures as high as  $-3^{\circ}\text{C}$ ; actual rain-making field trials began with the U.S. Air Force's Project Cirrus in 1948.

What makes these results surprising is that, despite its well-documented similarity to ice, AgI is essentially hydrophobic, or repels water, and the crystal's seeding ability is actually determined by a few

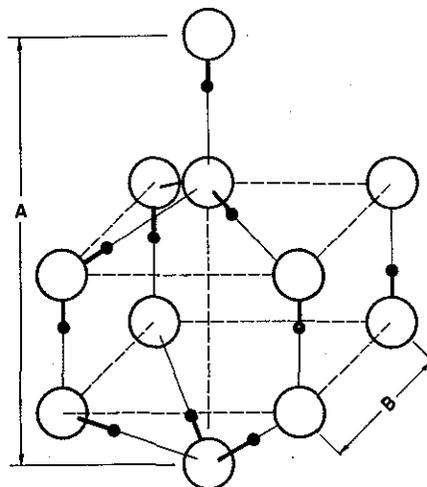


Fig 2 Hexagonal crystal structure of normal ice that is shared by silver iodide. The lattice dimensions for  $\text{H}_2\text{O}$  are  $A = 7.36\text{\AA}$ ,  $B = 4.52\text{\AA}$ ; while for AgI  $A = 7.49\text{\AA}$ ,  $B = 4.58\text{\AA}$ .

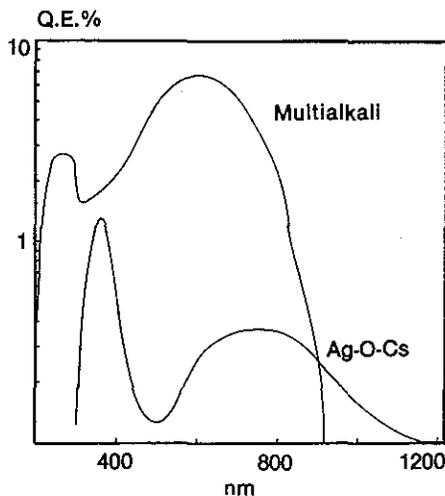


Fig 3 The quantum efficiency of a typical Ag-O-Cs photocathode is plotted. The multi-alkali curve is included for comparison. Though Ag-O-Cs is not nearly efficient over its full range, it remains sensitive much farther into the infrared.

hydrophilic sites scattered over its surface. These imperfections give the water molecules something to hang on to: perfect AgI is relatively ineffective. But so is a perfect ice crystal.

Silver iodide can be introduced to clouds by aircraft, or, more conveniently, with silver smokes by burning the salt in solution with some volatile solvent, such as acetone, or by sparking silver electrodes in the presence of iodine vapor. Russian scientists in the Transcaucas region have shot anti-aircraft shells full of AgI into hail-producing clouds and claim to have protected an area of  $10,000\text{ km}^2$  saving 30 million rubles by limiting crop damage.

Though cloud seeding works well enough in a laboratory environment, with the possible exception of the Soviet experiments, it has yet to reach its full potential. Many more atmospheric variables will have to be pinned down before weather control can consistently stop it from raining on your parade.

## In the Lab

To fully appreciate the invaluable role silver played in the genesis of science, imagine how far out of kilter the timetable of discovery would have been thrown without the photographic plate. Certainly it's possible that a Balmer or Bohr might still have cataloged and explained the visible spectrum of hydrogen and brought the first milestone of quantum mechanics in on schedule (though not without a lot of eyestrain). Yet the two open ends of the electromagnetic spectrum, starting with the ultraviolet and infrared, would have remained invisible, and with them all the secrets just waiting to be revealed. Radioactivity might have escaped Becquerel's notice, or crystal structure eluded Bragg, and even weak spectral lines in the visible could have gone ignored. But silver was there, its halide salts suspended in gelatin emulsions, coating the photographic plates that were bolted to spectrographs, x-ray diffractometers and cloud chambers, waiting, ready to absorb those tell-tale photons and crystallize into a latent image.

The real irony of silver halides (the fundamental photosensitive elements) is that they actually respond to a smaller portion of the spectrum than the human eye: only ultraviolet and blue light stimulates them. To extend their range into the green, red and infrared, sensitizing dyes must be added to the emulsions. To reach deeper into the ultraviolet and x-ray region plates are coated with fluorescent salts which reradiate at longer wavelengths. The resulting useful range of photography is from about 5 to 1500 nm.

Though photomultipliers, vidicons, and other photoelectric recording devices have largely replaced photographic detection, silver itself has kept pace with technology.

In fact, the silver-oxygen-cesium photocathode was one of the first to offer adequate sensitivity over a respectable spectral range (Fig 3). These cathodes are formed by evaporating silver on glass, or other suitable substrate, and oxidizing the film by heating in an oxygen atmosphere. Since the transmission of the Ag<sub>2</sub>O is close to total for the visible spectrum, the coating may be oxidized till it virtually disappears, resulting in a semitransparent cathode. After being exposed to cesium vapor, the plate is baked until the photocurrent stabilizes. Compared with a typical multi-alkali tube, the quantum efficiency of an Ag-O-Cs photomultiplier has a low yield. Yet the tube is sensitive to radiation into the infrared as far as 1200 nm and it is manufactured to suit specialized applications.

Once photoelectrons leave the cathode and begin to multiply, Ag-Mg-O dynodes show less fatigue than alkali-metal compounds, particularly at high current densities. Sometimes the photocathode is even eliminated, creating a dynode tube which is solar blind (immune to light above 300 nm), yet responsive to radiation in the vacuum ultraviolet, or to electrons, or to ions for mass spectroscopy.

On the spectrometer side of the phototube, infrared spectroscopists have pressed AgCl into windows and prisms to take full advantage of its wide transmission range of .4 to 24 μm. And unlike the better-known KCl and NaCl that gradually dissolve from moisture in the air, the silver salt is impervious to water, though this benefit is counterbalanced by a marked vulnerability to light. It tends to darken the silver chloride, clouding transmission in the infrared as well.

Whenever throughput in the visible is critical, silver mirrors are optimal. Freshly deposited Ag has unparalleled reflectivity between 400 and 700 nm (approaching 98% versus 90% for Al), and this enviable characteristic is preserved by overcoating to prevent sulfide formation. The only factor that keeps silver from dominating spectrometer optics (besides cost) is the way its performance plummets in the uv.

Even the source shows a profit when silver's afoot. Exploding-conductor excitation with thin films of silver was shown [3] to be convenient for qualitative emission spectroscopy over a wide concentration range, especially for microsamples in the multielement determinations common in pollution control. Even in less exotic sources, buffering the sample with AgCl not only stabilizes the arc, but selectively alters the volatilization to release the impurities while leaving the more refractory matrix behind. This sharp separation of analyte species yields an enhancement of up to three orders of magnitude over direct-burn systems [4].

A precious metal in any sense of the word, silver offers countless other helping hands in the laboratory. Chromatographic

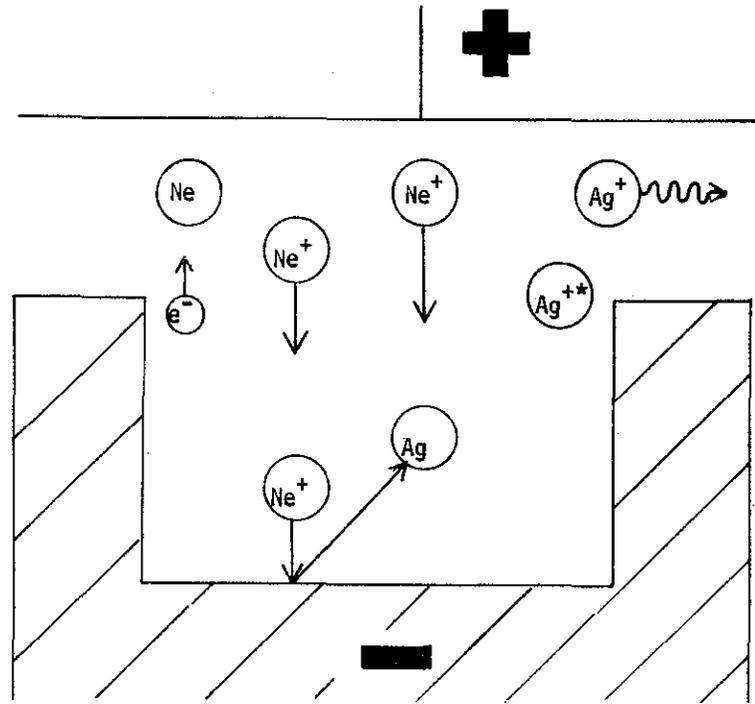
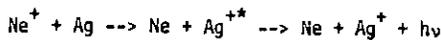


Fig 4 Hollow-cathode configuration for silver laser of Johnson et al. Free electrons accelerate toward the anode and ionize neon by collision. The gas ions travel to the cathode where they

knock Ag loose (sputtering). The Ag atoms are ionized and raised to excited states by further collisions.

columns packed with silver-nitrate-coated glass beads [5] are highly efficient in the analysis of aromatic hydrocarbons which have boiling points as high as 180 C. Normally the columns must be heated to vaporize the sample, but with the AgNO<sub>3</sub> packing, analyses can be routinely run at room temperature. But one of the most distracting developments is the construction of a silver laser.

Johnson et al. [6, 7] describe a cw silver-ion laser with transitions ranging from 324 to 503 nm. The hollow cathode geometry (Fig 4) of their device consists of a notched, rectangular bar of silver and a stainless-steel anode surrounded by a helium or neon atmosphere. High voltage applied across the electrodes accelerates free electrons toward the anode and they pick up enough kinetic energy to ionize the gas molecules they strike along the way. These positive ions are then accelerated toward the cathode where they knock off, or sputter, silver atoms into the discharge zone. Here other ions strike the silver atoms, ionizing and raising them to the excited state (Ag<sup>+</sup>\*) from which they emit radiation. This asymmetrical, thermal charge-exchange reaction follows the pathway



Instead of sputtering, most other metal lasers have ovens to convert the active species to a vapor. But with silver a 1000 C temperature would be required to vaporize enough atoms to support laser action, which has a threshold of about 10<sup>13</sup> atoms/cm<sup>3</sup>. With cathode sputtering, on the other hand, the electrodes stay relatively cool, never rising above 400 C.

Other workers [8, 9] have reported infrared laser oscillations with wavelengths as long as 840 nm. This impressive range, and power at 318 nm exceeding 350 mW, hold great promise for silver lasers.

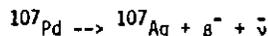
#### Pearls and Meteorites

Though silver has proven itself a loyal vassal ever since minting the first coin sealed the doom of the barter system, the metal isn't totally benign. Like countless substances, it has been linked (though by no means conclusively bound) to cancer. Despite reports of tumors developing after foils were implanted under the skins of rats [10], trauma, rather than the element itself, may be to blame for carcinogenesis. On the other hand, silver's extreme toxicity to marine organisms is too well documented to be questioned. Relatively harmless to higher forms of life, Ag is lethal to the American oyster at concentrations as low as 6 ppb, and the cunner, a small coastal fish, soon perishes when exposed to 0.5 ppm [11]. More dilute concentrations may

not bring immediate death, but might take their toll on growth, reproduction, and the ability of an individual fish to survive other stresses. Of all the heavy metals, only mercury is more deadly; silver is estimated to be 600 times as toxic as cadmium. The potential for environmental catastrophe is obvious once we realize that silver concentrations as high as 6.7 ppm have been found in sediments from Long Island Sound [12]. Also, of 92 ores examined spectroscopically by Hartley and Ramage [13], only four were silver free.

These ecological imperatives have intensified the search for more accurate determinations of silver. Unpolluted sea water contains about 0.1 ppb, yet flame spectrometric methods have not reached this detection limit and currently hover around 2 ppb. Recently, however, W.R. Kelly, F. Tera, and G.J. Wasserburg [14] reported success at 0.1 ppb through surface ionization mass spectroscopy. And repercussions of this research reach back through time to the birth of the planets.

Silver's potential as a solar system chronometer [15] hinges on its isotopic structure. Though there are 20-odd unstable isotopes, varying in half life from 5 seconds to a year, most native silver is a composite of almost equal portions of stable  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  (actually  $^{107}\text{Ag}/^{109}\text{Ag} = 1.081$ ). Sometime after the formation of the planets,  $^{107}\text{Ag}$  was produced from the beta decay of a now extinct isotope of palladium. This reaction, with a half life ( $T_{1/2}$ ) of 6.5 million years, followed the scheme



The original supply of  $^{107}\text{Pd}$  would have been created during the cataclysm of nucleogenesis when the heavier elements congealed at the beginning of the solar system. From that point on, the number of atoms of this isotope would begin to decrease exponentially while, as a conse-

quence, the abundance of  $^{107}\text{Ag}$  would increase as

$$^{107}\text{Ag} = ^{107}\text{Pd}(1 - e^{-t/\tau})$$

where  $\tau = 1.44T_{1/2}$

Now the amount of palladium trapped inside meteorites (the oldest known objects in our solar system) would be a function of the time elapsed between nucleogenesis and crystallization. And, because of beta decay, so would the eventual isotopic ratio of silver. An accurate measurement of that ratio therefore isolates the theoretical instant of a meteorite's birth.

We say theoretical here because the results, as with all radiometric dating techniques, depend on some necessary, though hopefully valid, assumptions. A nucleosynthetic model must be chosen to calculate the production rate of palladium [16]. And whether the synthesis was sudden, like a supernova, or took place over a continuous interval of time, during which some of the palladium already formed was allowed to decay [17], is open to conjecture.

Kelly et al. tackled both these models, turning their microanalytical technology on meteorites found at a variety of locations, as shown in Table 1. From their calculations, the oldest of these meteorites was formed at least 21 million years after the origin of the solar system.

### Super Silvers

A planetary probe that spins off into deep space after beaming back to earth the first close-ups of one of the outer planets, may have the sun as the primary source of its power. But the servo motors to unfold those massive wings lined with solar collectors and the guidance system to turn them into the solar wind probably drew their current from a bank of compact, light-weight silver-zinc batteries nested deep inside the probe's core.

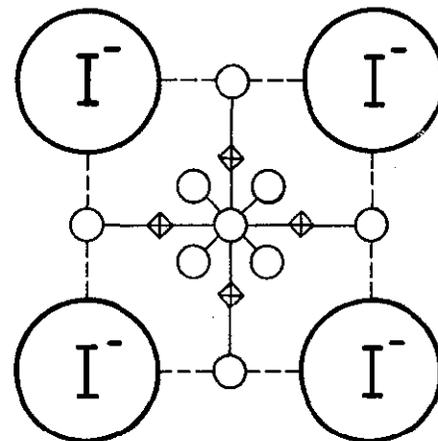


Fig 5  $\alpha$ -phase crystal structure in which AgI becomes a superionic conductor above 147C. The indicated points between the iodine anions are possible lattice sites for  $\text{Ag}^+$  ions.

Ever since the 18th century when Volta's silver-zinc pile set the stage for electrochemical science, these batteries have been the preferred way to go whenever high current densities and maximum capacities were critical and quarters cramped. Supplying perhaps 50 watt-hours per kilogram (1 watt-hr/cm<sup>3</sup>), Ag-Zn cells power everything from submarines scouting the ocean floor, to drills designed to bore into the lunar surface. In hearing aids, they've reunited the handicapped with the sound spectrum that runs from Aram Khatchaturian to Led Zeppelin. And in the trunk of a motorized car, they've driven over some of the roadblocks standing in the way of non-polluting, practical commuter transportation. Unfortunately, some of these barriers stubbornly stand, limiting the range of electric vehicles and tethering them for recharging 1/3 of each 24-hour period.

Research for more efficient energy storage devices is an accelerating race against evaporating fuel reserves. Besides the transportation impetus, there's the hope of diverting energy generated in off-peak hours, such as the early morning, to meet the surge in demand that comes with a waking population. Much of this current interest has collected around solid electrolyte batteries formed from ionic materials that have conductances comparable to liquid electrolytes, but without the attendant problems of corrosion, cost, and resistance to miniaturization.

TABLE 1  
Lower Limits of the Formation Age of Meteorites

Sample Site	Sudden Synthesis in million years	Continuous Synthesis in million years
Canyon Diablo	97	32
Toluca	87	21
Hoba	91	25
Santa Clara	99	34

Contrary to conventional conductors whose electrons transport the current, ionic conductors have few free electrons; it is the atoms themselves that move between the electrodes. We wouldn't, of course, expect these mobile ions to weave through a crystal as freely as the much smaller electrons and, under normal conditions, ionic solids have very low conductivities. Yet in certain compounds one ion species forms a rigid sublattice with many vacant sites for the more mobile ion species and when an EMF is applied, these latter ions freely hop from one site to the next, producing what is known as superionic conductivity.

The classic superionic conductor is AgI [18]. Under standard conditions, the crystal is stable in the  $\beta$ -phase or hexagonal wurtzite structure (Fig 2). But when heated above 147 C (420K, Fig 5) there's a sudden transition to the  $\alpha$ -phase which is a body-centered cubic iodine lattice with several possible sites for Ag ions. As a result the Ag ions are highly motivated and the conductivity jumps abruptly by 4 orders of magnitude.

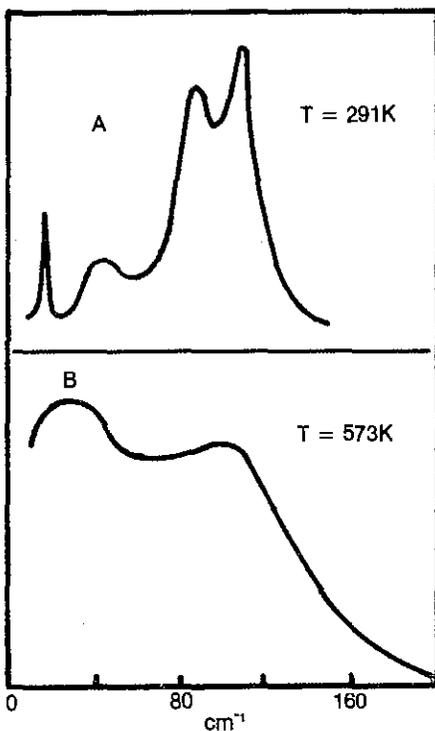


Fig 6 AgI Raman spectra for two temperatures, one below (A) and one above (B) the transition to superionic conductivity. Note how the major structural features are smeared at the elevated temperature. The general increase of detected radiation is not due to elastic scattering.

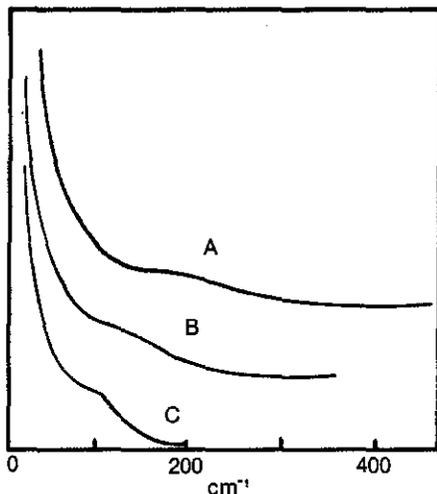


Fig 7 A comparison of Raman spectra of molten AgCl (A) and AgBr (B) to solid  $\alpha$ -AgI.

Measurements of laser-Raman scattering by M.J. Delaney and S. Ushioda, taken on a SPEX double monochromator, offer direct information on the dynamics and environment of the ions in the AgI lattice as a function of temperature [19, 20]. Since these experiments were run at varying temperatures, the accompanying change in the population of states in the sample crystal was allowed for to insure that any differences between spectra would indicate structural alterations and not simply be temperature effects.

The scattering intensity of these vibrational modes is proportional to  $\epsilon''$ , the imaginary part of the dielectric response function [21].

$$I = M(1 + n)\epsilon''$$

$$\text{where } n = (e^{h\nu/kT} - 1)^{-1}$$

is the Bose-Einstein occupation number.

Note that M is the Raman matrix element that depends on the square of the polarizability, and recall that the dielectric response function is a measure of the way atoms associate in a crystal. It's the factor  $(1 + n)$ , however, that reflects the thermal occupation of higher vibrational levels which, though temperature dependent, is not a fundamental consequence of the scattering process. So, to make a comparison of data at different temperatures more vivid, the intensity of Raman scattering in Fig 6 has been scaled by this factor.

The difference between the spectra from the  $\beta$ -phase (A) and the  $\alpha$ -phase (B) is quite striking. Above the phase transition,

the spectrum is dominated by an increase in lower-frequency scatter that accompanies the sudden jump in ionic conductivity--an increase that is not due to elastic scatter. The broad shoulder at about 100  $\text{cm}^{-1}$  is reminiscent of peaks in the  $\beta$ -phase and is probably due to optical vibrations of Ag ions against the iodine lattice. (Broadening, by the way, is a symptom of disorder as might appear in the liquid phase of a compound.) In the course of their work, Delaney and Ushioda were frequently piqued by this and other liquid-like behavior of  $\alpha$ -AgI, so they went on to compare its spectra with melts of AgBr and AgCl. The remarkably similar results are shown in Fig 7, uncompensated for thermal population. All three spectra show strong low-frequency scattering with a broad shoulder at higher frequencies.

A clue to the origin of these similarities was uncovered in the scattering mechanism in the solid phase of silver halides. AgBr and AgCl crystals are said to have a center of inversion at each site that forbids stimulation of first-order Raman effects, so their spectra are completely second order, involving two-phonon interactions. And second-order effects increase rapidly with temperature just like the scattering noted in the  $\alpha$ -AgI spectra. Furthermore, generalizing from other data on these materials, Delaney and Ushioda were confident that the silver-halide melt spectra preserved the dual-phonon nature of the solid, so they made a more critical analysis of the spectra of molten AgCl and solid  $\alpha$ -AgI. In Fig 8 the Intensity data was rescaled again, point by point, eliminating the disparities in the populations of the two phonon states

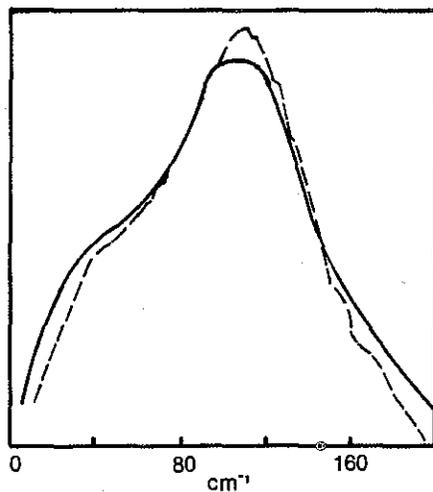


Fig 8 Molten AgCl (dotted line) and  $\alpha$ -AgI rescaled for the thermal population in two-phonon Raman scattering.

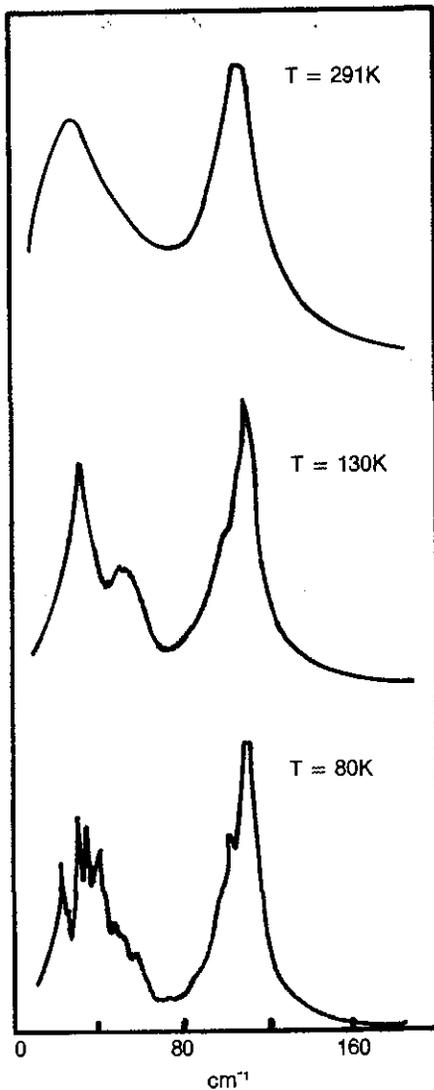


Fig 9 Raman spectra of  $\text{RbAg}_4\text{I}_5$  for various temperatures. Superionic conductivity sets in above 121.8K.

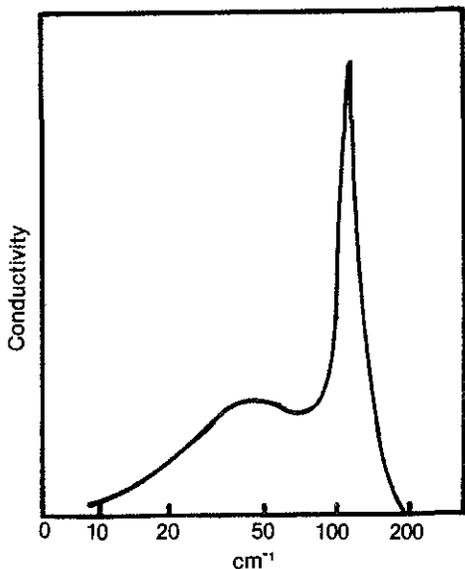


Fig 10 The conductivity of  $\text{RbAg}_4\text{I}_5$  as a function of scattering frequency.

with a factor of  $(n(\omega/2) + 1)^2$ , following reasoning similar to that applied in Fig 6.

The strength of the correlation between the spectra suggests that  $\alpha\text{-AgI}$  scattering is also due to second-order processes. Also, the broadening of the vibrational structure of molten silver halides comes from the loss of long-range order on melting. Coupling these observations, Delaney and Ushioda conclude that superionic  $\text{AgI}$ , at least with respect to Raman scattering, is molten, lacking the long-range order of a solid and having the structure of a liquid. (The observation that both  $\text{AgI}$  and  $\text{AgCl}$  peak at around  $110\text{ cm}^{-1}$  in these spectra has been interpreted by others [22] to indicate that above the transition temperature, silver ions prefer the sites marked in Fig 5, where the  $\text{AgI}$  distance is  $2.84\text{ \AA}$ , over the other sites available to them.)

Though  $\text{AgI}$  is the archetypical superionic conductor and the relative simplicity of its structure is ideal for exploring the mechanisms of silver hopping,  $\text{RbAg}_4\text{I}_5$  (an  $\text{AgI}$ -based compound) has the highest room-temperature conductivity of any solid electrolyte to date. The Raman spectra for different temperatures appear in Fig 9.

In contrast with  $\text{AgI}$ , room temperature  $\text{RbAg}_4\text{I}_5$  emits a single, narrow peak at about  $108\text{ cm}^{-1}$  in the higher frequency end of the spectrum which has been assigned [23] to the breathing mode of the iodine tetrahedron that surrounds the silver ion in both materials, though the  $\text{Ag-I}$  distance is reported to be slightly smaller in  $\text{RbAg}_4\text{I}_5$ . Also, in the superionic phase,  $\text{RbAg}_4\text{I}_5$  has two well-defined peaks, as compared with the broad humps of  $\text{AgI}$ , (Figs 6A and 9A).

As the temperature of  $\text{RbAg}_4\text{I}_5$  is lowered, a shoulder appears on the lower-frequency peak until it is fully resolved at 130K. Dropping from 130 to 80K the crystal undergoes a first-order phase transition and peaks appear that do not seem to be the results of simple splitting or increased resolution from diminished temperature broadening. Delaney and Ushioda intend to take a closer look at the behavior of these peaks with temperature in future experiments. The conductivity of  $\text{RbAg}_4\text{I}_5$  at room temperature (where it is superionic) can be plotted from this data with the equation

$$\sigma = \omega \epsilon''$$

that relates the conductivity  $\sigma$  to the imaginary part of the dielectric response function at a given frequency ( $\omega$ ). In Fig 10, note that the conductivity peak is near  $110\text{ cm}^{-1}$ , a frequency which appears to be fundamental in all the data presented and hints that the silver ions prefer sites similar to those in  $\text{AgI}$ .

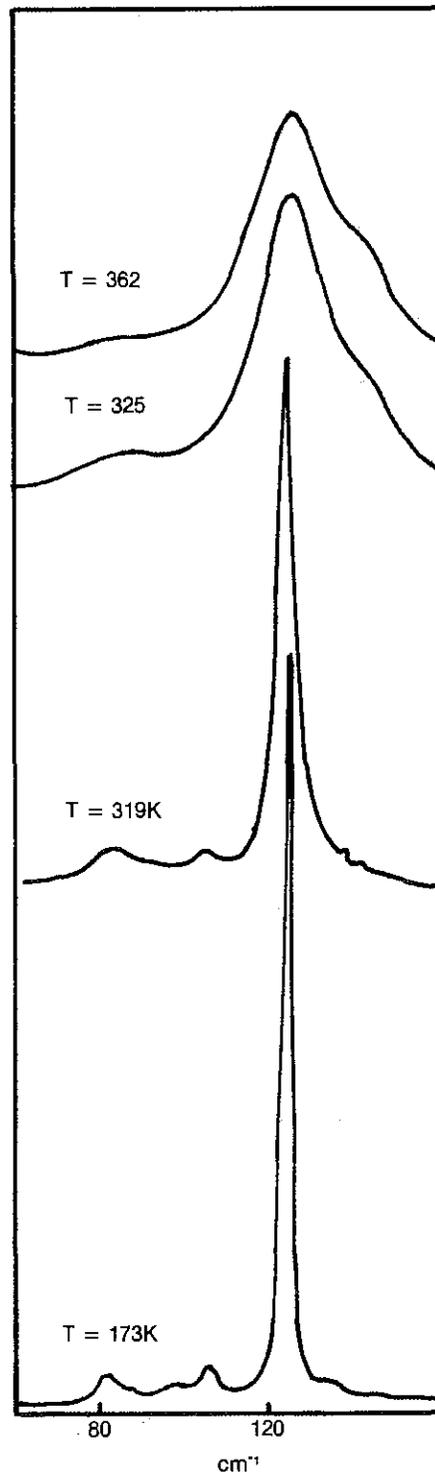


Fig 11 Raman spectrum above and below the phase transition of  $\text{Ag}_2(\text{HgI}_4)$ . The distinct band broadening above 323K identifies it as a potential superionic conductor.

Though  $\text{AgI}$  and  $\text{RbAg}_4\text{I}_5$  exhibit some striking similarities, a complete theoretical treatment of the light-scattering process in ionic conductors hasn't surfaced yet. But the expanding search for a link between spectra and cation motion has uncovered other solid electrolytes, such as  $\beta$ -alumina, which may very well propel an efficient electric car out of the realm of pipe dreams. Regardless of the outcome, research into AgI-type compounds has already produced some practical fallout.

D.F. Shriver et al [24] have already proposed Raman scattering as a screening technique for solid electrolyte candidates in preference to NMR which is limited by the absence of suitable nuclear properties in the mobile ions. Their spectra of  $\text{Ag}_2(\text{Hgl}_4)$  appears in Fig 11. As this material is heated in its  $\beta$ -phase, the by-now-familiar peak at about  $110\text{ cm}^{-1}$  begins to broaden till it merges with the peak at  $84\text{ cm}^{-1}$  as the temperature crosses the phase transition point which happens at  $323\text{K}$ . Note the drastic behavior of the  $123\text{ cm}^{-1}$  peak in the  $\alpha$ -phase. Not only has it broadened considerably, but a distinct shoulder rises at about  $141\text{ cm}^{-1}$ . This characteristic of line broadening, as we have seen time after time, can come with the loss of long-range order in the crystal above a phase transition, and so it tags the material as a potential superionic conductor. It's a straightforward procedure to run Raman spectra of a compound at a series of temperatures and, though the test does not guarantee the material will be a suitable electrolyte, it is an excellent screening tool indicating whether further, more complex tests are warranted.

Our last word on solid electrolytes is that a working chemical cell has already been built and tested by Takahashi and Yamamoto [25]. The design appears in Fig 12 and has the composition

$\text{Ag}/\text{RbAg}_4\text{I}_5/\text{Ag}_2\text{Te}$ ,  $\text{RbAg}_4\text{I}_5$  and graphite.

At present, the output of this cell is too inconsistent to make it a practical power source. Yet the design is responsive to miniaturization and the cell could be incorporated into an electronic circuit as an analog memory element, or as a coulometer to monitor the energy consumed by the components.

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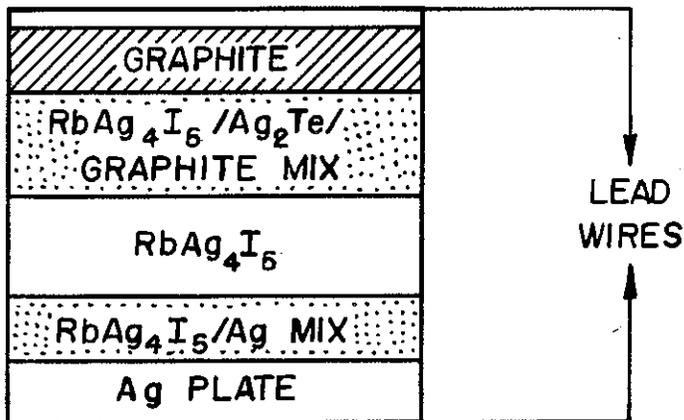


Fig 12 Schematic diagram of the electrochemical cell built by Takahashi and Yamamoto from superionic solid electrolytes.

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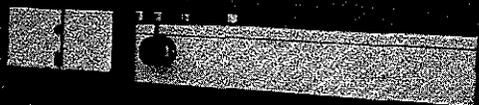
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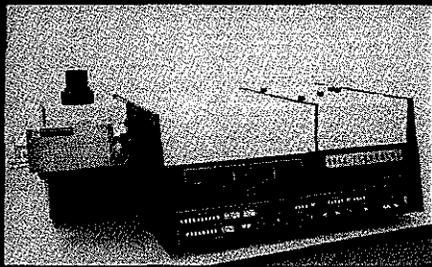
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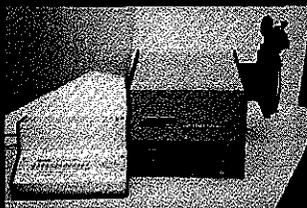
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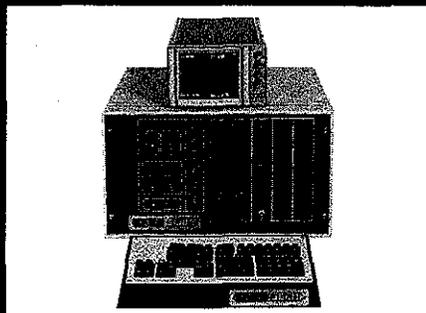
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