Semiconducting Properties of Tetramethylammonium Polyiodides and the Irradiation Effect*

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Polyiodides, a remarkable group of salts, are of the MI_n type, in which M is one of the larger alkali metal ions, a substituted ammonium ion or an arsonium ion, and $n=3$, 4, 5, 7 or 9. In triiodide crystals of a kown structure, the triiodide anions exist as separated individuals. In the higher polyiodides, the anion assembly is made up of a number of sub-units (I^-, I_3^- and I_2 molecules) which are loosely held together to form the more complex I_n system. The triiodide ion has been found to be linear in a number of salts with a large cation.(1) In tetramethylammonium pentaiodide,(2) there are approximately square nets of iodine atoms. An even more complex arrangement is found in tetramethylammonium enneaiodide;(3) five-ninths of the iodine atoms form rather densely-packed layers, while the remaining iodine atoms exist in the form of diatomic iodine pairs, which act as props between those layers. It is to be expected that the electrical behavior of polyiodide crystals will change in parallel with the transition in the nature of the intermolecular or interionic bond in polyiodides; I_3^- ions exist in more or less isolated units, I_5^- ions exist in a layered structure, and I_9^- ions form a three-dimensional network. It was pointed out in a preceding paper that, in organic polyiodides, the electrical resistivity and the activation energy for electronic conduction decreases with the increasing number of iodine atoms in the polyiodide ion, the influence of the cations being of subordinate importance.(4) The present study is concerned with the interrelation between the crystal structure and the electrical behavior in tetramethylammonium polyiodides and especially with the anisotropy of electrical properties in different crystallographic directions.

The effects of irradiation with charged particles or neutrons on semiconducting properties have been studied extensively for many semiconductors; such investigations have provided valuable information above the defects which behave as acceptor levels or as donor levels.(5,6) Studies of the effects of high-energy irradiation on electrical properties are also useful for an understanding of the nature of rather weak bonds in solids. Several examples studied in this line in relation to the dielectric relaxation phenomena of some mineral dielectrics have already been reported.(7,8) In the present investigation, the effects of X- and γ-irradiations on the electrical conductivity of tetramethylammonium pentaiodide will be studied.

Experimental

The preparation of the Compounds.—Crystals of tetramethylammonium polyiodide were grown by a

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1) R. C. Mooney and J. S. Slater, *Acta Cryst.*, **12**, 187 (1959).

2) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **75**, (1951).

3) W. J. James, R. J. Hach, D. French and R. E. Rundle, *Acta Cryst.*, **8**, 814 (1955).

4) S. Kusabayashi, H. Mikawa, S. Kawai, M. Uchida and R. Kiriyama, This Bulletin, **37**, 811 (1963).

5) J. W. Cleland, J. H. Crawford, Jr., K. Lark-Horovitz, J. C. Pigg and F. W. Yond, Jr., *Phys. Rev.*, **84**, 861 (1951).

6) H. Y. Fan and K. Lark-Horovitz, "Report of the Conference on Defects in Crystalline Solids," Bristol, 232 (1954).

7) R. Kiriyama and S. Kawai, *Mineral. J.*, **3**, 19 (1960).

8) R. Kiriyama and S. Kawai, *Inst. and Ind. Res. Osaka Univ.*, **21**, 111 (1964).

slow cooling of an alcoholic solution of tetramethylammonium iodide from its boiling point with an excess of iodine, as has been described in a previous report.[4)] Single crystals, composed of thin flakes 0.5—1 mm. thick and suitable for d. c. measurement, were obtained by cooling a solution with an adequate concentration from 80 to 35°C over a period of several weaks. The melting points agreed with those reported in the literature. Each individual crystalline phase was also identified by X-ray diffraction.

Measurements.—The temperature-dependence of anisotropic d. c. conductivity was measured in different crystallographic directions, perpendicular to and parallel to the iodine net in both $(CH_3)_4NI_5$ and $(CH_3)_4NI_9$. In $(CH_3)_4NI_3$, the measurements were carried out in two directions, perpendicular to and parallel to the cleavage plane. Various electrode materials were tested: indium amalgam, copper plate, silver paste and graphite. Graphite powder electrodes were used for the direct current measurement, because it was inert against iodine. The d. c. conductivity of the specimen was measured by a micro-micro ammeter, capable of measuring current down to 10^{-13} amp. with an applied potential of 90 V.

Preliminary experiments showed that iodine sublimed from polyiodide crystal on heating. This sublimation of iodine may be a cause of the time-dependent of the d. c. conduction. The time-dependence current could be avoided by enclosing the sample and electrodes in a 3 cc.-capacity glass tube tightly covered with Teflon plates and silicon grease at both openings. On both edges or both sides of a platy single crystal, graphite powder was pressed through platinum plates with wire springs. The electrode assembly was then put in a shield box connected to the ground side of the circuit in order to eliminate any stray field effects. The temperature was measured with a copper-constantan thermocouple located as close as possible to the specimen. The specimen was heated to about 20°C below the melting point, and then the conductivity measurements were made as it was slowly cooled.

The measurement of the thermoelectric power was also attempted for these materials. A test piece 13 mm. in dameter and about 1—2 mm. thick was molded by pressing the crystalline powder of polyiodide under 5 ton/cm².

Irradiation.—The radiation effect on the electric conductivity of $(CH_3)_4NI_5$ was also investigated. The crystal was subjected to about 4.1×10^6 r. of X-rays from a copper target tube with a beryllium window operated at 15 kVp and 15 mamp. γ-Irradiation was performed at about 5°C in order to avoid the annealing effect which appeared at higher temperatures. A brass container with the specimen was immersed into a water pool, at the bottom of which ^{60}Co has been placed, and kept there for the required period of time. The total dose attained was from 2×10^6 to 10^7 r.

Results and Discussion

The Temperature-dependence of the Conductivity.—When an external electric field was applied below 0°C, the current decreased with time and reached a steady value after 1 min. This phenomenon, however, could not be observed above 0°C, and the relaxation time of the anomalous current observed below 0°C is in the order of sec.-min.

Sufficient ohmic contact is attained with graphite electrodes below about 200 V./cm. of an applied field. As the thin single crystal was brittle and small, the application of a guard ring in order to eliminate the surface leakage current was abandoned. When a single crystal of $(CH_3)_4NI_5$ was kept in an evacuated condition for 20 min. at room temperature, a little iodine sublimed out from the surface of the crystal and a reddish-brown layer of $(CH_3)_4NI_3$ covered the surface of the crystal. This effect was useful as a means of knowing if the surface leakage current, if any, has any influence on activation energy. No change in the activation energy for d. c. conduction was detected, even when a $(CH_3)_4NI_5$ crystal was used which had been kept for 2 hr. in a vacuum prior to the measurement, until the color of the crystal surface changed sufficiently. The activation energies obtained in the present experiment must, therefore, be reliable values for the real bulk conduction.

The variation in the conductivity with the temperature was found to obey the usual equation of electrical conduction:

$$\sigma=\sigma_0\exp(-\varepsilon/2kT)$$

Figure 1 shows the temperature-dependence of the conductivity with an applied field parallel to and perpendicular to the iodine nets in the cases of $(CH_3)_4NI_5$ and $(CH_3)_4NI_9$ and to the cleavage plane in the case of $(CH_3)_4NI_3$. It is noticeable that the systematic increase in the number of iodine atoms within the polyiodide ion from $(CH_3)_4NI_3$ to $(CH_3)_4NI_9$ is accompanied by a gradual increase in the electronic conductivity.

The activation energies calculated from the conductivity data are given in Table I. As for $(CH_3)_4NI_3$, it may be seen in Fig. 1 that the

TABLE I. THE ACTIVATION ENERGY FOR THE CONDUCTIVITY OF TETRAMETHYLAMMONIUM POLYIODIDES

	$\varepsilon_\perp$, eV.*	$\varepsilon_\parallel$, eV.*
Triiodide**	2.15	2.15
Pentaiodide	1.36	1.39
Enneaiodide	1.69	1.36
Solid iodine	1.24—1.3[13)]	

* $\varepsilon_\perp$ ($\varepsilon_\parallel$) is the activation energy obtained in the direction perpendicular (parallel) to the nets of iodine atoms.

** Triiodide; normal and parallel to the cleavege plane.

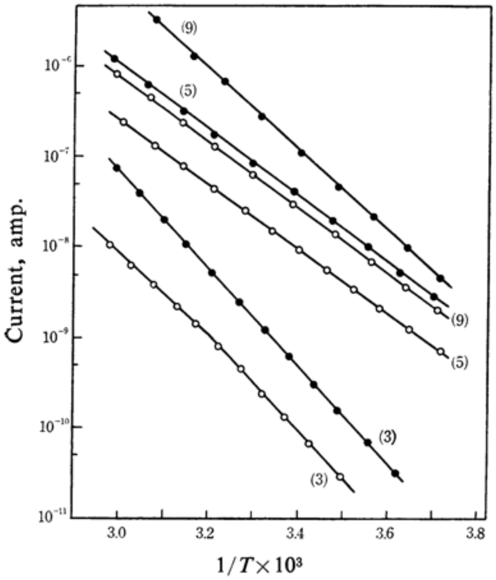

Fig. 1. Temperature-dependence of the electrical conductivity of tetramethylammonium polyiodide. Solid circles indicate the conductivity in the direction perpendicular to the nets of the iodine atoms (pentaiodide and enneaiodide) and to the cleavage planes (triiodide).
Open circles indicate that along the nets (pentaiodide and enneaiodide) and cleavage planes (triiodide). 9) tetramethylammonium enneaiodide, 5) tetramethylammonium pentaiodide, 3) tetramethylammonium triiodide.

plot of the logarithm of the conductivity versus the reciprocal temperature in the direction parallel to the cleavage plane gives two straight lines, with a break around 40°C. The activation energy for the upper part of the break is 1.68 eV., and for the lower part, 2.15 eV. Although a number of runs have been made on several samples, the same results were always obtained, and so, there was a good reproducibility. On the other hand, the temperature-dependence of the conductivity in the direction perpendicular to the cleavage plane gives a single straight line, and the energy of activation is 2.15 eV. It is remarkable that the activation energy in the low temperature range is apparently isotropic. In $(CH_3)_4NI_5$, the activation energy is smaller than that in $(CH_3)_4NI_3$. The values of the activation energy are almost the same both parallel to and perpendicular to the iodine nets. In $(CH_3)_4NI_9$, the values of the activation energy depend on the crystallographic direction; the value perpendicular to the iodine net is larger than that parallel to it, and the latter is the same as that of $(CH_3)_4NI_5$ within the range of experimental error.

Thermoelectric Power.—In order to determine the sign of the majority carriers, preliminary measurements of the thermoelectric power were performed on $(CH_3)_4NI_3$, $(CH_3)_4NI_5$ and $(CH_3)_4NI_9$. For all these compounds, the sign of thermo-voltage suggests that a positive-charge carrier is more mobile than a negative one at room temperature. This is quite analogous to the case of solid iodine, where the hole conduction also seems to be predominant judging from a study of space-charge-limited photocurrent.⁹⁾

The Interrelation between Structure and Conductivity.—The crystal structures of $(CH_3)_4NI_5$ and $(CH_3)_4NI_9$ are similar to that of solid iodine, all the compounds have a layer structure composed of iodine atoms (Figs. 2, 3). In $(CH_3)_4NI_5$, the I—I distances with in the V-shaped I_5^- ion are 2.93 and 3.14 Å, larger than the I—I distance in the I_2 molecule in crystalline iodine (2.68 Å) and considerably smaller than the van der Waals distance. Therefore, the interaction between the iodine atoms within the ions is expected to be strong enough to a partial charge transfer through the resonance of the covalent bond. The shortest distance between neighboring polyiodide ions is shown in Table II, the value for solid iodine being also included for purposes of comparison.¹⁰⁾ The distance between the neighboring polyiodide ions in $(CH_3)_4NI_5$ and also in $(CH_3)_4NI_9$ is shorter than the van der Waals distance, so some direct inter-anionic bonding must be

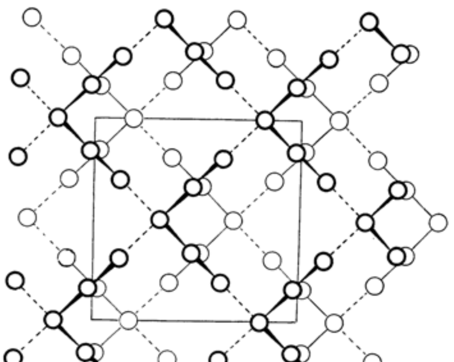

Fig. 2. Projection of the structure of tetramethylammonium pentaiodide on the c-face, showing the nets of iodine atoms in the upper plane and (in fainter line) that in the lower plane.

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9) A. Many, M. Simhony, S. Z. Weisz and J. Levinson, *J. Phys. Chem. Solids*, **22**, 285 (1961); A. Many, S. Z. Weisz and M. Simhony, *Phys. Rev.*, **126**, 1989 (1962).

10) A. I. Kitaigorodskii, T. L. Khotsyanova and Yu. T. Struchkov, *Zhur. Fiz. Khim.*, **27**, 780 (1953).

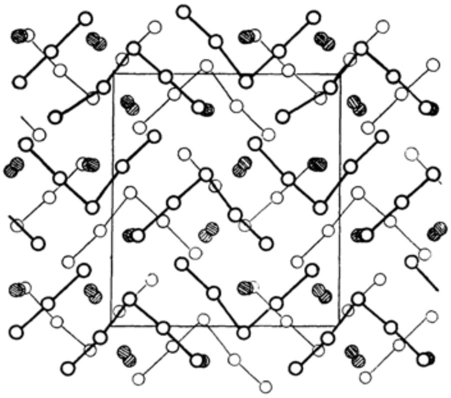

Fig. 3. Projection of the structure of tetramethylammonium enneaiodide on $(10\bar{1})$, showing the nets of iodine atoms in the upper plane and (in fainter line) that in the lower plane.

TABLE II. SHORTEST DISTANCE BETWEEN NEIGHBORING POLYIODIDE IONS

Anion	Cation	Distance, Å
Triiodide	Tetraphenylarsonium*	5.29
Triiodide	Cesium*	4.03
Pentaiodide	Tetramethylammonium	3.63
Enneaiodide	Tetramethylammonium	3.47, 3.67
Solid iodine		3.56

* Since the value in $(CH_3)_4NI_3$ has not yet been reported, the values in CsI_3 and $(C_6H_5)_4AsI_3$ are shown.

involved. The bond angle within and between polyiodide ions, 90° and 180° respectively, is direct evidence for the covalent nature originated by p orbitals of iodine atoms, as in solid iodine.11,12)

The distance between polyiodide ions in a single net in $(CH_3)_4NI_5$, 3.63 Å, is slightly larger than the I_2—I_2 distance reported for the I_2 crystal, 3.56 Å. It is, therefore, understandable that the activation energy for $(CH_3)_4NI_5$ (1.36—1.39 eV.) is somewhat higher than that for solid iodine (1.24—1.30 eV., the energy separation between π^* and σ^* bands).13) It may be expected that the fundamental process of the conduction will be the same in both polyiodide and solid iodine.

When different polyiodides are compared, it is interesting to note that the shorter the shortest distance between polyiodide ions, the smaller the activation energy for hole conduction. The energy band gaps are considered, therefore, to be determined essentially by the shortest distance between polyiodide ions.

The activation energy in $(CH_3)_4NI_5$ is almost the same both parallel to and perpendicular to the iodine net. The mechanism of electrical transport perpendicular to the layer is difficult to explain in the terms of a hopping mechanism because of the marked anisotropy of the atomic arrangement; that is, the distance between iodine layers is about 0.7 Å longer even than the interatomic distance in the layer. The semiconducting nature across the iodine layer in $(CH_3)_4NI_5$ suggests that the adjacent layers are held not only by the van der Waals force but also by another sort of intermolecular interaction. Although the shorter atomic distance of 4 Å between the layered iodine and the nearest molecular iodine I_2 interleaved in the $(CH_3)_4 \cdot NI_9$ lattice is shorter than that of the interlayer spacing of $(CH_3)_4NI_5$, the activation energy perpendicular to the layer of $(CH_3)_4NI_9$ is 0.3 eV. larger than that parallel to the layer. This discrepancy may be attributed to the following causes. The first is the imperfection of the crystal; that is, some sorts of stacking disorder in the direction perpendicular to the sheets should occur, because I_2 molecules lying between the layers sublime out rather easily. The second is that the I—I distance within the interleaved I_2 molecule is almost equal to that observed in the gaseous I_2 molecule. Thus the interatomic interaction within the iodine net through the interleaved I_2 molecule in $(CH_3)_4NI_9$ must be relatively weak compared with that between layers in $(CH_3)_4NI_5$.

As has been stated previously, an anomalous current was observed below 0°C, one which was characterized by the relaxation time in the order of sec.-min. Such a time-dependent polarization phenomenon is due to the relative displacement of ionic species rather than to than of electrons or holes.

Radiation Effects on Semiconducting Properties.—Since $(CH_3)_4NI_5$ forms a typical layer structure and is more stable than $(CH_3)_4NI_9$, the meaurements were carried out mainly on $(CH_3)_4NI_5$. It is interesting to note that the radiation-induced effect on the electrical conductivity is significantly different between X-rays and γ-rays; X-rays exert an increasing effect on the conductivity, while γ-rays exert a decreasing one.

The conductivity and the temperature-dependence of the crystal subjected to about 4.1×10^6 r. of X-rays are shown in Fig. 4. The X-rays used here are perfectly absorbed at the surface region of the crystalline specimen, because the absorption coefficient of iodine is very large. It seems, therefore, likely that the radiation damage caused by the incident X-rays is concentrated near the surface exposed to X-rays. In Fig. 4, the open circles on a

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11) R. Bersohn, *J. Chem. Phys.*, **36**, 3445 (1962).

12) J. L. Rosenberg, ibid., **40**, 1707 (1964).

13) T. S. Moss, "Photoconductivity in the Elements," Butterworths Scientific Publications, London (1952).

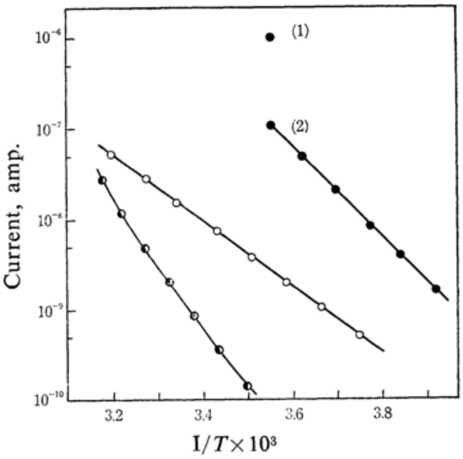

Fig. 4. Irradiation Effects on the temperature-dependence of the conductivity of tetramethylammonium pentaiodide with electric field along the nets of iodine atoms.
Open circles indicate unirradiated specimen. Solid circles indicate X-irradiated specimen 1) just after X-irradiation, 2) after about 24 hr. ◑ indicate r-irradiated specimen.

straight line denote the unirradiated specimen and the solid ones, the X-irradiated specimen. It is clear from this figure that the irradiation with X-rays considerably increases the conductivity. If the temperature of the irradiated specimen is raised above room temperature, an appreciable portion of the increment of conductivity will gradually vanish. The activation energy for the conduction of the annealed specimen, however, is greater than that of the unirradiated one (Table III).

TABLE III. ACTIVATION ENERGY FOR THE CONDUCTIVITY OF TETRAMETHYLAMMONIUM PENTAIODIDE IRRADIATED BY X- AND γ-RAYS

	$\varepsilon_{\parallel}$, eV.*	$\varepsilon_{\perp}$, eV.*
After the annealing for 24 hr. at room temp., X-irradiation of 4×10^6 r.	2.1	—
γ-rays, 2×10^6 r.	1.93	—
γ-rays, 4.8×10^6 r.	1.90	—
γ-rays, 1.2×10^7 r.	1.87	1.96
After annealing at 46°C, γ-irradiation of 4.8×10^6 r.	1.90	—

* $\varepsilon_{\perp}$ ($\varepsilon_{\parallel}$) is the activation energy obtained in the direction perpendicular (parallel) to the nets of iodine atoms.

The temperature-dependence of the conductivity of a γ-irradiated specimen exposed to about 2×10^6 r. is shown in Fig. 4. The conductivity is now actually lowered, and the apparent activation energy for the conduction is larger than that for the original specimen. However, the conductivity of the γ-irradiated specimen increases gradually with time when kept at room temperature. It happens, therefore, that the apparent activation evergy (3.12 eV.) of the γ-irradiated sample calculated directly from the $\log_{10} R$ against T^{-1} plot for the heating cycle includes the activation energy for the spontaneous change of the conductivity; the value must be larger than the true one. It has been found that a temperature of measurement of about 0°C or less is required in order to avoid such an annealing effect. Therefore, the true temperature-dependence of the conductivity of the irradiated materials should be measured in a low temperature region, thus avoiding any annealing process. The activation energies obtained for the specimens irradiated up to 1.2×10^7 r. are almost the same in both directions, parallel to and perpendicular to the iodine net (Table III).

If an irradiated crystal is stored at particular temperature, an appreciable portion of the radiation-induced change in conductivity is annealed out slowly, at a rate depending on the annealing temperature, and the value reaches a steady value asymptotically (Fig. 5b, 6). The curves of Fig. 6 indicate two types

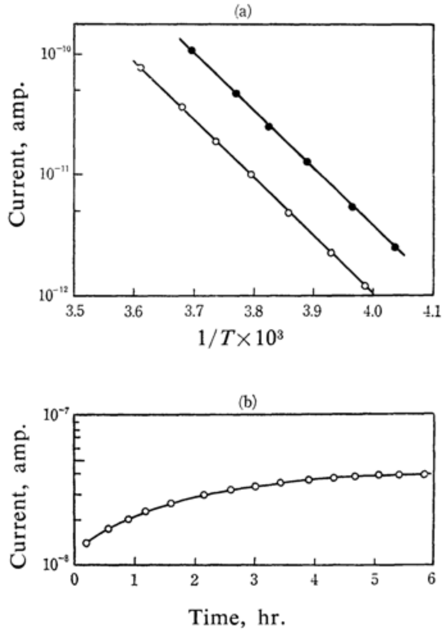

Fig. 5. Effects of annealing on the conductivity of specimen exposed to γ-rays of 4.8×10^6 r.
(a) Open circles indicate the temperature-dependence of the conductivity below 0°C just after γ-irradiation, solid circles that of specimen annealed out for about 8 hr. at 46°C.
(b) The variation of the conductivity of γ-irradiated specimen with time at 46°C.

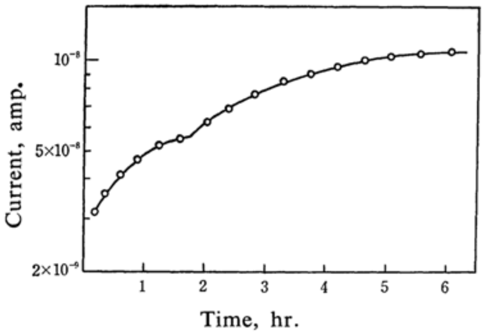

Fig. 6. The variation of the conductivity with time at 40°C for specimen irradiated by γ-rays of 4.8×10^6 r.

of annealing process; (i) at a higher annealing temperature, the curve is monotonous, (ii) when the temperature of annealing is decreased, there seems to be a tendency to have an intermediate step. Therefore, it is suggested that there are two separate processes involved in the recovering of the radiation-induced change. Such a long period of time was required for annealing at far lower temperatures that no exact measurements of the rate of annealing could be made. The magnitude of the conductivity at the starting point of annealing can, however, be estimated on the basis of the coductivity data obtained in the temperature region lower than 0°C. The logarithm of time taken to reach half the initial value in the second-stage annealing is plotted as a function of $1/T$. The $\log_{10} T_{1/2}$ versus T^{-1} plot is linear (Fig. 7). The activation energy obtained in the $k=A\exp(-E/kT)$ expression from the slope of the line in Fig. 7 is 1.55 eV.

The true activation energy thus estimated does not change between before and after the annealing, as Fig. 5 shows. It may be concluded that two types of radiation effects exist together, the first being a radiation-induced change which is gradually annealed out, even at room temperature, and the second being an effect which remains unchanged, even up to about 70°C.

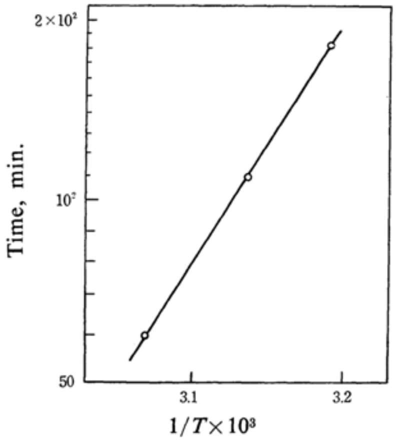

Fig. 7. The time to reach half the initial conductivity plotted as a function of $1/T$ for tetramethylammonium pentaiodide.

Possible Lattic Imperfections Produced by X- and γ-Irradiation.—Upon X-irradiation the conductivity of $(CH_3)_4NI_5$ increased, whereas upon γ-irradiation the conductivity decreased. Such facts can be understood if one assumes that the number of holes in the valence band is increased or decreased by the respective irradiations. The addition of acceptor levels below the Fermi level will increase the hole concentration in p-type semiconductors like $(CH_3)_4NI_5$, while, on the other hand, the addition of donor levels above the Fermi level will reduce the hole concentration in p-type semiconductors.

The passing of X-rays or γ-rays through the specimen must bring about extensive ionization and/or electronic excitation in the crystal lattice, which in turn will lead to bond rupture or bond rearrangement and atomic displacement. Cations, like I^+ or $I_2{}^+$, will be formed easily by the ionization action of moderate X-rays. These charged ions may act as an acceptor level in the crystal. Bond rearrangement will be caused, especially by γ-irradiation, as a resuls of the slight atomic displacement in the iodine net. Consequently, some anions, like $I_2{}^-$ or $I_3{}^-$, may appear in the original polyiodide lattic.

The value of the activation energy of annealing may serve as a clue for the explanation of the conduction mechanism, although the true features of the actual radiation damage will be considerably complicated. The good agreement between the activation energy of annealing, 1.55 eV., and the bond energy in the iodine molecule, 1.57 eV.,[14] suggests that the dissociation of the I_2 molecule takes place in the second stage of annealing. If the formation of the iodine molecule, I_2, in several sites of the iodine net is a true picture of the γ-irradiated effect, the electrical conduction in the original pentaiodide crystal, which may be attributed in part to some sort of charge transfer between V-shaped $I_5{}^-$ ions, will decrease to a certain extent because of the presence of the isolated I_2 molecule.

No significant change was observed in the diffraction pattern of the polyiodide crystal between before and after the irradiation. Therefore, the atomic displacement or the damage caused by irradiation must be negligibly

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[14] L. P. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, New York, (1960), p. 81.

small within the limits of diffractometer-sensitivity. Thus, it may be concluded that the main effect of the irradiation is the local formation of ions in the matrices of the complex overlapping of the electron clouds of polyiodide ions.

Summary

Measurements of the temperature-dependence of d.c. conductivity have been made with tetramethylammonium polyiodide in different crystallographic directions, perpendicular to and parallel to the nets of iodine atoms. The systematic increase in the number of iodine atoms from tetramethylammonium triiodide to tetramethylammonium enneaiodide is accompanied by a gradual increase in conductivity. The activation energy for the conductivity along the iodine net is determined mainly by the shortest distance between polyiodide ions. Such as in the case of crystalline iodine, hole conduction is predominant in polyiodide crystals. From the standpoint of structural considerations and the values of the activation energies, the fundamental process in the hole conduction seems essentially be the same in both polyiodides and solid elementary iodine.

The irradiation effects on the electrical conduction may be classified distinctly into two types: (i) the effects of irradiation which can easily be removed by annealing above about 30°C, and (ii) the effects which can not be overcome by heat treatment below 70°C. The conductivity increases on X-irradiation, indicating the production of some acceptor levels, while the conductivity decreases with γ-irradiation, a phenomenon which may be attributed to some sort of donor level formation.

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