and (32) and (33) for the surface heating effects become

$$\text{Joule:}\quad q_J \equiv -\rho_s d(J_i n_i)^2, \quad (40)$$

$$\text{Peltier:}\quad q_P \equiv -(\Pi_{ij}{}^R J_j{}^R - \Pi_{ij}{}^X J_j{}^X)n_i. \quad (41)$$

(Surface effects)

DISCUSSION

Starting with the isotropic theory of thermoelectricity we have postulated the fundamental relations (8) and from these have deduced without further assumptions the Ehrenfest-Rutgers equations (21). In addition, the irreversible effects of heat conduction and Joulean heat generation are included in the present theory in a natural way. Using our equations it is an easy matter to set down various boundary conditions appropriate to a given experimental arrangement, and thus one can easily derive the ordinary Kelvin symmetry relations which, as first shown clearly by Kohler,[7] are correct only for isothermal boundary conditions. If one applies adiabatic boundary conditions, he can derive more general relations which have been found by Kohler to give better agreement with experiment.

The author wishes to thank Mr. Erik Klokholm and Dr. D. P. Detwiler for several helpful discussions in connection with this work. Also, he wishes to express his appreciation for the encouragement as well as financial support he has received from the Squier Signal Laboratories. Finally, he thanks Dr. F. C. Nix for his continued interest and encouragement in the author's work.

PHYSICAL REVIEW VOLUME 92, NUMBER 4 NOVEMBER 15, 1953

Change of Electrical Conductivity of Sodium Chloride upon Bombardment with High-Energy Protons*

EDGAR A. PEARLSTEIN
Carnegie Institute of Technology, Pittsburgh, Pennsylvania
(Received July 15, 1953)

The conductivity of NaCl in the region 125°C to 400°C is considerably decreased by bombardment at room temperature with 10^{15} protons/cm^2 of energy 350 Mev. There are several temperatures where part of the effect anneals. A small decrease in conductivity still remains after heating to as high as 470°C. No satisfactory explanation for the results is evident.

A new method of measuring conductivity is described.

THE generally accepted picture of electrical conductivity of alkali halides is a motion of ions associated with the presence of lattice defects. Since nuclear radiation is known to produce lattice defects, it is of interest to study the conductivity of irradiated crystals and the annealing of the changes at various temperatures.

Single crystals of sodium chloride (obtained from the Harshaw Chemical Company) were bombarded with 350-Mev protons in the Carnegie Institute of Technology synchrocyclotron. Crystals of the order of a millimeter thick and a few square centimeters area were placed inside the cyclotron's vacuum chamber in the direct path of the circulating proton beam. Aluminum foil mounted alongside the crystals was used to measure the amount of irradiation by means of the reaction $Al^{27}(p,3pn)Na^{24}$.[1] It is estimated that the temperature of the crystals probably did not get higher than about 50°C during irradiation. Most crystals had been annealed in a helium atmosphere at 650°C after cleaving and before irradiation.

The conductivity measuring apparatus is shown in Fig. 1. This circuit compares the resistance of the crystal with the input resistance of the oscilloscope. This particular arrangement allows one to observe any polarization effects and to eliminate trouble with dc amplifier drift, or the capacitance of the crystals. The conductivity was measured over the temperature range from about 125° to 470°C, the lower limit being determined by the sensitivity of the apparatus, and the upper limit by failure of the electrodes on the crystal. The crystal holder holds two specimens at the same temperature so that a bombarded crystal can be directly compared with a "control" crystal (cut from the same large crystal as the bombarded one) which has not been bombarded. This gives one confidence about the reproducibility of the data. The maximum resistance detectable with the apparatus as shown is 2×10^{11} ohms. Electrodes were either graphite ("Dag") or silver conducting paint (Dupont 4817).

RESULTS

Figure 2 shows typical results, expressed as the ratio of the conductivity of a control crystal to that of an irradiated crystal. The arrows indicate time, the sequence starting from top left. The figure shows that there are several ranges of temperature where healing

* This work is supported by the U. S. Atomic Energy Commission. The results reported here were briefly described by the author at the meeting of the American Physical Society in Durham, North Carolina, March 28, 1953 [Phys. Rev. 91, 244 (1953)].

[1] L. Marquez, Phys. Rev. 86, 405 (1952).

takes place; it takes about one hour for healing at these temperatures. There are some ranges of temperature where there is no perceptible healing in several hours: 200° to 250° and 350° to 470°C. After all of this heat treatment, the conductivity at low temperatures is completely restored, but at higher temperatures it is still about 25 percent below that of an unirradiated crystal, as shown at the bottom of Fig. 2. This behavior is found in several specimens, having different amounts of bombardment in the vicinity of 10^{15} protons/cm^2. At present, nothing can be said about the dependence of the effects upon the amount of bombardment.

The bombarded crystals are strongly colored, and are kept in the dark after removal from the cyclotron. One specimen was partially bleached by exposure to skylight for several hours. Its conductivity was then measured. No differences were noted between it and a specimen which had not been bleached. Bombarded crystals are completely bleached, as far as the naked eye can tell, by heating to about 200°C.

DISCUSSION

It might seem that bombardment would increase the conductivity of an ionic crystal, since the conductivity is ionic, and heavy particle bombardment should produce extra vacancies. Calculations based on the formulas of Seitz[2] indicate that each 350-Mev proton should produce about three sodium vacancies per centimeter of path. As Fig. 2 shows, the conductivity is appreciably decreased rather than increased by the bombardment.

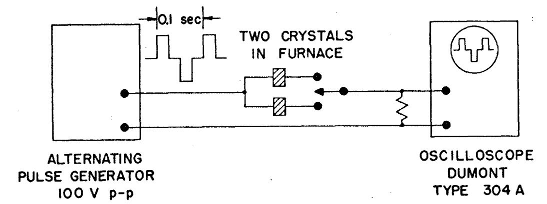

FIG. 1. Apparatus for measuring conductivity.

These results are not in good agreement with the results of Nelson, Sproull, and Caswell[3] at Oak Ridge. They irradiated potassium chloride crystals with gamma rays from cobalt 60, and fast neutrons from a pile. They got both increases and decreases in conductivity, depending on conditions. But in all cases annealing of the change in conductivity was almost complete after a few hours at 200°C. Differences between their results and the results reported in this paper might be caused by differences in material, or type, energy, and amount of radiation. (The amount of irradiation received in our experiment is, of course, very small when compared to, say, pile irradiation.) Also interesting in this connection is the work of Mapother,[4] who found that self-diffusion of NaCl was decreased during x-ray irradiation.

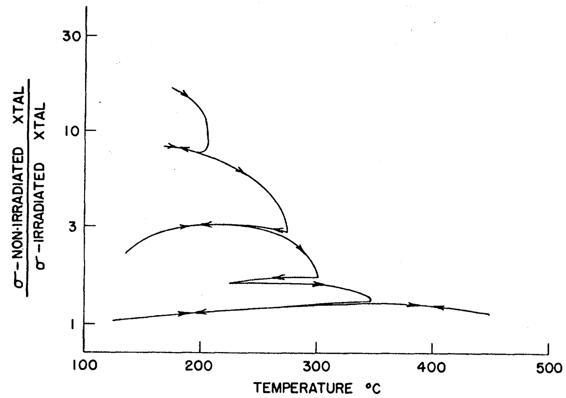

FIG. 2. Relative conductivity *vs* temperature for NaCl crystal irradiated with about 10^{15} protons/cm^2. The measurements started at the highest point on the curve and proceeded in time as indicated by the arrows.

It is hard to visualize a satisfactory mechanism to account for these results. Mechanisms involving only the electrical neutralization of vacancies by electrons or holes and non-equilibrium concentration of vacancies seem unlikely in view of the difficulty of completely annealing the specimens. Perhaps the motion of vacancies is impeded by mechanical distortions of the lattice in the vicinity of interstitial atoms or clusters of interstitials and/or vacancies; however it is possible that such distortions might have the net result of increasing, rather than decreasing the mobility of ions.[5]

It is intended to pursue this problem further with quantitative studies of annealing, dependence of the effects on the amount of bombardment, and correlation with optical effects.

The author is grateful to Professor R. Smoluchowski for advice and discussions.

[2] F. Seitz, Discussions Faraday Soc. No. 5 (1949).

[3] Nelson, Sproull, and Caswell, Phys. Rev. **90**, 364 (1953). Also, private communication.

[4] D. E. Mapother, Phys. Rev. **89**, 1231 (1953).

[5] A. W. Overhauser, Phys. Rev. **90**, 398 (1953).