

## Silver Bromide Crystal Counters\*†

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Single crystals of silver bromide and mixed crystals of sodium and silver chloride have been used to count ionizing radiation. The energy per ion pair in silver bromide for electrons was found to be approximately 5.8 ev. The mobility and the mean free path for the trapping of electrons in the conduction band of silver bromide crystals at 77°K were found to be 210 cm<sup>2</sup>/volt-sec and  $5 \times 10^{-4}$  cm<sup>2</sup>/volt, respectively. A study of the polarization of the counters for beta- and gamma-radiation was also made.

## I. INTRODUCTION

IN 1945, van Heerden<sup>1</sup> found that a single crystal of silver chloride can be used as a counter. Carefully annealed single crystals of silver chloride were placed between electrodes and cooled to liquid nitrogen temperature, where silver chloride is an insulator. With an electric field of several thousand volts per cm across the crystal, the ionization of a single particle or quantum was found to be observable. The magnitude of the pulse was found to be proportional to the energy of the incident particle under proper conditions. Since then there has been considerable interest in the investigation of various substances as counters of this type, and several other substances have been found to be satisfactory crystal counters; i.e., diamond,<sup>2-4</sup> single crystals of zinc sulfide,<sup>5</sup> and a mixed crystal of the bromide and iodide of thallium.<sup>6</sup>

It is the purpose of this paper to add silver bromide and a few other substances to the list of suitable crystal counters and to give an account of some of the properties of silver bromide crystal counters, such as the energy loss per ion pair, the mobility of electrons, and the polarization of silver bromide counters.

## II. EXPERIMENTAL PROCEDURE

## (A) The Growth of the Crystals

Single crystals of silver bromide were prepared from chemically pure silver bromide powder by Bridgman's method.<sup>7</sup> The lower two-thirds of the crystals grown in this way were clear and yellow in color. The upper portion was darker and opaque. In order to see whether or not these were single crystals, the clear portion was etched in a solution of hypo and viewed under strong white light. The crystals were found to be single when viewed in this way. They darkened appreciably when

exposed to white light; however, they regained their color when annealed at a temperature somewhat below the melting point. McFee<sup>8</sup> has investigated the growth of sodium chloride crystals by this method and has found that foreign atoms are concentrated in the upper portion of the crystals when grown in this way. In an effort to grow crystals which would be as free from impurities as possible, the lower portions of those grown from the powder were remelted and the process of growth repeated. These recrystallized samples were much lighter in color and had less tendency to darken on exposure to white light. The crystals used in these experiments are third and fourth crystallizations. They were pale yellow in color and had very little tendency to darken even when exposed to bright white light for several hours. The darkening mentioned previously is probably associated with the presence of impurities. All of the crystals, including those grown directly from the powder, were observed to count beta- and gamma-rays when properly annealed and cooled to liquid nitrogen temperature.

## (B) The Annealing of the Crystals

A silver bromide crystal that had been protected as much as possible from white light was cooled to liquid nitrogen temperature before annealing. When exposed to gamma-radiation from radium no pulses were observed. It was then heated in an annealing furnace to 380°C and cooled to room temperature in about 16 hours. When cooled to liquid nitrogen temperature and then exposed to gamma-rays it was observed to count. Similar behavior has been observed by van Heerden in silver chloride and by Hofstadter in a mixed crystal of thallium bromide and thallium iodide. Another crystal cut from the same sample was heated to about 300°C and cooled to room temperature in about 8 hours. This crystal, when cooled, responded to beta- and gamma-radiation; however, the pulse heights were about a third of those observed in the previous case. In order to establish a satisfactory annealing procedure the state of strain of a crystal of silver bromide was observed, as the temperature of the crystal was raised, by observing its strain pattern through crossed Nicol prisms. A sodium arc lamp was used as a light source in order to

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<sup>1</sup> P. J. van Heerden, *The Crystal Counter*, Utrecht Dissertation, 1945.<sup>2</sup> Wooldridge Ahearn, and Burton, *Phys. Rev.* **71**, 913 (1947).<sup>3</sup> L. F. Curtiss and B. W. Brown, *Phys. Rev.* **72**, 643 (1947).<sup>4</sup> Friedman, Birks, and Gauvin, *Phys. Rev.* **73**, 186 (1948).<sup>5</sup> A. J. Ahearn, *Phys. Rev.* **73**, 1113 (1948).<sup>6</sup> R. Hofstadter, *Phys. Rev.* **72**, 1120 (1947).<sup>7</sup> P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **60**, 305 (1925).<sup>8</sup> R. H. McFee, *J. Chem. Phys.* **15**, 856 (1947).

produce as little darkening as possible. Two plane parallel surfaces were cut on the sides of a crystal 0.8 cm thick, and the strain pattern was obtained on a photographic plate through the side of the crystal. It was found that strains begin to disappear at about 300°C and disappear rapidly above 350°C. Even at these high temperatures a longer exposure brought out some structure. The crystal was then cooled to room temperature in about 15 hours and a strain pattern obtained. This pattern showed very little change in cooling to room temperature in this manner. It was also found that there was no appreciable change in the strain pattern of the crystal on cooling the crystal to liquid nitrogen temperature in a period as short as a half hour. Also, repeated cooling from room temperature to liquid nitrogen temperature without annealing did not appreciably affect either the strain patterns or the counting properties of the crystal. The crystals were handled in a way similar to that described by Haynes.<sup>9</sup> A typical annealing schedule adopted for these crystals is shown in Fig. 1. Crystals annealed in this way were found to be quite uniform in their response to radiation.

### III. RESULTS AND DISCUSSION<sup>10</sup>

#### (A) The Energy Loss per Ion Pair

The energy loss per ion pair can be defined as the ratio of the energy of the incident particle to the number of secondary electrons produced by the particle in the absorbing medium. In the case of a gas this quantity is known to have a value of about 30 ev. Van Heerden has found that the analogous quantity in single crystals of silver chloride is 7.6 ev for beta-particles, a value which is considerably lower than that in a gas.

The energy loss per ion pair for beta-particles stopped by single crystals of silver bromide was determined in the following manner. Beta-particles from P<sup>32</sup> which have a maximum energy of 1.71 Mev were used as the source of radiation. The maximum pulse heights obtained from this source at four different values of electric field ranging from 1000 to 4000 volts/cm were estimated from photographs of the pulses. Figure 2 shows typical pulses obtained. These pulses were assumed to be due to 1.71-Mev beta-particles. The pulse heights were calibrated by comparison with pulses from a precision pulser. The number of electrons freed by the beta-particles was obtained from this data by comparison with the theoretical saturation curve of Hecht:<sup>11</sup>

$$N = N_0 \frac{\omega}{d} \left[ 1 - \exp\left(-\frac{d - \frac{1}{2}\epsilon}{\omega}\right) \right]. \quad (1)$$

This relation assumes that electrons are trapped in trapping centers which are distributed uniformly

<sup>9</sup> J. R. Haynes, Rev. Sci. Instr. **19**, 51 (1948).

<sup>10</sup> The apparatus used for this study was designed and built by R. Hofstadter. It is described in Nucleonics **4**, No. 4 (1949).

<sup>11</sup> K. Hecht, Z. Physik **77**, 235 (1932).

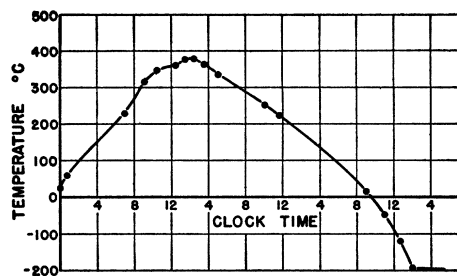


FIG. 1. Typical annealing and cooling schedule used for silver bromide crystal counters.

throughout the crystal.  $N_0$  is the number of electrons released by the beta-particles.  $N$  is the effective number of electrons contributing to the pulse height; that is,  $N = CV/e$ , where  $C$  is the crystal capacitance,  $V$  the pulse height in volts, and  $e$  the electronic charge.  $\omega$  is the mean free path for the trapping of electrons,  $d$  is the crystal thickness, and  $\epsilon$  is the penetration of the beta-particles into the crystal.

By fitting a curve of this type to the data obtained, one obtains values for  $N_0$  and  $\omega$ . The energy per ion pair is then  $(1.7 \times 10^6 / N_0)$  ev. The energy loss per ion pair at saturation fields for single crystals of silver bromide was found in this way to be 5.8 ev, a value lower than that found for silver chloride. The accuracy of this measurement is estimated to be within 10 percent. It is interesting to compare the energy loss per ion pair for silver chloride with the energy required to raise an electron from the filled band to the conduction band; i.e., the energy corresponding to the edge of the continuous optical absorption region. In the silver halides the position of this absorption edge is approximated by the position of the excitation levels, which are quite close to the absorption edge. From the

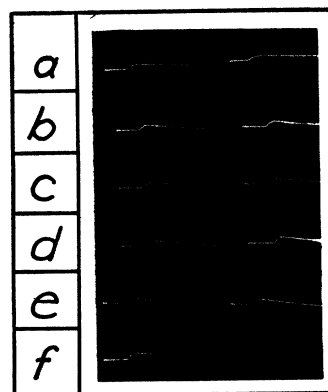


FIG. 2. Traces of typical pulses obtained from silver bromide crystal counters for energetic beta-particles from P<sup>32</sup>. Traces *a*, *b*, *c*, *d* were obtained at electric field strengths of 1870, 2730, 3640, and 4550 volts/cm, respectively. Traces *e* are due to a precision pulser with a rise time faster than that of the amplifier system. Traces *f* are due to gamma-rays from radium at a field strength of 3640 volts/cm.

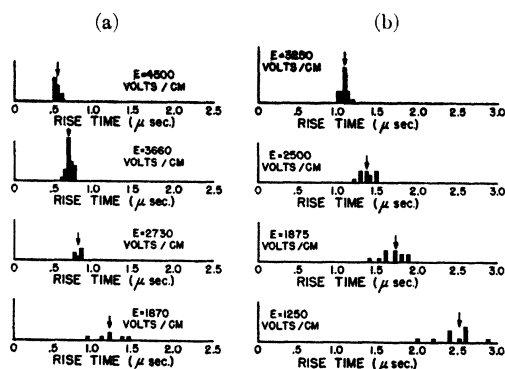


FIG. 3. The rise times of silver bromide crystal counter pulses due to energetic beta-particles from  $P^{32}$  observed at various field strengths. (a) crystal thickness 0.55 cm. (b) crystal thickness 0.8 cm. Each unit square represents one observation.

observations of Fesefeldt and Gyulai,<sup>12</sup> the continuous absorption edge for silver chloride occurs at about 5 ev and for silver bromide at about 4 ev. This is consistent with a lower value for the energy loss per ion pair in silver bromide as compared with that in silver chloride. It can also be said that approximately two-thirds of the energy of the incident beta-particle is effective in producing secondary electrons in both silver chloride and silver bromide, whereas in a gas such as hydrogen, about half of the energy of the incident particle is effective in freeing electrons.

The fact that saturation characteristics are obtained from the pulse size as the field is raised does not necessarily mean that most of the secondary electrons traverse the thickness of the crystal as the field is raised to saturation values. It would be possible that strains, etc., form one or more barriers in the crystal through

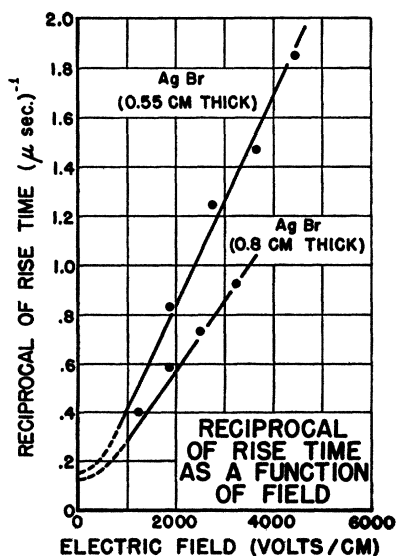


FIG. 4. Average rise times observed at various field strengths in two silver bromide crystal counters of different thicknesses.

<sup>12</sup> H. Fesefeldt and Z. Gyulai, *Nachr. Ges. Wiss. Göttingen* (1929), p. 226.

which electrons will not pass even at high fields. The pulse size in this case would also show saturation characteristics as the field is raised. However, the fact that the energy required to raise an electron from the filled band to the conduction band is relatively large, being about two thirds the energy loss per ion pair, indicates strongly that such barriers do not exist and that most of the secondary electrons do traverse the thickness of the crystal at field strengths that produce saturation in the pulse heights.

A value of  $5 \times 10^{-4}$  cm<sup>2</sup>/volt was found for the trapping mean free path for the secondary electrons from the curve fitting procedure. The uncertainty in this determination is somewhat greater than that for the energy per ion pair. This value is of the same order of magnitude as that found for silver chloride by Lehfeldt,<sup>13</sup> i.e.,  $4 \times 10^{-4}$  cm<sup>2</sup>/volt.

### (B) The Mobility of the Electrons

If the value of the electric field applied across the crystal is sufficiently high so that the mean free path for the trapping of secondary electrons is of the same order or larger than the thickness of the crystal, so that most of the secondary electrons travel the full thickness of the crystal, the rise time of the pulses is the time required for these electrons to traverse this distance. Thus, under these conditions the mobility of the electrons in the conduction band (the velocity of drift in unit field) can be obtained from a study of the rise times of the pulses. It can be seen from Fig. 2 that the slope of the pulse rise is reasonably constant indicating that most of the electrons do traverse the thickness of the crystal with a constant drift velocity. The mobility of electrons in silver bromide crystals at 77°K was determined in this way for two crystals, one 0.55 cm thick and the other 0.8 cm thick. The rise times of the pulses corresponding to various electric field strengths were measured for a number of pulses at each value of field. Figure 3 gives the results obtained in the form of histograms. It can be seen that the rise times measured in this way do not show a unique value at each value of field but rather a distribution about a mean value. This dispersion in the values of the rise times is seen to be greater at the lower field values. The dispersion in the values for the rise times is larger than the estimated error in measurement, being approximately two and five times the estimated error in measurement at the high and low values of field, respectively. It is unlikely that this dispersion is due to slight differences in the distances traveled by the electrons because one would then expect a correlation between the rise times and the corresponding pulse heights, slightly smaller pulses showing a faster rise time. No such correlation was found. Fluctuation in noise can, in general, give such a distribution;<sup>14</sup> however, it is felt that the dispersion is greater than can be accounted for by noise because the

<sup>13</sup> W. Lehfeldt, *Nachr. Ges. Wiss. Göttingen* (1935), p. 171.

<sup>14</sup> Suggested by R. H. Dicke.

peak noise level was only about 5 percent of the pulse height. It is possible that strains and other imperfections in the crystals cause local regions in which the mobilities are altered; that is, these imperfections may not be sufficient to cause appreciable trapping of electrons but may be sufficient to affect the mobility appreciably. In the absence of more complete knowledge, the mean value of the rise times at each field strength was estimated and used as the basis for the determination of the mobility. Figure 4 gives the results as a plot of the reciprocals of the average rise times as a function of the electric field strength. The mobilities obtained for the two crystals are 208 and 213 cm<sup>2</sup>/sec-volt for the 0.55-cm and 0.8-cm crystal, respectively. Correction has been made for the finite penetration of the beta-particles. The internal agreement is satisfactory. A Fröhlich-Mott formula, modified by Bardeen,<sup>15</sup> for the mobility of electrons in the conduction band of ionic crystals given in Eq. (2) gives a value of 308 cm<sup>2</sup>/sec-volt in silver bromide at 77°K. The agreement with the theoretical value is reasonable. A further study of mobilities at different temperatures and for other substances is contemplated.

$$v = 2 \left( \frac{3}{\pi m k \theta} \right)^{\frac{1}{2}} e a_0 (e^{\theta/T} - 1) \frac{K K_0}{K - K_0}, \quad (2)$$

where  $\theta = (hc/k\lambda)(K/K_0)^{\frac{1}{2}}$ .  $\lambda$  is the absorption eigenwavelength = 124 microns (Barnes),<sup>16</sup>  $T$  is the absolute temperature, and  $a_0$  is the radius of first Bohr orbit. The effective mass of the electron,  $m$ , in the conduction band is taken to be the mass of the free electron.

### (C) Polarization Effect

The polarization effect in crystal counters, which can be observed as a gradual decrease in pulse height as the number of counted events increases, is of interest because it limits the usefulness of these counters in many applications.

A preliminary study of the polarization effect in silver bromide counters due to beta-particles from P<sup>32</sup>, which produce ionization in a thin layer of the crystals, and to gamma-rays from radium, which produce essentially volume ionization in these crystals, was made by observing the counting rate as a function of the number of events counted. A discriminator was used to exclude pulses smaller than a given height. In both cases, the counting rate decreased slowly as the number of counted events increased. The decrease in counting rate was more rapid for gamma-rays than for beta-particles. However, after prolonged exposure to the radiation, the counting rate became erratic and rose considerably above the initial counting rate in both cases. At low discriminator levels, a little above noise level, spurious counts appeared after a much smaller number of counts than at higher discriminator

levels; however, in all cases spurious counts were observed eventually. It is believed that these spurious counts arise from an increase in the conductivity of the crystal. Observation of the conductivity of the crystal by means of a sensitive galvanometer showed that the conductivity does increase with exposure of the crystal to radiation and does so in an erratic manner, similar to the behavior of the counting rate. Subsequent warming of the crystal to room temperature and re-cooling to liquid nitrogen temperature restored the insulating properties of the crystal considerably.

In order to investigate the polarization effect more fully, a ten-channel discriminator was used to obtain pulse height distributions as a function of the number of counted events. Figure 5 gives the results obtained for beta- and gamma-rays. The polarization effect was evaluated from these data in the following manner. The pulse height is proportional to the total distance

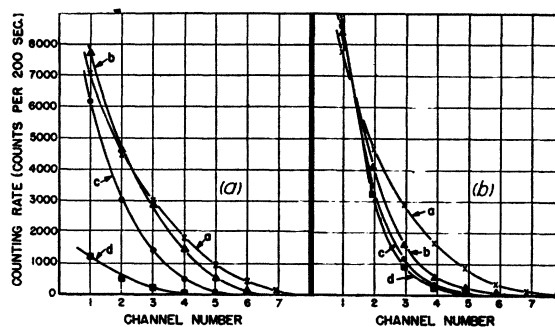


FIG. 5. Pulse-height distribution curves for beta-particles from P<sup>32</sup> and gamma-rays from radium obtained by means of a ten-channel discriminator. The channel number is proportional to pulse height. Pulses larger than 10 volts were counted, and the channel width was 10 volts. (a) Beta-particles from P<sup>32</sup>. Effective crystal area—0.4 sq cm; Crystal thickness—0.6 cm; Field strength—3300 volts/cm. Curve a after 40,000 counts, curve b after  $0.2 \times 10^6$  counts, curve c after  $0.5 \times 10^6$  counts, and curve d after  $0.7 \times 10^6$  counts. (b) Gamma-rays from radium. Effective crystal area—1 sq cm; Crystal thickness—0.7 cm; Field strength—2860 volts/cm. Curve a after 20,000 counts, curve b after  $0.25 \times 10^6$  counts, curve c after  $0.5 \times 10^6$  counts, and curve d after  $0.75 \times 10^6$  counts.

traveled by the secondary electrons. From these data we cannot follow the effect of polarization on a pulse due to a given energy radiation; however, we can obtain the over-all effect of polarization on all the pulses by observing the change in the pulse height distribution with the number of particles counted. The total distance,  $D$ , traveled by the secondary electrons released in unit time by the radiation is proportional to<sup>17</sup>

$$\sum_{\text{channel number}} (\text{counting rate})(\text{channel number}).$$

The behavior of  $D$  with the number of counted events gives the over-all effect of polarization on the pulse heights. Figure 6 gives the results for beta- and gamma-rays. It can be seen that the polarization occurs much

<sup>15</sup> J. Bardeen, by private communication to R. Hofstadter.

<sup>16</sup> R. B. Barnes, Z. Physik **75**, 732 (1932).

<sup>17</sup> The channel number is proportional to the pulse height, and thus to the total distance traveled by the electrons for a given pulse.

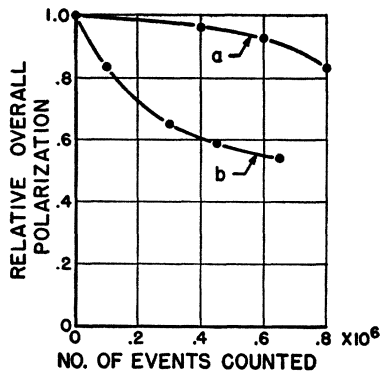


FIG. 6. Over-all polarization effect caused by (a) beta-particles from  $P^{32}$  (surface ionization), and (b) gamma-rays from radium (volume ionization). Data reduced for crystal area of 1 sq cm.

more quickly for gamma-rays (volume ionization), than for beta-particles (surface ionization).

The general behavior of the polarization effect for beta- and gamma-radiation can be accounted for along the lines suggested by Hofstadter.<sup>18</sup> The positive holes left by the displacement of electrons by the field do not move in the field.<sup>13</sup> Thus, a positive space charge builds up in the crystal with the number of events counted. Also, at near saturation fields, most of the electrons traverse the full thickness of the crystal and do not contribute very much to the space charge. Thus, the initial polarization effect can be ascribed to the positive space charge alone. The effect of the positive space charge is to change the potential distribution in the crystal, resulting in regions in the crystal where the electric field, and thus the mean free path for the trapping of electrons,  $\omega$ , is small. Of course, there will be regions where the electric field is higher than the original value; however, this does not affect the pulse size appreciably at near saturation fields.

In the case of beta-particles for which the ionization takes place in a thin layer of the crystal, the positive space charge is localized in this thin layer. The net result is to increase the field strength in the region of positive space charge above the original value and to reduce it in the remaining region of the crystal. Thus, the decrease in the pulse height can be attributed to a decrease in the mean free path in the region of the crystal outside the region of positive space charge. Assuming a uniform distribution of positive holes in a layer of crystal thickness,  $t$ , it can be shown that the mean free path is

$$\omega = [E_0 - (2nel/kd)]vT, \quad (3)$$

where  $E_0$  is the original field strength,  $n$  is the number of secondary electrons,  $d$  is the thickness of the crystal, and  $T$  is the average time for which an electron is free. It can be seen that the reduction in the mean free path depends on the relative thickness of the region of space charge as compared to the thickness of the crystal.

For example, polarization effects are thus expected to occur more slowly for alpha-particles, which do not penetrate very deeply into the crystal, than for beta-particles of comparable energies. The pulse heights decrease slowly in the region of saturation fields and more rapidly as the field, and thus the mean free path, reaches a value corresponding to the "knee" of the pulse-height saturation curve given by Eq. (1). This general behavior is shown by the experimental polarization curve for beta-particles.

For gamma-rays the positive space charge is distributed throughout the crystal. Assuming a uniform distribution of space charge, it can be shown that the mean free path for the trapping of electrons is

$$\omega = [E_0 - (2\pi ne/kd)(d - 2x)]vT, \quad (4)$$

where  $E_0$  is the original electric field strength,  $x$  is the position in crystal (positive in direction of motion of secondary electrons), and  $d$  is the crystal thickness. It can be seen that the effect of the positive space charge is to increase the mean free path above the original value in one-half of the crystal and to decrease it in the remaining half. Thus, the pulse heights caused by the motion of electrons in one-half of the crystal (region of large mean free path) are not appreciably affected, while those caused by motion of electrons in the remaining half of the crystal are decreased in height with the number of counted events. This general behavior is shown in the experimental polarization curve in that polarization occurs relatively rapidly at the beginning and then more gradually.

#### (D) Other Crystals

In addition to silver bromide crystals, single mixed crystals of silver chloride and sodium chloride were observed to count beta-particles and gamma-rays. A single crystal of the mixture, containing approximately 15 percent sodium chloride by weight after annealing and cooling to liquid nitrogen temperature, gave pulses approximately one-third the height of silver chloride pulses. Another crystal, containing approximately 50 percent by weight of sodium chloride, gave pulses about  $\frac{1}{8}$  that of the pulses from silver bromide. The fact that mixed crystals of sodium chloride and silver chloride count while sodium chloride crystals do not indicates the following: first, sodium atoms in the lattice of silver chloride crystals do not cause appreciable trapping of electrons; second, the fact that sodium chloride is not a counter cannot be attributed to trapping centers due to impurities in the sodium chloride crystals because a substantial amount of such impurities are present in the mixed crystals.

The author is indebted to Professor R. Hofstadter for his continuous interest and aid in all phases of these experiments. He wishes to thank C. Graves, E. Dexter, L. Hamner, and C. Lambert for their technical aid and H. Schrader for his help with drawings and photographs.

<sup>18</sup> R. Hofstadter, *Nucleonics* 4, No. 4 (1949).

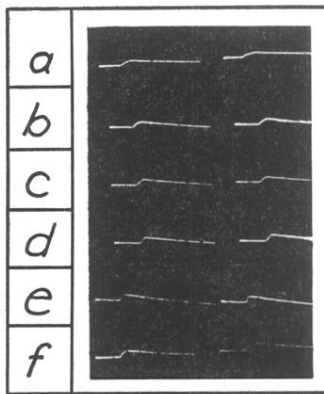


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