$=1.4$, whereas the theory predicts the value 2 for this ratio. In view of the inadequacies of the theoretical model applied to the present case, the agreement between prediction and experience is quite good. For comparison, the results of Steenland suggest that for potassium chromic alum $H_0 \sim 15$ oersteds, and it was found by de Klerk, Steenland, and Gorter[12] that $T_c = 0.004°K$. [The value of T_c obtained by Daniels and Kurti[13] was, however, 0.011°K.]

Garrett[14] has recently extended Van Vleck's exchange-interaction theory of the antiferromagnetic state and obtained the interesting result that, on this model too, a critical curve is to be expected which is not very different in form from that predicted by the Sauer-Temperley dipole-interaction theory. Garrett's theory, however, predicts unity for the ratio $kT_c/\mu H_0$. Whereas dipole interaction is present and of roughly the same order of magnitude in all low-temperature paramagnetics, exchange interaction appears only in some cases and varies greatly in magnitude in these. Kurti has pointed out[15] that the discrepancy in values of δ/k, the crystalline field splitting, in chromic methylammonium alum derived from adiabatic demagnetization experiments,[5] 0.269 degree, and from the most recent paramagnetic resonance measurements of Baker and Bleaney (unpublished), 0.255 degree, can be resolved if a small amount of anisotropic exchange coupling is assumed to be present in this salt. If this is the case, then exchange contributes about seven times as much as does dipole-interaction to the specific heat in the $1/T^2$ region [$b = CT^2/R = 7\times10^{-3}$ and 10^{-3}, respectively] and might therefore be deduced to be an important factor in bringing about the antiferromagnetic transition. On the other hand, there is no evidence (yet reported) of exchange in the potassium chromic alum. In the case of cobalt ammonium sulfate it is found[3] that the dipole-interaction contribution to the specific heat in the $1/T^2$ region is somewhat greater than the exchange contribution: $b(\text{dipole}) = 1.9\times10^{-3}$ and $b(\text{exchange}) = 0.8\times10^{-3}$.

Thus no clear-cut picture of the relative importance of the two types of interaction in bringing about a transition emerges from the existing experimental data. Their interpretation is hampered by the fact that the much simplified theoretical models treated so far bear little relation to complicated state of affairs existing in actual crystals, where both exchange and dipole-dipole interactions may be present and where the ions themselves are magnetically anisotropic.

[12] de Klerk, Steenland, and Gorter, Physica **15**, 649 (1949).
[13] J. M. Daniels and N. Kurti, Proc. Roy. Soc. (London) **A122**, 243 (1954).
[14] C. G. B. Garrett, J. Chem. Phys. **19**, 1154 (1951).
[15] N. Kurti (private communication).

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Fluorescent Response of NaI(Tl) to Nuclear Radiations*†

F. S. Eby‡ and W. K. Jentschke
University of Illinois, Urbana, Illinois
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The dependence on thallium concentration of the fluorescent response of NaI(Tl) to gamma rays and charged particles has been examined for crystals containing known mole fractions of Tl in the range from 0.00006 to 0.008. Scintillations were detected with a photomultiplier tube and pulses were displayed on an oscilloscope and recorded photographically. Plots of integrated pulse height *vs* energy for alpha-particle excitation show a region of nonlinearity which decreases with increasing Tl concentration. At sufficiently high alpha-particle energies a linear relation is approached for all crystals. No deviations from linearity were observed in plots of pulse height *vs* energy for deuterons or protons in crystals containing a Tl mole fraction of 0.0013. The fluorescent efficiency increases sharply with Tl concentration for mole fractions smaller than about 0.0015 and decreases for higher concentrations, this behavior being more pronounced for deuteron than for alpha-particle excitation. Four separate decay processes characterize the pulse shapes. In addition to the main part of the pulse, which has a rise time (mean life) of about 5.9×10^{-8} sec and a long, concentration dependent, exponential decay (decay constant 2.3 to 3.5×10^{-7} sec, independent of exciting radiation), there are two faster decays: 1, an emission with a decay constant of 1.2×10^{-8} sec from crystals containing Tl mole fractions less than about 0.0002; and 2, a 1.5×10^{-8} sec decay from high Tl content crystals excited by particles having a large specific energy loss. The emission spectrum consists of two bands centered at about 3500 A and 4100 A, their exact positions depending upon the Tl concentration and shifting toward longer wavelengths with increasing Tl concentration. The 1.2×10^{-8} sec emission is from the short wavelength band, and the other emissions are from the band at 4100 A. The dependence of the integrated pulse height on the Tl concentration and specific energy loss of the exciting particle are discussed, and possible explanations of the various decay processes are suggested.

I. INTRODUCTION

An important factor in determining the fluorescent response of a thallium activated sodium iodide crystal, or more generally any activated alkali halide phosphor, is the magnitude and uniformity of the activator concentration. There is often a considerable variation in the Tl concentration throughout a large

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† A preliminary report of some of the results was given at the Washington meeting of the American Physical Society in May, 1953, Phys. Rev. **91**, 495 (1953).
‡ Now at the University of California Radiation Laboratory, Livermore, California.

NaI(Tl) scintillation crystal, and that this may in some cases materially effect the total fluorescent response for gamma-ray excitation has been shown by the group at the Harshaw Chemical Company.[1]

In the present work we have investigated the Tl concentration dependence of the response for heavy particle and gamma-ray excitation of crystals containing mole fractions of Tl in the range from 0.00006 to 0.008 mole Tl/mole NaI as a function of the energy of the exciting radiation. Previous measurements have shown that the fluorescent response of commercially available NaI(Tl) crystals resulting from excitation by gamma rays, fast electrons, protons, or deuterons increases linearly with the energy of the bombarding particles[2] but that the response to energetic alpha particles deviates from linearity over an energy range of at least 10 Mev.[2,3] In order to determine the Tl concentration dependence of this nonlinearity and to obtain information about the luminescent efficiency for excitation by particles having a high specific energy loss, most of the present measurements of the total fluorescent response were performed using alpha particles.

Measurements of the characteristic decay times and emission spectra for crystals containing different Tl concentrations provide information about the processes taking place within the crystal which are responsible for its luminescence. Decay-time measurements were made for 23-Mev and 4.7-Mev alpha-particle, 11.5-Mev deuteron, and Ni^{60} gamma-ray excitation of the crystals. Radioactive sources were used for gamma rays and low-energy alpha particles. The University of Illinois cyclotron provided a source of high-energy protons, deuterons, and alpha particles.

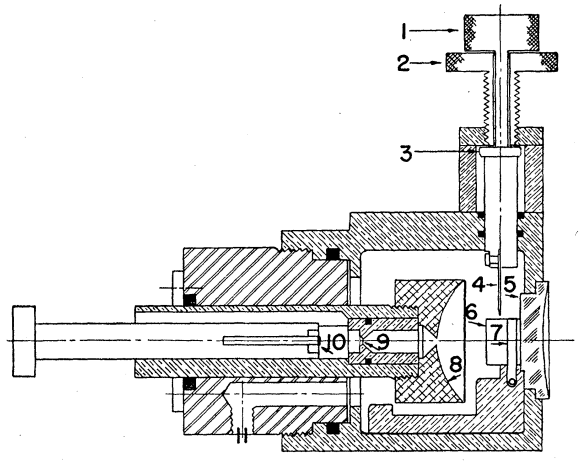

FIG. 1. Chamber used in measurements of scintillation response to low-energy alpha particles. 1, 2—knurled knobs, 3—key, 4—razor edge, 5—Lucite window, 6—NaI(Tl) crystal, 7—retaining strap, 8—hemispherical mirror, 9—foil, 10—Po alpha source, 11—pump-out port. Rotating knurled knob 2 forces piston down and presses razor into the upper edge of crystal cleaving it in two.

All measurements were carried out at room temperature and only prompt ($<10^{-6}$ sec) radiations were observed. Previous accounts of the long-lived radiations from NaI(Tl) have been given by Bonanomi and Rossel[4] and more recently by Emigh and Megill.[5]

II. EXPERIMENTAL PROCEDURE

For the investigation of the response to low-energy alpha particles clear crystals of dimensions 1.2 cm×1.0 cm×0.8 cm were inserted in the chamber shown in Fig. 1. The chamber was evacuated to a pressure of about 10^{-2} mm Hg and the crystals cleaved, exposing a fresh surface to the incident collimated beam of particles from a polonium alpha source. The source was moved along a tube at atmospheric pressure, and the energy of the particles incident on the crystal was determined by the distance of the source from a foil separating the tube and the evacuated chamber and the thickness of the foil. Range-energy curves given by Bethe[6] for alpha particles in air were used in obtaining the energy from the known equivalent air path.

Scintillations from the crystal were observed through a Lucite window with a selected RCA 5819 photomultiplier tube. A hemispherical mirror behind the crystal served to increase the efficiency of light collection, and a drop of oil (Dow Corning 703 fluid) between the crystal surface and the window was used to increase the optical contact between these surfaces. Output pulses from the photomultiplier tube were integrated with an *RC* time constant of 5×10^{-6} sec and fed into a Los Alamos type model 100 pluse amplifier[7] whose gain settings were selected to maintain the output pulse heights in the known linear regions of amplification. Data were recorded by making time exposures of the pulses displayed on the triggered sweep of an oscilloscope (Tektronix 511). Each film was exposed to pulse heights corresponding to several different energies at a common amplifier gain setting and a series of ten voltage calibration lines extending from the base line to 100 volts. A Po alpha source deposited on the vacuum side of the foil furnished particles having an energy of 5.3 Mev, and the resulting pulse heights served as a constant check on the stability of the apparatus.

In order to observe the response to alpha particles of higher energy the chamber was connected directly to the vacuum system at the cyclotron exit port. The magnetically analyzed beam from the cyclotron was collimated by a set of slits 2 mm in diameter and passed through an absorber section containing several movable aluminum absorbers before entering the chamber

[1] Harshaw, Kremers, Stewart, Warburton, and Hay, Atomic Energy Commission Report NYO-1577, September 10, 1952 (unpublished).
[2] Taylor, Jentschke, Remley, Eby, and Kruger, Phys. Rev. **84**, 1034 (1951).
[3] R. H. Loveberg, Phys. Rev. **84**, 852 (1951).
[4] J. Bonanomi and J. Rossel, Helv. Phys. Acta **25**, 725 (1952).
[5] C. R. Emigh and L. R. Megill, Phys. Rev. **93**, 1190 (1954).
[6] H. A. Bethe, Revs. Modern Phys. **22**, 213 (1950).
[7] W. C. Elmore and M. Sands, *Electronics* (McGraw-Hill Book Company, Inc., New York, 1949).

containing the crystal. The response of the crystals to alpha particles of 10, 15, and 23 Mev was observed relative to Po alpha particles from the chamber foil. A more detailed examination of the response of a crystal containing a mole fraction of Tl of 0.0013 was carried out by mounting the crystal directly on the photomultiplier tube which was positioned inside a large evacuated chamber behind an absorber wheel containing 15 different aluminum absorbers. The range-energy curves of Aron, Hoffman, and Williams[8] were used in the determination of the particle energies.

For the observation of luminescent decay times, the crystals and photomultiplier tube were located in a dry air chamber immediately in front of the beam port of the cyclotron. The beam was brought out of the port through a one-mm hole covered by a 1.15 mg/cm^2 polyethylene terephthalate foil and traversed about two cms of air before striking the crystals. A thin Lucite light pipe was employed in front of the 5819 tube to provide a flat surface for mounting the crystals, which were freshly cleaved immediately preceding the data runs. Dow Corning 200 fluid was used between the crystals and Lucite and between the Lucite and photomultiplier tube for improving optical contact. The signal taken from the last dynode of the 5819 was fed directly into the amplifier of a high-speed triggered sweep oscilloscope (Tektronix 517), and the *RC* time constant (about 2×10^{-9} sec) was determined by the 170-ohm input impedance of the oscilloscope and the interdynode and stray capacitances. Pulses appearing on the face of the oscilloscope tube were recorded photographically. Time calibration was provided by a 51-Mc sinusoidal signal from a crystal-controlled oscillator.

For decay-time measurements using gamma-ray excitation the large statistical fluctuations on the pulses made the use of time exposures impractical. The luminescent decay times of a crystal containing a mole fraction of Tl of 0.00095 were obtained for excitation by Ni^{60} gamma rays and Po alpha particles by photographing single pulses on the face of a Tektronix 517 oscilloscope with an oscillograph record camera (Du Mont type 295). Smoothed-out "average" pulses were constructed for gamma rays and for alpha particles by adding together a large number of single pulses.

Emission spectra of the crystals for excitation by 12-Mev H_2^+ ions were observed with a Hilger quartz spectrograph. Freshly cleaved crystals were mounted in a bracket in front of the beam port of the cyclotron. A beam density of about 2×10^{-8} ampere/cm^2 over a circular area of one mm diameter produced sufficient light in the crystals to obtain photographs of the spectra for exposure times of the order of a minute with the spectrograph slit 10 cm in front of the crystal. A wavelength calibration was furnished by a Hg arc source which was positioned between the crystal bracket and the spectrograph.

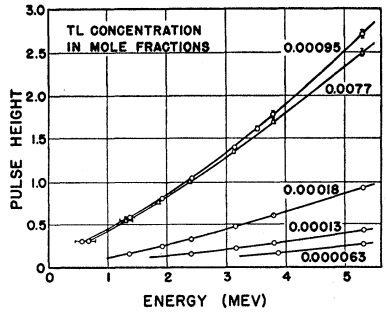

FIG. 2. Pulse heights resulting from low-energy alpha-particle excitation of NaI(Tl) crystals containing various Tl concentrations. The ordinate scale is the same as in Fig. 3.

Approximate values for the Tl concentrations of the crystals, as determined by semiquantitative spectrographic analysis, were obtained from the Larco Nuclear Instrument Company from whom the crystals were purchased. More exact values for the crystals used in the experiments were obtained by several different chemical methods. A tracer technique similar to that discussed by Moreau *et al.*[9] was used in which the Tl was chemically separated from the crystals and later recombined with radioactive I^{131} which was counted. Another and more convenient method of comparable accuracy which was used is the Thionalid method described by Prodinger[10] and others[11,12] in which the crystalline thallium complex ($C_{12}H_{10}ONS$) is precipitated quantitatively from solutions containing tartrate and cyanide. This method is specific for thallium and has a sensitivity of one part in 10^7.

In spite of the fact that high accuracy is possible in determining the total amount of Tl in the samples which are analyzed chemically, the determinations of the Tl concentrations associated with the volumes actually used in the measurements (on the average about 1/50th of the volumes which were analyzed chemically) may be somewhat in error as a result of local variations in the concentration within the crystals.

III. EXPERIMENTAL RESULTS

Pulse Height *vs* Energy and Tl Concentration

The dependence of the mean integrated pulse height on the energy of incident alpha particles having energies of 5.3 Mev or less is shown in Fig. 2 for crystals with five different Tl concentrations. Data for crystals with Tl mole fractions of 0.0025 and 0.0045 were also obtained and lie between the curves shown for crystals with Tl mole fractions of 0.0077 and 0.00095. Pulse heights

[8] Aron, Hoffman, and Williams, Atomic Energy Commission Report AECU-663 (UCRL-121, Second Revision) September 26, 1950 (unpublished).

[9] Moreau, Chovin, and Daudel, Compt. rend. **219**, 127 (1944).

[10] W. Prodinger, *Organic Reagents Used in Quantitative Inorganic Chemistry* (Elsevier Publishing Company, Inc., New York, 1940).

[11] R. Berg and E. S. Fahrenkamp, Z. Anal. Chem. **112**, 162 (1938).

[12] R. Fresenius and G. Jander, Haundbuch der Analytischen Chemie (Springer-Verlag, Berlin, 1942), Vol. 3.

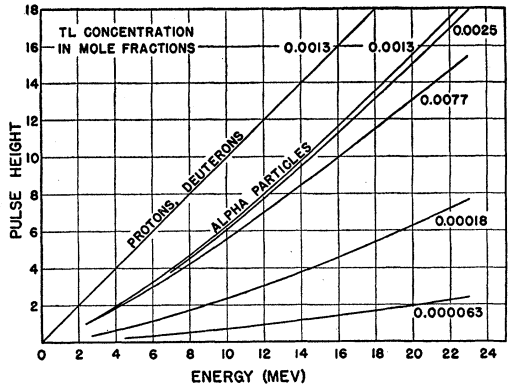

FIG. 3. Pulse heights resulting from alpha-particle and deuteron excitation of NaI(Tl) crystals containing various Tl concentrations.

were measured for two different crystals from the same melt for each Tl concentration. No deviations greater than experimental uncertainties were observed in these measurements, and each of the curves shown has been constructed from the combined data for both crystals.

The uncertainties in pulse heights associated with the points were assigned on the basis of the spread in pulse heights resulting from the finite resolution of the crystal and photomultiplier tube and the spread in alpha-particle energy caused by straggling. Knowledge of the energy coordinate was limited by the accuracy of the experimental determination of the air-equivalent thickness of the chamber foil. Unfortunately, the large uncertainties associated with the low-energy data prevent an accurate overlapping with the measurements of Allison and Casson[13] who determined the response for alpha particles with energies below 0.3 Mev.

Figure 3 shows the response of the various crystals to higher-energy alpha particles, protons, and deuterons. Data for a commercial scintillation crystal (mole fraction of Tl, about 0.0013) were obtained for 15 alpha-particle energies between 4 Mev and 23 Mev. The individual measurements of mean pulse height

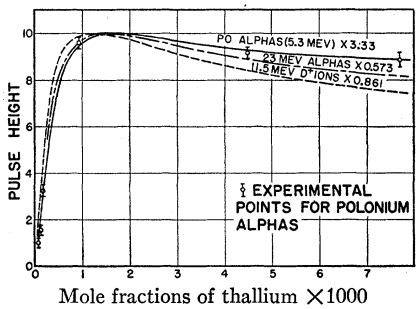

FIG. 4. Variation in pulse height resulting from alpha-particle and deuteron excitation of NaI(Tl) crystals as a function of the Tl concentration.

[13] S. K. Allison and H. Casson, Phys. Rev. **90**, 880 (1953).

were in all cases within one percent of the curve shown. The energy values of the incident cyclotron particles overlap the energy of Po alpha particles which serves as a check point on the low energy side. The response to protons and deuterons was found to be linear within the accuracy of the measurements, in agreement with previous work.[2] The curves for the other crystals were drawn on the basis of the ratios of the measured pulse heights for alpha particles of 10, 15, and 23 Mev relative to Po alpha particles and indicate that the response of NaI(Tl) to alpha particles increases with Tl concentration for mole fractions smaller than about 0.0013 and decreases for higher concentrations. The linearity, however, shows a steady improvement with Tl concentration. This is apparent from plots of the specific fluorescent *vs* the specific energy loss of the particle which are presented later.

A plot of pulse height *vs* Tl concentration for alpha particles of two different energies and deuterons of 11.5 Mev is shown in Fig. 4. The points on the curve

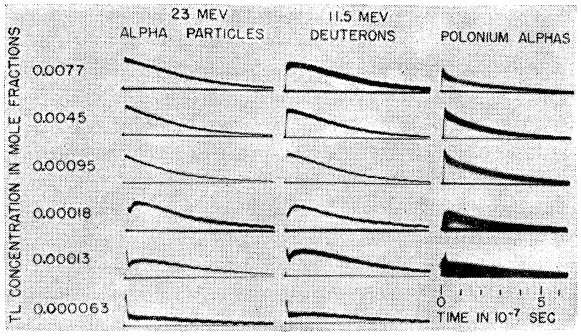

FIG. 5. Oscillograms of pulses (time exposures) resulting from the excitation of NaI(Tl) crystals by deuterons and high- and low-energy alpha particles.

for Po alpha particles are average values obtained for two different crystals from the same melt. The uncertainties associated with the points are based upon the reproducibility of the measurements which is limited by such factors as the crystal geometry, optical coupling, and slight variations in the Tl concentration. The curves for 23-Mev alphas and 11.5-Mev deuterons were derived from the measured ratios of the pulse heights for the energetic particles relative to pulse heights for Po alpha particles. Since pulse heights due to alpha-particle excitation vary in a more nearly proportional manner with the particle energy for high Tl content crystals than for low, the alpha-particle pulse heights in Fig. 4 tend to increase relative to deuteron pulse heights with increasing Tl concentration. The deuteron curve is in agreement with the data obtained by the Harshaw group[1] for Cs^{137} gamma-ray excitation within the accuracy of the respective experiments. This is to be expected in view of the similarity of the pulse heights *vs* energy relations for deuterons and gamma rays.

Luminescent Decay Times and Emission Spectra

Figure 5 shows oscillograms of pulses resulting from the excitation of crystals containing different concentrations of Tl by 23-Mev alpha particles, 11.5-Mev deuterons, and Po alpha particles. Each of the oscillograms represents a time exposure of the oscilloscope face and is made up of between 5000 and 30 000 individual pulses. The pulse heights were adjusted to a convenient size by changing the magnitude of the photomultiplier tube high voltage and were all taken with the same amplifier gain. The ripples superimposed on the 23-Mev alpha and deuteron pulses are due to pick-up from the cyclotron oscillator which was in synchronism with the particle bursts. The leading edges of the pulses are limited by the rise time (approximately 7×10^{-9} sec) of the amplifier, and the pulses can be relied upon to represent quantitatively the rate of light emission from the crystals only for times greater than about 3×10^{-8} sec. For times shorter than this the pulse shapes are to some extent influenced by the characteristics of the amplifier and have only qualitative validity.

Four separate decay processes characterize the pulse shapes: 1, that giving rise to the spike appearing on the leading edges of pulses from crystals with low Tl concentrations; 2, the initial rapid decay of Po alpha pulses for crystals abundant in Tl; 3, the rise of the main pulse; and 4, the relatively long decay of the main pulse. Figure 6 shows the measured exponential rise and decay times (mean lives) of the main pulse as a function of the Tl concentration. The points shown are average values obtained from several sets of data. Times were measured by making enlargements of oscillograms and transferring the ordinates of the traces to semilog paper. The uncertainties indicated in the figure were assigned on the basis of the widths of the traces and reproducibility of measurements made on different crystals from the same melt and represent the extreme values which could reasonably be assigned from any of the oscillograms. The rise-time characteristic of the main pulse is clearly evinced on semilog plots of pulses from both the 23-Mev alphas and the deuterons and, within the accuracy of the measurements is independent of Tl concentration and equal to 5.9×10^{-8} sec. The decay times for a given Tl concentration are the same for alpha particles and deuterons for times greater than about 2×10^{-7} sec after the start of the pulse. No indication was found of the presence of after-pulses on the segments of the curves which were used in the measurements. After-pulses generally do not appear until more than a microsecond after the start of the main pulse in the 5819 tube.[14]

The spike characteristic of low Tl concentration crystals has a decay time (mean life) of about 1.2×10^{-8} sec and the initial fast decay of the Po alpha pulses has a decay time of approximately 1.5×10^{-8} sec.

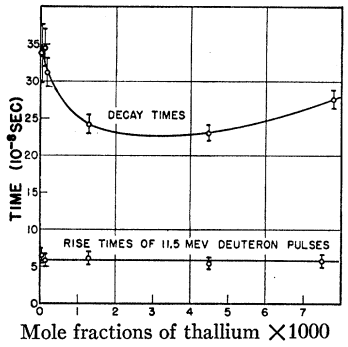

FIG. 6. Rise and decay times (mean-lives) of the main pulse resulting from deuteron excitation of NaI(Tl) crystals as a function of the Tl concentration. The decay times are the same as for excitation by other heavy particles.

The luminescent decay time of a crystal containing a mole fraction of Tl of 0.00095 was determined for Ni^{60} gamma-ray excitation from a smoothed-out "average" pulse which was obtained by numerically adding together a number of single pulses. Figure 7 shows a typical pulse due to a single gamma ray and below it an "average" pulse representing the sum of 75 single pulses. The irregularities of the gamma-ray pulse are the result of statistical fluctuations in the rate of light emission from the crystal. The shape of the smoothed pulse is similar to that observed for deuteron excitation, and the measured decay time is the same within the accuracy of the measurement.

The total emission spectrum, including phosphorescent components as well as prompt radiations, was measured for 11.5-Mev H_2^+ ion excitation of crystals containing various Tl concentrations and was found to consist of two broad bands. For crystals containing a mole fraction of Tl of 0.000063 the emission occurs in a band centered at 4100±50 A with a full width at half maximum of 800±50 A and a band (with about 60 percent of the maximum intensity of the first) centered at 3200±50 A and having a width of 450

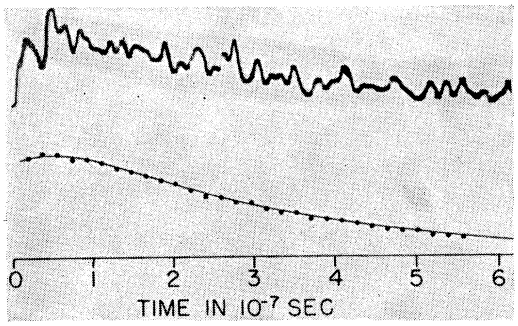

FIG. 7. Oscillogram of a single pulse from a NaI(Tl) crystal (containing a mole fraction of Tl of 0.00095) excited by a gamma ray from a Ni^{60} source and an "average" pulse obtained by adding together 75 single pulses.

[14] J. S. Allen, Los Alamos Report LA-1459, Aug., 1952 (unpublished). See also Mueller, Best, Jackson, and Singletary, Nucleonics **10**, No. 6, 53 (1952).

±50 A. The short wavelength band decreases in relative intensity and shifts toward longer wavelengths with increasing Tl concentration. For a Tl mole fraction of 0.0045 the short wavelength band has a maximum intensity of about 35 percent that of the long wavelength band and is centered at 3430±50 A. The position of the maximum in the long wavelength band is insensitive to the Tl concentration for mole fractions smaller than 0.0045. Our measurements on this band are in agreement with those reported earlier by Hofstadter[15] who excited NaI(Tl) with gamma rays. For a Tl mole fraction of 0.0077 the long-wavelength band is centered about 4400±50 A and has a width at half-maximum of 900±50 A. The short-wavelength band has a relative maximum intensity about 20 percent as great and is centered at about 3450 A. A shift in the wavelength of the emission spectrum with Tl concentration has been found in other alkali halide phosphors and has been described by Pringsheim.[16]

By inserting an appropriate optical filter between the crystal and photomultiplier tube it is possible to observe practically unattenuated the prompt radiation from the short wavelength band and to greatly reduce contributions from the long wavelength band. Pulses were observed from crystals excited by 23-Mev alpha particles alternately with and without a Corning 7–54 Red Purple Corex A filter (89 percent transmission at 3200 A decreasing to 10 percent at 2400 A and at 4000 A). The insertion of the filter between a crystal with a mole fraction of Tl of 0.000063 and the photomultiplier tube resulted in about a 10 percent decrease in the height of the spike on the leading edge and a decrease in the height of the rest of the pulse by a factor of about five with no detectable change in the decay times. The insertion of the filter between the photomultiplier tube and crystals containing mole fractions of Tl greater than 0.00095 decreased the pulse heights by a factor of five or more without detectable changes in either the shapes of the pulses or the decay times. In particular there is no apparent indication of a fast spike component of the pulses from crystals containing Tl mole fractions greater than 0.00018. It should be noted, however, that our experimental equipment was not well suited for such an observation. The heights of the spikes shown on the pulses of Fig. 5 are severely limited both by the response of the 5819 tube (short wave cutoff at about 3100 A) and the relatively slow rise time of the amplifier.

Excitation of a "pure" NaI crystal (mole fraction of Tl less than 10^{-7}) with 11.5-Mev deuterons and 23-Mev alpha particles resulted in pulses similar to the 23-Mev alpha pulse in a crystal with a Tl mole fraction of 0.000063 (Fig. 5). The height of the spike resulting from deuteron excitation was 0.77±0.06 times the height resulting from alpha particle excitation. The two lowest Tl concentration crystals also showed about this ratio. There was no evidence that the decay time of the spike depends upon either the Tl concentration or the specific energy loss of the particle. The intensity of the long component was about the same for deuteron as for alpha particle excitation, as is also the case for crystals with a Tl mole fraction of 0.000063. The maximum intensity of the long component relative to the spike was about one-half that of the pulse shown in Fig. 5 and the decay time of the long component about twice as long as the pulse in Fig. 5.

Two alternative possibilities suggest themselves to account for the absence of the spike component from crystals with high Tl concentrations. Either the processes which give rise to this emission are not present in high Tl content crystals, or the processes are present but the light is absorbed by the Tl before it escapes from the crystal. The long-wave absorption band in NaI(Tl) peaks at 2930 A.[17] In order to decide between these possibilities, experiments were performed with two crystals, one as a scintillator and one as a filter. The use of an RCA type C7140 A end-window photomultiplier tube (short wave cutoff at about 2100 A, relative sensitivity of 55 percent at 3200 A) enhanced the response to the short wavelength radiation by a factor of 2 or 3 relative to the long wavelength component. 23-Mev alpha particles and 11.5-Mev deuterons were used to excite the spike in a "pure" crystal. The pulses were essentially unchanged by the insertion of another pure crystal (about 3 mm thick) between the phototube and the crystal being bombarded. After the insertion of a crystal containing a Tl mole fraction of about 0.001 (also about 3 mm thick) between the phototube and the pure crystal which was bombarded, the spike component was decreased in intensity by a factor of about 3 and the long component remained essentially unchanged.

The fact that the spike was not entirely removed in this case indicates that its absence from crystals with Tl concentrations greater than 0.00018 must be explained by assuming the processes which give rise to this radiation are not present, or are at least not important, in high Tl content crystals. The accuracy of the experiment was not sufficient to ascertain whether or not the energy absorbed by the filter crystal appeared in the long component.

Prolonged bombardment of the crystals by 23-Mev alpha particles (integrated flux of about 10^{14} particles/cm^2) produced no measurable change in the intensity or decay time of the spike component.

IV. DISCUSSION

The response of Tl-activated alkali halide phosphors to excitation by light in the visible and ultraviolet regions has been the subject of numerous experimental

[15] R. Hofstadter, Phys. Rev. **75**, 796 (1949).
[16] P. Pringsheim, Revs. Modern Phys. **14**, 132 (1942).
[17] See, for example, P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

investigations, and in an early theoretical study based on the experimental work of Pohl and his co-workers Seitz[18] interpreted the absorption and emission spectra of these phosphors in terms of the excitation of the thallous ions which were assumed to occur substitutionally in the lattice. Later, Williams[19] succeeded in describing quantitatively the behavior of KCl containing dilute concentrations of Tl and was able to calculate the absorption and emission spectra at various temperatures.

Charged particles, however, lose their energy almost completely to the base material, and very little is known about the details of the mechanism for the transfer of the absorbed energy through the crystal. In addition, it appears that once the luminescent centers have been excited in crystals containing high activator concentrations the radiative processes do not occur in a manner in all ways similar to that exhibited for the optical excitation of crystals containing only small amounts of the activator.

In the following we shall consider the various prompt decay processes ($<10^{-6}$ sec) evident in NaI(Tl), the specific fluorescence as a function of the specific energy loss of the particle, and the dependence of the light emission on the Tl concentration and type of particle responsible for the excitation.

Energy Transfer and Decay Processes

Upon entering the crystal a fast charged particle loses its energy principally to the electronic system producing excitons and free electrons with a wide range of energies, and toward the end of its range a non-negligible fraction of its energy is expended in exciting lattice vibrations. The migration of free electrons, holes, and excitons and certain resonance processes appear as possible mechanisms responsible for the transfer of energy within the crystal. The number and types of centers which are excited evidently depends upon their concentrations and their relative cross sections for intercepting the carriers. During the period of energy migration several different types of excited levels are created whose characteristic de-excitation times can be observed in the pulses.

As was noted earlier the main part of the light pulse is characterized by a rise time of about 5.9×10^{-8} sec and a decay time which depends upon the Tl concentration and varies between 2.3×10^{-7} and 3.5×10^{-7} sec. A minimum of two excited states is necessary to describe this behavior, one state of the luminescent centers (radiative state) and at least one other state, not necessarily associated with luminescent centers, which decays nonradiatively into it. An approximate ratio for the relative initial (before appreciable light is emitted) populations of these states can be estimated by fitting to the deuteron pulses of Fig. 5 curves describing the ordinary radioactive decay law for the radiation of the daughter substance when both the mother and daughter levels are populated at zero time.

The question as to whether the rise or the relatively long decay of the pulse is characteristic of the radiative state cannot be definitely resolved on the basis of the present results. If it is assumed that the rise is characteristic of the radiative state the ratio of the initial populations of the radiative state to the nonradiative state which decays into it varies between about 0.1 and 0.2 having a maximum for a Tl mole fraction of about 0.002. If the alternative assumption is made the ratio ranges between 1 and 3, again with a maximum for a Tl mole fraction of about 0.002.

The fact that in either case the relative initial population of the radiative state increases with Tl concentration for low concentrations, seems to support the supposition that the Tl is indeed the luminescent center. It has been suggested that the function of the Tl is restricted to the trapping process and nonradiative transition.[4] It is difficult to see why, if this is so, the initial population of excited luminescent centers should increase with increasing Tl concentration, unless the actual process is somewhat more complicated than has been assumed here and three states are involved: a nonradiative state, an excited state in Tl, and a short-lived light-emitting state not in Tl.

The dependence of the integrated pulse height on the Tl concentration, which is discussed later, indicates that the rise time of the main pulse (5.9×10^{-8} sec) is probably the one associated with the radiative state and that the relatively long decay is apparently characteristic of the nonradiative state. In this case it must be supposed that most of the energy which is emitted in prompt radiations has passed through the nonradiative state and that the process giving rise to the main part of the pulse is a type of host-sensitized luminescence.[20]

The initial (approximately 1.5×10^{-8} sec) decay characteristic of Po alpha pulses from crystals with Tl mole fractions of 0.00095 and greater apparently represents an additional emission which exists under the conditions of high Tl concentration and large specific energy loss of the primary particle and suggests the possibility that another excited state of the luminescent center can be formed, perhaps by the capture of more than a single carrier during the energy transfer process. In view of the fact that this fast decay was not accentuated on the pulses which were observed after placing an ultraviolet filter between the photomultiplier tube and crystal, which was excited by 23-Mev alpha particles, it must be concluded that the emitted light is not much different in energy than that associated with the level giving rise to the main pulse. Although precise measurements could not be made of the magnitude of the contribution of this emission to the integrated

[18] F. Seitz, J. Chem. Phys. **6**, 150 (1938).
[19] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).
[20] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953) contains references to previous work.

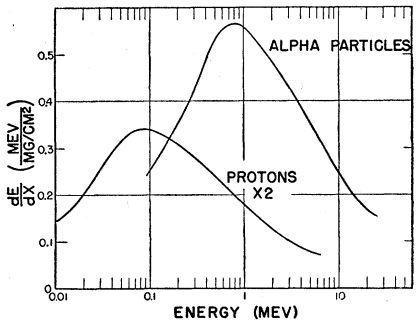

FIG. 8. Specific energy loss for alpha particles and protons in NaI.

pulse height it appears probable that it is to a large extent responsible for the increased linearity of the pulse height *vs* energy relation for high Tl content crystals.

Pulses from crystals containing Tl mole fractions of 0.00018 or smaller are characterized by an additional fast decay not apparent from crystals with higher Tl concentrations. This emission, which lies on the short wavelength side of the main band, is relatively less sensitive to the specific energy loss of the primary particle than the main pulse and is more prominant the lower the Tl concentration. Its presence in a "pure" crystal indicates that it has its origin in the base material. Since the decay time, 1.2×10^{-8} sec, is comparable to the lifetime expected for an exciton in a crystal containing this concentration of impurity atoms[21,22] it seems possible that this emission is associated with the extinction of excitons generated along the particle track. The fact that no strong characteristic luminescence has been observed when an alkali halide crystal is irradiated in the first fundamental band (presumably the most direct means of producing excitons) makes this explanation seem unlikely, however.§ Also the fact that the decay time is insensitive to the Tl concentration and remains essentially unchanged after the crystal has been exposed to prolonged particle bombardment is not in accord with this explanation. The efficiency for the production of this radiation is greater for deuterons than for alpha particles (which have a higher specific energy loss) which suggests that it does not owe its existence to imperfections created by heavily ionizing radiations.‖ Although this radiation was present from crystals containing low Tl concentrations which were obtained from the Larco Nuclear Instrument Co. as well as a "pure" NaI crystal obtained from the Harshaw Chemical Co., the possibility that it arises as a result of some impurity in the crystal cannot be definitely ruled out.

Specific Fluorescence *vs* Specific Energy Loss

The extent to which the specific energy loss of the incident particle influences the efficiency of light production in the crystal may be observed by plotting the specific fluorescence, dL/dx, obtained by differentiating a curve of pulse height *vs* residual range of the particle in NaI, as a function of the specific energy loss, dE/dx, of the incident particle. Unfortunately, the ranges of the particles and values of dE/dx in NaI have not been measured and must be inferred from existing data on other materials.

Figure 8 shows a plot of dE/dx *vs* energy for alpha particles and protons in NaI which has been calculated on the basis of stopping power and range-energy measurements of several different investigators and the assumption of the additivity law for combining the individual values of the stopping powers of Na and I. The dE/dx values for alpha particles with energies less than 2 Mev were constructed from the measured stopping powers of different substances relative to air[23] and the dE/dx values for air as given by Bethe.[24] In the region from 2 to 8.77 Mev the values were found by interpolation of dE/dx *vs* E curves based on ThC′ alpha particle range-energy measurements of Rosenblum.[25] For energies higher than 8.77 Mev Bethe's theoretical expression[24] was used for calculating the stopping powers using experimental values of the mean excitation potentials given by Mano.[26] Values of dE/dx for protons with energies below 2 Mev were obtained by interpolation of available experimental data on the rate of energy loss of protons in various metals,[27] and a point at 6.3 Mev was found by interpolation of the measured stopping power values of Marmier.[28] Values of dE/dx for alpha particles inferred from Aron's[29] theoretical dE/dx values for protons agree within ±5 percent with the values obtained by use of Mano's

[21] D. L. Dexter and W. R. Heller, Phys. Rev. 84, 377 (1951).
[22] F. Seitz, Revs. Modern Phys. 26, 7 (1954) mentions calculations of the lifetime of an exciton by Toyozawa.
§ *Note added in proof.*—No evidence was found of a similar fast fluorescent response from crystals of KI, KCl, or NaCl which were subjected to bombardment by 23-Mev alpha particles. These crystals were all observed to fluoresce weakly when exposed to a 10^{-8} ampere/cm² beam of 6-Mev protons (violet in the case of KI, green for KCl and NaCl, and an intense coloration was produced in the crystals after an exposure of about 15 sec (green in KI, violet in KCl, and yellow in NaCl). This behavior is strikingly different from that of NaI which fluoresces brilliantly (blue) and exhibits no perceptible coloration as a result of the bombardment.

‖ *Note added in proof.*—Subsequent work has shown that this radiation is excited by gamma rays and that the fluorescent efficiency is very nearly the same as for proton or deuteron excitation.
[23] Landolt-Börnstein and Roth-Scheel, *Physikalisch-Chemische Tabellen* (Springer Verlag, Berlin, 1936), fifth edition, Third Supplementary Volume, Second Part.
[24] See for example, E. Segrè, *Experimental Nuclear Physics* (John Wiley and Sons, Inc., New York, 1953), Vol. 1, Part II.
[25] S. Rosenblum, Ann. phys. 10, 408 (1928).
[26] G. Mano, Ann. phys. 1, 407 (1934).
[27] S. K. Allison and S. D. Warshaw, Rev. Modern Phys. 25, 779 (1953).
[28] F. P. Marmier, Helv. Phys. Acta 24, No. 1 (1951).
[29] W. A. Aron, thesis; University of California (UCRL 1325) (unpublished).

values for the excitation potentials in Bethe's formula for the region of alpha particle energies above 16 Mev. At 25 Mev the dE/dx values for alphas in NaI calculated from the works of Aron, Marmier, and Mano are in agreement to within 2 percent. The dE/dx values for alpha particles with energies greater than about 3 Mev seem to be consistent with those shown for protons. For lower energies dE/dx values for alpha particles are smaller than, and not directly comparable with, values for protons because of electron pickup and consequent change in the effective charge of the alpha particle. The curves for protons and for alpha particles with energies greater than 2 Mev are thought to be reliable to within ± 8 percent. The curve for alpha particles with energies less than 2 Mev is not more certain than about ± 10 percent.

Curves of dL/dx *vs* dE/dx are shown in Fig. 9 for crystals with three different Tl concentrations and indicate the amount of light dL emitted as a result of the particle's losing energy dE in traversing a path dx within the crystals. The relative uncertainties associated with the individual curves range from about 5 percent for low values of dE/dx to about 15 percent for the highest dE/dx values.

The straight portions of the curves occurring for low dE/dx values correspond to the region of linear pulse height *vs* energy response. Although the curve representing the Tl mole fraction 0.00018 is nonlinear throughout the energy range in which data were obtained, it seems probable that at sufficiently high alpha particle energies a region of linear response is approached for all the crystals. The range in dE/dx for the curve with a Tl mole fraction of 0.0013 has been extended by the inclusion of data for protons with energies up to 6 Mev. The maximum dE/dx value for protons is approximately that for 18-Mev alpha particles. The extent to which dL/dx is independent of the details of the way in which particle energy is lost is illustrated by the accuracy with which the response of the crystal to low energy alpha particles can be predicted from a knowledge of dE/dx and the dL/dx curve of Fig. 9. Figure 10 shows the measured pulse-height values of Allison and Casson[13]

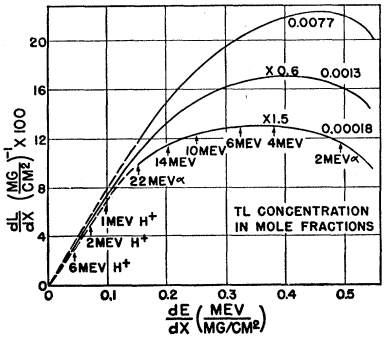

FIG. 9. Variation of the specific fluorescence, dL/dx, of NaI(Tl) with the specific energy loss, dE/dx, of the incident particles. L is in the same units as in Figs 2–4. dx is in mg/cm² of NaI.

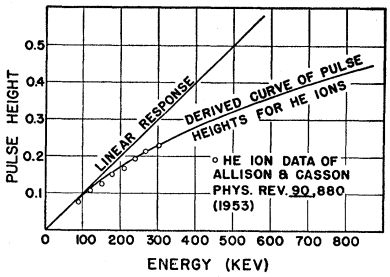

FIG. 10. Pulse heights resulting from excitation of a commercial NaI(Tl) crystal by alpha particles with energies below 350 kev. Pulse height scale is the same as in Figs. 2–4.

and a derived curve using data from Fig. 8 and the curve for a Tl mole fraction of 0.0013 from Fig. 9 with the assumption that dL/dx depends only on dE/dx. Because of the relatively large uncertainties in the low energy region of Fig. 8, the derived curve is probably not more accurate than ± 10–15 percent. Comparison of the pulse heights from low-energy alpha particles and the line representing linear response suggests that the thermal spike[30] produced in the wake of a slow alpha particle can have only slight, if any, deleterious effect on the fluorescent efficiency.

Although the Tl concentration exerts a strong influence on the absolute values of the specific fluorescence, the dependence on dE/dx is relatively insensitive to Tl concentration, and the number of activator ions present within the range of migration of the energy is clearly not the dominant factor responsible for the bending over of the curves for high values of dE/dx in NaI(Tl). The saturation of the specific fluorescence with increasing dE/dx is a characteristic of most of the common scintillators[31] and is usually somewhat more pronounced in organic materials. That the behavior of dL/dx is indeed a property of the bulk material and is not to be associated with "surface effects" has been demonstrated for NaI(Tl) by der Mateosian and Yuan.[32]

For reasons which will be mentioned later, it appears that most of this effect is tracable to processes taking place during the time in which the energy is transferred from the neighborhood of the particle track to the various trapping centers. Simple models of the type which have been used with some success to describe quantitatively the behavior of dL/dx *vs* dE/dx in

[30] A short discussion and references are given in the book by Shockley, Hollomon, Maurer, and Seitz, *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952).

[31] Reference 2; see also G. T. Wright and G. F. J. Garlick, Brit. J. Appl. Phys. 5, 13 (1954); W. T. Link and D. Walker, Proc. Phys. Soc. (London) **A66**, 767 (1953) have given a curve for KI(Tl). The situation in the case of KI(Tl) is somewhat confused. Link and Walker report a deviation from linearity in the pulse height *vs* energy curves for protons and deuterons. The paper by Franzen, Peele, and Sherr, Phys. Rev. **79**, 742 (1950) and preliminary unpublished results of the group at Chalk River (private communication) indicate a linear response.

[32] E. der Mateosian and L. C. L. Yuan, Phys. Rev. **90**, 868 (1953).

organic scintillators are, however, probably not applicable to the case of NaI(Tl) since it is evident that all of the prompt radiations emitted by the crystal do not arise from a single source and that energy is being transferred within the crystal for an appreciable time after the start of the pulse. It would seem that a theoretical treatment taking into account all of the factors which are apparently involved in the energy transfer and emission processes in NaI(Tl) would contain so many parameters that it would not easily lend itself to convincing experimental verification by curves of the type shown in Fig. 9.

Dependence of Light Emission on Tl Concentration and dE/dx of the Primary Particle

The increase in the integrated pulse height with Tl concentration for crystals containing mole fractions of Tl less than about 0.0015 (Fig. 4) is evidently the result of the greater probability for exciting luminescent centers due simply to their increased abundance. The pulse heights resulting from a given excitation tend to decrease, however, for mole fractions greater than about 0.0015. In view of the fact that the emission spectrum shifts toward longer wavelengths with increasing Tl concentration and more nearly matches the response of the photomultiplier tube, the decrease in light intensity for high Tl concentrations is possibly somewhat greater than is indicated by the pulse heights.

In order to explain the decreased fluorescence of phosphors with high activator concentrations, several theories have been proposed[33,34] which postulate that concentration dependent quenching mechanisms compete with the process of light emission in the de-excitation of the luminescent centers. Such processes, if present, might be expected to alter the decay times of the excited centers and to result in faster decays the higher the activator concentration. Although evidence of this behavior is definitely not present in the measured decay times of the pulses (Fig. 6), a decrease in the rise times with Tl concentration sufficient to account for the decrease in the pulse heights, while not obvious, (Fig. 6) is not inconsistent with the present measurements. A concentration-dependent quenching process which takes place before appreciable light has been emitted from the crystals would not be apparent in either the rise or the decay times of the pulses. As has been mentioned previously, the ratio of the initial populations of the radiative to the nonradiative state which decays into it decreases with Tl concentration for mole fractions greater than about 0.002. Although this decrease could be explained by assuming that fewer luminescent centers are excited during the energy transfer process, it is perhaps more plausible to assume that a concentration dependent quenching mechanism operates to deplete the radiative level before appreciable light is emitted.

It seems probable that the pulses rise with a time constant characteristic of the luminescent centers and that the decays of the pulses are determined by the nonradiative states. This assumption is to some extent supported by the fact that the long decay has been found to be present in the luminescence of NaI crystals which were supposedly free of Tl, both in the present work and in the earlier observations of Bonanomi and Rossel.[4] No rise component was apparent in the pulses from pure crystals observed in the present work. The existence of the long decay from pure crystals presumably indicates that the "nonradiative" state may either luminesce weakly or lose its energy to some other imperfections in the crystal which later radiate. It is not entirely clear why the decay time of this state should depend on the Tl concentration in the manner shown in Fig. 6. It seems probable that the decay time decreases with increasing Tl concentration for mole fractions less than about 0.003, mainly as a result of the increased probability for the state's transferring its energy to the luminescent centers as these become more abundant. The subsequent increase in decay time with Tl concentration, however, indicates that other factors must also be considered.

There is no evidence from the present work that the magnitude of the specific energy loss of the primary particle exerts an influence on the decay times of either the radiative or the nonradiative states, as seems to be the case for certain organic phosphors.[35] Although the time constant associated with the rise of the main pulse could not be measured for Po alpha excitation, it was found to be the same, within the accuracy of the measurements, for deuteron and 23-Mev alpha excitation. The decay time (after about 2×10^{-7} sec) is the same for alpha particle and deuteron excitation. Apparently the difference in the relative efficiencies for fluorescence in NaI(Tl) by deuteron or by alpha-particle excitation must be explained entirely on the basis of the probability of exciting the radiative and various nonradiative states during the initial energy transfer process.

The authors would like to acknowledge their indebtedness to Mr. G. de Pasquali who performed the chemical analyses of the crystals which were used in the measurements.

[33] P. D. Johnson and F. E. Williams, J. Chem. Phys. **18**, 1477 (1950).

[34] H. Kallman and M. Furst, Phys. Rev. **79**, 857 (1950).

[35] Bittman, Furst, and Kallmann, Phys. Rev. **87**, 83 (1952).

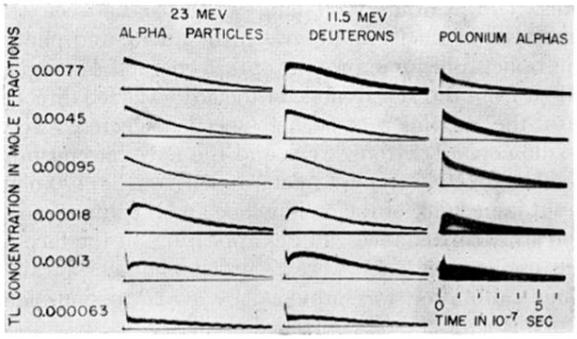

FIG. 5. Oscillograms of pulses (time exposures) resulting from the excitation of NaI(Tl) crystals by deuterons and high- and low-energy alpha particles.

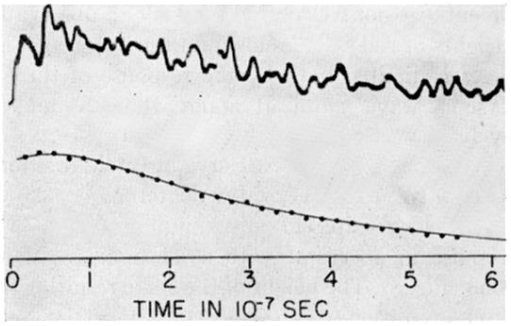

FIG. 7. Oscillogram of a single pulse from a NaI(Tl) crystal (containing a mole fraction of Tl of 0.00095) excited by a gamma ray from a Ni^{60} source and an "average" pulse obtained by adding together 75 single pulses.