Response of Sodium Iodide Crystals to Alpha Particles and Electrons as a Function of Temperature*†

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In an attempt to determine the mechanism causing the lower scintillation efficiency of α particles in NaI(Tl) crystals relative to the scintillation efficiency of electrons, the response of pure NaI and thallium-activated NaI crystals to α particles and electrons was studied as a function of temperature. Crystals were grown for this investigation both by the Bridgman and Kyropoulos methods. The magnitude of the scintillations per unit of energy loss in the crystals varied with temperature in a way which agreed with predictions of qualitative theories. The ratio of the α-particle response to the electron response per unit energy, though a constant with temperature for the crystals grown by the Bridgman method (α response/e^- response $= \sim 0.7$) showed an interesting temperature dependence for crystals grown by the Kyropoulos method. For a "pure" NaI crystal grown by the Kyropoulos method this ratio attained a value as high as 1.5 at $-150°C$, indicating that the α particle was more efficient than the electron at this temperature. In view of this, proposed explanations for the lower efficiency at room temperature such as "local saturation" of scintillation centers or the loss of energy by "hard collisions" are re-examined. A temperature-dependent effect in the resolution of α-particle peaks is also reported and discussed.

INTRODUCTION

THE response of NaI(Tl) crystals to α particles and electrons has been the subject of investigations by several groups.[1,2] There is general agreement that below ~ 10 Mev the scintillations caused by α particles are ~ 0.7 times as large as those caused by electrons for a given energy loss in the crystal. Allison and Casson[1] considered three possible explanations for the lower scintillation efficiency of the α particles: (a) the specific ionization of the α particle is great enough to saturate the luminescence centers in the immediate vicinity of the ionizing event; (b) the spectrum of the light excited by the α particle differs from that of the electrons and is detected less efficiently by the photomultiplier; (c) direct transfer of energy to the atoms of the crystal becomes important for heavier ions and this energy is not available to the scintillation centers. These authors give an involved argument which seems to rule out explanation (a), they did not test explanation (b), and they present evidence showing that explanation (c) might be important for ions as heavy as neon. Eby and Jentschke[2] concluded from a study of the fluorescent response of NaI(Tl) to ionizing particles as a function of thallium concentration that the difference in the relative efficiencies for scintillations must be explained "entirely on the basis of the probability of exciting the radiative and various nonradiative states during the initial transfer process." Some recent work on the fluorescence of alkali halides[3] suggested to us that it

would be of interest to determine this relative scintillation efficiency for α particles and electrons in unactivated NaI crystals and to see how this efficiency varies with temperature for both pure and thallium-activated NaI crystals.

EXPERIMENTAL DETAILS

Our previous experience with the detection of α particles in NaI(Tl) crystals taught us that one can obtain well resolved peaks if the α source is dispersed throughout the scintillation crystal.[4] In the present work the scintillation crystals under investigation were grown by the Bridgman and Kyropoulos methods.[5,6] In all cases, an α source was added to the melt so that activity was uniformly dispersed throughout the resulting crystals. In the Bridgman method the powdered materials from which the crystal is to be formed are placed in a Vycor glass vessel, attached to a vacuum system, and heated to drive off all water of hydration. The vessel is then sealed under vacuum and suspended in a tubular electric furnace which is supported in a vertical position. The temperature in the center of the oven is maintained at $50°C$ above the melting point of the material of the host crystal (in this case NaI) while the vessel is slowly lowered out of the furnace into a cool region at the rate of ~ 0.25 in. hr^{-1}. This method generally produces large single crystals.

In the Kyropoulos method, one melts the powdered materials in a crucible, and dips a cooled pointed rod into the surface of the melt. A crystal forms on the cool tip of the rod. The latter is slowly withdrawn, a portion of the crystal being kept in contact with the melt. With NaI melts, we produced by this method clear

[1] S. K. Allison and H. Casson, Phys. Rev. **90**, 880 (1953).
[2] F. S. Eby and W. K. Jentschke, Phys. Rev. **96**, 911 (1954).
[3] J. Bonanomi, Helv. Phys. Acta **25**, 725 (1952); B. Hahn and J. Rossel, Helv. Phys. Acta **26**, 271 (1953). The increase in the scintillation efficiency of NaI at low temperatures first reported

by the above authors has been confirmed by the present authors, Phys. Rev. **95**, 598(A) (1954), and by W. Van Sciver and R. Hofstadter, Phys. Rev. **97**, 1181 (1955).

[4] E. der Mateosian and L. Yuan, Phys. Rev. **90**, 868 (1953).
[5] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).
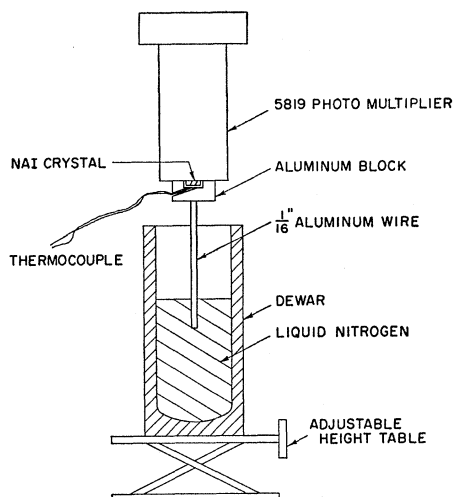[6] Kyropoulos, Z. anorg. u. allgem. Chem. **154**, 308 (1926).

FIG. 1. Arrangement for cooling scintillating crystals. The temperature of the crystal as measured with a thermocouple was changed by raising or lowering the Dewar flask. Temperatures were maintained constant to within half a degree centigrade during readings.

crystalline masses which were not single crystals. Our criterion for the recognition of single crystals is that the cleavage planes throughout the crystalline mass be parallel. Since thallium salts are quite volatile at the melting point of NaI, and toxic, NaI(Tl) crystals were grown by a modified Kyropoulos method. The technique
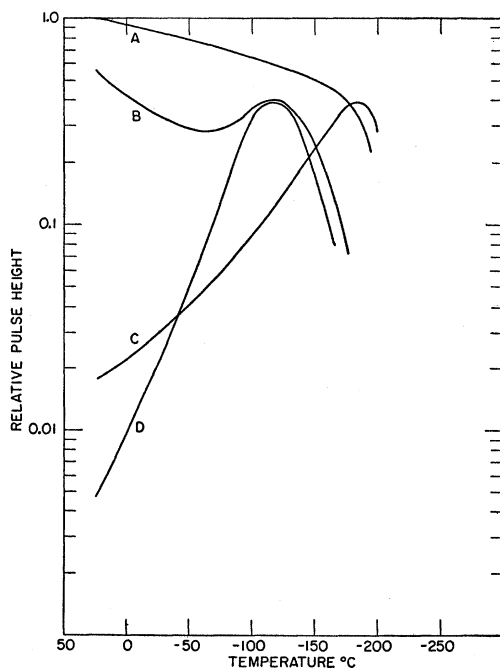

FIG. 2. Temperature dependence of the response of sodium iodide crystals to alpha particles. Curve A: thallium-activated sodium iodide grown by the Bridgman method. Curve B: thallium-activated sodium iodide grown by the Kyropoulos method. Curve C: sodium iodide grown by the Bridgman method. Curve D: sodium iodide grown by the Kyropoulos method.

employed in this case is to place NaI, thallium iodide and traces of α emitters in a Vycor glass vessel, evacuate, heat to 700°C, seal off the vacuum system, and maintain this temperature while one small region of the glass vessel is cooled sufficiently to start a small clear crystalline mass growing in the melt. The whole vessel is then cooled, broken open, and the clear portion is cut free of the solidified mass.

By these procedures, four types of crystals were prepared for investigation. NaI crystals with and without thallium activator were grown by the Bridgman method, unactivated NaI crystals were grown by the Kyropoulos method and, finally, Tl-activated NaI crystals were grown by the modified Kyropoulos method. All the crystals were α-radioactive with internal sources.

The crystals were mounted on 5819 RCA multiplier tubes and provision was made to cool them (Fig. 1). The crystals were cut about 4 mm square and 2 mm thick, the size being kept small to minimize effects due to temperature differences between different parts of the crystals. The temperature was measured with a thermocouple and the response of the crystal was studied as a function of temperature both for polonium α particles (5.3 Mev) and Cs^{137} gamma rays (661 kev). The gamma rays, of course, give rise to photoelectrons in the crystal and it is the photoelectrons which are compared with the α particles.

EXPERIMENTAL RESULTS

In Fig. 2, the response to α particles as a function of temperature is compared for pure and thallium-activated NaI crystals grown by the Bridgman and Kyropoulos methods. An interesting fact emerges from these curves; namely, although the response of thallium activated crystals is greater than that of "pure" NaI crystals by factors greater than 50 at room temperature, the crystals are indistinguishable below −115°C in one case and −180°C in the other. Similar curves differing only in detail were obtained for the γ-ray response.

Having measured the response to α and γ radiations as a function of temperature for all four types of crystals, we plotted the ratio of the α-particle response to the γ-ray (or e^-) response per unit energy in each case (Fig. 3). It is seen that the ratio of the α- to γ-ray response is independent of temperature for both "pure" and thallium-activated NaI crystals that have been grown by the Bridgman method and that the value of this ratio is ~ 0.7. The crystals grown by the Kyropoulos method however, show a temperature dependency, and in the "pure" NaI crystal the α- to γ-response ratio assumes a high value of 1.5 at approximately −150°C, indicating that the α particle has a higher scintillation efficiency than the γ ray under these conditions.

The α-particle and electron pulses were analyzed with an Atomic Instrument Company single-channel pulse-height analyzer and the shapes of the peaks as well as

their heights were recorded as a function of temperature for the various crystals. It was noticed that the resolution of the α-particle peaks (width at half-height, ΔE over E) in several samples showed a temperature dependence which was independent of the peak height. A most extreme example is shown in Fig. 4 in which the α-pulse distribution is a single peak at some temperatures but separates into double peaks at others. Other samples showed greatly broadened and distorted peaks in some temperature range but did not separate into two distinct peaks. Although the crystals grown by the Kyropoulos method exhibited this effect to a far greater degree than did the Bridgman crystals, the latter were not free of the effect, as is shown in Fig. 5.

DISCUSSION OF RESULTS

Three significant results were obtained through this investigation which warrant consideration: (1) the effect
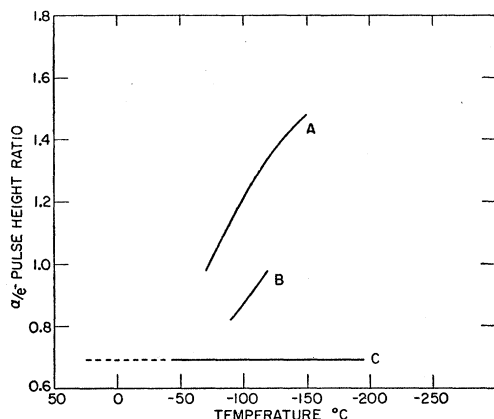
FIG. 3. Ratio of pulse heights for α particles and electrons as a function of temperature. Curve A: sodium iodide grown by the Kyropoulos method. Curve B: thallium-activated sodium iodide grown by the modified Kyropoulos method. Curve C: both thallium-activated and "pure" sodium iodide crystals grown by the Bridgman method.

of Tl activation on pulse height becomes progressively smaller as the temperature of a NaI crystal is decreased until at temperatures of -115 to $-180°C$ it is negligible; (2) the ratio of the alpha particle to electron response of the crystal (per unit energy) may be a function of temperature, and under certain conditions can become greater than 1; (3) a good portion of the width of α-particle peaks in NaI crystals can be due to effects which are not statistical in nature and which have strong temperature dependencies.

A relatively simple "explanation" open to investigation can be proposed for the third effect. This anomalous resolution is most pronounced in crystals grown by the Kyropoulos method. This method produced clear multi-crystalline masses. If these crystals differed slightly in their response to α particles as well as in the variation of their response with temperature, one could explain the observed phenomena. The crystal can be pictured
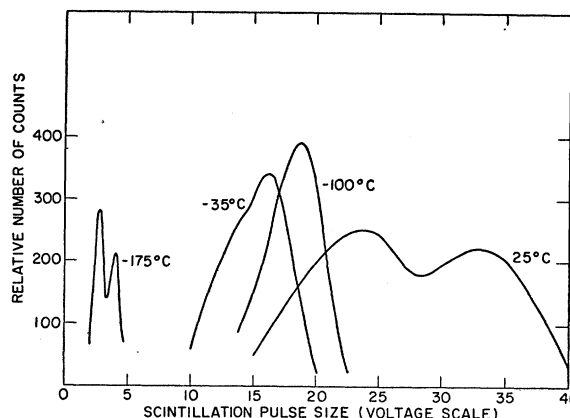
FIG. 4. Extreme example of temperature dependence of resolution for a sodium iodide crystal grown by the Kyropoulos method. The pulses are due to Po[210] α particles contained in the crystal.

as being formed of many regions each with a slightly different response to the α particle.[7] Changes in temperature heighten, or lessen, the differences among the individual responses of the regions. These regions will in general have to be large compared to the range of the α particle ($\sim 5\mu$). If they are sufficiently large, one will be able to test this theory by splitting crystals into smaller ones and comparing the response of the parts with that of the original whole crystal. (One such experiment has been performed and seems to be in agreement with this explanation.)

The other two phenomena are undoubtedly more complex in nature and one should proceed with caution in considering them. The phenomena have been demonstrated repeatedly with a given crystal sample; how-
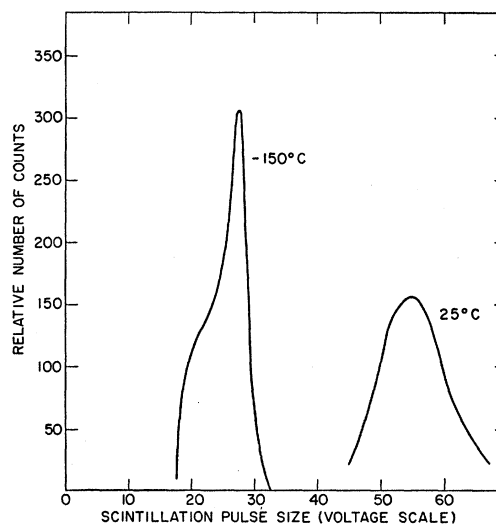
FIG. 5. Temperature dependence of resolution for a thallium-activated crystal grown by the Bridgman method.

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[7] Phenomena such as "zone purification" could cause the different regions of the crystalline mass to differ in scintillation properties.

ever, in most cases only a few crystals have been grown by the same method, and consequently there is no strong evidence yet that the differences between crystals that we ascribe to the different methods of growth will always appear. Another fact to remember is that we refer to some crystals as "pure" NaI crystals and to others as thallium-activated. This is obviously open to criticism since we add minute amounts of Po to all the crystals. Furthermore, one of the authors has found in the process of growing many NaI(Tl) crystals containing traces of radioactive elements, that sodium iodide plus thallium iodide at 700°C will dissolve measurable amounts of normally insoluble materials such as gold, platinum, tantalum, and hafnium metals as well as hafnium oxide. Since all the crystals used in the experiments were grown in contact with Vycor glass, and the Kyropoulos (unmodified) crystals were grown in contact with both Vycor glass and platinum, these crystals may have unknown amounts of impurities in them. However, the same author also found that the thallium activation of the NaI was not affected at room temperature by the addition of other substances in so far as light output per scintillation was concerned, provided the added matter was less than one-tenth the thallium in weight. Since the crystals with and without thallium activation are grown under similar conditions (as far as the introduction of impurities) it is a safe assumption that the difference between them is due to the thallium and that the action of the thallium is not greatly affected by the impurities. In this respect, then, it is permissible to speak of "pure" and thallium-activated crystals.

The amplifiers used had a decay time of $\sim$10 to 15 μsec. As a result, they were insensitive to pulses which were much slower than this in their natural decay time. Bonanomi[3] in an extensive study of the temperature dependence of the luminescence of alkali halide crystals reported at least four components in the scintillation of NaI and we have observed components in addition to the ones he reports. Some of these components have lifetimes as long as seconds at -115°C and would not be observed by our equipment. Consequently, our data are a comparison of the integrated light output of the fast components in a scintillation with lifetimes less than $\sim$20 μsec. With these reservations in mind, we can consider the results of our experimentation qualitatively.

Luminescent phenomena in crystals have been studied by many investigators, and qualitatively[8] and quantitatively[9] precise theories have been advanced. It is proposed that the valence electrons in a crystalline solid have energy levels which are grouped together into continuous regions or bands separated by semiforbidden

regions. Normally the electrons fill the lowest bands but they may be excited to higher energy levels. If this should be a level in a higher empty band, the excited electron is free to move about and the crystal becomes conductive. The vacancy in the filled band will act like a positive hole and it too is free to migrate in the crystal. There may also be levels in the forbidden regions (electron traps) to which the electron may be excited, but in which the electron is not generally free to move. If there are impurity atoms in the crystal, they may give rise to discrete energy states in a forbidden band. The migration of holes and electrons in the conduction band can cause the concentration of the excitation energy in traps and impurity centers.

An excited center may decay either through a radiative (emission of light) or nonradiative transition. If the probabilities P_1 and P_2 for these transitions to take place were to be determined mainly by the probability that a metastable state makes a transition by the absorption of thermal energy, so that

$$P_i = S_i e^{-E_i/kT}, \quad i = 1, 2,$$

the fraction of the energy arriving at excited states which is converted into visible light is expressible as

$$n = \frac{1}{1 + (S_2/S_1)e^{-(E_2-E_1)/kT}}, \tag{1}$$

where S_1, S_2 are constants, E_1, E_2 are activation energies, k is Boltzmann's constant, and T is temperature. If the constant E_2 associated with the emission of heat is greater than E_1 associated with the emission of light, the efficiency of luminescence will be large at low temperatures and becomes small as the temperature is raised. This is the type of behavior exhibited by the "pure" alkali halides,[3] as is shown in Fig. 2.

Seitz[8] has considered the effect of thallium activation in alkali halide crystals and has explained phosphorescence phenomena by a model in which two adjacent ions cooperate to form one "center." At these centers, electrons can be excited into metastable states which decay by thermal activation. The significant feature of this model is that the magnitude of the activation energies for the two processes are reversed from the above case, so that the light emission efficiency is greater at high temperatures and becomes smaller as the temperature is decreased.

It has furthermore been shown that when crystals of this type are subjected to particle excitation (as is the case in both our α-particle and γ-ray studies, since in the latter case it is a secondary electron which excites the crystal) the energy is given up to the bulk material of the crystal and transferred to the activation centers. The thallium is too low in concentration to account for the primary interactions between the atoms in the crystal and the exciting particle (see F. Seitz[8]).

The curves of Figs. 2 can now be explained in either one of two ways. The pure crystal has centers in which

[8] F. Bloch, Z. Physik **52**, 555 (1928); R. W. Gurney and N. F. Mott, Trans. Faraday Soc. **35**, 69 (1939); F. Seitz, Trans. Faraday Soc. **35**, 74 (1939); G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, New York, 1949).

[9] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).

a portion of the energy of the exciting particle can gather and be radiated as visible light or dissipated as heat. The thallium-activated crystals are essentially the same as a pure crystal in which thallium ions are sparsely dispersed. An exciting particle in either crystal gives up its energy to the crystal with which it interacts and a portion of the energy is quickly concentrated at the luminescent or trapping centers. Here it is converted into light or heat, the relative amount of each being a function of the temperature. The thallium-activated crystal will have at least two kinds of luminescent centers, one similar to those in the "pure" crystals, the other composed of thallium ions. The temperature dependence of the "pure" crystal is described by expression (1). The temperature behavior of the thallium-activated crystals can be described by a simple addition of two effects, the radiations of the host crystal type centers and that of the thallium ion centers. In addition, since the thallium-activated crystals give as much light as the pure crystals below certain temperatures, the amount of energy which ends up in the centers associated with the host crystal must be the same whether thallium is present or not, and all of the energy which ends up in the thallium-ion type centers must either be converted into heat at low temperatures, or be emitted as light in a time long compared with the RC of the circuits.[10]

An alternative explanation, which in a sense is simpler, is to picture the thallium-activated crystal as again having the two kinds of centers, but that as the temperature is lowered the passage of energy to the thallium ions becomes less and less efficient, until at sufficiently low temperatures only the host-type centers are operative.

In Fig. 2, one notices that the temperature at which the thallium-activated crystal begins to act like its unactivated counterpart is dependent upon the method of growth of the crystals. It is known that the rapid cooling of a crystal freezes into it more electron traps and imperfections than if the crystal were cooled slowly. Thus, the Kyropoulos method would be expected to produce crystals with more electron traps and perhaps associated luminescence centers than would the Bridgman method. If the division of energy between the two types of emission centers were to involve a mechanism of the type proposed by Klasens[11] for phosphors with two activators, the distribution of energy could be a function of temperature and the relative numbers of the two kinds of emission centers. This would result in different temperatures at which the thallium activators would become inoperative for the two kinds of crystal preparations. The fact that the two pure crystals peak at different temperatures suggests that more than one center is involved.

SCINTILLATION EFFICIENCIES

The greater light efficiency of α particles relative to electrons under certain conditions is still unexplained. Hitherto, all but one of the models which have been proposed to explain the difference in scintillation efficiencies of electrons and alpha particles have been effects which can only reduce the alpha scintillation efficiency. The suggestion of Eby and Jentschke[2] that the difference is due to a mechanism which allows the α particle and electron to distribute its energy in different ways between radiative and nonradiative states is the only one which will allow for the α particle to become more efficient than the electron. Again, this may best be understood in terms of a model utilizing many traps and luminescent centers. The sensitivity of the photocell to radiations of different wavelengths could play a role in emphasizing certain of the centers at the expense of others just as the RC of the circuit could emphasize components in the light pulse with decay times lying in a certain range. But these are not a necessary part of the model. Local saturation of scintillation centers and "hard" collisions may still play a role in scintillation phenomena but their effects must be limited to that of modifying the fundamental processes which distribute energy among the many states present in the crystal.[12]

CONCLUSION

A study of the temperature dependence of the response to α particles and electrons of "pure" and thallium-activated NaI crystals grown by the Bridgman and Kyropoulos methods revealed that under certain conditions, the scintillation efficiency of α particles relative to electrons for unit energy becomes greater than one. In view of this observation, one must look more critically at the "local saturation" and "hard" collision theories as an explanation for the fact that at room temperature in NaI(Tl) crystals this relative efficiency assumes the value ∼0.7. It was also found that in certain crystals α-particle peaks exhibited marked changes in resolution as a function of temperature and that this phenomenon was observed to a small degree even in good NaI(Tl) crystals. The interesting possibility is suggested of improving the resolution of a NaI(Tl) or other crystal by controlling its temperature.

Finally, it was seen that the temperature dependence of the response to particles of both "pure" and thallium-activated crystals is in agreement with qualitative theories.

ACKNOWLEDGMENTS

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[10] More precisely, the sum of the two must be equal to the output of the host centers in pure NaI crystals. If there is still some light given off by the Tl centers, then one must demand that the host centers give off less light by precisely the same amount in order to keep the light equal to the output of a pure crystal.

[11] H. A. Klasens, Nature **158**, 306 (1946).

[12] In a study of scintillation phenomena in NaI and CsF crystals W. J. Van Sciver has recently reported [Stanford University Report HEPL-38 (unpublished)] that the emission spectra of NaI crystals differ for electron and α-particle excitation. This again suggests that several luminescence centers are involved and that electrons and alpha particles may distribute their energy in different ways among these centers.