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THERMOLUMINESCENCE STUDIES OF THE GAMMA-IRRADIATED FERROELECTRICS ROCHELLE SALT AND GUANIDINE ALUMINUM SULFATE HEXAHYDRATE

J. W. Gilliland, Jr.

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HEALTH PHYSICS DIVISION

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J. W. Gilliland, Jr.*

DATE ISSUED

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I. INTRODUCTION

Cady[1] presents a thorough treatment of the history and properties of Rochelle salt. Some of the more interesting points are briefly summarized in the following paragraphs.

A. History of Rochelle Salt

The chemical properties of Rochelle salt and its value in medicine have been recognized ever since it was first produced, in 1672, by Pierre de la Seignette, an apothecary of La Rochelle on the coast of France. However, it was not until 1880 that its remarkable physical properties were observed when the Curie brothers included it in their first studies of the piezoelectric effect. Since that time Rochelle salt has become of importance primarily because of the extremely large piezoelectric effect and because of the electric anomalies along its x-axis.

Pockels in 1894 first discovered the anomalous dielectric behavior in the x-direction during the course of his experiments in which he made the first quantitative measurements of the piezoelectric effect in Rochelle salt. In an earlier paper by Borel, however, low normal values had been given for the dielectric constants along all three axes, and the anomalous behavior along the x-direction was not given much consideration until 1917.

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[1] W. G. Cady, PIEZOELECTRICITY (McGraw-Hill Book Company, Inc., New York, 1946), pp. 510-530.

Interest was then revived in the physical properties of Rochelle salt for their application to h-f underwater signaling. Since this time the properties of Rochelle salt have been given the attention of a number of prominent investigators.

A. M. Nicolson published the first descriptions of technical applications along with properties and methods of producing the crystals. His papers record some of the earliest observations of the electric response to various stresses and the converse; the dependence of the reactance of Rochelle salt crystals on frequency; and the evidence of hysteresis. A few years later J. Valasek published a series of papers which treated the characteristic dielectric and piezoelectric properties. He introduced the term "two Curie points" for Rochelle salt and pioneered in working out the analogy between the dielectric properties of Rochelle salt and ferromagnetism. Interest in the internal properties and structure theories of Rochelle salt began to develop generally around 1929 due to publications by Shulvas-Sorokina and later ones by I. Kurchatov and his collaborators.

B. Properties of Rochelle Salt

Rochelle salt is the potassium sodium salt of tartaric acid with four molecules of water of crystallization, represented by the structural formula as shown in Figure 1. The molecule, and hence the crystal, is enantiomorphous as shown in the figure. Tartaric acid from which the salt is produced occurs in many

fruits, mainly grapes, and is found naturally only in the dextro form. Thus, the name Rochelle salt generally refers to the "d-Rochelle salt."

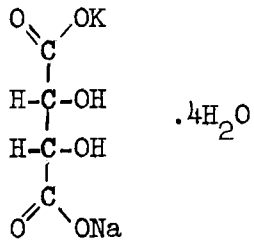

Figure 1. Structural Formula of Rochelle Salt

The molecular weight of Rochelle salt is 282.184, and the density at 25°C is given by Mason as 1.775 ± 0.003 gm/cm^3. It is very soluble in water to the extent of 1.50 moles (420 gm.) per liter of water at 0°C and 4.90 moles (1,390 gm.) per liter at 30°C. It may be crystallized from its saturated solution below 40°C either by cooling or evaporation and forms clear colorless crystals. The 40°C limit must be observed since above this temperature sodium tartrate is deposited, and the crystal itself changes above 55.6°C to a mixture of Na and K tartrates and their saturated solution. This is an irreversible process known commonly as the "melting" of Rochelle salt.

According to Vigness, changes in the dimensions of the crystal due to changes in temperature are related by an almost exactly linear function in all three directions, the only peculiarity being a slight bend at the upper Curie point for the Y- and Z-directions. Vigness's expansion coefficients have the following values: In the

X-direction, 12° to 35°C - 58.3×10^{-6}; Y-direction, 12° to 24°C - 35.5×10^{-6}, 24° to 35°C - 39.7×10^{-6}; Z-direction, 14° to 24°C - 42.1×10^{-6}, 24° to 35°C - 43.6×10^{-6}. The coefficient of volume expansion calculated from these data is approximately 1.4×10^{-4}.

Rochelle salt forms primitive orthorhombic crystals with tetramolecular units having the edges:

$$a_o = 11.93 \text{ A}, \quad b_o = 14.30 \text{ A}, \quad c_o = 6.17 \text{ A}^2$$

Each of the three axes possesses two-fold symmetry, and the three planes formed by the axes are reflection planes.

Between the Curie points, the Seignette-electric region, Rochelle salt possesses a domain structure with a monoclinic lattice. Mueller concludes that the domains in Rochelle salt are of the order of one centimeter in extent.[3] Ubbelohde and Woodward report that Rochelle salt actually breaks up into subcrystalline domains in a thermodynamic transition of "the second kind" or continuously over a range of temperatures which begins at +24.5° and terminates at about -20°C.[4] They show that in this range a "single" crystal of Rochelle salt is in reality made up of subcrystalline units which all have their a-axis in common and their

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[2] R. W. G. Wyckoff, CRYSTAL STRUCTURES (Interscience Publishers, Inc., New York, 1953), Vol. 4, Chapter III, Text p. 66.

[3] W. G. Cady, op. cit., p. 632.

[4] A. R. Ubbelohde and I. Woodward, Nature 155, 170 (1945).

b- and c-axes respectively equal but which differ in that the angle between these two axes is either 90° 2' or its supplement 89° 58' apparently at random. These two components are most clearly distinguished by X-ray methods around the middle of the transition range, 0°C. The process is reversible, and at temperatures outside the range, either above or below, the domains coalesce, and the specimen again possesses all the properties of a single crystal.

Marutaki reports that most domains in Rochelle salt consist of thin parallel plates perpendicular to the b-axis with some also perpendicular to the c-axis, though generally fewer in number.[5] Mitsui and Furuichi give the widths of these domains as varying from 0.5 to 0.001 cm.[6]

Beevers and Hughes first worked out the crystal structure for Rochelle salt in 1940.[7] The structure is naturally quite complicated since there are 28 atoms per molecule and 4 molecules per unit cell. The tartrate ion is found to lie approximately in three planes, each half lying in a plane inclined at 60 degrees to the plane of the carbon atoms, and it is bonded to the sodium and potassium both directly and through the medium of water molecules. The structure has an arrangement of positive ions lying rather close together in sheets perpendicular to the b-axis.

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[5] M. Marutake, J. Phys. Soc. Japan 7, No. 1, 25-29 (1952).

[6] T. Mitsui and J. Furuichi, Phys. Rev. Series 2, 90, 193-202 (1953).

[7] C. A. Beevers and W. Hughes, Proc. Roy. Soc. (London) A177, 251-259 (1940).

The sodium atoms have a coordination group of six being neighbored by two oxygens and one hydroxyl from the tartrate and three waters. The potassium atoms have two dissimilar positions in the structure, half of the atoms occupying each. One has a coordination group of four, two oxygens from the tartrate groups and two waters, while the other has a coordination group of eight consisting of two oxygens and two hydroxyls from the tartrates and four water molecules.

Some modifications, which are discussed later, have been made recently in the Beevers and Hughes structure due to X-ray examinations by Sundara-Rao, Maggi, and Pepinsky and single crystal neutron diffraction study by Frazer, Danner, and Pepinsky.[8]

As stated earlier, Rochelle salt is characterized by the large piezoelectric effect and its electric anomalies along the X-direction. The piezoelectric constant, d_{14}, which relates the polarization in the X-direction to a shearing stress in the YZ-plane, and the dielectric constant, k'_x, show a sharp rise inside the Seignette-electric range with maxima at the Curie points. The crystal shows spontaneous polarization in this region, and a non-linear relation exists between polarization and field and also between polarization and strain, both showing hysteresis. The

[8] G. Shirane, F. Jona, and R. Pepinsky, Proc. Inst. Radio. Engrs. 43, 1738 (1955).

strict paraelectric state in which polarization is linearly related to strain, or field, is found above 32°C and below -26°C. Between these temperatures and the Curie points, the nearness to the Seignette-electric region produces a curvature in the relationship although no hysteresis occurs.

In Mason's development of the ferroelectric theory of Rochelle salt, it was assumed that the ferroelectric dipole was due to the displacement of a proton in the hydrogen bonds of the Beevers and Hughes structure, and he was able to get two Curie points which agreed with observations.[9] In his treatment, however, he had to assume that the dipole itself varied with temperature because of thermal expansion.

Ubbelohde and Woodward explain the spontaneous polarization of Rochelle salt as due to the stretching of hydrogen bonds and illustrate the mechanism by use of the potential energy curve for a hydrogen atom between two oxygen atoms as follows.[10] If such a free hydrogen bond is less than 2.592 A, there is minimum potential energy at the middle of the bond and the hydrogen occupies that position, thus producing no permanent polarity. However, when the bond is stretched beyond this amount, as for example by thermal

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[9] W. P. Mason, PIEZOELECTRIC CRYSTALS AND THEIR APPLICATIONS TO ULTRASONICS (D. Van Nostrand Company, Inc., New York, 1950), p. 237.

[10] A. R. Ubbelohde and I. Woodward, Proc. Roy. Soc. (London) A185, 448-465 (1946).

expansion of the crystal, the middle of the bond becomes a maximum in the potential energy distribution so that the hydrogen occupies either of two minima bringing it closer to one or the other of the oxygens, thereby producing a polarization. When an electric field is applied, spirals containing hydrogen bonds extending throughout the crystal become polarized when the hydrogen atoms can jump over the potential barrier at the middle of the bond so as to assume the configuration with polarity in the same sense as the field. This explanation is compatible with the observed rise in Curie temperature with application of hydrostatic pressure.

Vernon says that although the ferroelectric state is probably due to chains of hydrogen bonds along the direction of spontaneous polarization, it seems doubtful that hydrogen bonds are very important since deuterating Rochelle salt produces only slight changes in the Curie temperatures as compared with changes produced in potassium dihydrogen phosphate by the same method.[11] He says further that this effect must be very structure dependent in Rochelle salt since none of its isomorphs has been found to be ferroelectric.

With the recent modifications in the Rochelle salt structure from the neutron diffraction studies mentioned earlier, Mitsui has developed a theory of ferroelectric properties in Rochelle salt

[11] R. C. Vernon, Am. J. Phys. 23, No. 4, 183-191 (1955).

which does not depend on hydrogen bonds.[12] A significant deviation from orthorhombic symmetry was found to exist in the case of the H on $O_{(5)}$ (using the notation of Beevers and Hughes) in that two orientations are possible. If one orientation is adopted in one part of the structure on one $O_{(5)}$ and the other orientation is adopted for a "pseudosymmetrically related mate," a net hydrogen displacement of almost 1A results with the principal component along the x-axis. The assumption in this development is that the $(OH)_{(5)}$ is a rotatable dipole with two equilibrium positions along the x-axis; and that, being a hydroxyl group of the tartrate ion, it should be rigid insofar as elongation is concerned. Thus, the ferroelectric dipole variation with temperature cannot be assumed, and the lower Curie point is derived from the asymmetric potential. This point represents the main difference between Mitsui's theory and previous ones, because otherwise the general features and conclusions do not depend upon whether the ferroelectric dipole is in hydrogen bonds or the hydroxyl groups.

C. Some Radiation Effects in Rochelle Salt

Coolidge and Moore reported the decomposition of Rochelle salt which was exposed to cathode rays as evidenced by evolution of gas bubbles when the crystal was warmed to melting.[13] Zheludev, et al.,

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[12] T. Mitsui, Phys. Rev. 111, 1259-1267 (1958).

[13] W. D. Coolidge and C. N. Moore, J. Frank. Inst. 202, 730 (1926).

also report that decomposition occurs within the crystal when irradiated with Co^{60} gammas in an exposure field of about 10^5 r/hr, and, according to them, the decomposition results in the emission of gases (H_2, CO, CO_2, CH_4) in amounts of five molecules per 100 ev.[14]

Zheludev and Iurin report that exposure of Rochelle salt to Co^{60} gammas (10^5 r/hr) results in anomalies in the hysteresis loop and eventually results in complete loss of hysteresis but causes little change in the piezoelectric effect.[15] They found that the piezoelectric coefficient g_{14} was almost the same as in an unirradiated crystal after doses had been administered high enough to destroy completely the hysteresis effect, and that the amount of decomposition at these doses results in loss of one tartrate ion in several thousand. The disappearance of the hysteresis effect is attributed to an increase in the interstitial layer between the domains and to the formation of atomic or ionic inclusions between the individual cells within a given domain, resulting from the decomposition. It was shown by photographs that the Rochelle salt maintains its domain structure even at high doses where hysteresis disappears.

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[14] I. S. Zheludev, M. A. Proskurini, V. A. Yurin, and A. S. Boberkin, Soviet Research in Physics, Collection No. 5, 19-21 (1956).

[15] I. S. Zheludev and V. A. Iurin, Bull. Acad. Sci. USSR, Physical Series, No. 2, 20, 193-196 (1956).

Some other radiation effects in Rochelle salt have been studied by Krueger, et. al., of Clevite Corporation and Yockey of Oak Ridge National Laboratory.[16] Some of these results are as follows:

With increasing doses, the maxima in the dielectric constant become less pronounced and move closer together until only one low, broad maximum occurs at exposures of 10^7 r. Measurements on the frequency constant of Rochelle salt, which normally has its minima at the Curie points, show that with increasing doses these minima also become less pronounced and move closer together, and at exposures of 10^7 r the value remains almost constant at about 1800 over the entire range from -18 to +24°C.

The stiffness coefficient, c_{44}^D (constant displacement), shows little or no change until dosages approach 10^7 r, where a gradual decrease indicates a mechanical loosening of the lattice. In contrast, c_{44}^E (constant field), is very sensitive to radiation. Low doses produce sharpening of the Curie dips, and between 10^5 r and 10^6 r the Curie points have shifted drastically and are less well defined. At doses greater than 10^6 r, one broad dip is found in the stiffness-temperature curve which becomes stiffer over-all with dose.

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[16] H. H. A. Krueger, W. R. Cook, Jr., H. Jaffe, and H. P. Yockey, private communication.

It was shown by use of an X-ray monochromator that the effect of gamma rays on Rochelle salt was first to increase and then to decrease the perfection of the crystal. The former is explained by the authors as probably due to a dislocation diffusion mechanism and the latter as the breaking of bonds and displacement of atoms.

D. Guanidine Aluminum Sulfate Hexahydrate

Guanidine Aluminum Sulfate Hexahydrate, $C(NH_2)_2\ NH.AlH(SO_4)_2 .6H_2O$, (abbreviated GASH) and its isomorphs make up a relatively new class of ferroelectric compounds which was first reported by Holden, et. al.[17] The crystal is trigonal with perfect clevage in the basal plane. It belongs to the space group P31m and has three molecules to the unit cell. The guanidine ion probably exists as a resonance hybrid with the structure shown in Figure 2, and, if this is correct, it has trigonal symmetry itself, the carbon lying in the plane of the three nitrogens with the hydrogens and nitrogens offering the possibility of N-H-O bonding to the sulfate ions and

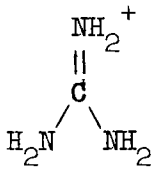

Figure 2. Probable Structure of the Guanidine Ion in GASH

[17] A. N. Holden, B. T. Matthias, W. J. Merz, and J. P. Remeika, Phys. Rev. 98, 546 (1955).

the water molecules.[18] Merz, et. al., report that at room temperature very symmetrical square hysteresis loops are obtained with GASH.[19] They also report that it is similar to Rochelle salt in that it is a weak ferroelectric with spontaneous polarization at room temperature of about 0.35 microcoulombs per square cm. The small signal dielectric constant of GASH at room temperature along the trigonal axis is only about 6 as compared to 5 perpendicular to this axis.[18] The Curie temperature is probably about 200-300°C but could not be determined accurately since the crystal begins to lose water of crystallization above 100° so that above this temperature reproducible results were not attainable.[19] The properties were found to vary from point to point in a crystal particularly between material grown on the basal faces and that grown on the prism faces. GASH was found to have only weak piezoelectric properties.

E. Thermoluminescence

Thermoluminescence is a luminescence produced in a substance when the temperature of that substance is raised. This definition says nothing about how the luminescence is induced; however, it is most commonly encountered in substances which have been exposed to ionizing radiation.

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[18] A. N. Holden, W. J. Merz, J. P. Remeika, and B. T. Matthias, Phys. Rev. 101, 962 (1956).

[19] W. J. Merz, J. P. Remeika, A. N. Holden, and B. T. Matthias, Phys. Rev. 99, 626 (1955).

During recent years considerable amounts of work have been done in studying thermoluminescence in many crystalline substances, particularly the alkali halides, in an effort to gain a better understanding of the physics of the solid state and damage produced by ionizing radiation.

II. THEORY

A. Interactions of Radiation with Matter

When gamma rays pass through matter, three primary interactions result due to the photoelectric effect, Compton effect, and pair production. Each of these effects produces primary electrons which in most cases are energetic enough to cause further ionization and excitation in the medium as a secondary process. Atomic displacements and decomposition of molecules are important results of irradiation, because of interactions between the energetic electrons and atoms. Atomic displacements in crystalline materials produce interstitials and vacancies in the lattice and have important consequences on the properties of the crystal. Dienes and Vineyard[20] and Seitz and Koehler[21] have treated the problem of displacements for charged particle irradiations as well as neutron irradiations. In gamma irradiations the direct bombardment of primary and secondary electrons and recoils from the primary gamma ray event can produce displacements. Also, there are two other possible mechanisms for displacement production in gamma irradiations.[20] The first of these, suggested

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[20] G. J. Dienes and G. H. Vineyard, RADIATION EFFECTS IN SOLIDS (Interscience Publishers, Inc., New York, 1957).

[21] F. Seitz and J. S. Koehler, "Displacement of Atoms During Irradiation," SOLID STATE PHYSICS, F. Seitz and D. Turnbull, Editors (Academic Press, Inc., New York, 1956), Vol. 2, p. 308.

by Seitz, proposes that excitons are produced in the crystal by radiation. The exciton is a combination of a hole and an electron in an excited state. The hole acts as a positive charge and the electron is supposedly attracted to form a state similar to the hydrogen atom. This phenomenon may be thought of as an excited state of an atom or ion, the excitation moving from one cell of the lattice to another. The excitons move through the crystal until they encounter an irregularity in the lattice at which point the energy is discharged into the lattice producing a localized "hot spot" which can produce dislocations and vacancies. Also, free electrons and holes may recombine and liberate energy into the lattice sites.

The other possibility for displacement production suggested by Varley is that an atom or ion may lose two or more of its outer electrons due to primary or secondary ionization. In this case its position might become highly unstable due to surrounding ions and thus be ejected to an interstitial position.

B. Electron Traps

When a crystalline material is irradiated with ionizing radiation such as gamma rays, ionization occurs and electrons are excited into the conduction band. In this state an electron is free to move through the crystal until it finds a position of lower potential energy. The electron may assume a position of lower potential by one of two processes - recombination or

trapping. The process of recombination is the case in which an electron recombines with a positive hole, that is, with an atom or ion in the crystal which possesses one electron less that it normally has in that crystalline structure. Thus, "recombination" implies that the electron returns to its ground state. In the case of trapping however, the electron assumes a metastable position with potential energy between the conduction state and ground state. Trapping may occur in several ways. The electron may become trapped at a lattice imperfection such as a negative ion vacancy. It may become attached to an impurity in the crystal. Also, if the temperature of the crystal is sufficiently low, the electron may polarize the surrounding material and become self-trapped.[22] Thus, several different types of traps may exist in a crystal, and there is for each type of trap a characteristic energy of activation for release of the electron. A simplified model of the electron trap is shown in Figure 3. In order to be excited into the conduction band, an electron must be supplied at least energy E_c. From the conduction band, an electron may then fall into a trap or return to a positive hole left in the filled band, yielding a quantum of light.

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[22] J. A. Ghormley and H. A. Levy, J. Phys. Chem. 56, 549 (1952).

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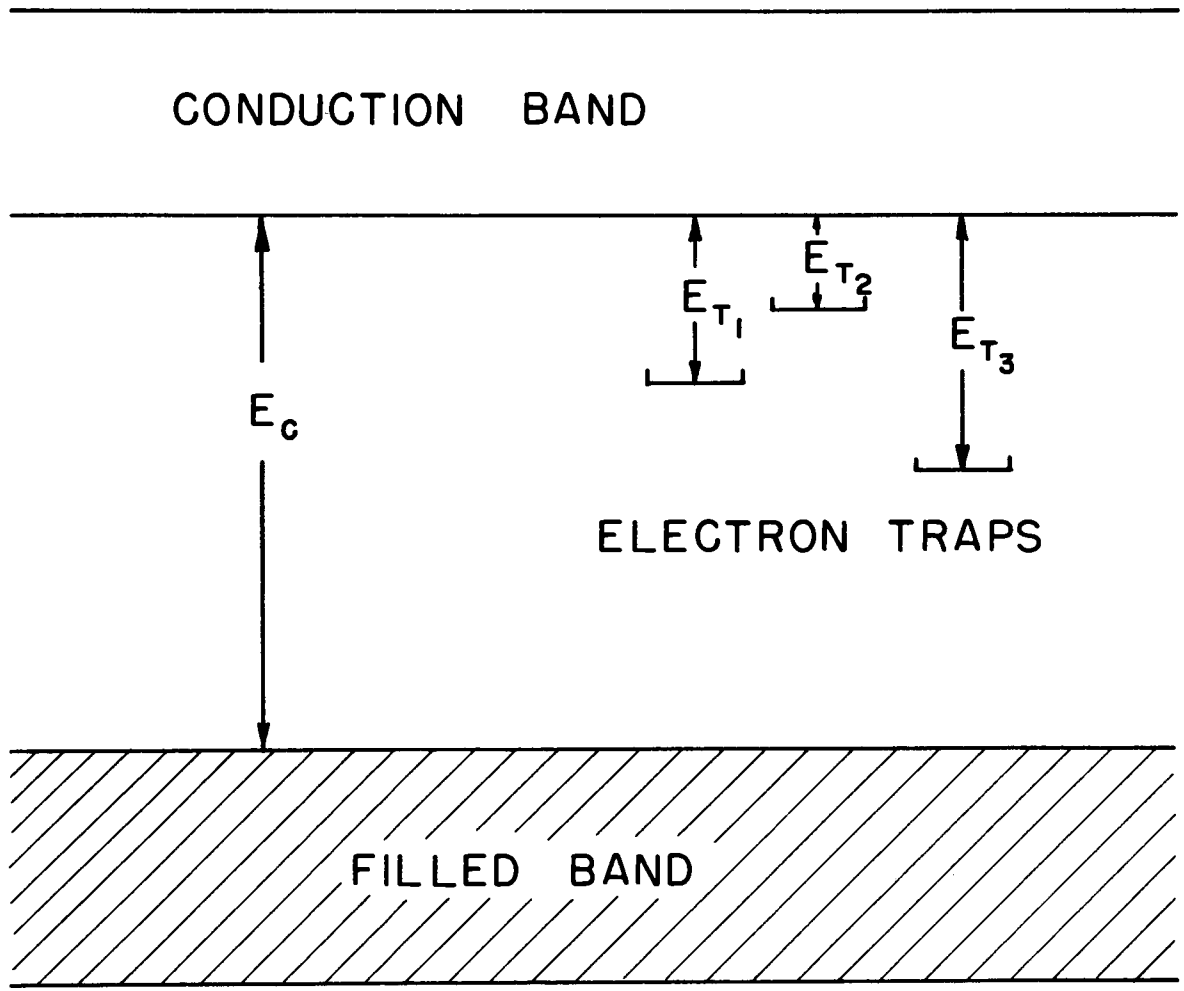

Figure 3. Electron Energy Model for Thermoluminescence

C. The Glow Curve

In order to be released from a trap of depth E, an electron must absorb at least an amount of energy E. Thus, when a substance is irradiated at low temperatures and then warmed at a constant rate, maxima will be observed in the glow curve at different temperatures corresponding to the various trap depths which are present in the crystal. The probability p of an electron escaping from a trap of depth E at temperature T is given by the Boltzmann factor,

$$p = se^{-E/kT}$$

where k is Boltzmann's constant and s is a constant although it may vary slightly with temperature.[23] Randall and Wilkins have calculated the form of the glow curve when E is single valued and the temperature rises at a constant rate. They assume there is no retrapping but that when an electron is released from a trap it goes directly to a luminescence center. Under these conditions their theoretical curve rises exponentially at first reaching a maximum and falling to zero. The temperature of maximum glow varies slightly with rate of warming. From their theoretical calculations, Randall and Wilkins give the following approximation

[23] J. T. Randall and M. H. G. Wilkins, Proc. Roy. Soc. (London) A184, 372 (1945).

for converting maximum glow temperature to trap depth:

$$\text{trap depth} = 25\ kT$$

where k is Boltzmann's constant and T is temperature of maximum glow in degrees K. This expression appears to be more nearly correct at slow rates of warming than at fast rates.

Garlick has extended the development of Randall and Wilkins to include retrapping for the case when the capture cross section is the same for a trap as for an empty luminescence center.[24] This treatment results in a fundamental change in the form of the decay at constant temperature from exponential to hyperbolic. There is also considerable modification of the glow curve. For example, the half-intensity width is larger by a factor of about two than for the case when retrapping was neglected. In either case the temperature of maximum emission is proportional to the trap depth, the half-intensity width increases with temperature, and the peak intensity decreases with temperature if the number of electrons trapped remains constant. For complex trap distributions generally found in phosphors, the theoretical treatment becomes complex, and it is difficult to determine whether retrapping is important or not, but Garlick cites experimental evidence which shows that the neglect of retrapping is justified to a considerable extent.

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[24] G.F.J. Garlick, "Some Studies of Electron Traps in Phosphors," PREPARATION AND CHARACTERISTICS OF SOLID LUMINESCENT MATERIALS, National Research Council (John Wiley and Sons, Inc., New York, (1948), pp. 87-114.

III. APPARATUS

The sample holders used in the gamma irradiations are similar to that used by Grossweiner and Matheson in their experiments on the thermoluminescence of ice.[25] A vertical cross section of the assembly is shown in Figure 4. The sample holder sits down on the base over the small vertical arm containing a copper constantan thermocouple which was attached at the top of the arm by an arc discharge. The two flat surfaces make good contact, thus producing a good heat path between the thermocouple and the sample. It was found that the temperature gradient between the thermocouple and sample was undetectable when a second thermocouple was fastened directly to the sample. The weight of the sample holder actually rests on the top of this arm and not at the base. The thermocouple signal was fed into a Brown recorder calibrated to record the temperature from -200°C to +100°C as a function of time. The heater was made from coiled nichrome wire wound noninductively inside a cylindrical frame made of lavite and was covered with asbestos tape to prevent shorting. A Variac was used to regulate the current in the coils and thus the rate of warming.

The sample holders, as well as the base plate and thermocouple arm, were made of 2S aluminum. The teflon was used in this apparatus

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[25] L. J. Grossweiner and M. S. Matheson, J. Chem. Phys. 22, 1514 (1954).

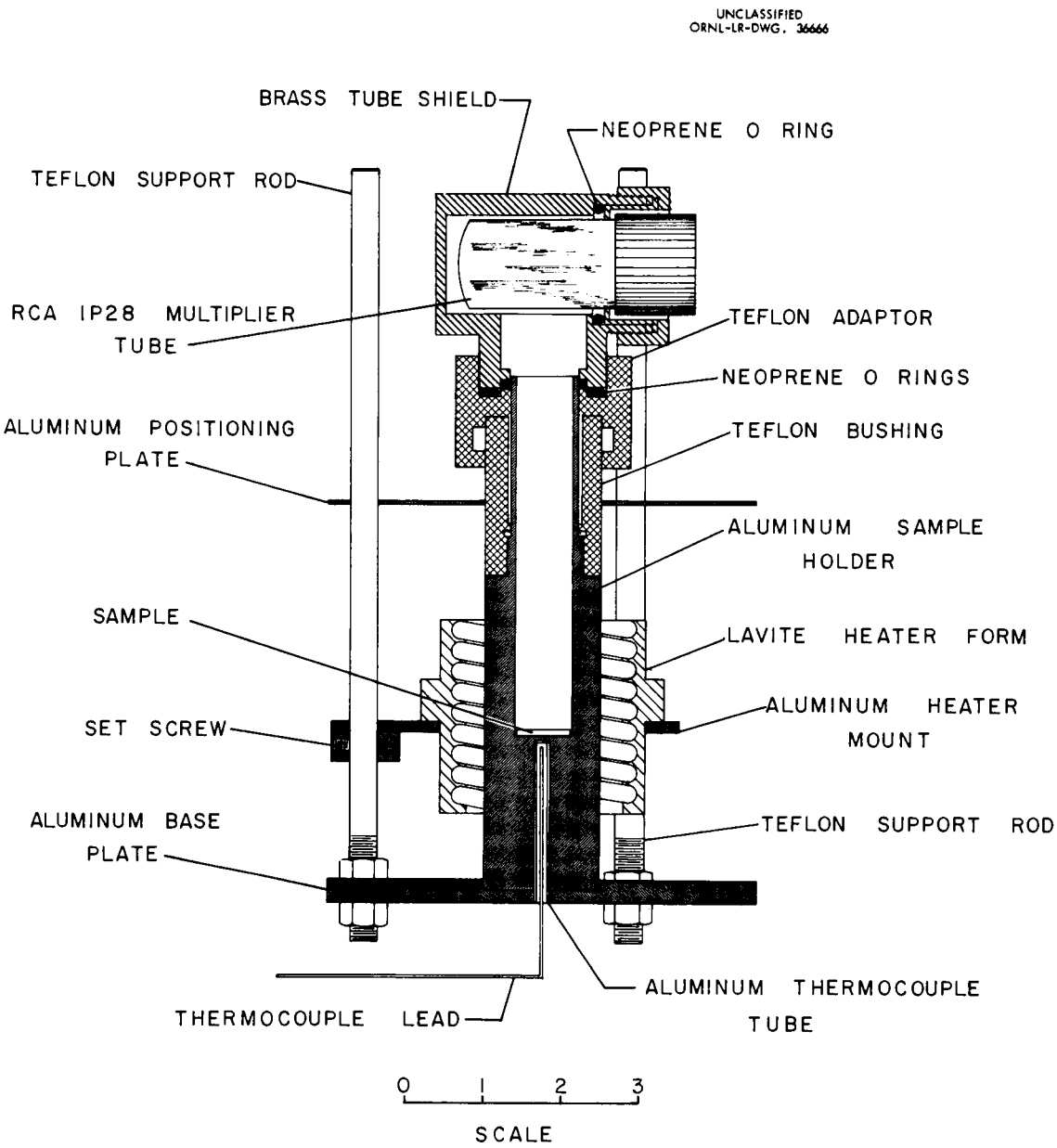

Figure 4. Vertical Cross Section of Assembly for Thermoluminescence Measurements

because it is a poor heat conductor, it will stand the temperature extremes used in the experiments, and it will stand rather high doses of radiation before becoming brittle. The 1P28 photomultiplier tube was enclosed in a brass shield which fitted down onto the sample holder, the connection being made light-tight by a rubber O-ring. There was a small hole in the top of the brass shield to which was fixed a small coiled tube blackened on the inside. This arrangement allowed the air to expand during warming without raising the pressure inside the holder but let no light in. A photograph of this assembly is shown in Figure 5.

During the irradiations a teflon cap was placed on the sample holder which was kept cold inside a Dewar flask of liquid nitrogen as shown in Figure 6.

The high voltage was supplied to the 1P28 photomultiplier by an Atomic Instrument Company super-stable high voltage power supply. The current was then amplified by a Kiethly micromicroammeter, Model 410, which uses a feed-back circuit (as shown in Figure 7) and was recorded as a function of time on a Speedomax recorder.

Two different irradiation facilities were used in these experiments - the cobalt garden and a cobalt-60 facility in Building 4501. The cobalt garden is an underground storage facility for cobalt-60 gamma sources with a chamber for lowering samples into place to be irradiated. Figure 8 is a diagram of this facility. A flux of about 3.5×10^6 r/hr was obtained inside the sample holder with this facility.

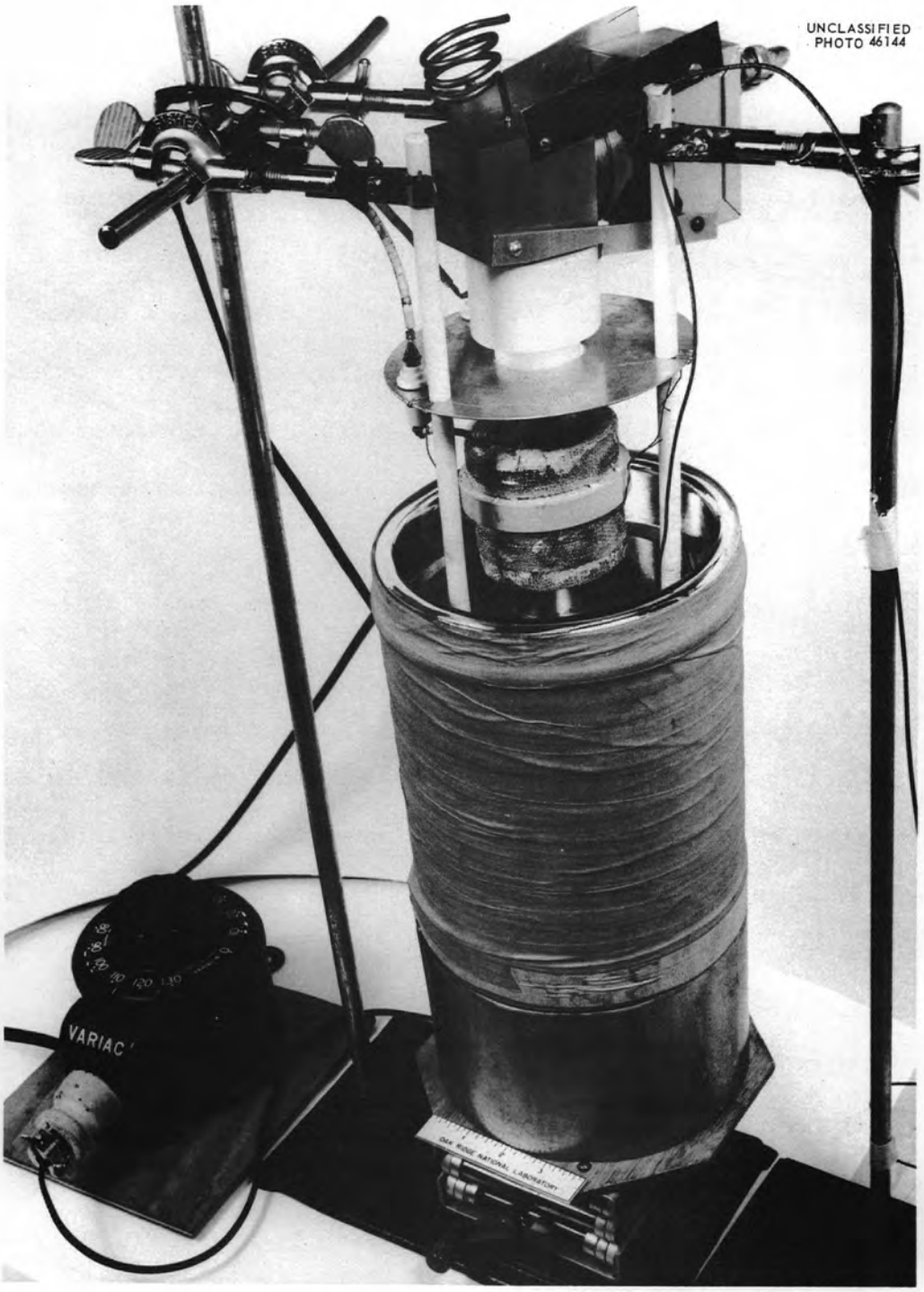

Figure 5. Photograph of Assembly for Thermoluminescence Measurements

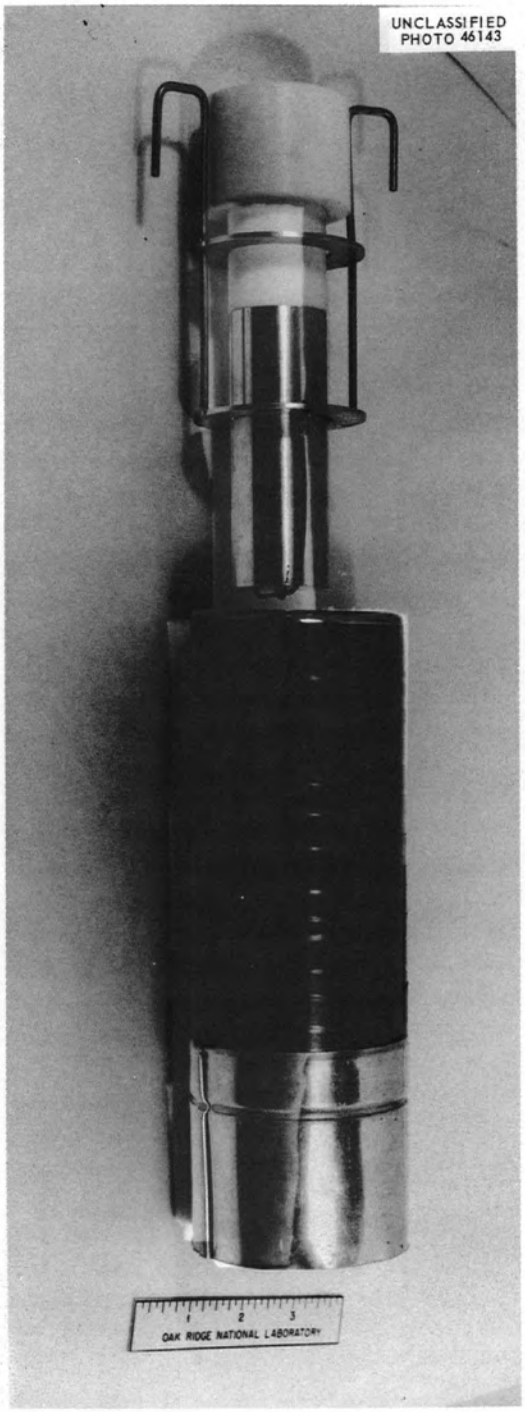

Figure 6. Sample Holder with Teflon Cap, Dewar Flask and Support

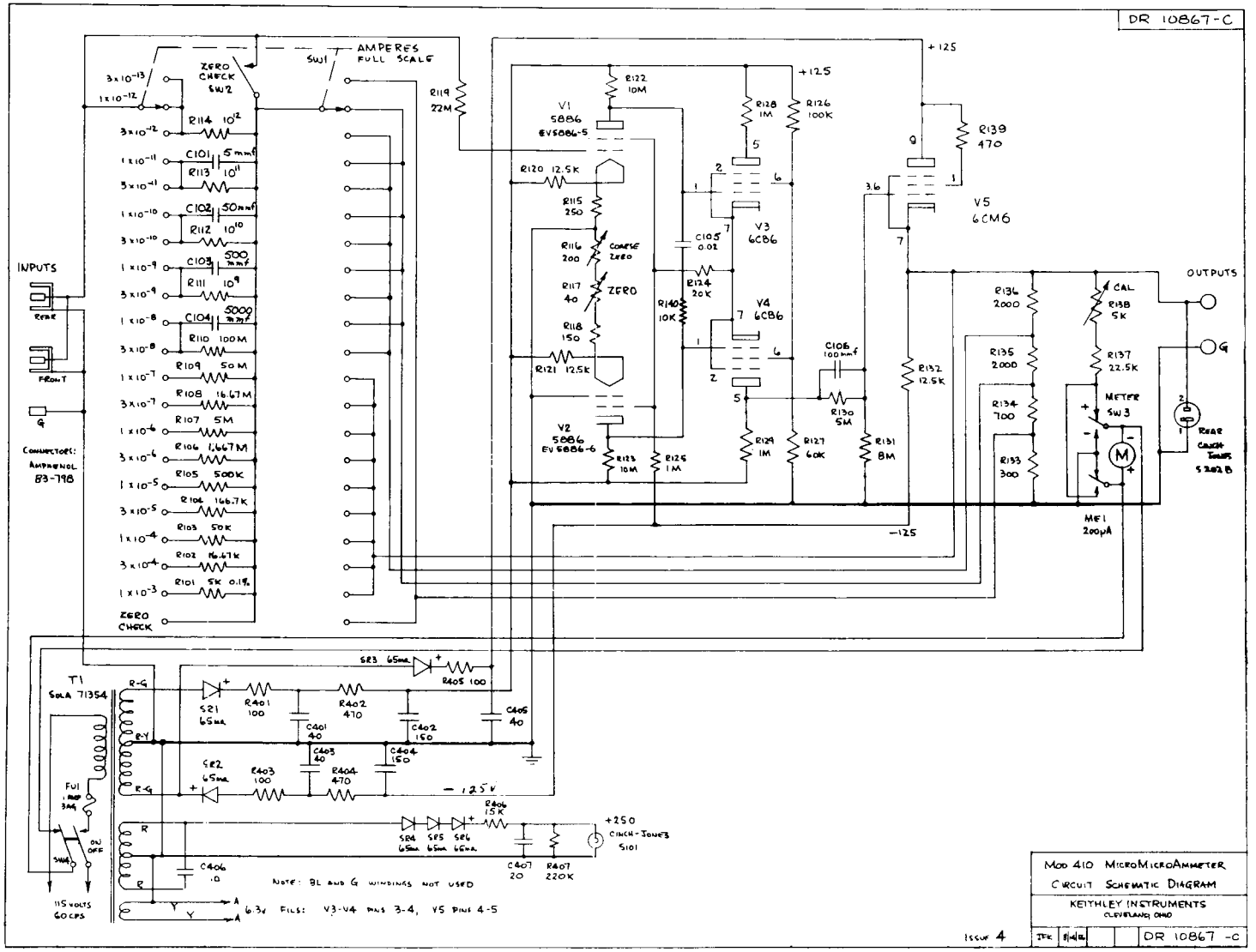

Figure 7. Circuit Diagram of Kiethly Micromicroammeter, Model 410

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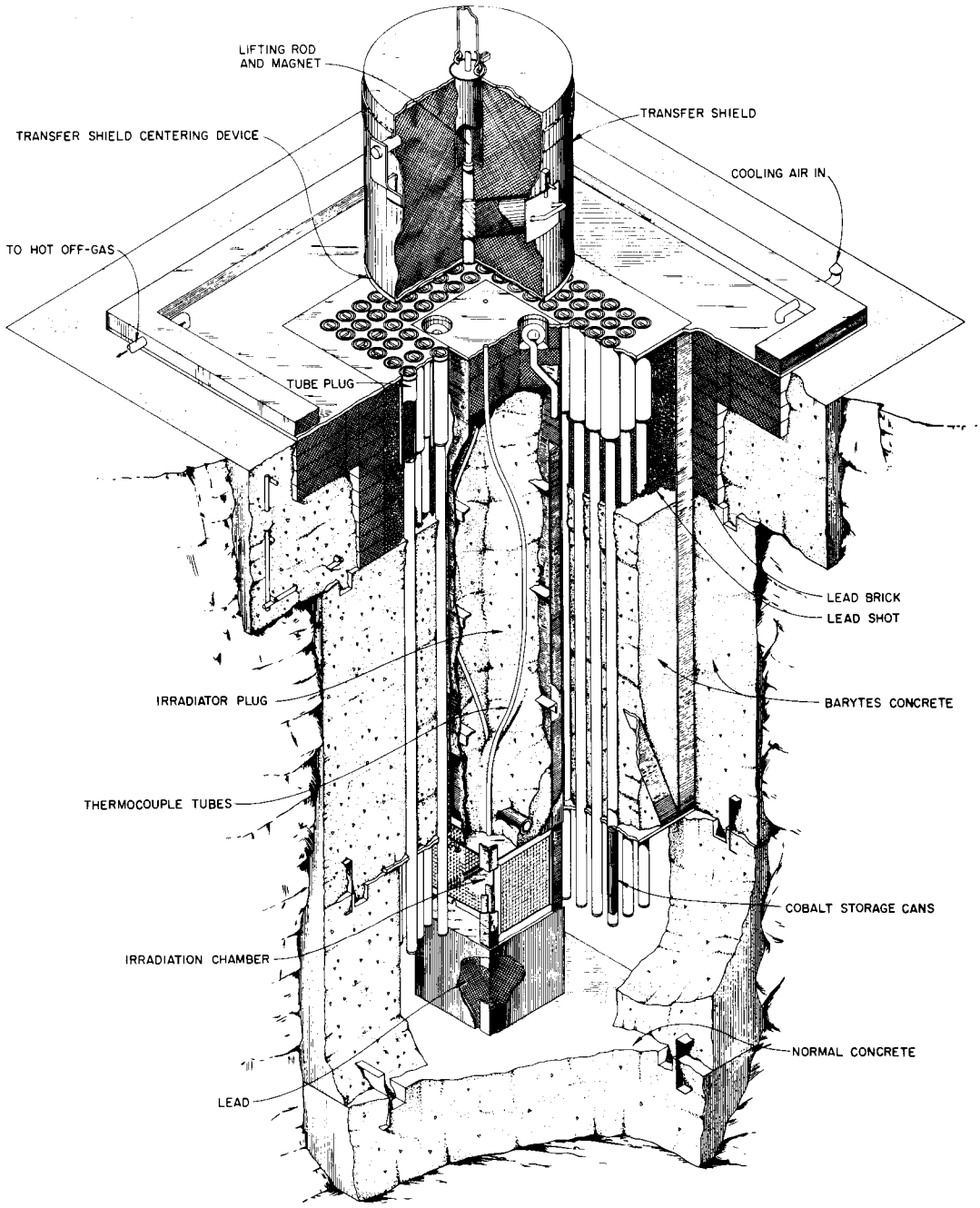

Figure 8. Cutaway View of Cobalt Garden and Irradiation Chamber

The other facility in Building 4501 which was used is the 1100 curie cobalt-60 source which produced a flux of about 55,000 r/hr inside the sample holder. This source is shielded and operated similarly to the one described by Ghormley and Hochanadel.[26]

[26] J. A. Ghormley and C. J. Hochanadel, Rev. Sci. Instr. 22, No. 7, 473-475 (1951).

IV. EXPERIMENTAL PROCEDURE

Most of the samples used in these experiments were in the form of single crystals, although some were in the form of powders. The single crystals were obtained from the Clevite Corporation in the form of thin plates. The Rochelle salt plates were about 2 mm thick, and the GASH plates were about 1 mm thick. The crystals were first cut to the desired shape. In the case of the Rochelle salt, the crystals were shaped so as to just fit the sample holder; that is, they were circular with a diameter just under 3/4 inch. The GASH crystals had irregular shapes, but the magnitude of the light output seemed not to be affected appreciably by this variation in the geometry. After the crystals had been cut to size, they were etched in distilled water in order to remove any surface impurities. For this step the crystal was simply held with small tweezers and dipped in a beaker of distilled water several times. It was then blotted dry with tissue paper and allowed to dry in the air for a few minutes. Before being cooled down and irradiated, the crystal was weighed, usually on an analytical balance or occasionally on a triple beam balance.

It should be mentioned that inasmuch as Rochelle salt tends to lose some of its water of crystallization when the humidity is too low, both the crystals and powders were stored in a desiccator over a saturated solution of Rochelle salt.

The only powdered samples used were a few Rochelle salt samples. In preparation of these powders, the reagent grade chemical purchased from General Chemical Division, Allied Chemical and Dye Corporation, was recrystallized twice from its water solution. The crystals thus obtained were allowed to dry in the desiccator mentioned above for several hours (at least overnight) and were ground to a powder with a mortar and pestle. The powders were then passed through sizing screens, and samples were taken from the fraction which passed 100 mesh and was retained by 170 mesh copper screen. The samples were weighed out (about 1 gm) and packed into the sample holders for irradiation. A few Rochelle salt powders were prepared without any recrystallization so that they still retained all the impurities present in the reagent chemical.

Very scrupulous care must be given to the preparation of the sample holders before irradiation since the uncleaned surface of the aluminum, that is, the aluminum oxide film of the surface, will produce a thermoluminescence glow of its own, making it impossible to tell what part, if any, of the glow is being produced by the crystal. The following procedure reduced this "background" glow to insignificant proportions. First, the holders were rinsed several times alternately with a sodium hydroxide solution (10%) and water until bubbles formed readily on the side of the holder when the caustic solution was added, showing that the Al_2O_3 film had been dissolved and the NaOH was reacting with the aluminum. The holders

were then rinsed thoroughly with water and polished with a fine abrasive which removed the black residue left on the surface by repeated etching and kept the surface shiny and highly reflective. Finally, the holders were washed with soap and water, rinsed with distilled water, and dried under a heat lamp.

Using the arrangement shown in Figure 6, irradiations were made in one of the two facilities described previously. In order to keep ice formation on the sample holder to a minimum, a paper cap was placed over the Dewar flask at all times while the sample holder was being kept cold. No ice formation could be detected inside the sample holder either visually or by the thermoluminescence.

The next step in the procedure was the determination of the glow curve. The large Dewar flask shown in the assembly photograph of Figure 5 was filled with liquid nitrogen and raised with the laboratory jack to cool the base plate and heater and was left in this raised position so that the level of the liquid nitrogen was above the aluminum positioning plate. The sample holder was then transferred from the Dewar flask to a flat-bottom can filled with liquid nitrogen; the lights in the room were turned off; the teflon cap was removed; and the photomultiplier assembly was placed on the holder. This operation is illustrated in Figure 9 which shows the photomultiplier assembly about to be placed on the sample holder. Since the holder was cold, it was handled with tongs which fitted into small holes in the teflon jacket. The flat-bottom can was used since some forcing

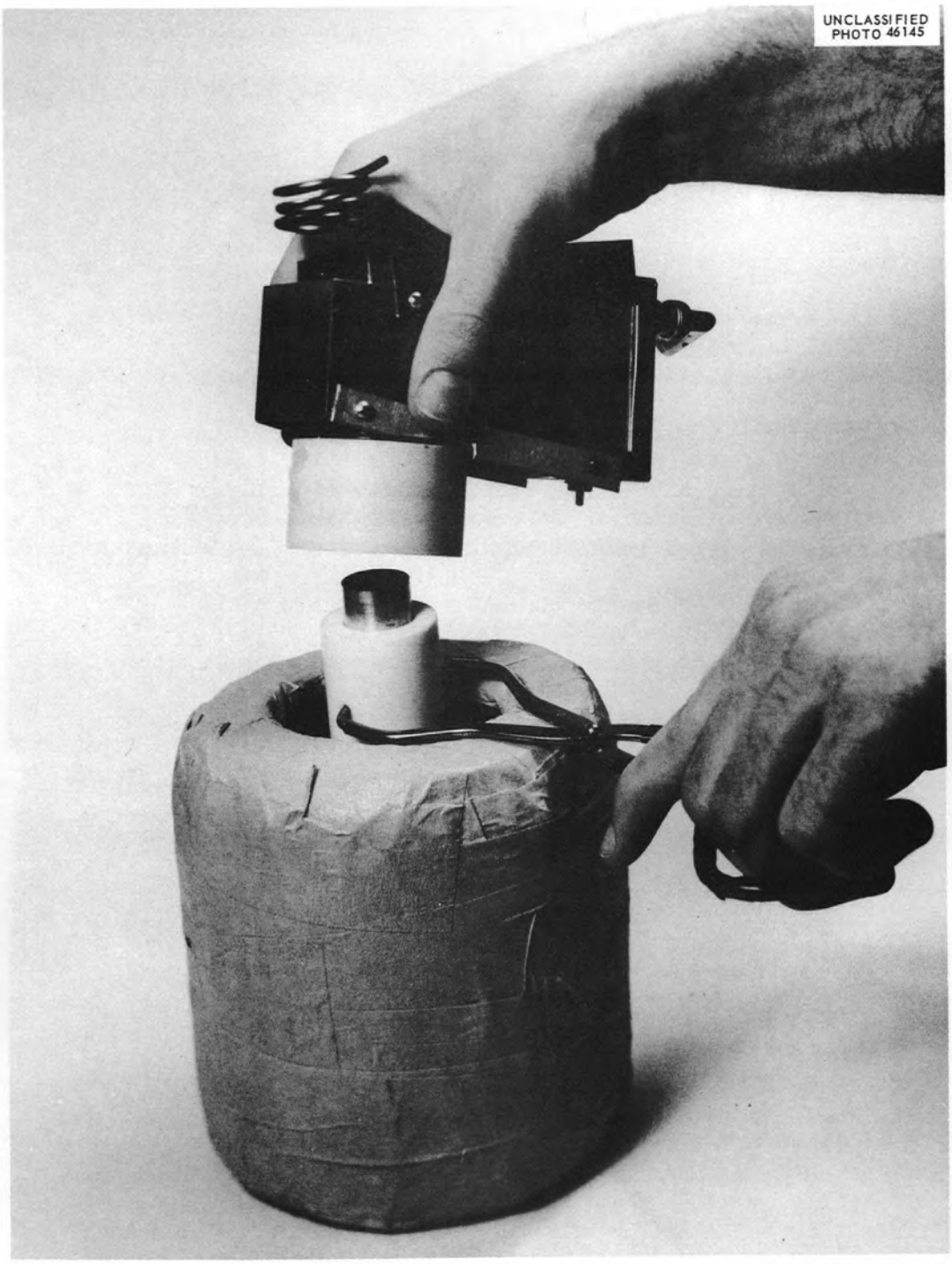

Figure 9. Photograph Showing Method of Transferring Sample Holder

was required in order to get the photomultiplier assembly to seat properly on the holder. Once this operation was completed and the lights were turned on again, the transfer was made onto the base plate and thermocouple arm. The two transfers from one liquid nitrogen bath to another were made quickly enough so that the sample holder was not warmed up appreciably. With the sample holder seated on the thermocouple arm, the cables from the high voltage supply and amplifier were connected to the photomultiplier tube; and the two recorders, one for temperature vs. time and one for glow intensity vs. time, were synchronized at "zero" time. Then the warm-up was begun. The large Dewar flask was lowered so that the level of liquid nitrogen was just below the base plate of the assembly, and the heater was turned on immediately. An approximately linear rate of warming was easily obtained between -196 and 0°C by making only about four separate settings on the Variac regulator.

V. RESULTS

Rochelle salt single crystals were irradiated with varying doses up to about 3.5×10^6 r. These crystals were than warmed to 0°C or in some cases almost to "melting." In each case no light was observed from the crystal.

The output current from the photomultiplier tube is given by the equation

$$I_o/A = ne/t$$

where I_o is the output current, A is the amplification of the photomultiplier tube and is equal to 600,000 at an operating voltage of 900 volts which is about what was used, n is the number of photoelectrons, e is the electronic charge, and t is time. The dark current of the photomultiplier was about 0.3×10^{-9} amps, and a rise in the output of about 0.5×10^{-10} could be detected easily. Thus, substituting this value into the equation above and solving for n, one obtains the value n = 500 photoelectrons per second. The response of the Cs_3Sb photocathode of the 1P28 tube varies from about 0.09 photoelectron per quantum for light of 4000 A to 0.2 at 3100 A.[27] Thus, in order to make a conservative estimate, it will be assumed that the average response of the photocathode will be 0.1 photoelectron per quantum.

[27] L. Apker, E. A. Taft, and J. Dickey, J. Opt. Soc. Am. 43, 78 (1953).

With this assumption, then 500 photoelectrons would be produced by 5000 photons on the photocathode. If it is further assumed that the geometry of the arrangement is 50%, then 10,000 photons per second would have to be produced in the crystal in order to produce an output of 0.5×10^{-10} amps from the photomultiplier tube. Thus, if any light at all is produced in the Rochelle salt, it must be produced at a rate significantly lower than this 10,000 sec^{-1} limit, even with doses of 3.5×10^{6} r. Since the average weight of the crystals was about 0.8 grams, this would set a limit of less than 12,500 photons per second per gram in Rochelle salt with an exposure of 3.5×10^{6} r and heating at 12°C per minute.

Since the wave length is assumed to be about 4000 A, the total amount of energy released in the form of light during the warm-up from -196°C to 0°C would be less than 6.2×10^{-5} ergs gram. This value for total energy would be even less if it were calculated for a shorter wave length, because, although the energy per photon would rise, the response of the Cs_3Sb photocathode would increase up to 3100 A, thus reducing by a greater factor the number of photons necessary to give an equivalent rise in the output signal.

When the irradiated Rochelle salt was warmed to above 0°C and removed from the sample holder, it was as clear and colorless as an unirradiated specimen. However within one or two minutes it attained a yellowish-brown color which was more intense for higher doses. This would seem to indicate that some sort of metastable state was produced

by the radiation which was excited into transition by visible light and not excited thermally or which was excited by a combination of the effects of heat and visible light. This phenomenon would warrant further investigation to see whether or not is is temperature dependent.

Although no light was observed from the single crystals of Rochelle salt, the less pure Rochelle salt powders did show some thermoluminescence. Figure 10 shows the glow curve obtained from a sample of reagent grade Rochelle salt powder with no recrystallization, which was irradiated at liquid nitrogen temperature with 78,000 r of Co^{60} gammas. In Figure 10 as well as in the glow curves that follow, the dark current of the photomultiplier has been subtracted out so that the part shown is due only to the luminescence. In this case there is a prominent glow peak at about -61°C, which corresponds to a trap depth of 0.42 ev according to Randall's and Wilkins' approximation. When the reagent chemical is recrystallized twice from water solution, this glow peak is no longer present, and although there is some indication of a very small glow peak around -135°C, it is very minor and requires high doses of about 500,000 r in order to be seen at all. This small effect undoubtedly could be removed also by further purification since it was not observed in the pure Rochelle salt single crystals.

Guanidine aluminum sulfate hexahydrate was irradiated with doses from 10^4 to 3.5×10^6 r, and three glow peaks were observed. The glow

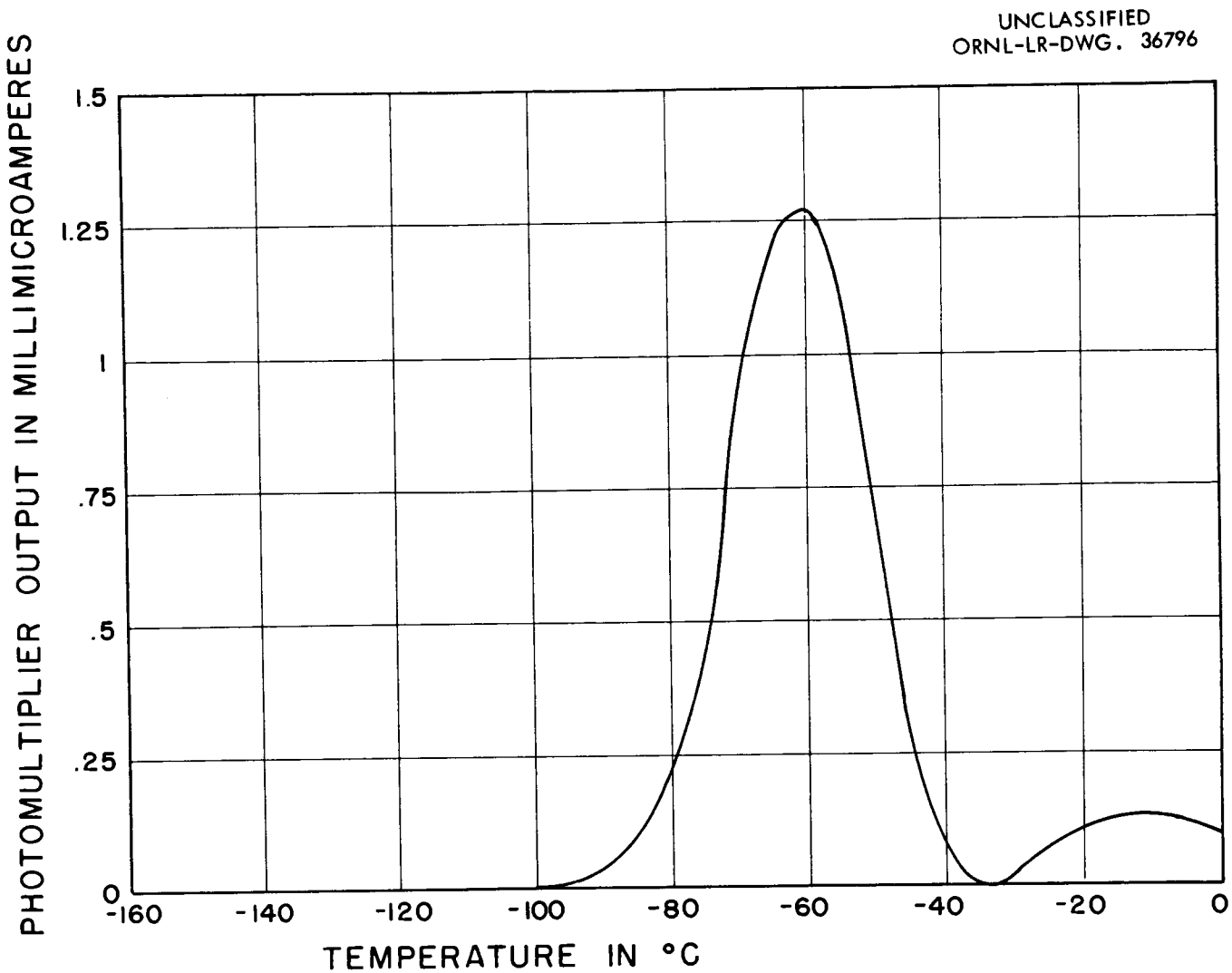

Figure 10. Glow Curve of Reagent Grade Rochelle Salt Powder, 1 gram sample, 78,000 r, warming rate = 12°C/min

curves for the various doses are shown in Figures 11, 12, 13, and 14. In Figure 11, for which the dose was 10^4 r, the peak at -146°C appears only as a shoulder on the larger peak at -119°C. However, Figure 12 shows that with a dose of 10^5 r the -146° peak has grown much larger than the -119° peak, and at 10^6 r (Figure 13) no peak can be seen at -119° at all, but it is completely covered by the lower temperature peak. There is, however, a slight deflection in the curve on the high temperature side of the peak in Figure 13 showing that the peak around -119°, although small in comparison, is still operative. However, at 3.5×10^6 r (Figure 14) no indication of this peak can be seen at all, and the glow curve appears to result from an essentially single valued trap depth.

Using the approximation of Randall and Wilkins,

$$\text{Trap depth} = 25\ kT$$

or

$$0.1\ ev = 50°K$$

the peaks at -146°C and -119°C correspond to traps of depth 0.25 ev and 0.31 ev respectively.

The third trap observed with GASH is a low broad peak with a maximum around -5°C, corresponding to trap depth of about 0.54 ev. This peak can only be seen easily in the glow curves for doses of 10^5 and 10^6 r (Figures 12 and 13). A dose of 10^4 r does not seem to be sufficient to produce noticeable effects in this range, and with a dose of 3.5×10^6 r the peak is poorly resolved because of a small

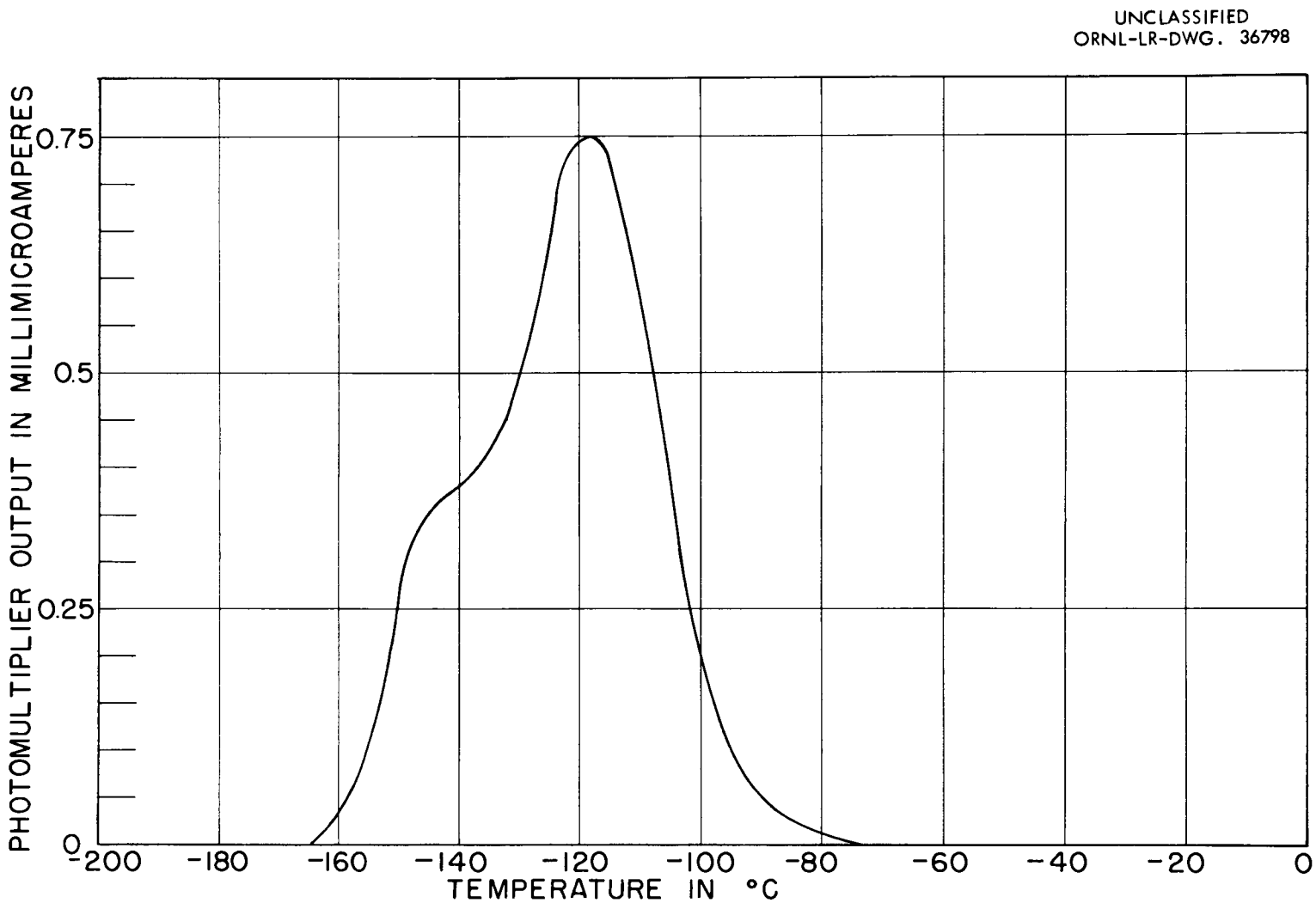

Figure 11. Glow Curve of GASH, 0.161 gram sample, 10^4 r, warming rate = 12°C/min

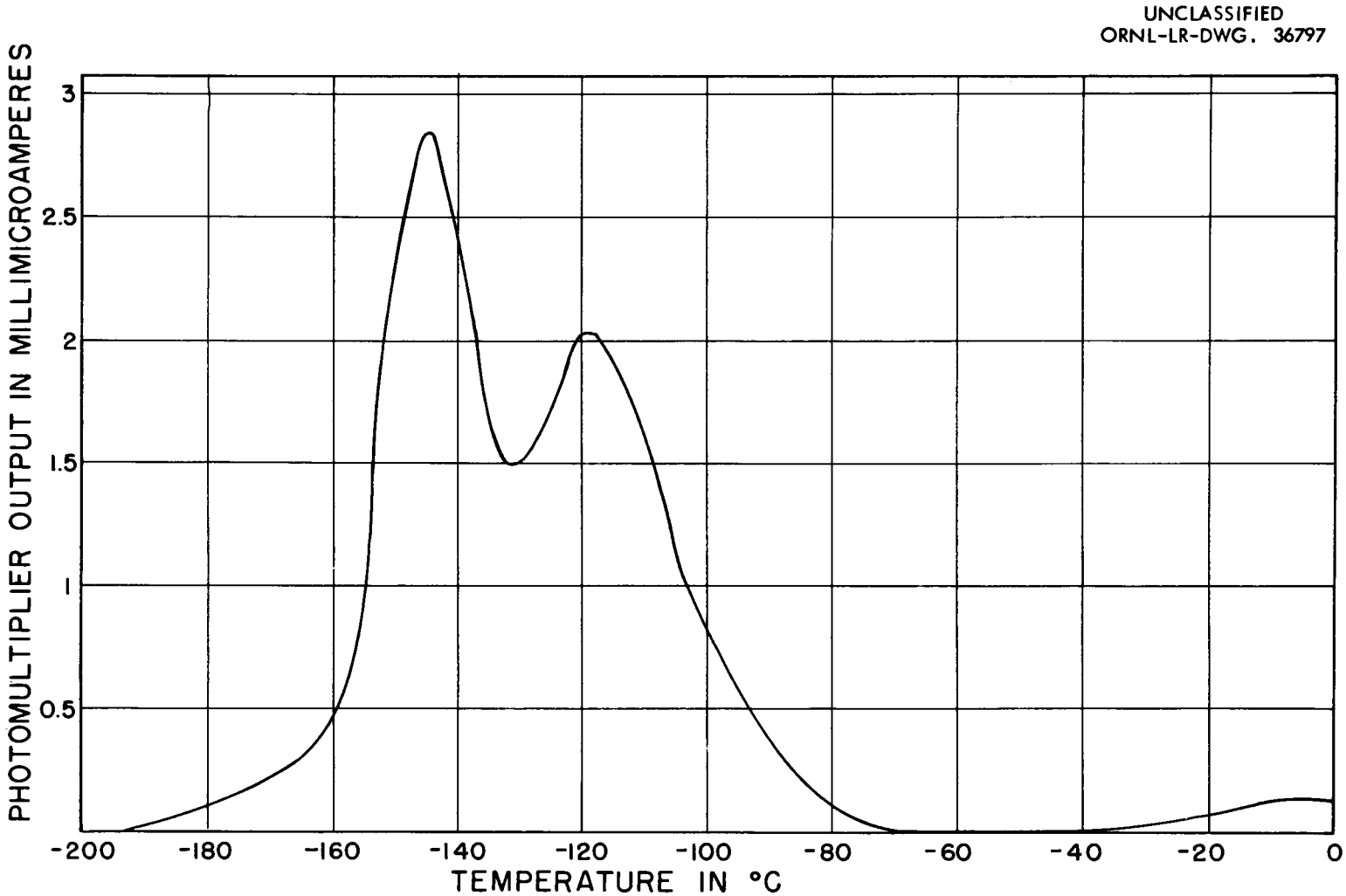

Figure 12. Glow Curve of GASH, 0.266 gram sample, 10^5 r, warming rate = 12°C/min

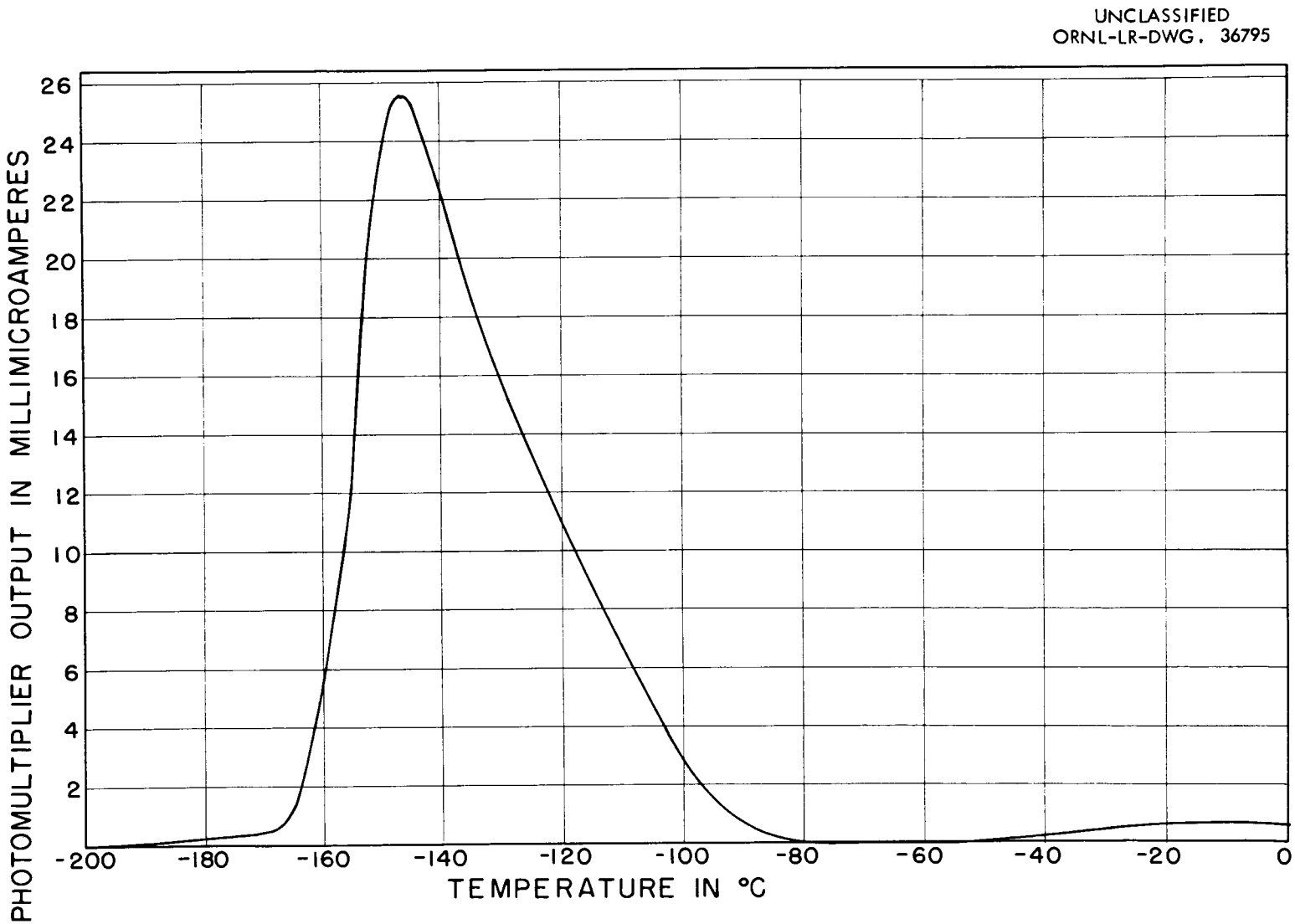

Figure 13. Glow Curve of GASH, 0.413 gram sample, 10^6 r, warming rate = 12°C/min

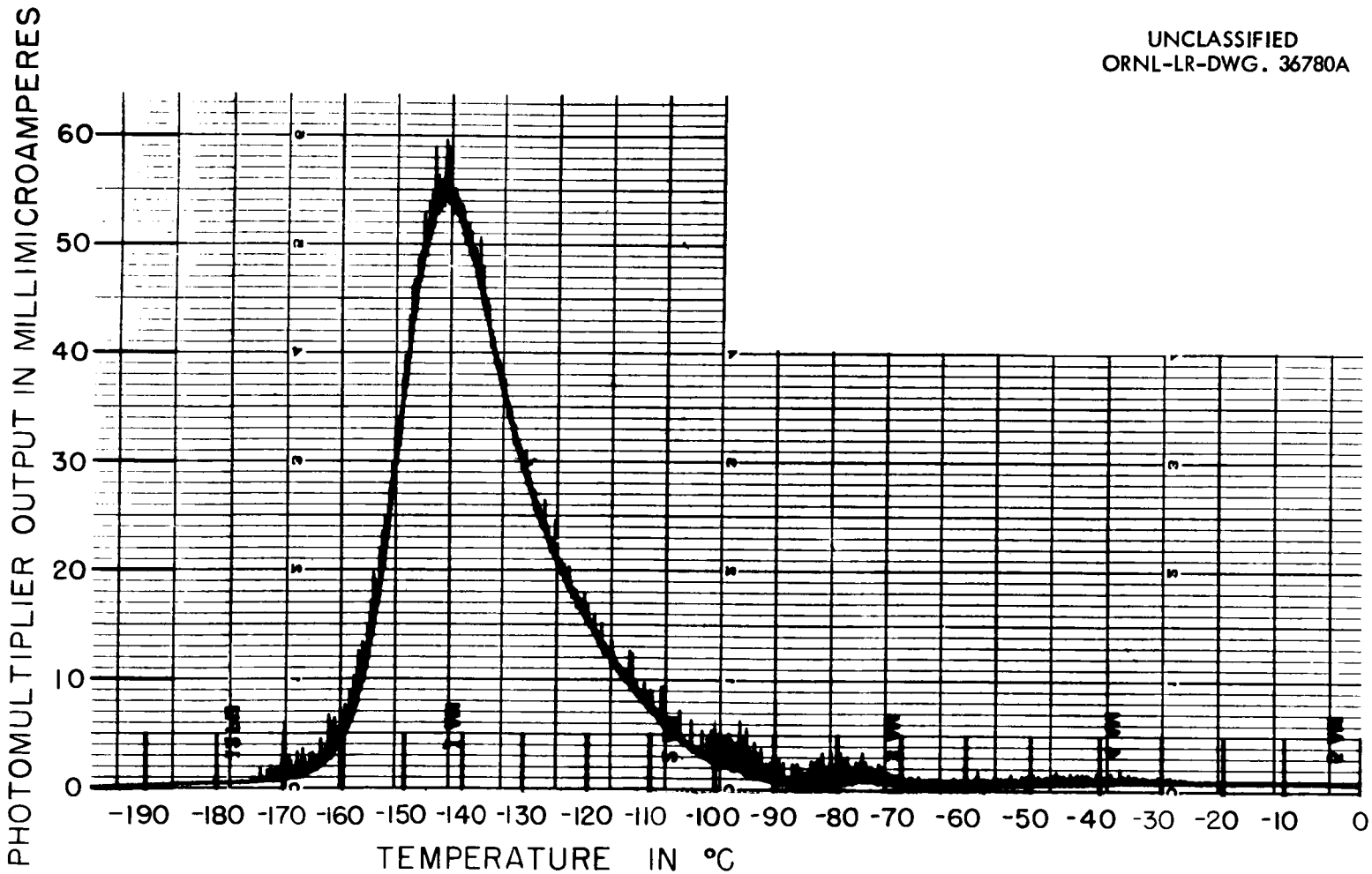

Figure 14. Glow Curve of GASH, 0.216 gram sample, 3.5×10^6 r, warming rate = 12°C/min

diffuse glow following the large peak at -146°C and to many spurious signals superimposed on the glow curve up to about -25°C. This effect will be noticed by comparing Figure 14 with Figure 13.

Figure 14 is a reproduction of a glow curve as recorded on the Speedomax recorder which is presented in order to show the spurious signals as they occur on the glow curve. In this case many closely spaced signals occurred between about -175°C and -25°C. Only a few randomly spaced spurs were observed on one of two GASH samples at 10^6 r, and at lower doses none were observed.

In Rochelle salt the occurrence of spurs varies greatly from one sample to another but does seem to have some dose dependence, although they were observed in some samples which were unexposed to radiation and were observed upon cooling as well as upon warming the crystals. This fact suggests that these spurs are likely due to a triboluminescence produced by the thermal expansion and contraction of the crystal. A fatigue was noted also in that when a sample was cooled and warmed several times, fewer spurs would result than when the crystal was fresh.

Some observations of these spurious signals from Rochelle salt were made by putting an oscilloscope across the output of the Kiethly amplifier. The signals observed were of the order of 10 microseconds duration and slightly distorted because of the comparatively slow response time of the amplifier, 10 milliseconds.

VI. CONCLUSION

Samples of Rochelle salt and guanidine aluminum sulfate hexahydrate were irradiated with various doses of Co^{60} gammas up to 3.5×10^6 r at liquid nitrogen temperature after which they were warmed at a constant rate and observed with a 1P28 photomultiplier tube. Pure Rochelle salt single crystals were found to yield no thermoluminescence glow which is detectable, and it is estimated that the minimum amount of detectable luminescence by the method used is less than 10,000 photons per second. The reagent grade Rochelle salt powder was found to produce a glow peak at about -61°C which was removed completely by two recrystallizations from water solution. This peak corresponds to a trap depth of about 0.42 ev.

Guanidine aluminum sulfate hexahydrate showed three glow peaks at -146°C, -119°C, and about -5°C, corresponding to trap depths of 0.25 ev, 0.31 ev, and 0.54 ev respectively. The major peak at -146°C becomes more prominent as the dose is increased to 3.5×10^6 r. At low doses (10,000 r) the -119°C peak is largest but becomes completely concealed by the lower temperature peak at 3.5×10^6 r. The low and very broad peak at -5°C is most easily seen at intermediate doses of 10^5 and 10^6 r. At lower doses it becomes undetectable, and at higher doses it is poorly resolved because of interference from a low diffuse glow following the large peak at -146°C and from spurious signals.

The spurious signals observed from Rochelle salt on an oscilloscope were found to be of the order of 10 microseconds duration. It is suggested that these spurious signals may be the result of triboluminescence in the crystal produced by thermal expansion or contraction.

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