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Comments and Addenda

The section Comments and Addenda is for short communications which are not appropriate for regular articles. It includes only the following types of communications: (1) Comments on papers previously published in **The Physical Review** *or* **Physical Review Letters.** *(2) Addenda to papers previously published in* **The Physical Review** *or* **Physical Review Letters,** *in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section must be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts follow the same publication schedule as articles in this journal, and page proofs are sent to authors.*

Optical spectroscopy of scintillations occurring in unirradiated glycine and triglycine sulfate: *L*-alanine

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Several research groups have reported observations of scintillations in well-known ferroelectric crystals. Previously we reported similar activity occurring in unirradiated glycine (nonferroelectric) but did not report the optical spectrum associated with the scintillations. In this paper we present the optical-spectroscopy results for scintillations occurring in single crystals of glycine and *L*-alanine-doped triglycine sulfate (LATGS). Seven lines were identified in glycine and eight lines in LATGS, all belonging to the second positive system of N_2. The spectrum results from an electrical discharge from the crystal surface, which has a layer of N_2 adsorbed onto it, to ground.

In recent years several research groups have reported observations of intense scintillations (electrical discharges) in ferroelectric crystals[1-6] and, in one case, in a nonferroelectric crystal.[7] Yockey and Aseltine[1] conducted a thorough study of potassium dihydrogen phosphate (KDP) that had been irradiated by γ rays and subjected to a temperature ramp. The optical spectrum of the scintillations occurring in KDP was recorded, yielding nine lines that were identified and assigned to the second positive system of N_2. It was suggested that the second positive N_2 spectrum resulted from electrical discharges from the crystal to the ambient nitrogen gas that had evolved from the liquid N_2 which was being used to cool the sample. By replacing the liquid N_2 with liquid Ar, efforts were made to photograph an Ar spectrum. This experiment did not yield an Ar spectrum; instead, it produced the second positive N_2 spectrum. The authors suggested that the appearance of the N_2 spectrum was due to the fact that the experimental apparatus was not designed to be evacuated and therefore small amounts of N_2 diffused into the immediate vicinity. Some of the scintillations were partially polarized, indicating that they came from internal breakdown of the crystal. A model based upon the strong internal fields that exist in ferroelectrics was proposed to explain the scintillations. Real charge liberated in the crystal by ionizing radiation was most likely trapped at domain boundaries. These domains anneal and coalesce over a broad temperature range, thereby releasing real charge to the surface of the crystal. It was noted that the crystal must be in the ferroelectric phase during irradiation and that scintillations are peculiar to ferroelectrics.

Cooke and Alexander[7] have observed intense scintillations and current pulses in glycine which result from heating or cooling the sample between 77 and 300 K. Glycine did not require irradiation for the scintillations to manifest themselves, and furthermore, available evidence indicates that glycine is nonferroelectric.[8] If the scintillations observed in glycine are due to the same physical effect that produces scintillations in ferroelectrics, then the model of Yockey and Aseltine will require modification to explain scintillations adequately. Although Cooke and Alexander[7] did not propose a model to explain the scintillations in glycine, it was suggested that they probably occur as a result of a temperature gradient that exists across the sample. Current pulses accompanied the scintillations and the direction of the measured current flow was dependent upon the direction of the temperature gradient. No optical spectrum was reported for the scintillations occurring in glycine.

In this paper we report optical-spectroscopy results

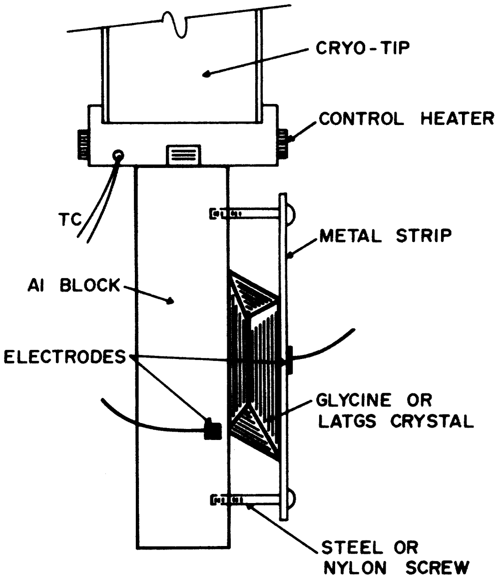

FIG. 1. Sample holder used in detecting scintillations in glycine and LATGS.

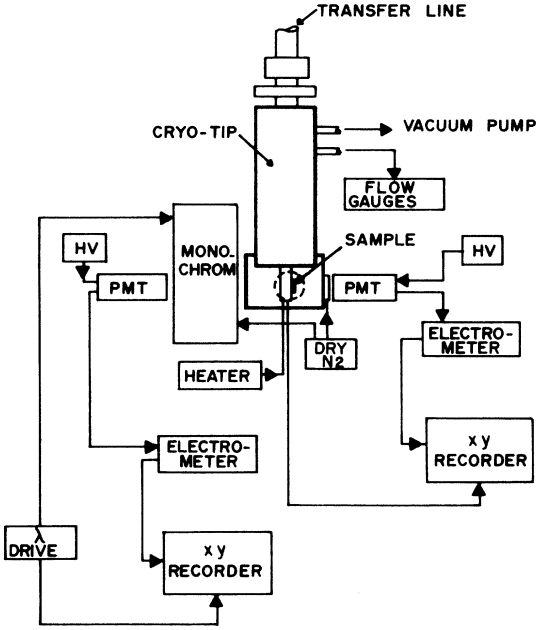

FIG. 2. Block diagram of experimental apparatus used in detecting scintillations in glycine and LATGS.

for scintillations occurring in single crystals of glycine and *L*-alanine-doped triglycine sulfate (LATGS). By scanning the spectrum slowly with a monochromator, we have identified seven lines in glycine and eight lines in LATGS, all of which belong to the second positive system of N_2. We believe that the N_2 spectrum is due to molecular nitrogen that has been adsorbed onto the crystal surface which is subsequently excited by the electrical discharges. The ubiquitous presence of N_2 on the surface of crystals might explain why other workers have identified the spectra of scintillations as that belonging to the second positive system of N_2.

Single crystals of glycine ($4 \times 4 \times 7$ mm^3) or LATGS ($4 \times 7 \times 10$ mm^3) were placed on an aluminum-block sample holder (shown in Fig. 1) and inserted into an evacuated (10^{-5} Torr) cryostat. Following evacuation, the crystal was cooled at a nonlinear rate of about 30 K/min to 77 K and subsequently heated at a rate of about 10 K/min to 280 K. The tail section of the cryostat was provided with two quartz windows so that the optical radiation produced by the scintillations could be simultaneously detected by two photomultiplier tubes (PMT's). One PMT recorded the total light emitted regardless of its wavelength, whereas the second PMT was placed at the exit slit of a $\frac{1}{4}$-m monochromator and detected only that radiation possessing a particular wavelength. The output of each PMT was amplified by an electrometer and recorded on an *xy* recorder. A block diagram of the experimental apparatus is shown in Fig. 2.

The scintillation spectrum was obtained by the following method: (i) subject the crystal to a temperature ramp to produce frequent occurrence (4–5/sec) of scintillations, (ii) detect the occurrence of a scintillation by observing a signal on recorder 1, (iii) scan the spectrum slowly (10 nm/min) with the monochromator and observe the signal on recorder 2, (iv) when both recorders produce a signal in coincidence, note the wavelength reading of the monochromator, (v) after the most intense lines have been identified, repeat the experiment several times by setting the monochromator dial at the identified wavelength and observing the coincidence signal of the two recorders, (vi) As a final check on the position of the spectral line, move the monochromator dial 0.3 nm to each side of the line and see if a coincident signal is observed; if not, then the spectral line has been properly identified. An estimate of the resolution of the monochromator was made by recording a mercury spectrum and determining the full width at half maximum of the 253.7-nm line (FWHM $\sim$0.3 nm) and also noting that the doublet at 313 nm could barely be resolved. Although a reasonable estimate of the accuracy of the spectral lines is ± 0.3 nm, as determined by the monochromator resolution, the accuracy of the wavelength dial is only ± 1.0 nm. Therefore, the spectral lines presented in Table I are only quoted with an accuracy of ± 1.0 nm. A previous attempt to photograph the spectrum by passing the radiation through a quartz-lens arrangement and focusing it onto the entrance slit of a 1-m monochromator was unsuccessful. Type-O plates were used as the detector but, unfortunately, were of insufficient sensitivity to reproduce the spectrum.

TABLE I. Summary of spectroscopy results (wavelengths in nanometers).

Glycine	TGS:*L*-alanine	Second positive N_2^a
	312.9 ± 1.0	313.60 (8)[b]
315.4 ± 1.0	315.6 ± 1.0	315.93 (9)
336.8 ± 1.0	336.6 ± 1.0	337.13 (10)
357.3 ± 1.0	357.3 ± 1.0	357.69 (10)
371.0 ± 1.0	370.8 ± 1.0	371.05 (8)
375.2 ± 1.0	375.2 ± 1.0	375.54 (10)
380.0 ± 1.0	379.9 ± 1.0	380.49 (10)
390.0 ± 1.0	390.8 ± 1.0	389.46 (7)

[a] Taken from R. Pearse and A. Gaydon, *The Identification of Molecular Spectra*, 4th ed. (Wiley, New York, 1976).

[b] Relative intensities of the spectral lines according to Pearse and Gaydon.

Prominent spectral lines produced by a scintillation in glycine are shown in Table I. Seven lines are identified and compared with the second positive system of nitrogen as given by Pearse and Gaydon.[9] Column 3 of Table I represents the prominent lines of the transitions occurring between the $C\,^3\pi_u$ and the $B\,^3\pi_g$ states of N_2. The numbers in parentheses are the relative intensities of each spectral line as determined by Pearse and Gaydon. Also presented in Table I are the spectral lines resulting from scintillations in LATGS. These lines also correspond to the second positive system of N_2.

The spectroscopy results of Table I exhibit reasonable agreement with the data of Yockey and Aseltine[1] for γ-irradiated KDP. A noteworthy exception is the presence of a spectral line at 390.0 nm in glycine and 390.8 nm in LATGS, which was absent in KDP. The first negative system of N_2^+ exhibits a very strong line at 391.4 nm, and, due to the uncertainty in our measurements, it is possible that the 390.8 ± 1.0-nm line in LATGS belongs to this system. Robertson and Baily[4] have reported the spectrum associated with scintillations in irradiated and unirradiated triglycine sulfate (TGS) and identified five lines associated with the second positive system of N_2.

Spectroscopy results of the present work, and all previous work, indicate that the predominant optical spectrum produced by a scintillation is that belonging to the second positive system of N_2. We attribute this to a layer of N_2 that has been adsorbed onto the surface of crystals due to their exposure to the ambient environment. This layer is probably not removed by evacuation at 10^{-5} Torr. When a discharge occurs at the surface of a crystal it will produce a N_2 spectrum because of this adsorbed layer. Discharge-energy data[10,11] indicate that the energy associated with a scintillation is sufficient to ionize molecular N_2. Thus the spectrum of the scintillations provides very little information concerning the internal charge producing mechanism but fortuitously appears as a surface effect. The details of the transition layer (e.g., TGS-N_2-atmosphere) are clearly beyond the scope of this paper; however, this transition layer may explain the polarization exhibited by KDP as reported by Yockey and Aseltine.[1] The mechanism whereby a scintillation is produced in a ferroelectric or nonferroelectric crystal is unclear, and we offer no model in the present work. We can, however, offer some insight into the problem that should be valuable in future theoretical developments.

Apparently the scintillation phenomenon cannot be based upon ferroelectricity. This conclusion is supported by the following experimental facts: (i) scintillations are observed in glycine—a nonferroelectric crystal; (ii) scintillations are observed in pressed pellets of glycine, indicating that domain structure is unimportant; (iii) scintillation activity in ferroelectric crystals does not appear to depend upon the orientation of the ferroelectric axis with respect to the direction of the temperature gradient. We cleaved a single crystal of TGS such that the ferroelectric axis was perpendicular to one of the crystal faces. Scintillations were observed for two orientations of the crystal; viz., ferroelectric axis parallel to the sample holder and ferroelectric axis perpendicular to the sample holder (see Fig. 1). From previous work[7] it was known that the scintillations resulted from a discharge from the upper surface of the crystal to the lower surface via the metal strap and screws. Thus, we expected frequent occurrence of scintillations when the ferroelectric axis was perpendicular to the sample holder surface but not when it was parallel. Several measurements indicated that the scintillations were independent of the ferroelectric axis orientation.

In conclusion, we have shown that the emission spectra of scintillations observed in nonferroelectric and ferroelectric crystals are identical and we attribute this spectrum to an adsorbed layer of molecular N_2 through which the discharge occurs. In addition, any theory proposed to explain electric discharges in crystals subjected to a temperature gradient should not be based on ferroelectric phenomena.

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