ment requires introducing neither Planck's constant ($\hbar$), the mass of the helium atom (m), nor the inner or outer undetermined radii (a and b) of quantized vortices. Besides relying thus upon less profound physical concepts, the result requires no adjustment to experiment.

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[1]H. Hall and W. Vinen, Proc. Roy. Soc. (London) A238, 204 (1956).

[2]H. Hall and W. Vinen, Proc. Roy. Soc. (London) A238, 215 (1956).

[3]L. Onsager, Suppl. Nuovo cimento 2, 249 (1949).

[4]R. Feynman, Progress in Low-Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1955), Vol. 1, Chap. II, p. 36.

[5]Additional dynamic complications for rotating systems (Coriolis effects) are neglected as higher order in Ω for absorption (quadratic).

[6]Recalling that temperature waves support no first-order pressure fluctuations, we recognize that second-order processes assume primary importance.

[7]Local density deviations from the ambient contribute positively to the potential energy, regardless of sign (consider the potential energy content of ordinary sound).

[8]In contrast to the normally adiabatic nature of second sound, involving no actual conversion between phases.

[9]Upon conversion from superfluid, for example, there results a small portion of normal fluid travelling in the wrong direction, with consequent frictional retardation and degeneration of kinetic energy. The reverse process presents greater subtleties.

[10]Note that whether in "closing" the normal component enters regions of greater or less wave energy remains immaterial, as either process produces irreversible energy transfer (thus the absolute value signs). Such a consideration also enters integration of Eq. (4), following.

[11]Note independence on domain size upon normalization for density calculation.

[12]The present result remains valid only for conditions wherein the wavelength greatly exceeds the domain size ($\lambda \gg a$). A re-evaluation would be necessary for the opposite extreme, and in fact, for high enough frequencies ($\lambda \ll a$), the effect may conceivably disappear.

TUNNELING-ASSISTED PHOTON EMISSION IN GALLIUM ARSENIDE *pn* JUNCTIONS

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When a gallium arsenide *pn* junction is biased in the forward direction with a voltage nearly equal to the energy gap, efficient radiative recombination is observed. We shall show evidence that this recombination involves tunneling of carriers across the space charge region of the *pn* junction.

The mechanism is believed to consist of an electron from the conduction band of the *n*-type region tunneling to a virtual state (in the energy gap) from which it makes a radiative transition to the valence band of the *p*-type region, thus recombining with a hole.

The possibility that photon-assisted tunneling may occur in germanium tunnel diodes has been proposed by Aigrain[1] and by Sommers,[2] but, to the best of our knowledge, no clear-cut evidence for this mechanism has been reported.[3] However, the converse effect, field-assisted absorption of photons,[4] has been observed in a number of materials[5] including GaAs.[6]

For our experiment, GaAs *pn* junctions were made between degenerately doped regions either by alloying a tin dot to a zinc-doped crystal or by diffusing zinc into a degenerate *n*-type crystal. The diodes were operated at liquid helium temperature. The forward current-vs-voltage characteristic of these diodes shows that when the applied voltage is nearly equal to the energy gap (about 1.5 eV at 4.2°K), the current rises very rapidly with increasing voltage. It is under this bias condition that an infrared emission of near band-gap energy is obtained. The emission spectrum, which has the form of Fig. 1, peaks at an energy somewhat lower than the gap, and shifts to higher energies as the current increases. A shift from 1.450 to 1.479 eV was obtained with a change in current density from about 70 to 1000 A/cm^2.

The exact value of the energy gap is not known because the material is heavily doped. However, previously reported measurements[7] of photovoltaic threshold, absorption edge, and V-I characteristics (voltage at which the current rises rapidly)

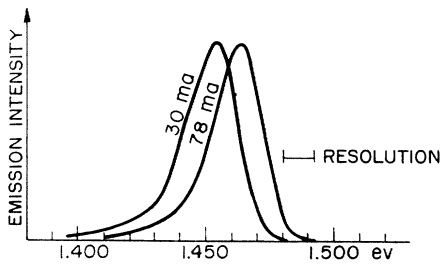

FIG. 1. Emission spectra of a GaAs *pn* junction at 4.2°K for two currents through the junction.

all indicate that the traffic of carriers involves transitions with an energy difference of 1.49 ± 0.01 eV at 4.2°K. Having found no evidence for discrete levels accounting for this energy difference, we have assumed that in our GaAs the energy gap is narrower than in pure material by about 0.04 eV. Actually, tunneling-assisted photon emission can also occur with discrete levels. But for the sake of relative simplicity, let us describe the phenomenon in the case of the shrunken gap model.

According to the tunnel-assisted photon-emission mechanism (Fig. 2), at 0°K, the most intense emission should occur at a photon energy,

$$h\nu_{\text{peak}} = eV - \epsilon_p + \epsilon_n m_1/m_2,$$

where V is the voltage across the pn junction, ϵ_p and ϵ_n the energies of the Fermi levels with respect to the nearest band edge, m_1 the effective mass of the conduction band, and m_2 the light-hole effective mass of the valence band (in nearly all the units tested the doping level was such that $\epsilon_p m_2 > \epsilon_n m_1$). The term $(-\epsilon_p + \epsilon_n m_1/m_2)$ is imposed by momentum conservation, for we are dealing with direct transitions. The lowest photon energy obtainable is $h\nu_{\text{min}} = eV - (\epsilon_n + \epsilon_p)$ corresponding to transitions between the band edges at the boundaries of the space charge region. Because the barrier width through which the electron must tunnel increases as the kinetic energy of the electron in the conduction band decreases, the tunneling probability for carriers involved in the lowest energy photon emission decreases. Furthermore, the number of carriers making these transitions goes as the density of states and therefore decreases between the Fermi level and the band edge. Hence, the emission spectrum is expected to decrease rapidly between $h\nu_{\text{peak}}$ and $h\nu_{\text{min}}$, in qualitative agreement with the observation. A theoretical treatment of this mechanism is under way.

The dependence of emission intensity with current is shown in Fig. 3. Beyond a certain current, the emission is proportional to the current as expected from a very efficient process. The emission efficiency was calculated from the data of Fig. 3, taking into account the following: (1) geometrical factors of the optics involved assuming isotropic distribution of emission intensity inside the semiconductor, (2) refraction at the GaAs-air interface, and (3) multiple internal reflections assuming negligible absorption. The detector (PbS at 195°K) in series with the optics used for the spectral measurement was calibrated against a standard lamp whose spectral radiance is known with an accuracy of 15%. A quantum efficiency of about 100% is obtained in the range where the emission intensity is proportional to the current, if one assumes that none of the light emitted in the direction away from the detector ever reaches the detector. But, if the light emitted away from the detector is reflected towards the detector by the electrode opposite the exit surface, then a quantum efficiency of about 50% is obtained.

The author is indebted to Mrs. M. Massoulié

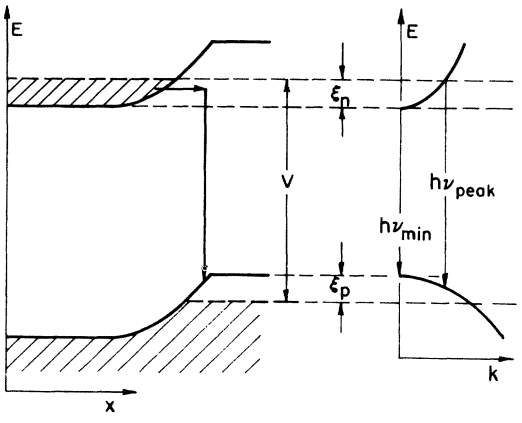

FIG. 2. Schematic description of the tunnel-assisted photon-emission mechanism.

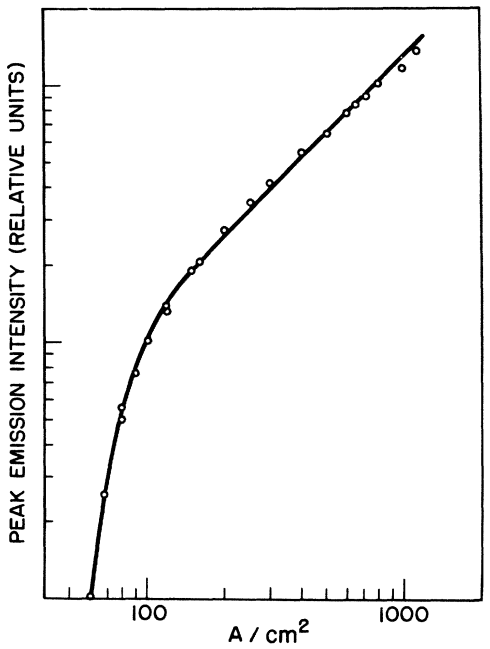

FIG. 3. Emission intensity vs current density through the pn junction.

for her assistance, to Dr. M. LaMorte for sample preparation, and to Miss M. Gabler for the final processing.

[1]P. Aigrain (private communication, 1959).
[2]H. S. Sommers, Jr., Phys. Rev. 124, 1101 (1961).
[3]J. I. Pankove, Ann. phys. 6, 331 (1961).
[4]W. Franz, Z. Naturforsch. 13A, 484 (1958); L. V. Keldysh, J. Exptl. Theoret. Phys. (U.S.S.R.) 34, 962 (1958) [translation: Soviet Phys.-JETP 34, 665 (1958).
[5]R. Williams, Phys. Rev. 117, 1487 (1960); 126, 442 (1962). L. V. Keldysh, V. S. Vavilov, and K. I. Bricin, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovakian Academy of Sciences, Prague, 1961), p. 824.
[6]T. S. Moss, J. Appl. Phys. 32, 2136 (1961).
[7]J. I. Pankove and M. Massoulié, Bull. Am. Phys. Soc. 7, 88 (1962); J. Electrochem. Soc. 11, 71 (1962).

FERROELECTRICITY IN POTASSIUM NITRATE AT ROOM TEMPERATURE

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Potassium nitrate (KNO_3) was reported to be ferroelectric in the phase-III modification which occurs stably in the temperature range of 110°C to 125°C at atmospheric pressure.[1] Now ferroelectric behavior, at room temperature, has been observed in KNO_3. The phenomenon, as evidenced by a hysteresis loop, completely vanished within several hours after the earlier samples were prepared. Therefore, our ferroelectric observation was thought to be due to the existence of phase III as a metastable state at room temperature. Subsequent x-ray diffraction analysis verified that we in fact had phase III at room temperature and atmospheric pressure, and further refinement in the fabrication technique has extended the lifetime to several weeks.

The samples were prepared from reagent grade KNO_3 powder which had been dried at 130°C under a vacuum of approximately 10 microns of mercury for several days. The dried powder was then melted onto a copper substrate which served as one of the electrodes. Various materials have been used as the second electrode, e.g., air-drying silver paint, colloidal graphite, mercury, and metallic foils attached while the KNO_3 was still molten. These elements have been made as thin as 2×10^{-3} cm. It has been noted that any moisture, either in the original powder or absorbed from the atmosphere after the layers are formed, greatly influences the ferroelectric behavior of these elements.

Figure 1 shows a typical hysteresis loop taken at 60 cycles per second using a standard Sawyer and Tower[2] circuit. The observed coercive field is of the order of 6 kV/cm and the value of the spontaneous polarization thus far observed is approximately 3.5 $\mu C/cm^2$. The flat part of the loop corresponds to a dielectric constant of about 16 while the steep part corresponds to a value of about 10^4. It can be seen from Fig. 1 that these layers show nearly perfect saturation. The ratio of the maximum slope to the minimum slope, i.e., the so-called "squareness ratio," for this sample was of the order of 600:1. Evidently, the thin layers show a high degree of orientation. This is supported by the fact that for layers of the order of thickness of 2×10^{-2} cm, the saturation is not nearly so perfect nor is the squareness of the loop so pronounced (of the order of 100:1). Furthermore, this material seems to demonstrate true coercivity as may be seen from Fig. 2 which shows a series of minor loops obtained by multiple exposure of the photographic plate for various applied fields. No definite information can be given as to the switching time of these elements

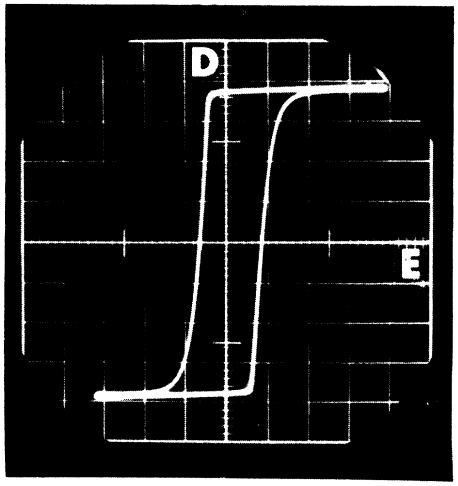

FIG. 1. Typical 60-cps hysteresis loop of KNO_3 at 20°C.