claim a 5% accuracy for their calculation while Pines claims 20% for his. Unfortunately, we do not have as yet an independent experimental value for this spin contribution. However, these two different types of calculation do give the same result, and in the case of lithium, for which χ_s has been measured, the calculations are in good agreement with the experimental value.

Thus we conclude, that if the value of the orbital contribution is that given by the Landau-Peierls formula, the susceptibility of sodium is anomalously high.

If either of the values for $\chi_s + \chi_c$ in Table II are accepted as correct, then our experimental value is seen to imply a surprisingly small value for the orbital diamagnetism. Using the free electron χ_s, we obtain $\chi_0 = +(0.25 \times 10^{-6})$; using the Kohn and Kjeldaas value, we obtain $\chi_0 = +(0.07 \times 10^{-6})$. The value of $-(0.23 \times 10^{-6})$, expected on the free-electron theory, differs from both of these by several times the estimated error.

We have no explanation of these disparities. While it is true that according to the band theory of metals, the Landau-Peierls formula does not give the complete orbital susceptibility,[16] it would be surprising if the correction terms were responsible.

Finally, we shall discuss the low-temperature data. The decrease in susceptibility by 4.5% from room temperature to 55°K is roughly what is to be expected from the change in the Fermi level with density. Below 77°K, we have found no sign of an anomaly similar to that found in the Knight shift in sodium[12] which changes by 5% between 77°K to 55°K. Thus we conclude that, at least in the limited temperature range 77°K to 55°K, the behavior of the Knight shift is not due to a rapid change in the density of states.

Note added in proof.—After submitting this paper, we received a preprint of a paper by Schumacher and Slichter which gives the results of their measurement of the conduction electron spin susceptibility in sodium. (This paper is to appear soon in *The Physical Review*.) They obtain for χ_s a value per g of $(0.96 \pm 0.1) \times 10^{-6}$ cgs units corrected to room temperature. If one uses the value of 0.96×10^{-6} to calculate the orbital diamagnetism as described in the discussion above, one obtains $\chi_0 = -0.03 \times 10^{-6}$. This is still much less than the free electron value of -0.23×10^{-6}. However, the uncertainties in the values of χ_s, χ_c and the total χ are now such that a combination of extreme values of these quantities can lead to a χ_0 close to the free electron value. Hence, the existence of a substantial deviation of the actual orbital diamagnetism from the free electron value, while appearing most likely from the data, is not definitely established.

ACKNOWLEDGMENTS

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[16] A. H. Wilson, Proc. Cambridge Phil. Soc. 49, 292 (1953); E. N. Adams, Phys. Rev. 89, 633 (1953).

Electroluminescence of GaP

G. A. WOLFF, R. A. HEBERT, AND J. D. BRODER
Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey
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Electroluminescence has been observed in GaP single crystals. Above a threshold current the intensity of the emitted light is proportional to the ac and dc passing through the crystals. The orange color of the light emission probably is due to the presence of Ga as activator, while the brilliant, deep red luminescence is observed in crystals where Zn is a possible activator. The temperature dependence of the luminescence is negligible in the range from liquid nitrogen temperature to 160°C. The impact excitation mechanism of Piper and Williams is proposed.

SINGLE crystals of GaP have been prepared[1] which were found to emit orange-colored light when either dc, or ac (up to 20 000 cps) is applied. Massive In, Ga, Hg, Cd, Zn, Pb, conducting glass, and point contacts of W were used as electrodes. Above a threshold current, the light intensity is proportional to the ac and dc passing through the crystals (Fig. 1), as has been found for SiC[2] and ZnS:Cu[3]; it increases exponentially with

voltage. Since rectification is found in the crystals, the light output in the forward direction is less than in the reverse direction. This also holds true when ac is applied; the light pulses observed are in phase with the applied voltage and are sinusoidal. This was determined with an oscilloscope by synchronizing the photomultiplier (RCA 5819) output with the voltage applied (Fig. 2). There were no out-of-phase pulses observed. The decay time, as derived from the ac measurements, is less than 25 μsec. Using dc, the light emitted from the majority of the crystals appears in the vicinity of the

[1] Wolff, Keck, and Broder, Phys. Rev. 94, 753 (1954).
[2] Lehovec, Accardo, and Jamgochian, Phys. Rev. 83, 603 (1951); 89, 20 (1953).
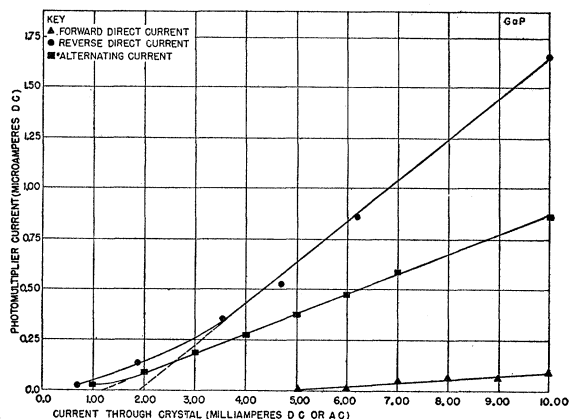[3] W. W. Piper and F. E. Williams, Phys. Rev. 87, 151 (1952).

FIG. 1. The intensity of the electroluminescence, given as the photomultiplier current, as a function of the current passing through the crystal.

FIG. 2. Oscillogram of photomultiplier current (lower curve) synchronized with the current through the crystal (60 cps; upper curve). The current is nonsinusoidal due to nonohmic characteristic and rectification in the crystal. More intense emission is observed during the reverse current interval.

cathode. The temperature dependence of the luminescence is negligible. Light is also emitted when a layer of GaP powder, or a layer of a suspension of GaP powder in a dielectric, is placed between a metal and a conducting-glass electrode. When GaP crystals are bombarded with electrons from a Van de Graaff generator, the same orange-colored luminescence resulted. Neither fluorescence, phosphorescence, thermoluminescence in the visible range, nor photoconductivity has been observed.

The electroluminescence begins at 5600 A, which is close to the end of the absorption edge of GaP (5300 A). It can be concluded from this that the emission is a direct electron-hole recombination but it is more likely an electron-hole recombination through an activator, having the energy term close to the valence band. The GaP crystal might very well be self-activated, since it has been grown from a solution in Ga.[1] As a result of adding Zn or Cu to the Ga solvent prior to preparing the GaP solution and crystallization, GaP crystals having a brilliant, deep red electroluminescence were obtained and these were of a much higher efficiency than the crystals showing the orange luminescence. The spectral range of the red luminescence begins at about 6800 A as was found from the spectra recorded photographically. In this instance, there was definite shift of the emission toward longer wavelengths. Probably the spectra extend beyond 8900 A, where the film sensitivity is negligible.[4] Whether or not Zn or Cu was the activator responsible for the red luminescence is yet to be determined, but the evidence points to Zn in relatively small amounts. The crystals were prepared in quartz tubes, which would indicate the possibility of Si as a co-activator. There was no noticeable effect upon the orange luminescence as a result of doping the crystals with elementary C, Si, Ge, Mn, or S.

GaP:Zn corresponds very largely to ZnS:Cu. GaP is isoelectronic with ZnS and has the same crystallographic structure. Among the colored III-V compouuds, AlP (light yellow), AlAs (brown) and GaP (orange),[5] there is strong indication that GaP will have good luminescent properties since it is closely related to ZnS. Since, however, GaP has a much lower energy gap than ZnS—close to that of CdS—and the semiconductor properties are more pronounced, with the bonding energy much higher than ZnS, basic differences in the properties of these two luminescent materials are to be expected.

It is proposed that impact excitation as suggested by Piper and Williams[3,6] for ZnS:Cu, causes the electroluminescence in GaP at the metal-semiconductor barrier. It was found that in one out of ten cases luminescence did not occur in the vicinity of the cathode. From this, it may be concluded that recombination of injected minority carriers from a p-n junction captured by the activator system[2,7] is a second possibility for luminescence, although it is as yet impossible to prepare p-n junctions in GaP crystals to confirm this point. By doping with S, n-type material only was obtained. It was dark in color and had relatively low resistivity.

It might be worthwhile to mention that electroluminescence was also observed in GaAs and Si by means of a snooperscope, but the luminescence was irregular, fading, disappearing and reappearing as the current passed through the crystals.

[4] *Note added in proof.*—A second type of luminescence of a yellow-green color, seen in Zn-doped crystals, consists of the red band mentioned in the text and a band in the range of 5300 A to 6300 A, with a maximum at 5900 A.
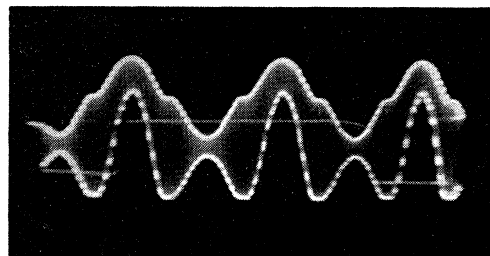
[5] Absorption edges as determined in our laboratory are located at about 4000 A, 5730 A, and 5200 A which corresponds to energy gaps of approximately 3.1 ev, of 2.16 and 2.39 ev.
[6] W. W. Piper and F. E. Williams, Brit. J. Appl. Phys. Supplement 4, 39 (1955); F. E. Williams, Advances in Electronics 5, 158 (1953).
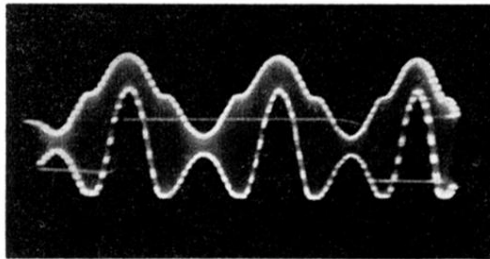[7] M. Schoen, Z. Naturforsch. 8a, 442 (1953).

FIG. 2. Oscillogram of photomultiplier current (lower curve) synchronized with the current through the crystal (60 cps; upper curve). The current is nonsinusoidal due to nonohmic characteristic and rectification in the crystal. More intense emission is observed during the reverse current interval.