

TABLE III. Approximate line width in gauss.

Line width in gauss	KCl			NaCl	KBr	LiF
	$Cl^{35}-Cl^{35}$	$Cl^{35}-Cl^{37}$	$Cl^{37}-Cl^{37}$			
	2.4	2.0	1.6	7.5	4	17

The variation of the splitting with the angle θ between the bond direction and the magnetic field enables us to determine the admixture of s and p functions on the halogens. We have obtained 30% s and 70% p for both KCl and NaCl. For $|\psi(0)|^2$, we have obtained $1.9 \times 10^{24} \text{ cm}^{-3}$.

The KBr spectra are more difficult to analyze because of second-order effects and quadrupole effects. However, the analysis indicates the existence of Br_2^- molecule-ions. Second-order effects play also an important part in LiF. A tentative analysis suggests that the bond direction of the F_2^- molecule-ion is (110).

Typical values of the observed line widths are listed in Table III. It appears that the predominant relaxation is due to hyperfine interaction. Spin-spin interaction seems also to play a role, and this indicates that high local concentrations of color centers might be formed by x -irradiation.

A full account of the present investigations will be published in a forthcoming paper. The analysis of the results was only possible through the advice of C. P. Slichter and the continuous help of T. G. Castner.

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¹ See, e.g., Kip, Kittel, Levy, and Portis, *Phys. Rev.* **91**, 1066 (1953).

² F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

³ D. Dutton and R. Maurer, *Phys. Rev.* **90**, 126 (1953).

⁴ R. Sternheimer, *Phys. Rev.* **84**, 244 (1953).

Effect of Proton Irradiation upon the Electrode Potential of Tungsten

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NUCLEAR irradiation may be expected to alter the electrochemical and chemical properties of metals. As a preliminary study we have measured the effect of proton irradiation upon the electrode potential of tungsten in aqueous salt solutions. Tungsten wire specimens 0.012 in. in diameter were chosen since previous investigations¹ have shown that at room temperature the radiation effects in this material are quite stable. Reproducible and steady electrode potential measurements were obtained by means of the following procedure. The tungsten surfaces were degreased with alcohol and acetone, immersed in a strong aqueous solution of ammonia for several minutes, and washed with an oxygen-free saturated solution of KCl in dis-

tilled water. The specimens were then placed in an oxygen-free saturated solution of KCl in distilled water, and their electrode potentials were measured against a saturated calomel cell with a vacuum-tube potentiometer. The solution and the standard cell were kept at 30°C in a thermostat. The results obtained are shown in Table I.

First of all it should be pointed out that after bombardment the wires were very slightly radioactive (about 1000 counts per minute), presumably because of some minor impurities. This activity is much too weak to produce any significant changes in the electrolyte and thus the observed effects have to be ascribed to radiation-induced changes in the metal. It appears that the effect of proton irradiation upon the electrode potential of tungsten is large and actually it is much greater than the effect of severe cold work. At first glance the magnitude of the observed effect is surprising in view of the fact that the diameter of the wire is less than one percent of the mean free path of the 260-Mev proton in tungsten. It should be remembered, however, that the majority of the radiation effects produced under these conditions appears to be caused by highly effective secondary nucleons produced in inelastic collisions rather than by elastic collisions of the incident protons.¹ The results indicate also that the change in electrode potential increases with the intensity of the proton beam as expected. The greater change obtained with protons of 130-Mev energy than with 260-Mev protons is rather difficult to understand and may not be real. In all cases the potentials of the irradiated specimens are anodic (less noble) to the annealed specimens, which means that irradiation makes the tungsten more reactive chemically.

The experiments show that irradiation alters significantly the electrochemical properties of metals, and that such measurements may be used to study the nature and extent of the effects produced. One would expect the change of the electrode potential to be associated with production of localized lattice imperfections at the metallic surface. These defects are primarily dislocations formed either by displacement spikes or by collapse of vacancy clusters. Other defects such as vacancies and interstitials, even if they were sufficiently stable in the interior of the grains, would probably disappear rather rapidly near the surface. The

TABLE I. Electrode potentials of proton irradiated tungsten.

Treatment	Proton irradiation	Electrode potential ^a millivolts (anodic)
Annealed ^b	none	0
Cold drawn	none	22
Annealed and irradiated	$1.9 \times 10^{15}/\text{cm}^2$ at 130 Mev	72?
Annealed and irradiated	$1.8 \times 10^{15}/\text{cm}^2$ at 260 Mev	39
Annealed and irradiated	$6.8 \times 10^{15}/\text{cm}^2$ at 260 Mev	47
Annealed and irradiated	$2.2 \times 10^{16}/\text{cm}^2$ at 260 Mev	84
Irradiated and annealed ^b	$2.2 \times 10^{16}/\text{cm}^2$ at 260 Mev	0

^a The electrode potentials are reported *versus* the annealed tungsten.

^b The annealed specimens were heated for 2 hours at 900°C in an argon atmosphere.

existence of such a gradient of defects near the surface is indicated by the recent observations of the effect of irradiation on the solubility rate of Fe_2O_3 in hydrochloric acid.²

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¹ Pearlstein, Ingham, and Smoluchowski, Phys. Rev. 98, 1530 (1955).

² M. Simnad and R. Smoluchowski, J. Chem. Phys. (to be published).

Radiative Transitions in Semiconductors

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RADIATION produced by carrier injection has been observed from GaSb, GaAs, InP, and the Ge-Si alloys at room temperature and 77°K. The spectral distributions of the radiation are maximum at energies close to the best estimates of the band gaps of these materials; consequently, the evidence is that the radiation is due to the direct recombination of electron-hole

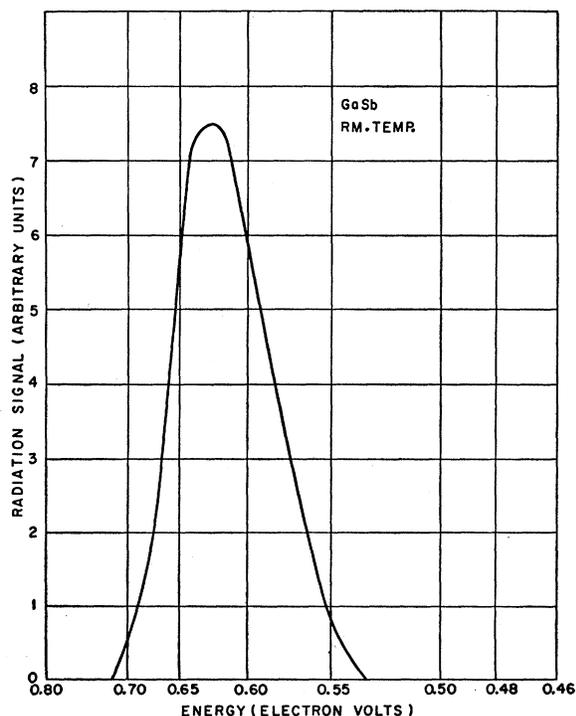


FIG. 1. Spectral distribution of recombination radiation from GaSb at room temperature.

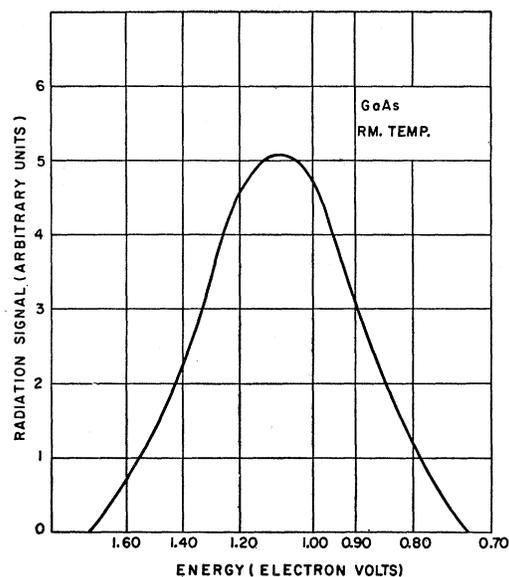


FIG. 2. Spectral distribution of recombination radiation from GaAs at room temperature.

pairs. Direct electron-hole recombination radiation from a semiconductor has been previously observed from Ge and Si by Haynes and Briggs¹ and from SiC by Lehovec *et al.*²

The radiation was obtained by injecting minority carriers into 0.02 in. thick samples of material by means of point contacts or by broad area injecting contacts of silver paint applied to the surface of an appropriately etched semiconductor. The samples were soldered to kovar rings and mounted on temperature-controlled copper blocks. The diodes were pulsed by a 50% on-off square wave generator operating at 100 cps; currents up to 1 amp/cm² were passed in the forward direction. Radiation was detected by a dry-ice cooled PbS cell. The spectral distribution of the radiation from GaSb and GaAs was obtained by using a Perkin-Elmer monochromator with a fused quartz prism.

Figure 1 shows the spectral distribution of the radiation from GaSb at room temperature. The peak of the emission line occurs at 0.625 eV. This is to be compared with the value of 0.67 eV for the band gap of GaSb obtained by Blunt *et al.*³ from absorption measurements. The present sample was *n*-type having a free carrier density of $\sim 10^{17}/\text{cm}^3$.

Figures 2 and 3 show the lines observed from GaAs at room temperature and 77°K, respectively. The peak of the radiation occurs at 1.10 eV at room temperature and at 1.19 eV at 77°K. If we assume a linear variation of the line position with temperature, the line position is given by $1.22 - 4 \times 10^{-4}T$ electron volt. If we attribute the radiation to the recombination of injected holes and electrons with the emission of a photon and the simultaneous absorption or the emission of a phonon, the line positions are at variance with the value of 1.35 eV