## Electrical Properties of Gold-Germanium Alloys*

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(Received July 14, 1953)

Recent studies[1–3] have shown that zinc, and copper, as well as the third and fifth column elements, can act as activator elements in germanium. The present note deals with gold, which is shown to be an acceptor capable of taking up electrons at two distinct energy levels. The first acceptor level is 0.15 ev above the filled band, the second (trapping) level is 0.20 ev below the conduction band.

Gold-germanium alloys have been made using cp gold wire (exact purity unknown), gold wire (99.96 percent), and gold ingot[4] (purity checked in the G. E. Research Laboratory and found to be 99.99 percent or better). Consistent results were obtained using these materials.

Gold was added during growth of the single crystals in proportions ranging from 0.01 to 0.1 percent. *N*-type crystals showed an increase in resistivity at the point of addition; *p*-type crystals showed a decrease. The segregation coefficient (ratio of gold in the solid to that in the liquid) was found to be about $1.5\times 10^{-5}$, assuming that each gold atom furnished two acceptor states. The solubility of gold appears to be about $10^{15}$ atoms/cm$^3$.

Figure 1 shows Hall effect data, which also give the density of carriers, for samples cut from a gold-doped germanium ingot. Temperatures of measurement ranged from 77°K to 400°K. The steep slope is in contrast to the behavior of the usual impurities (including zinc and copper), for which the Hall curve is practically constant in this temperature range. The slopes indicated an ionization energy of ~0.20 ev for the *n*-type samples, ~0.15 ev for the *p*-type sample.

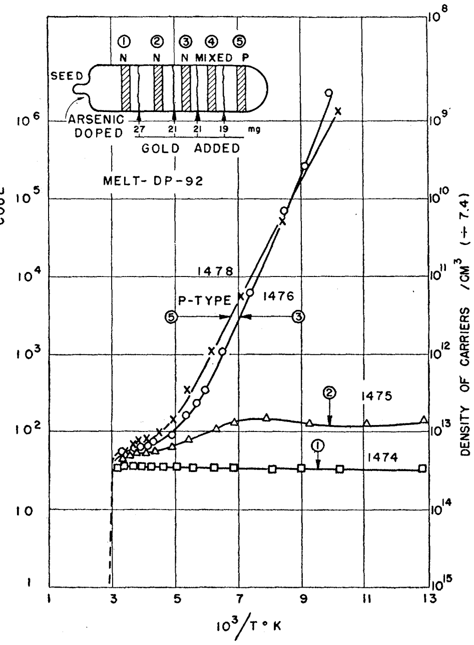

Fig. 1. Hall coefficient *vs* $1/T$°K for a series of germanium samples cut from wafers containing progressively increasing amounts of gold. The crystal was originally *n*-type before gold was added. Each successive wafer is more *p*-type as the result of the addition of gold, as well as the normal segregation process. The scale at the right represents (1/7.4) times the actual density of carriers.

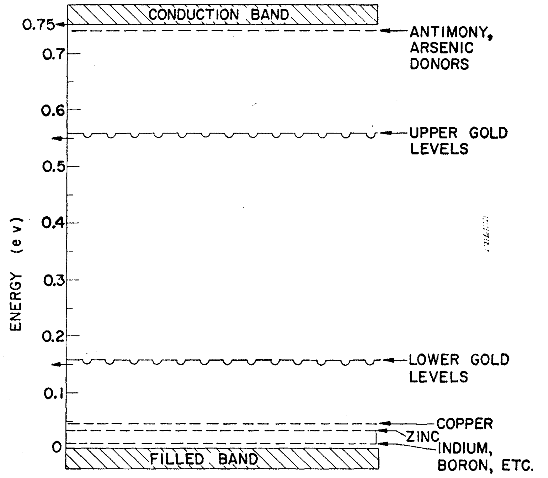

Fig. 2. Impurity level spectrum of germanium, based upon published work to date. Indicated are the acceptor levels of gold, as well as those of zinc and copper and the third column elements. The donor levels are those characteristic of the fifth column elements. The upper gold level is seen in conduction processes mainly as an electron trap, whereas the lower gold levels act both as electron traps and high-ionization energy acceptors.

The observed results may be accounted for in terms of the scheme of Fig. 2. Acceptor levels at 0.20 ev below the conduction band and 0.15 ev above the filled band are indicated. The observed properties are then determined by the degree to which these levels are filled by electrons from donor impurities. If no such impurities are present, the crystal is *p*-type.

These experiments also showed that the number of upper gold levels was equal to the number of lower gold levels, to within experimental error (±25 percent). This might be accounted for if each gold atom accepts one, then a second electron, to become Au$^-$ and Au$^{--}$.

Several interesting properties have been discovered in gold-doped germanium at 77°K: (a) a slow-decay component has been found in the photoconductivity following illumination in the infrared; (b) current-pulsing, in some samples, leads to immediate loss of conductivity, followed by its slow reappearance; (c) new photoconductivity bands in the infrared, apparently associated with the levels discussed here, have been found by R. Newman. The phenomena, which will be discussed in detail in later reports, appear to be related to disturbance of the equilibrium between the various traps and the conduction bands.

By proper compensation of impurities, resistivities at 77°K as high as $5\times 10^7$ ohm cm have been obtained. This is an aid in the doing of experiments in which the relatively high conductivity of germanium has been a hindrance.

The high ionization energy of gold in germanium also leads to simplification of the problem of studying germanium in the impurity ionization range, since many of these experiments can now be done in the range 77°K to room temperature.

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* Some of these results were presented at the 1953 Durham meeting, American Physical Society [Phys. Rev. **90**, 208 (1953)].

[1] W. C. Dunlap, Jr., Phys. Rev. **85**, 945 (1952).

[2] C. S. Fuller and J. D. Struthers, Phys. Rev. **87**, 526 (1952).

[3] F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953).

[4] I wish to thank M. D. Fiske for a supply of this gold.

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## Scintillation Response of Organic Phosphors

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(Received March 23, 1953; revised manuscript received July 14, 1953)

The scintillation efficiencies and decay times of organic phosphors depend upon the nature and energy of the absorbed particles. From the available experimental data concerning these quantities we may infer the nature of the quenching processes which occur for ionizing particles and calculate the scintillation response of these phosphors.

For fast electrons internal conversion of energy by electronically excited molecules is almost certainly the predominant quenching process. It is consistent with the efficiency being independent of electron energy, and Birks[1] has shown that it can quantitatively explain the low values found. For more heavily ionizing particles the scintillation efficiency may become very small, yet the accompanying decrease in decay time is relatively slight.[2] This indicates that the additional quenching is due to bimolecular processes, e.g., neighboring ionized and electronically excited molecules may interact to form new chemical entities (such as dianthracene in anthracene), excited molecules may be affected adversely by the coulomb fields of neighboring ions and return non-radiatively to the ground state, and interaction between excited molecules may occur leading to non-radiative dissipation of their electronic energy. This latter process is discussed by Black[3] who shows that it can provide an interpretation of the experimental data. This author also considers the effects of migration of energy out of the excitation column. However, due to the rapidity with which the bimolecular processes occur, expansion of the excitation column may be neglected whether taking place by resonance exchange of energy between molecules[4] or by photon emission and reabsorption.[1] Considering then that quenching of fluorescence is due to the combined effect of monomolecular and bimolecular processes in the excitation column, one may readily calculate the scintillation efficiency.

In penetrating a distance $\Delta x$ the particle loses energy $(dE/dx)\Delta x=\epsilon_0\Delta x$ to the molecules along or near its path. At a time $t$ after absorption the excess electronic energy of the molecules in this length of the excitation column is $\epsilon$, and we have

$$d\epsilon=-(p+k+a\epsilon)\epsilon dt, \tag{1}$$

where $a\epsilon$= rate of energy dissipation by bimolecular quenching processes, $k$= rate of energy dissipation by monomolecular quenching processes, and $p$= rate of energy dissipation by fluorescence emission. The total fluorescence emission from these molecules is

$$dL=p\Delta x\int_0^\infty \epsilon dL=\frac{p}{a}\ln\left(1+\frac{a}{p+k}\cdot\frac{dE}{dx}\right)\Delta x. \tag{2}$$

When $dE/dx$ is small this may be written in the approximate form

$$\frac{dL}{dx}=\frac{p}{p+k}\cdot\frac{dE}{dx}\Bigg/\left(1+\frac{1}{2}\cdot\frac{a}{p+k}\cdot\frac{dE}{dx}\right), \tag{3}$$

in agreement with the semi-empirical expression proposed by Birks.[5] The total scintillation emission excited by the particle is

$$L=\int_0^x dL=\int_E^0 \frac{dL}{dE}\cdot dE. \tag{4}$$

When $dE/dx$ is small, Eq. (4) reduces to $L=pE/(p+k)$; thus the constant $p/(p+k)$ denotes the phosphor efficiency for fast electrons. For the particular case of anthracene the complete integration of Eq. (4) has been performed using a graphical method. The differential energy loss $dE/dx$ was calculated from the theoretical stopping formula, except for alpha particles with energies below 10 Mev for which a semi-empirical method based on the range-energy curves for air was used;[6] the constant $p/(p+k)$ is 0.05 for anthracene, and the ratio $a/p$ was determined from the data for 5-Mev protons to be 0.23. The curves obtained are illustrated in Fig. 1 and compared with the experimental data.[7,8] The agreement is very satisfactory, and since the response of all organic phosphors is very similar we may expect this in other cases.

A point of interest concerns the decay time of fluorescence, which is longer when excited with particles than with ultraviolet quanta. This has been interpreted as the result of additional absorption and emission processes undergone by fluorescence photons emitted from initially ionized molecules;[1] an alternative explanation is that particle excitation involves an effective delay in the emission of fluorescence by ionized molecules due to the finite time of ion recombination. It is hoped that measurements of decay times and efficiencies of fluorescence excited by radiations in the wavelength range 3000A to 100A will resolve this question; such measurements are in progress in this laboratory.

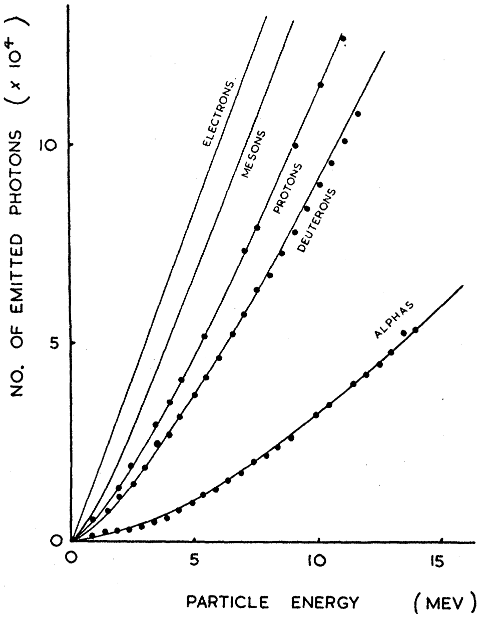

FIG. 1. Scintillation response of anthracene to ionizing particles. ——— theoretical curves; ● experimental observations.

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[2] Bittman, Furst, and Kallman, Phys. Rev. **87**, 83 (1952).
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[8] Frey, Grim, Preston, and Gray, Phys. Rev. **82**, 372 (1951).

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## Variable Activation Energy and the Motion of Lattice Defects*

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(Received June 30, 1953)

IN a recent paper, Overhauser[1] successfully analyzed isothermal annealing curves of irradiated copper on the basis of a variable activation energy, i.e., an activation energy which depends on the number of disturbances left in the lattice. The writer was concerned with the analysis of this type of annealing kinetics in another connection[2] and arrived at some general conclusions on the basis of a simple example. It is the purpose of this note to summarize the results briefly.

Let $n$ denote the number of lattice disturbances present at any time $t$, and assume that over the range of interest the activation energy, $E$, decreases linearly with increasing $n$. This simple case can be handled analytically. The source of this functional dependence of $E$ on $n$ is most likely the strains introduced in the lattice by the disturbances, particularly intersitial atoms.[1,3] A linear dependence is a reasonable approximation to the relation derived by Overhauser[1] on the basis of lattice strains. $E$ is expressed, therefore, as

$$E/k=E_0/k-\alpha n/k, \tag{1}$$

and the general rate equation for the disappearance of $n$ is

$$dn/dt=-\nu n^\gamma e^{-E_0/kT}e^{\alpha n/kT}. \tag{2}$$