Some Effects of Neutron Bombardment on MgO Crystals*

WILLIAM C. SCHIEVE, MARTIN A. POMERANTZ, AND ROMAS A. SHATAS†
Bartol Research Foundation of the Franklin Institute, Swarthmore, Pennsylvania
(Received May 6, 1959; revised manuscript received December 2, 1959)

Electrical conductivity and post-bombardment conductivity induced in MgO crystals by electron irradiation have been investigated following exposure to neutrons in the Brookhaven pile (integrated epi-cadmium fluxes of 4.2×10^{16} n/cm^2 and 5.1×10^{17} n/cm^2, respectively). A change in carrier lifetime was observed. No change in the temperature dependence of the yield was detected, indicating that the mobility of the charge carriers is unaffected by these irradiations. The 1.4-ev shallow trap previously observed was split into two levels by the neutron bombardment. This supports the association of this level with the 2.2-ev optical transition. Optical absorption measurements were conducted in the 0.6 to 3.0-ev range, and a previously unreported peak has been observed at 0.74 ev.

I. INTRODUCTION

WHEN a single crystal of MgO is bombarded by high-energy electrons, an electrical conductivity is induced.[1] Electrons lifted into the conduction band (and corresponding holes in the filled band) act as mobile charge carriers until they are captured by trapping centers. Measurements of this bombardment-induced conductivity have yielded information about carrier lifetime and mobility.[2]

Furthermore, under certain conditions, it has been observed that a conductivity persists following the cessation of the electron bombardment. This post-bombardment conductivity, which decays at a rate depending upon temperature, is a consequence of the re-emission into the conduction band of carriers captured in shallow traps. These carriers eventually recombine, or are captured by deeper trapping centers. From measurements of the temperature dependence of the rate of decay of the post-bombardment conductivity, the thermal energy level of shallow trapping centers can be determined.[3]

The purpose of the present work was to investigate the effects of neutron irradiation upon the aforementioned phenomena in MgO. Previously, Day[4] had measured the photoconductivity induced in MgO by neutron bombardment, and concluded that displacement effects saturate at neutron doses of 10^{15} n/cm^2. More recently, Clarke[5] has investigated the optical absorption induced in MgO by neutron irradiation. He studied the region 1.2 to 6.0 ev quite thoroughly. In the present experiments, optical absorption measurements were made in conjunction with the observations of electron-bombardment effects, with particular emphasis upon the 0.6 to 3.0-ev region.

II. LIFETIME AND MOBILITY EFFECTS

The phenomenon of electron bombardment-induced conductivity in MgO is represented by the following relationship:

$$m=\delta\mu_d\tau V_c/d, \tag{1}$$

where $m=I_c/I_p$ is the ratio of induced current to the primary electron beam current, δ is the number of internal secondary electrons (or holes) raised into the conduction band by one primary electron per unit path, μ_d is the average carrier drift mobility, V_c is the potential across the sample of thickness d, and τ is the mean lifetime of the carrier in the conduction band.

Previous measurements of m at a number of temperatures yielded values of $\tau\approx5\times10^{-10}$ sec for unirradiated MgO samples.[2] The relationship between lifetime and density of trapping centers is

$$N=1/v_0\sigma\tau, \tag{2}$$

where N is the number of traps per cm^3, v_0 is the average thermal velocity, and σ is the average capture cross section of the trapping centers. Taking σ to be 10^{-15} cm^2 gives $N=10^{18}$ cm^{-3}, which is in agreement with the impurity content of these crystals as determined spectrographically.[6] This analysis shows: Ca-100 parts per million, Fe-20 parts per million, Si-10 parts per million, Mn, Ta, Cu, and Ag-lesser quantities.

An MgO crystal[7] typical of a number investigated previously was subjected to two successive neutron irradiations in the Brookhaven pile, and the bombardment-induced conductivity was measured after each exposure. The epi-cadmium integrated fluxes were 4.2×10^{16} n/cm^2 and 5.1×10^{17} n/cm^2, respectively. The experimental procedures for observing bombardment-induced conductivity have already been described.

As seen in Table I, $\delta\mu_d\tau$ [see Eq. (1)] decreased only slightly during the first irradiation. However, the second irradiation reduced the bombardment-induced conductivity by a factor of 10. Furthermore, the

* Assisted by the Office of Ordnance Research, U. S. Army.
† Present address: Philco Corporation, Research Division, Philadelphia, Pennsylvania.
[1] M. A. Pomerantz, R. A. Shatas, and J. F. Marshall, Phys. Rev. **99**, 489 (1955).
[2] J. F. Marshall, M. A. Pomerantz, and R. A. Shatas, Phys. Rev. **106**, 432 (1957).
[3] R. A. Shatas, J. F. Marshall, and M. A. Pomerantz, Phys. Rev. **109**, 1953 (1958).
[4] H. R. Day, Phys. Rev. **91**, 822 (1953).
[5] F. P. Clarke, Phil. Mag. **2**, 607 (1957).
[6] Spectrographic analysis was performed by the University of Missouri Spectrographic Service.
[7] The MgO crystal was identical with that described in reference 2.

TABLE I. Summary of effects of neutron irradiation upon bombardment-induced conductivity in MgO.

Integrated flux (n/cm^2)	Experimental value of $\delta\mu_d\tau$ at 294°K	Experimental estimate of total trap density (cm^{-3})	Theoretical estimate of neutron-produced trap density (cm^{-3})
0	1.5 ±0.2	10^{18}	···
4.2×10^{16}	1.1 ±0.1	···	8×10^{18}
5.1×10^{17}	0.16±0.01	10^{19}	1×10^{20}

bombardment-induced conductivity at all temperatures over the range covered (200°K to 525°K) was one-tenth the corresponding pre-irradiation value. Thus, the *form* of the bombardment-induced conductivity *vs* temperature curve[2] is unaffected by the neutron irradiations.

As has been reported previously,[2] the mobility of charge carriers is influenced by more than one scattering mechanism. Any change in the relative effects of these scattering mechanisms would alter the form of the aforementioned curve. It is unlikely that different scattering effects should be changed by a constant ratio at all temperatures. Hence, the present results reveal that the mobility is unaffected by neutron irradiations of the magnitude cited. Consequently, the decrease in m is ascribed to a change in the lifetime, τ, arising from neutron-produced trapping centers.

After the first irradiation, the density of such traps was of the same order of magnitude as that of the trapping centers originally present in the raw crystal. Following the second irradiation, the number of traps was increased tenfold, thus decreasing the lifetime by a corresponding amount. This quantitative conclusion is based upon the tacit assumption that the average capture cross section of trapping centers (impurities) in the raw crystal itself is nearly the same as for centers produced by neutron irradiation.

Unfortunately, information concerning the energy spectrum of neutrons to which the specimen was exposed was not available. However, a rough estimate of the damage can be arrived at if it is assumed that the epi-cadmium flux is entirely in the fission neutron spectrum. On the basis of the theory of Khinchin and Pease,[8] displacement densities of 8×10^{18} cm^{-3} and 1×10^{20} cm^{-3} are produced by the two irradiations. With the above assumptions, this represents a theoretical estimate of the upper limit of the displacements produced by these irradiations.

The hole temperature during irradiation was 70°C. Annealing effects were carefully watched for following the irradiation. The measurement of the bombardment-induced conductivity at room temperature after the specimen was received at our laboratory indicated no detectable annealing for periods as long as 99 days. Any room temperature annealing of displacements must effectively have taken place during the two irradiations in the pile. As far as annealing is concerned, the relative conditions of the crystals were the same during and after the two irradiations. During the high temperature measurements of the bombardment-induced conductivity, the measurements were repeated at low temperatures to guard against spurious effects due to annealing. A similar procedure was applied later during the post-bombardment conductivity measurements. Some annealing was observed at temperatures above 450°K, but this proceeded at a rate which did not interfere with the measurements.

These results are not in accord with Day's estimate that the damage saturates at 10^{15} n/cm^2 irradiation in MgO. The number of displacements is still increasing at 10^{17} n/cm^2. Day's conclusion has also been criticized by Khinchin and Pease.[8]

III. POST-BOMBARDMENT CONDUCTIVITY

A detailed discussion of post-bombardment conductivity has been presented previously.[3] In particular, since this phenomenon represents the transfer of electrons from shallow traps into the conduction band, measurements of post-bombardment conductivity provide information about the properties of these centers. At high temperature, experiment and theory reveal that the post-bombardment conductivity of an MgO crystal decays in accordance with an exponential law. The density, n, of electrons in the conduction band is given by

$$n=C\exp(-t/\tau), \tag{3}$$

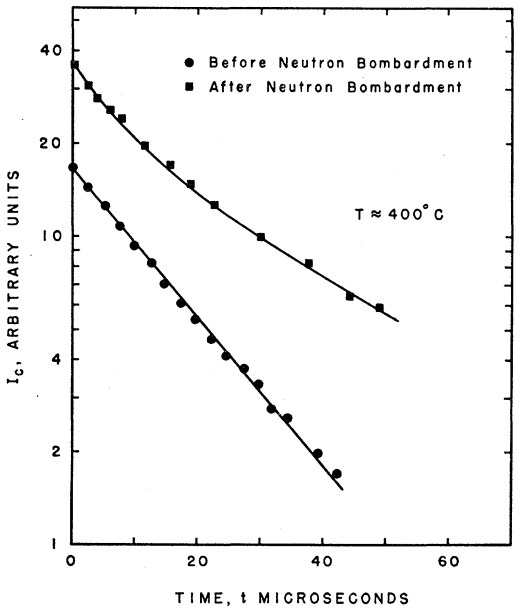

FIG. 1. Effect of 4.2×10^{16} n/cm^2 neutron irradiation upon post-bombardment conductivity in MgO.

[8] G. H. Khinchin and R. S. Pease, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 6.

where C is a function of parameters relating to the energy level scheme of the trapping centers, and τ is a characteristic decay time constant. If the post-bombardment conductivity is associated with more than a single predominant level at a particular temperature, the decay would be represented by a sum of exponentials with different characteristic decay times.

In the case of a single level, the time constant for the decay of the post-bombardment conductivity depends upon temperature in the following manner:

$$\tau = \tau_0 \exp(E/kT). \quad (4)$$

Here, τ_0 is also a function of the parameters relating to the center, and depends only weakly upon temperature, and E is the thermal ionization energy of an electron in a particular shallow center.

A level characterized by a thermal activation energy equal to 1.4 ev has previously been investigated. A semilogarithmic plot of post-bombardment conductivity as a function of time at 400°C is shown in Fig. 1 (circles). The straight-line relationship indicates the predominance of a single level, tentatively identified with the 2.2-ev photoconductivity peak.[3]

Clarke[5] has made a detailed study of the absorption spectra of MgO crystals following neutron irradiations, and has observed that with integrated fluxes of 10^{18} n/cm^2 and larger, the 2.2-ev level becomes two levels separated by about 0.1 ev. It appeared desirable to explore this effect by the post-bombardment conductivity technique, and, as is shown in Fig. 1 (squares), neutron irradiation of 4.2×10^{16} n/cm^2 produces a significant change in the 1.4-ev level. The decay can

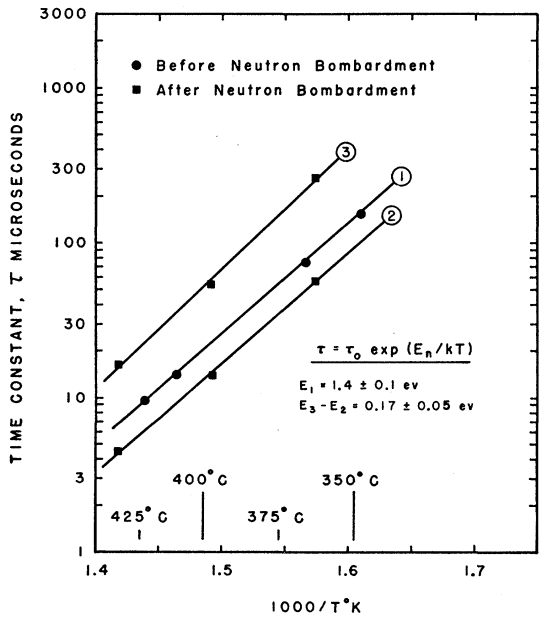

FIG. 2. Effect of 4.2×10^{16} n/cm^2 neutron irradiation upon temperature-dependence of decay time-constant.

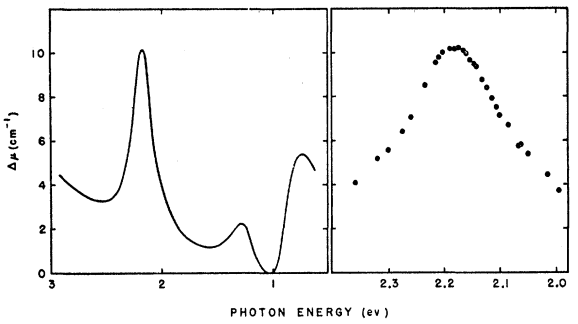

FIG. 3. Induced absorption coefficient vs photon energy following 5.1×10^{17} n/cm^2 neutron irradiation. Detailed plot of 2.2-ev peak is shown.

no longer be described by a single exponential function. However, the experimental curve can be fitted by two exponentials with different time constants.

Similar measurements of the variation of post-bombardment conductivity with time were obtained at various temperatures. Figure 2 reveals the effect of neutron bombardment upon the temperature dependence of the characteristic decay times of carriers trapped by the 1.4-ev level. The single level present initially (curve 1) having energy E_1 has been split into two levels (curves 2 and 3) having an energy difference E_3-E_2 of the order of 0.1 ev. This adds weight to the earlier hypothesis that the 1.4-ev thermal energy gap disclosed by the post-bombardment conductivity method corresponds to the 2.2-ev optical transition observed in absorption and photoconductivity measurements.

IV. OPTICAL ABSORPTION

In order to check the splitting of the 1.4-ev level described above, optical absorption data were obtained concurrently on the irradiated samples. The measurements of absorption induced in the 3.0- to 4.3-ev range agree with those already reported by Clarke. Figure 3 shows absorption changes in the 0.6- to 3.0-ev region produced by an irradiation of 5.1×10^{17} n/cm^2. It is evident in the expanded plot of irradiation-induced absorption coefficient *vs* photon energy that the splitting of the 2.2-ev peak is not detectable by this method. However, this is not in disagreement with the observations of Clarke. His results indicate that the doublet is brought out only by more intense irradiation. Thus, the post-bombardment conductivity technique for investigating the electron energy level scheme of trapping centers appears to be more sensitive, at least in the present example, than the optical absorption measurements at room temperature.

It is also of interest to point out the existence of a peak at 1.27 ev, which has also been reported by Clarke. Photoconductivity associated with this level has been investigated by Day. This absorption peak presumably

corresponds with the 0.7-ev level determined earlier by the post-bombardment conductivity method.[3]

Finally, it is seen in Fig. 3 that an additional peak is present at 0.74 ev following neutron irradiation. This has not been reported previously. This peak is not observed in annealed unirradiated crystals. Furthermore, it is enhanced by subsequent electron bombardment, and is observed to decay afterward.

V. ACKNOWLEDGMENT

It is a pleasure to express our appreciation to Dr. J. F. Marshall for many helpful discussions.

PHYSICAL REVIEW VOLUME 117, NUMBER 6 MARCH 15, 1960

Superconductivity of Dilute Indium-Mercury Alloys*

MORTON D. REEBER
International Business Machines Corporation, Research Laboratory, Poughkeepsie, New York
(Received October 12, 1959)

Measurements were made of the critical magnetic field for the transition from the superconducting to the normal state in polycrystalline rods of the substitutional solid solution In-Hg, containing 0–7 atomic percent Hg. The treatment given these alloys was designed to assure homogeneity in composition in which case the transitions to the normal state were found to be similar to those for pure elemental superconductors. It was, moreover, possible to distinguish between properties that are characteristic of the ideal alloy system and properties which arise from structure within the specimen. T_c, the transition temperature at zero field, was measured as a function of composition and was found initially to decrease (up to a concentration of 1.75 atomic percent Hg) after which it began to increase with added Hg concentration. The width of the transition to the normal state, as measured by the variation of specimen resistance in a longitudinal magnetic field, was found to show a regular dependence upon composition, and also reached a minimum value at 1.75 atomic percent Hg. The superconducting properties of pure indium were measured and used as a standard. For indium it was found that:

$$T_c=3.407\pm0.002°\text{K};\quad H_0=293\pm2\%\ \text{oersted};$$

and $(dH_c/dT)\,|\,_{T_c}=-155.5\pm3\%$ oersted/°K.

INTRODUCTION

THE characteristic properties of a pure elemental superconductor, relatively free from strains and inhomogeneities, are usually found to embody a discontinuous change in resistance at the critical temperature, a well-defined, reproducible, and unique critical field, and exclusion of magnetic flux upon entering the superconducting state.[1] Experiments with alloys, impure or strained elements, and compounds frequently reveal, in contrast to pure elemental materials, strikingly different properties.[1–4] For example, high magnetic fields may be required for the restoration of the full normal state resistance, the Meissner-Ochsenfeld effect is often incomplete and does not coincide with the loss of electrical resistance, the transition between states frequently takes place only over large field and/or temperature intervals, and currents flowing in the specimen often affect the transition, as measured by resistance techniques, in a manner which suggests that the supercurrent is localized in small regions of the specimen. Such behavior has, more often than not, been inferred to be the normal inherent behavior of alloys.[1]

On the other hand, not all alloys are found to behave in the manner described above. Stoichiometric compounds and certain alloys,[5–7] when prepared with great care have occasionally exhibited transition characteristics similar to those of pure elemental superconductors. This suggests the possibility that homogeneity of the system might be a significant factor in making a solid solution alloy behave like a pure elemental superconductor.

We have attempted to investigate this possibility by a careful study of the indium-mercury alloy system, chosen because of its convenient critical temperature and critical field range, and the ease with which the material could be cold worked and annealed. Moreover, both elements are available in extremely pure form and it was therefore hoped that detrimental effects due to the presence of unknown impurities would thereby be avoided.

EXPERIMENTAL PROCEDURE

The alloys used for these measurements were prepared from 99.999% pure indium[8] and triple-distilled mercury. The materials were weighed, placed in a Pyrex tube, sealed off in vacuum, melted, mixed vigorously, and quenched in an oil bath. Quenching was of particu-

* This work was supported in part by the Department of Defense.

[1] For a general discussion of the properties of pure elemental and alloy superconductors see D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952).
[2] W. J. deHaas and J. Voogd, Commun. Phys. Lab. Univ. Leiden No. 208b (1930).
[3] P. R. Doidge, Proc. Roy. Soc. (London) **A248**, 553 (1955).
[4] B. G. Laserew and A. A. Galkin, J. Phys. (USSR) **8**, 371 (1944).
[5] D. Shoenberg, Nature **142**, 874 (1938).
[6] B. G. Laserew and I. E. Nakhutin, J. Phys. (USSR) **6**, 116 (1942).
[7] J. W. Stout and L. Guttman, Phys. Rev. **79**, 396 (1950).
[8] Johnson Matthey & Company, Catalog No. 380.