Radiation-Induced Recombination and Trapping Centers in Germanium. I. The Nature of the Recombination Process*

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Extensive measurements on irradiated germanium indicate that previous analyses of the recombination process are incorrect. A model which explains the observations in both *n*- and *p*-type material is presented. According to this model, the recombination level lies 0.36 ev above the valence band in gamma-irradiated *n*-type germanium. Presumably due to the extensive perturbation caused by neutron irradiation, the level lies slightly lower in neutron-irradiated material. Trapping levels which are not present in antimony-doped germanium occur in arsenic-doped material ~0.17 ev above the valence band. Other trapping levels are observed only in high-resistivity antimony-doped samples. It has not been possible, from the data presented, to determine the values of hole and electron capture cross sections associated with the recombination level; however, the ratio σ_p/σ_n has been determined: Its value is ~1000.

INTRODUCTION

THE study of the recombination behavior of irradiation-induced defects in semiconductors should be very useful in determining the nature of those defects. Some recent reviews[1,2] indicate the importance of recombination measurements in radiation effects studies. Lifetime measurements have a great advantage over other electrical measurements because of their sensitivity to radiation-produced defects; very low concentrations of defects playing the role of recombination centers can be detected. The reason that lifetime measurements are more sensitive than those depending upon carrier concentration is that, in a well-prepared, unirradiated germanium specimen, the number of recombination centers present is very small compared with the extrinsic carrier concentration.

Due to rather fortuitous circumstances involving primarily the limited range of carrier concentration in the material investigated in the past,[2] some erroneous conclusions have been drawn about the nature of radiation-induced recombination centers in Ge. The data previously reported could largely be explained on the basis of rather simple models. However, the data to be presented here indicate that a more sophisticated explanation of the recombination process is necessary. The temperature dependence of carrier lifetime varies among samples having different resistivities (apart from those differences predicted by the simple Hall[3]-Shockley-Read[4] theory), among samples having different doping impurities, and among samples exposed to different types of irradiation. It is the purpose of this paper to present a model which will explain these various results.[5]

Many of the data to be presented here arose in the annealing studies of radiation-induced recombination centers. However, discussion of this annealing behavior will be reserved for a later paper.

RESULTS

All lifetime measurements were made by observing the transient decay of photoconductivity in bulk specimens following a light pulse. For details of the experimental procedure, the reader is referred elsewhere.[2,6] The irradiations were carried out at 35°C and took on the order of several hours. Thus, any defects unstable below this temperature would have annealed.

The recombination data herein reported arose from an effort to determine the annealing behavior of radiation-induced recombination centers in germanium. Since the nature of gamma-ray-induced damage is expected to be simpler than for the case of neutron bombardment and since the recombination process is better understood in *n*- than in *p*-type materials, emphasis has been placed on *n*-type germanium irradiated with Co^{60} gamma rays. Since annealing results based on lifetime measurements at a fixed temperature would not be very meaningful if there were a change in the recombination process, the effect of annealing upon the recombination process, as indicated by temperature dependence of lifetime, was determined. Figure 1 shows lifetime plotted logarithmically as a function of reciprocal temperature for an antimony-doped, 15 ohm-cm specimen[7] before and after gamma-ray exposure and after several annealing treatments. At low temperatures an increase in the lifetime with decreasing temperature is noted in the post-irradiation curves. An analysis of this behavior in terms of a trapping process will be given in the discussion. Similar results have been observed by others, both in gamma-ray-[8] and reactor-neutron-[9] irradiated

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† Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[1] G. K. Wertheim, J. Appl. Phys. **30**, 1166 (1959).

[2] O. L. Curtis, Jr., J. Appl. Phys. **30**, 1174 (1959).

[3] R. W. Hall, Phys. Rev. **87**, 387 (1952).

[4] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

[5] General Discussion of the Faraday Society, "Radiation Effects in Inorganic Solids," Saclay, France, April 11–12, 1961.

[6] O. L. Curtis, Jr., Ph.D. thesis, University of Tennessee, 1961 (unpublished).

[7] In the sample designation, the second pair of letters is the chemical symbol for the doping agent, and the number is the resistivity in ohm-cm.

[8] S. M. Ryvkin and I. D. Yarosketskii, Fizika Tverdogo Tela **2**, 1966 (1960).

[9] A. Czachor and J. Piekoszewski, J. Appl. Phys. (to be published).

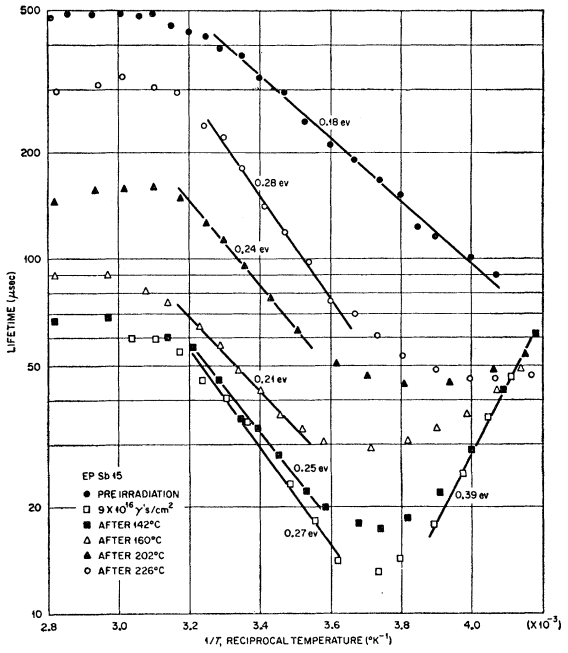

FIG. 1. The recombination behavior of 15 ohm-cm antimony-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

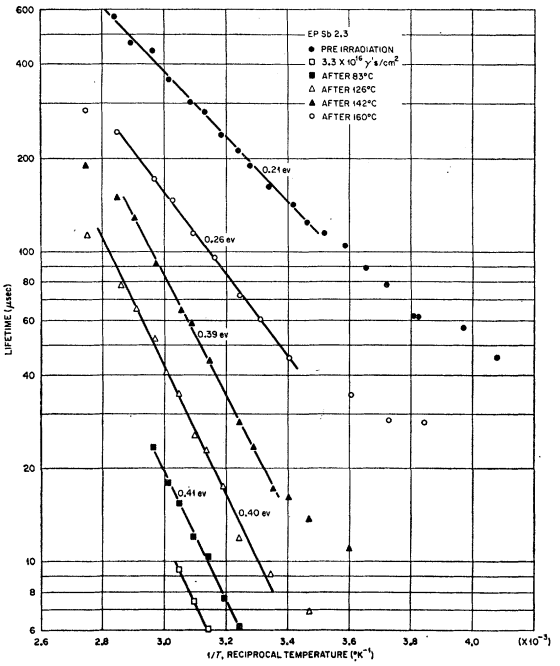

FIG. 3. The recombination behavior of 2.3 ohm-cm antimony-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

specimens. Another important point is that the slopes of the post-irradiation curves are much steeper than observed previously[2] for similar material.

Figure 2 exhibits the temperature variation of recombination for a 3.7 ohm-cm antimony-doped specimen following irradiation and thermal treatment. Note here the very steep slope of the $\ln\tau$ vs $1/T$ curve, with no indication of trapping in the range of measurement. On the basis of simple theory, after subtracting 0.04 ev from the indicated slope (an approximate correction for the $T^{\frac{3}{2}}$ temperature variation of the density-of-states function N_v), the position of the recombination level as measured from the valence band should be obtained.[2]

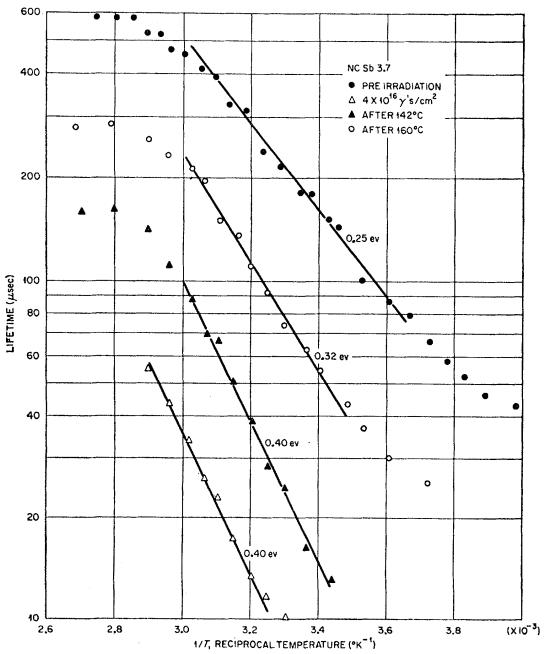

FIG. 2. The recombination behavior of 3.7 ohm-cm antimony-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

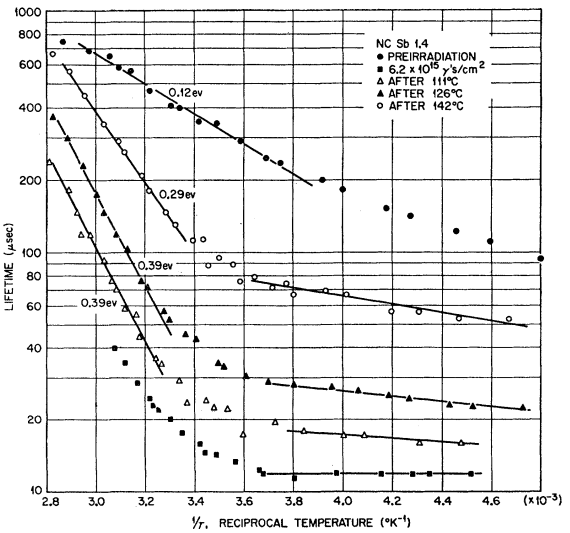

FIG. 4. The recombination behavior of 1.4 ohm-cm antimony-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

For all the samples whose annealing behavior was investigated, the temperature dependence of lifetime was obtained following each anneal. However, in the interest of clarity, only a few of the resulting curves are shown for each specimen. In Figs. 3 and 4, for 2.3 ohm-cm and 1.4 ohm-cm, antimony-doped material, the behavior is very similar to that displayed in Fig. 2. Again, the post-irradiation slope is quite steep and no trapping is observed. For NCSb 1.4, the measurements were extended to lower temperatures than for the other specimens.

Compared to the other antimony-doped specimens, the recombination behavior of UMSb 1.3 was anomalous. Figure 5 illustrates this fact. The slopes here have lower values than those shown in Figs. 2–4.

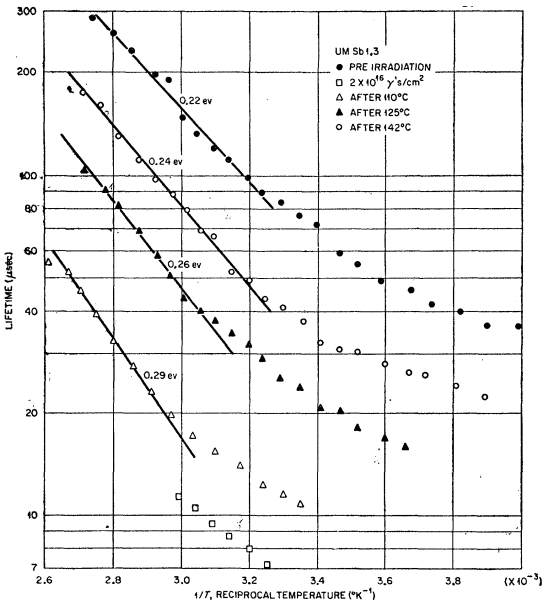

FIG. 5. The recombination behavior of 1.3 ohm-cm antimony-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

The recombination behavior is quite different in arsenic- and antimony-doped material. There are also important differences in the annealing behavior of recombination centers for these two types of doping.[6,10] In Figs. 6 through 8 the results of lifetime measurements for three arsenic-doped specimens are shown. In these three figures strong trapping is observed. In fact, for the high-resistivity specimen, NCAs 20, the trapping seemed to persist into the intrinsic range. Furthermore, the traps seem to anneal at a much higher temperature than did the recombination centers. (In fact, it appeared that the trap concentration actually increased following annealing at the lowest temperature.)

It is evident from these data that, although irradiation by Co^{60} gamma rays is expected to produce a simple

[10] W. L. Brown, W. M. Augustyniak, and T. R. Waite, J. Appl. Phys. **30**, 1258 (1959).

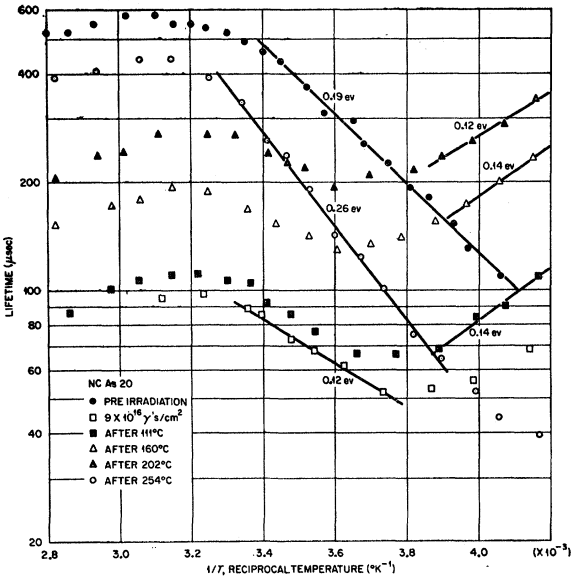

FIG. 6. The recombination behavior of 20 ohm-cm arsenic-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

type of damage, even in this restrictive case, different types of recombination behavior occur in *n*-type germanium. In this paper we shall attempt to explain these results and to extend that explanation to include material which has undergone other types of irradiation.

DISCUSSION

The approach most commonly used in the analysis of recombination data obtained from irradiated semi-

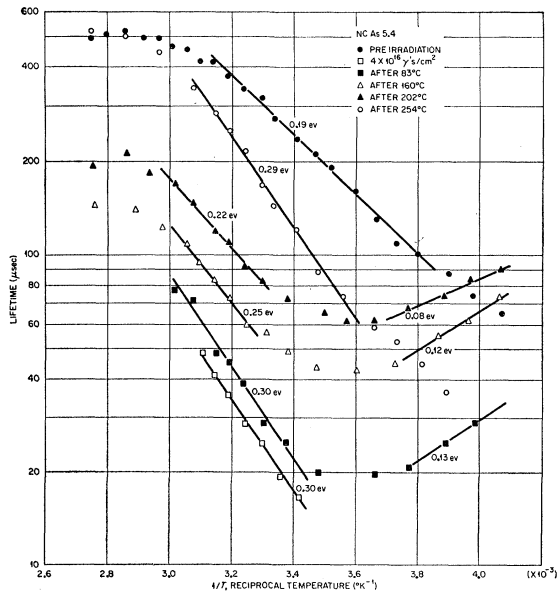

FIG. 7. The recombination behavior of 5.4 ohm-cm arsenic-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

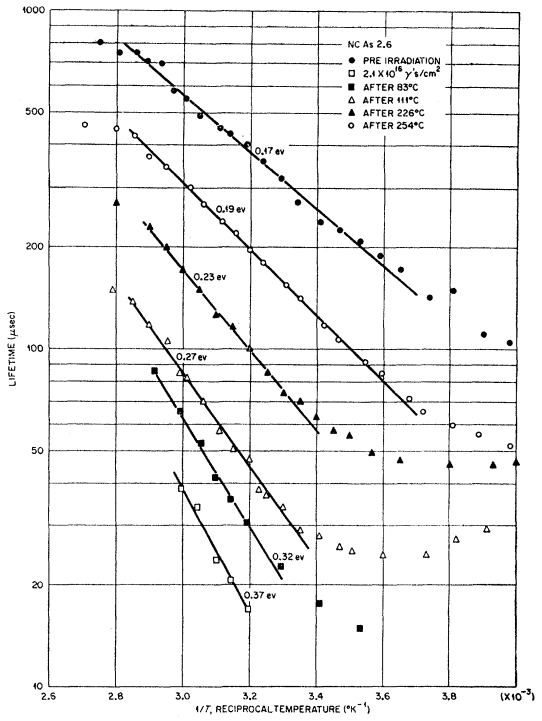

FIG. 8. The recombination behavior of 2.6 ohm-cm arsenic-doped germanium following irradiation by Co^{60} gamma rays and successive one-hour anneals.

conductors is to assume the presence of a single recombination level. Using the analysis of Hall,[11] Shockley, and Read,[12] the properties of such a recombination center can be obtained. However, the data presented here indicate that such an approach is not correct. Rather, the influence of trapping levels must be considered in treating the recombination problem. A number of observers have reported trapping levels present in irradiated germanium.[12–16] However, these observations were made at lower temperatures than those used here. Evidence will be presented that in some cases trapping levels affect the recombination behavior, even in the room-temperature range.

Wertheim[17] has extended the calculations of Hall, Shockley, and Read to the consideration of recombination in the presence of trapping levels. Ryvkin and Yaroshetskii[8] have treated the problem differently, obtaining solutions in certain limiting cases. For the case in which the recombination level is located below the Fermi level and above the trapping level,[18] the result of Wertheim's calculation can be written in the following way:

$$\tau=\frac{p_{1r}}{c_{nr}nN_r}+\frac{1}{c_{nr}n}+\frac{N_tp_{1r}}{c_{nr}nN_rp_{1t}}+\frac{N_t}{c_{pr}N_rp_{1t}}+\frac{1}{c_{pt}p_{1t}}+\frac{1}{c_{pr}N_r}, \quad (1)$$

where the symbols used are defined in Table I. This relationship is subject to certain assumptions, described by Wertheim. The six terms of Eq. (1) display four types of temperature dependence. Assuming temperature independence of capture probabilities, plotting the magnitude of the terms logarithmically as a function of reciprocal temperature yields straight lines with four different values of slope. Correcting for the $T^{\frac{3}{2}}$ temperature dependence of the density-of-states function, $(p_{1r}/c_{nr}nN_r)$ and $(N_t/c_{pr}N_rp_{1t})+(1/c_{pt}p_{1t})$ yield the energy-level positions of the recombination and trapping levels, respectively. The term $(N_tp_{1r}/c_{nr}nN_rp_{1t})$ gives the difference in position between the trapping and recombination levels. The terms $(1/c_{nr}n)$ and $(1/c_{pr}N_r)$ are temperature independent.

The results of Eq. (1) may be applied in a very straightforward manner to the experimental data. In Fig. 9 an attempt has been made to synthesize representative temperature dependence of lifetime by adding three terms of Eq. (1) which affect the recombination behavior in arsenic-doped material. Here, the effect of the temperature dependence of the intrinsic carrier concentration has been included by replacing n by $n+p$ where both n and p include the intrinsic contribution. This correction can only be approximate due to the assumption made in obtaining Eq. (1) that n is very large compared with p. The points shown in Fig. 9 are the result of adding the three terms indicated in the figure. Inspection of Fig. 9 makes the results for arsenic-doped material quite understandable. For instance, the curve for[19] $N_d=3\times10^{14}$ cm^{-3} corresponds to a sample resistivity of about 5 ohm cm and the shape of this curve is very similar to the lower four curves of Fig. 7. The

TABLE I. List of symbols.

c_{nr}—Electron capture probability at a recombination center.
c_{pr}—Hole capture probability at a recombination center.
c_{pt}—Hole capture probability at a trapping center.
N_r—The number of recombination centers.
N_t—The number of trapping centers.
n—The equilibrium electron concentration.
n_{1r}—The electron concentration for the case in which the Fermi level lies at the recombination level.
p_{1r}—The hole concentration for the case in which the Fermi level lies at the recombination level.
p_{1t}—The hole concentration for the case in which the Fermi level lies at the trapping level.
τ—The time constant of decay of excess carriers; the carrier lifetime.

[11] R. N. Hall, Phys. Rev. **87**, 387 (1952).
[12] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).
[13] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).
[14] H. Y. Fan, Phys. Rev. **92**, 1424 (1953).
[15] R. G. Shulman, Phys. Rev. **102**, 1451 (1956).
[16] J. W. Cleland and J. H. Crawford, Jr., J. Appl. Phys. **29**, 149 (1958).
[17] G. K. Wertheim, Phys. Rev. **109**, 1086 (1958).
[18] It can be shown that Eq. (1) holds so long as the trapping levels lie below the Fermi level (not necessarily below the recombination levels).
[19] N_d, the concentration of chemical donors, is equal to the extrinsic electron concentration, n.

data of Figs. 6 and 8 are also well explained on the basis of Fig. 10. At high temperature some of the experimental lifetime values are lower than predicted; this fact is undoubtedly due to the approximations made in accounting for the contribution to recombination of intrinsic carriers. If p becomes comparable with n, then the recombination equation will change completely, becoming more complicated than Eq. (1). For samples in which trapping centers affect the recombination to such high temperatures as demonstrated in Fig. 9, it is not possible to obtain the position of the recombination level with any accuracy.

In Fig. 1 a rather steep slope in the trapping portion of the lower curves for this highest resistivity, antimony-doped specimen is seen. Evidently, the trapping level in this specimen is much higher than in the case of arsenic-doped material. However, there may be a contribution to the slope due to the fact that the carrier concentration is decreasing with decreasing temperature in this range. The Hall curves for n-type material indicate a freezing out of carriers at an energy level 0.20 ev below the conduction band.[20] These levels are introduced at a rate[21] of $\sim 5\times 10^{-4}$/gamma-cm so the change in carrier concentration resulting from the filling of these levels would be $\sim 4\times 10^{13}$ in this case, or about one-half of the room-temperature value. The position obtained by Ryvkin and Yaroshetskii[8] for the trapping level in near-intrinsic germanium was $E_t - E_v = 0.24$ ev. Shulman reported a trapping level at $E_t - E_v \approx 0.28$ ev in electron-irradiated material.[15] Hall measurements have also demonstrated the presence of an energy level in this region ($E_t - E_v = 0.26$ ev).[20] Although Figs. 2 and 3 do not display trapping behavior similar to that of Fig. 1, the reason that points are not included for lower temperatures in the case of the curves following anneal at 160°C is that the photoconductivity decay curves became nonexponential, evidently due to the fact that trapping was beginning to occur. Since Eq. (1) was derived on the basis of a single time constant, it cannot be applied to these low-temperature data.[22] However, the trapping does not appear to be important in the higher temperature range. Assuming no dependence of capture probability on temperature, the recombination center lies ~ 0.36 ev above the valence band in these antimony-doped specimens. Even though arsenic-doped material displays the presence of trapping levels not present in antimony-doped material, it seems reasonable to assume no difference in the position of the recombination level. Although it cannot be proved that the same recombination center is effective in both arsenic- and antimony-doped material, the analysis shown in Fig. 9 indicates that this conclusion is reason-

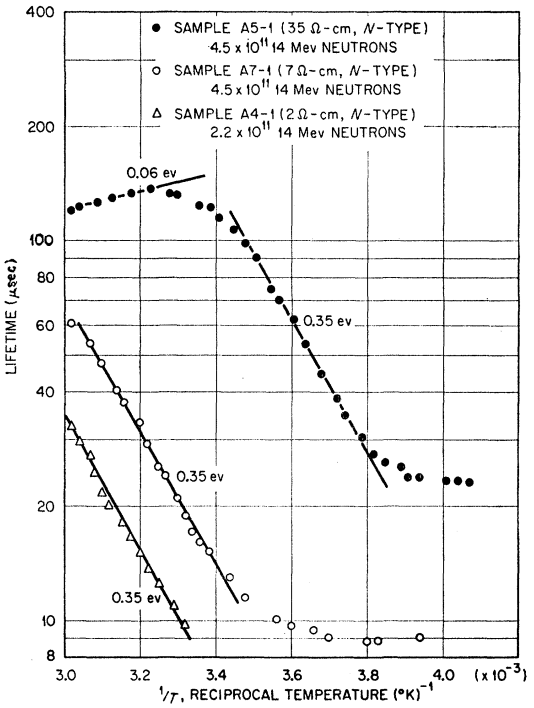

FIG. 10. The recombination behavior of antimony-doped germanium following irradiation by 14-Mev neutrons. From reference 6.

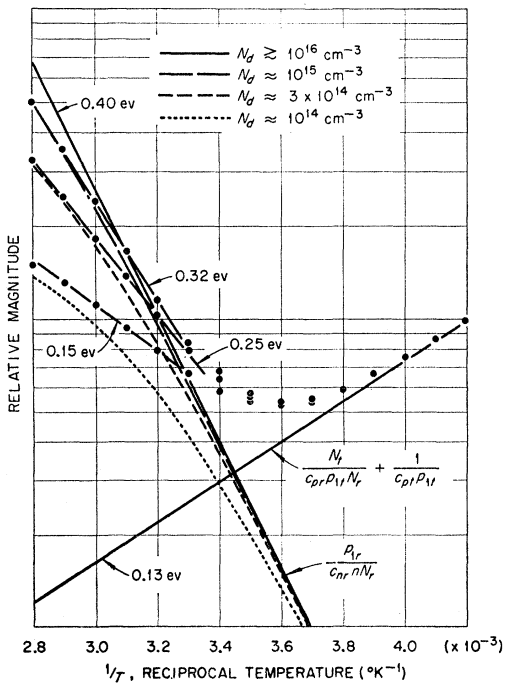

FIG. 9. The result of adding three terms of the recombination equation including the effect of intrinsic carriers. The apparent slopes are indicated for comparison with the experimental data.

[20] J. W. Cleland, J. H. Crawford, Jr., and D. K. Holmes, Phys. Rev. **102**, 722 (1956).
[21] J. W. Cleland (unpublished data).

[22] Let us emphasize that trapping can manifest itself in two ways. The photoconducting decay may remain exponential and the behavior of Eq. (1) is observed. However, there are solutions to the problem which do not manifest simple exponential decay. This is the situation observed in the samples of Figs. 2 and 3.

able. Thus, the differences in recombination behavior between arsenic- and antimony-doped material can be attributed to a trapping level present in γ-irradiated arsenic-doped material, 0.17 ev above the valence band, which is not present in irradiated antimony-doped germanium.

Samples cut from two ingots obtained from one source displayed recombination behavior which was anomalous as compared with the other antimony-doped specimens. A typical example of this behavior is shown in Fig. 5. Comparison with Fig. 4 shows that this difference in behavior is not due to a difference in carrier concentration. It has been shown,[5] however, that this behavior can be explained on the assumption that a high concentration of trapping centers is present in the unirradiated crystal. This is not the only possible explanation, and the presence of such traps has not been proved.

It should be noted that the model proposed here is quite different from that used to explain recombination behavior in previous papers[2] in which the effect of trapping centers was neglected. On the basis of the few studies then available, it was postulated that recombination occurs through an energy level located $\sim$0.20 ev below the conduction band and that the hole capture probability limits the recombination and is temperature dependent.[23] The earlier data are easily explained on the basis of the present model. For most of these samples $N_d \sim 10^{14}$ cm^{-3} and the corresponding curve in Fig. 9 agrees well with the data.

The present model also adequately accounts for the results of reactor and 14-Mev-neutron irradiation.[2,24] Figure 10, taken from reference 24, shows the result of irradiating three antimony-doped samples of different resistivity with 14-Mev neutrons. Evidently, the rate of introduction of traps relative to the rate of production of recombination centers by 14-Mev neutrons is considerably less than in the case of gamma irradiation. Also, there is some indication that the position of the recombination center is slightly lower in the forbidden gap, 0.32 ev above the valence band.[25] Figures 11 and 12 demonstrate results for n-type germanium irradiated with reactor neutrons. These data are from an exploratory investigation of the annealing behavior of neutron-induced defects.[26] Other data,[2] mostly on $\sim$15 ohm-cm material, indicate a slope for the recombination curves of $\sim$0.24 ev. The data were, quite logically, interpreted on the basis of recombination at a level known to be present in neutron-irradiated germanium $\sim$0.20 ev below the conduction band (again correcting for the temperature dependence of the density of states function). On the basis of present data, however, the explanation is that reactor-neutron irradiation represents an intermediate condition in which the traps are more important than in the case of 14-Mev-neutron irradiation but less important than for gamma-ray irradiation. The position of the recombination level in this case is estimated to be $\sim$0.33 ev above the valence band.

Comparing the experimental data with Eq. (1), certain conclusions may be drawn concerning the relative magnitude of the terms in the recombination equation. Specifically, $p_{1r}/c_{nr}nN_r \gg 1/c_{pr}N_r$ in the higher temperature range. Therefore, $p_{1r}/c_{nr}n \gg 1/c_{pr}$; but

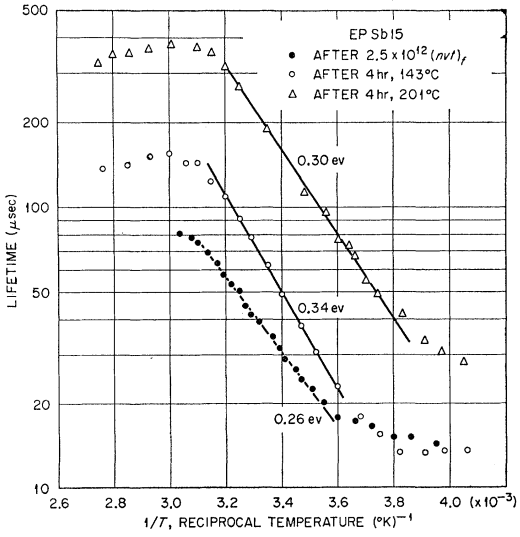

FIG. 11. The recombination behavior of 15 ohm-cm antimony-doped germanium following irradiation by reactor neutrons and successive anneals.

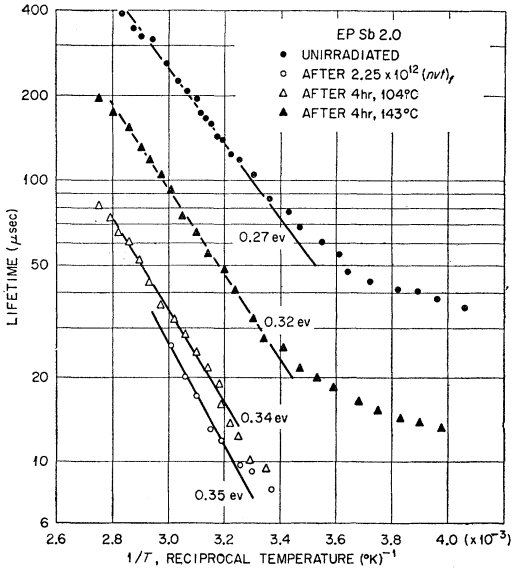

FIG. 12. The recombination behavior of 2.0 ohm-cm antimony-doped germanium following irradiation by reactor neutrons and successive anneals.

[23] Ryvkin and Yaroshetskii[8] also concluded that the recombination center was at $E_c - E_r = 0.20$ ev, even though they considered trapping. However, the samples which they used were all near intrinsic at room temperature.

[24] O. L. Curtis, Jr., and J. W. Cleland, J. Appl. Phys. **31**, 423 (1960).

[25] This is the position obtained previously[24] for this case, without considering trapping effects.

[26] O. L. Curtis, Jr., and J. H. Crawford, Jr., Bull. Am. Phys. Soc. **5**, 196 (1960).

$n \gg p_{1r}$. Thus, $c_{pr} \gg c_{nr}$. In Fig. 4 the nearly temperature-independent portion of the curves presumably corresponds to the condition that $1/c_{pr}N_r \gg p_{1r}nN_r$. These two terms are approximately equal at $1/T = 3.35 \times 10^{-3}$ °K^{-1}. At this temperature, $c_{pr}/c_{nr} \approx n/p_{1r}$, where n, the concentration of electrons in NCSb 1.4, is approximately 1.1×10^{15} cm^{-3}, and p_{1r} at the stated temperature is 2.8×10^{12} cm^{-3}, or $c_{pr}/c_{nr} \approx 400$. Making the usual assumption that $c \approx \sigma\langle v \rangle$, where $\langle v \rangle$ is the mean thermal velocity at the temperature of measurement, $\sigma_{pr}/\sigma_{nr} \approx 1000$. This is in excellent agreement with a similar calculation based on the data of Fig. 10, for the case of 14-Mev-neutron irradiation. The flatness of the lower portions of Figs. 4 and 10 indicates that c_{pr} is very nearly temperature independent.

Since the electron-capture process is rate limiting, it can be argued that the recombination center responsible for recombination in n-type germanium would be highly ineffective in p-type material. Actually, the rate at which the lifetime is degraded by irradiation in p-type germanium is lower than in n-type material[27] but large enough to indicate the action of a different recombination center. In spite of this fact, it is of interest to see if an analysis such as that carried out for n-type material might be of assistance in understanding the recombination center in p-type germanium. Figures 13–15, taken from references 2 and 24, demonstrate the results of irradiating p-type, gallium-doped material with Co^{60} gamma rays, reactor neutrons, and 14-Mev neutrons. There is no reason *a priori* to assume that behavior such as given by Eq. (1) holds for p-type material. That is, it is not known if a trapping level is effective in the temperature range of interest. However, attempts to treat the behavior in p-type material on the basis of a single recombination level have not been successful. For conditions of small N_r and low injection level, the Hall-[11]Shockley-Read[12] recombination equation may be written for p-type material ($p \gg n$):

$$\tau = n_{1r}/c_{pr}pN_r + (1/c_{nr}N_r)(1 + p_{1r}/p). \quad (2)$$

If the recombination center in question lies well above the Fermi level, $p_{1r}/p \ll 1$; and Eq. (2) reduces to:

$$\tau = n_{1r}/c_{pr}pN_r + 1/c_{nr}N_r. \quad (3)$$

This equation follows directly from the equation for p-type material corresponding to Eq. (1), when the effects of trapping centers are neglected. On the other hand, if the center lies below the middle of the gap, the

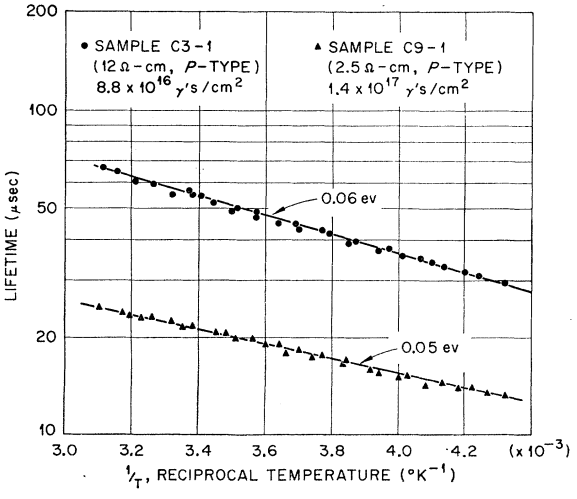

FIG. 13. The recombination behavior of gallium-doped germanium following irradiation by Co^{60} gamma rays. From reference 5.

[27] O. L. Curtis, Jr., J. W. Cleland, and J. H. Crawford, Jr., J. Appl. Phys. **29**, 1722 (1958).

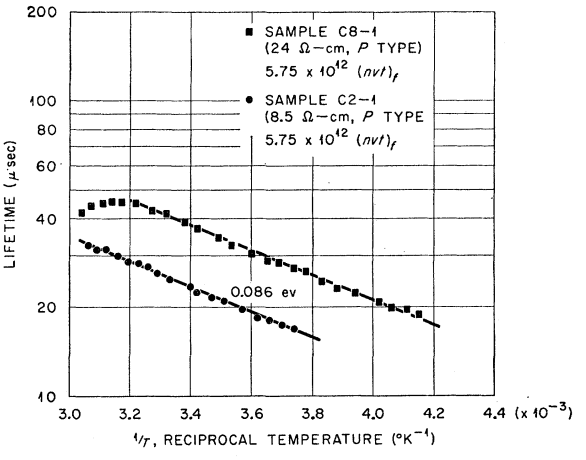

FIG. 14. The recombination behavior of gallium-doped germanium following irradiation by reactor neutrons. From reference 5.

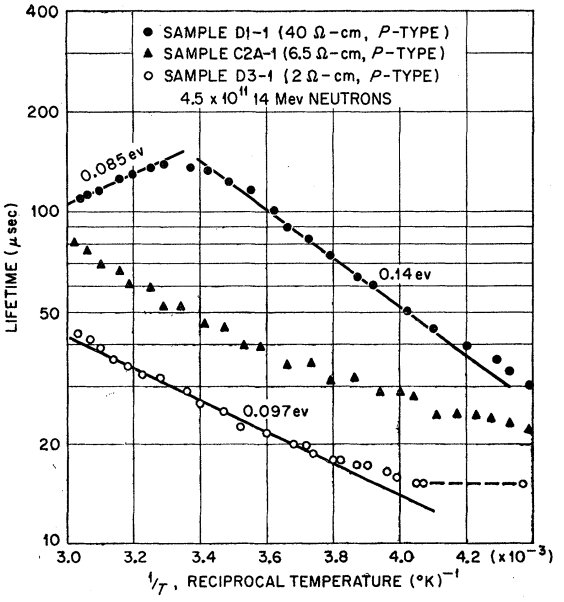

FIG. 15. The recombination behavior of gallium-doped germanium following irradiation by 14-Mev neutrons. From reference 6.

term containing n_{1r} becomes extremely small; and

$$\tau = 1/c_{nr}N_r(1+p_{1r}/p). \quad (4)$$

It has been noted that levels near the center of the band gap are most effective for recombination. If such recombination centers are operative in p-type specimens, Eq. (3) would be expected to hold. Then the $\log\tau$ vs $1/T$ curve should have a slope at high temperatures similar to that for n-type material if hole capture is rate limiting, or should display no temperature dependence if electron capture is rate limiting. Inspection of Figs. 13 through 15, however, reveals a small slope, $\approx$0.09 ev in the case of reactor-neutron exposure and $\approx$0.06 ev for gamma-irradiated specimens, with a somewhat higher value for 14-Mev-neutron irradiation. It is, therefore, tempting to conclude that the recombination center lies near a band edge and either Eq. (3) or (4) is applicable, depending on whether the level lies near the conduction band or near the valence band. However, due to the fact that the temperature-dependent terms contain either n_{1r} or p_{1r}, a level at the position indicated would be 10^{-4} as effective as a level near the center of the band gap (for the same capture cross sections). This would tend to make such an explanation doubtful. It might be that the second term in Eq. (3) is dominant and the temperature variation observed is due to temperature dependence of electron capture probability.

Wertheim and Pearson[28] have attributed similar behavior in plastically deformed germanium to temperature dependence of capture probability. For recombination at a charged center, a variation in capture probability with temperature might be expected. However, the data of Figs. 13 through 15 cannot be explained simply on the basis of a temperature variation of capture probability. Note that the temperature behavior is approximately the same in Figs. 13 and 14 for the two p-type samples of different resistivity, yet the values of the lifetime at the same temperature are quite different. This would indicate that a temperature dependence of c_{nr} cannot be responsible for the temperature dependence of lifetime since electron capture does not appear to be the limiting process. (The term in question, $1/c_{nr}N_r$, is carrier-concentration independent.) The behavior apparently cannot be ascribed to variations in c_{pr} since the term in Eq. (2) involving c_{pr} also involves n_{1r}. The behavior can be explained,[26] but with some difficulty, on the basis of coupled levels. However, it might be more satisfactory to use an explanation involving recombination in the presence of traps. Equation (1) was derived for n-type materials, but is easily shown that the solution is completely symmetrical for p-type material with the trapping and recombination levels above the Fermi level. In this case the proper expression is

$$\tau = \frac{p_{1r}}{c_{pr}pN_r} + \frac{1}{c_{pr}p} + \frac{N_t n_{1r}}{c_{pr}pN_r n_{1t}} + \frac{N_t}{c_{nr}N_r n_{1t}} + \frac{1}{c_{nt}n_{1t}} + \frac{1}{c_{nr}N_r}. \quad (5)$$

This relation introduces a new type of temperature dependence, not predicted by the simple theory. The experimental results are not inconsistent with the premise that the lifetime in gallium-doped, p-type material irradiated with Co^{60} gamma rays and reactor neutrons obeys the following relation:

$$\tau = N_t n_{1r}/c_{pr}pN_r n_{1t}; \quad (6)$$

and the temperature dependence shown in Figs. 13 and 14 would correspond to the difference in position between the recombination and trapping levels. The difference in the case of 14-Mev-neutron irradiation is presumably due to other terms from the recombination equation becoming important. For Eq. (6) to hold, the number of traps must be large compared with the number of recombination centers; and the recombination process must be hold-capture limiting ($c_{nr} \gg c_{pr}$). Since the pre-irradiation recombination behavior in these gallium-doped specimens is not unlike the post-irradiation case, the trapping centers entering Eq. (5) may be present in the unirradiated material. On the other hand, these trapping levels may result from a gallium-defect complex. As is true for the case of n-type material, the position of the recombination level appears to be nearer the center of the gap in the case of neutron irradiation. Again, this is probably due to the extensive local perturbation produced by neutrons, which would cause a spreading out of the energy levels. The energy levels nearest the center of the band gap, being most effective, would dominate the recombination process. Thus, it is possible to explain recombination behavior in p-type germanium by assuming a high concentration of trapping centers in unirradiated material. Although this argument explains the observed behavior in these particular specimens, it is only tentative and predicts a variation in behavior depending upon the method of preparation. The behavior observed in indium-doped material is somewhat different from that discussed here.[6] Specifically, there is no evidence for the trapping centers present in the unirradiated material. These two mate-

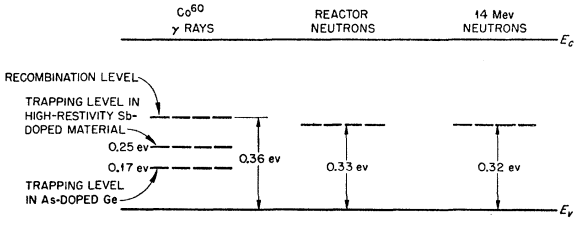

FIG. 16. The energy-level structure proposed to explain the recombination behavior of n-type Ge exposed to various kinds of irradiation.

[28] G. K. Wertheim and G. L. Pearson, Phys. Rev. **107**, 694 (1957).

rials (gallium and indium-doped germanium) were obtained from two sources, and the difference in recombination behavior may reflect a difference in preparation rather than a difference in dopant.

Figure 16 displays the energy-level structure proposed to explain the recombination behavior of n-type germanium exposed to various kinds of irradiation. It is not possible from the present data to locate these levels for p-type material. In n-type germanium the energy level responsible for recombination apparently is shifted slightly downward in the case of neutron irradiation. The experimental results strongly indicate that the same defect is responsible for recombination in neutron- and gamma-irradiated material. The following speculative hypothesis, which is also useful in analyzing the annealing, behavior is offered to explain the recombination data. A germanium atom may be displaced to a nearby interstitial site which is stable, and less energy is required to displace an atom to this position than to produce completely separated vacancies and intersitials. This might be resonable on the basis that the strains produced by a vacancy would be partly compensated if the interstitial remained close to the vacancy. Furthermore, there might be an electrostatic interaction between the two. Wertheim[29] has obtained evidence that such close-spaced pairs occur in silicon. In this picture the energy level primarily responsible for carrier removal is associated with the coupled defect and the recombination center is either an isolated vacancy or interstitial.

This hypothesis would account for the difference in relative rate of introduction of recombination centers between gamma and neutron irradiation. In the case of Co^{60} gamma irradiation, most of the Compton and photoelectric electrons which create displacements have only enough energy to produce relatively close-spaced Frenkel pairs and relatively few isolated defects are produced. On the other hand, with 14-Mev neutrons the average energy imparted to the germanium atoms is large, and so, relatively few germanium atoms would receive just enough energy to form a coupled pair. The case of reactor-neutron irradiation would, of course, be intermediate. The difference in trapping behavior observed for the various radiations would indicate that a trapping level below the center of the gap is introduced by these close-spaced pairs. On the basis of the measurements of Ryvkin and Yarosketskii,[26] this level lies $\sim$0.25 ev above the valence band. Previously we have attempted to explain the difference in rate of lifetime change compared with carrier removal on the basis of a difference in capture probabilities for the different types of irradiation.[2]

Unfortunately, it is impossible to determine the absolute values of capture probabilities and cross sections for recombination simply on the basis of the results presented here. The reason for this is that the number of recombination centers cannot be determined since their introduction rate is not known. (In earlier work,[2] when the energy level at 0.20 ev below the conduction band was thought to be responsible for recombination, the rate of introduction of this level as inferred from changes in carrier concentration was assumed to be identical with the rate of recombination-center introduction.) Furthermore, the addition of a trapping term to the recombination expression complicates any determination of capture probabilities even if the number of centers were known. However, upon examining the annealing behavior, it will be seen that under certain assumptions the values of the electron-capture probability and cross section can be obtained for the recombination centers.

The annealing results show that the stability of recombination centers depends upon the impurity concentration. This, together with the complications imposed by the trapping process, indicates that any analysis of recombination behavior based solely on the variation of lifetime with carrier concentration is invalid. It has previously been stated,[26] on the basis of the temperature behavior, that such an analysis for p-type material could not be made. Nonetheless, recent work has been based on such a method.[30]

SUMMARY

This study emphasizes the fact that the nature of the chemical dopant strongly influences the position and role of radiation-induced defects. In arsenic-doped germanium, trapping levels are introduced approximately 0.17 ev above the valence band which are not present in antimony-doped material. High-purity antimony-doped material displays the presence of a different trapping level, which is not effective in medium or low resistivity (medium or high antimony concentration) material. This level lies approximately 0.25 ev above the valence band[8] and may correspond to a level observed through Hall measurements.[20] By considering the effect of these different trapping levels, the recombination behavior in n-type germanium irradiated with Co^{60} gamma rays can be explained on the basis of a single recombination level located approximately 0.36 ev above the valence band. The ratio of the capture cross sections σ_p/σ_n for this level was found to be approximately 1000. The same value for this ratio was obtained from 14-Mev neutron irradiated material.

Evidence from the annealing data suggests that the recombination center may be a vacancy.[6] The number of isolated vacancies appears to be fairly small as compared with the number of coupled, vacancy-interstitial pairs in the case of Co^{60} gamma irradiation. These coupled pairs may be responsible for the energy level located 0.20 ev below the conduction band commonly observed[20] through Hall measurements. It is even more likely that

[29] G. K. Wertheim, Phys. Rev. **111**, 1500 (1958).

[30] See, for instance, J. J. Loferski and P. Rappaport, J. Appl. Phys. **30**, 1181 (1959).

they are responsible for a trapping level about 0.25 ev above the valence band. The behavior in p-type germanium which previously was not explained can be accounted for quite reasonably on the basis that a high concentration of trapping centers initially present in the material is effective in the room-temperature range. Differences in the recombination behavior among types of irradiation can be explained on the basis that particles which impart higher energy to the germanium atom produce larger numbers of isolated vacancies as compared with the number of vacancy-interstitial pairs. There is apparently a small shift in the position of the energy level for the free vacancy in the case of neutron irradiation. This is probably due to the heavy, localized damage produced by neutron irradiation.

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Calculation of Excitation Energies in "Tightly-Bound" Solids*

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An approximate method of computing the energy of a localized excitation in a solid described by the Heitler-London scheme is presented. The overlap of the excited electron with wave functions centered on neighboring atoms is explicitly taken into account through terms of second order. The use of a Schmidt orthogonalization process avoids questions of convergence of the overlap series expansions found in other methods. Some further simplifying assumptions which are of possible use in ionic crystals are subsequently introduced. The formalism is applied to the system Ne : Ar. In this case it is found that the electrostatic excitation energy predicted for the $3p^6\,{}^1S-3p^54s\,{}^1P$ transition using the approximation identical to the symmetric orthogonalization method is appreciably smaller than that given by an "exact" application of the present theory. Questions concerning the reliability of some previous calculations are thus raised.

I. INTRODUCTION

THOUGH rather exhaustive investigations of the ground state and band structure of various specific crystals have been made in the past, interest in detailed, *ab initio*, calculations for nonconducting excited states of solid systems (e.g., excitons, impurity states) has flourished only recently.[1–4]

The systems considered in the work just cited are either rare-gas or alkali-halide crystals, and the calculations proceed to make use of the tight-binding (Heitler-London) scheme, which is known to be a good description of the ground states. The problem of the nonorthogonality of heterocentric atomic wave functions, which arises even in calculation of the ground-state energy of the systems, becomes much more formidable when spatially diffuse atomic functions are introduced in the description of an excited state.

Thus far, all of the computations have adopted the method of symmetric orthogonalization (introduced by Löwdin[5] in the calculation of alkali-halide cohesive energies) to account for the overlapping of atomic functions in both the ground and excited states. The resulting expressions for the energy are then expanded in a power series which is terminated at terms of the second order in the overlap integrals. This procedure is known to be very useful for the ground state,[5] but in excitation energy calculations very serious questions of the convergence of the expansion arise.[1,4]

However, in practice it is found that the only overlaps which contribute appreciably to the energy of the optical excitations are those involving the spatially diffuse excited electron. Thus, it seems natural to develop a formalism for such states using a Schmidt orthogonalization procedure, neglecting all other overlaps from the outset.[6] The convergence difficulties of the symmetric orthogonalization scheme are thereby avoided completely.

We shall, for simplicity, consider only transitions which may be described in terms of a single excited atomic state, neglecting "configuration interactions." We shall generally use the word "atom" to describe the constituent units of the crystal, whether they be ions or neutral atoms.

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[1] R. S. Knox, J. Phys. Chem. Solids **9**, 238, 265 (1959).
[2] N. N. Kristoffel, Optika i Spektroskopiya **7**, 45 (1959) and references to earlier papers, therein.
[3] N. D. Potekhina, Optika i Spectroskopiya **8**, 437 (1960).
[4] A. Gold, J. Phys. Chem. Solids **18**, 218 (1961).
[5] P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.
[6] The Schmidt procedure has been used previously in a limited, approximate treatment of the F center in ionic crystals. See the review by B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 10.