Energy Levels in Irradiated Germanium

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The energy levels found in germanium irradiated by different particles seem at first to be mutually inconsistent. It is possible tentatively to reconcile the differences by consideration of clustering and association of defects. Four levels are ascribed to single vacancies and interstitials. A crude theory is constructed to explain these levels, particularly their asymmetrical distribution in the energy gap, and to assign each to a definite defect. This theory differs somewhat from a previous one due to James and Lark-Horovitz; some differences in experimental predictions are discussed in particular.

INTRODUCTION

A CONSIDERABLE amount of the work on radiation damage in semiconductors has been directed toward determining the energy levels introduced by the defects. James and Lark-Horovitz[1] proposed a simple model (JLH) which has been used as a reference point for the discussion of experimental results. Indeed, Cleland, Crawford, and Pigg[2] have been able to fit their results on room-temperature neutron irradiation of germanium to this model very successfully. On the other hand, the results of low-temperature neutron bombardment and the Purdue results obtained with electron and deuteron irradiation have not been consistent with the JLH model.

The experimental situation is summarized in Fig. 1 taken from a recent Purdue report. Along the top row are listed the various bombarding particles with which results have been obtained. Below each are the levels observed after such bombardment, labeled with the energy difference in ev from the nearer band edge. The numbers in parentheses have been added for reference below.

It is clear that for a detailed understanding of the levels introduced by radiation much more experimental work is required, and any conclusions based on currently available evidence are necessarily tentative. We believe, however, that such conclusions are in order, having suggestive value at least. A discussion of these points comprises Sec. I. Section II will be concerned with an alternative to the JLH level scheme. In Sec. III, the latter model will be described and compared to the present proposal.

I

A major difficulty in the interpretation of experiments such as those summarized in Fig. 1 is that neither experimentally nor theoretically do we have any detailed picture of the defects. While it is true that we can scarcely imagine any defects other than vacancies and interstitials, we have very little knowledge of their spatial arrangement.

Qualitatively we may consider two aspects of this problem. We shall call these association and clustering. By association we refer to a situation where two or more defects are so close together that the localized electronic levels must be considered as belonging to the group rather than to the individual defects. By clusters we shall mean groups of defects, usually larger than those found associated, which are significantly closer together than would be expected if the defects were distributed at random in the crystal but such that the effect of neighboring defects may be viewed merely as a perturbation. Neither of these notions is new, of course, though the definition of association is tailored for our present purposes.

It is clear that association, if it occurs, will cause different states and energy levels from those found with isolated defects. From clustering we expect that the levels may be altered by the interaction of states on neighboring defects. We expect broadening in particular, though a shift is also quite possible.

It is easy to conjecture how these two factors, association and clustering, may vary with type of radiation. In the case of electrons of 4.5 Mev, we expect that on the average only enough energy will be transferred in a collision to displace about 1 atom in addition to the primary knock-on.[3] Thus clustering is minimized. As-

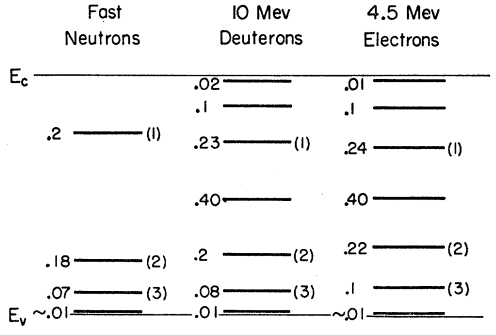

FIG. 1. Energy levels in Ge after various types of irradiation. Energies are indicated by the distance (in ev) from the nearer band edge. [Adapted from H. Y. Fan and K. Lark-Horovitz, Special Report, Purdue University, June, 1957 (unpublished)].

[1] H. James and K. Lark-Horovitz, Z. physik. Chem. **198**, 107 (1951).
[2] Cleland, Crawford, and Pigg, Phys. Rev. **98**, 1742 (1955); **99**, 1170 (1955).
[3] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 305.

sociation, on the other hand, appears quite likely, for there are many small energy collisions, both primary and secondary, which will be unable to knock atoms very far. In the case of deuterons, there will be an average of 10–15 secondaries per primary knock-on, so that small clusters are likely. In this case it is well to realize that roughly half the displacements will be made by atoms which have only enough energy left for one displacement. In these cases we expect the displaced atoms not to travel far from either its original site or the atom which knocked it out; thus, again, association seems likely.

In the case of neutron irradiation, on the other hand, each neutron will collide only once in a typical specimen, giving up about 1% of its energy. This will be enough to produce of the order of thousands of displacements in a rather small volume, say 10^5 atoms[4]; actually the release of such a large amount of energy in a small region will probably produce a "displacement spike," a region of local melting.[3] In this region we may expect the vacancies and interstitials to be fairly randomly distributed as a result of the high temperatures; in particular, we do not expect a high degree of association, for pairs of defects which do not recombine will probably become separated during the period at high temperature. In short, neutrons may be expected to produce little association, but, of course, a high degree of clustering.

With these preparations, we may consider Fig. 1. We observe that the neutron column contains only four levels. While these are not the same as any of those in the column, we may imagine a relation between each and the levels in the other columns which have the same numeral in parentheses. These levels are rather close; furthermore they change monotonically as expected degree of clustering increases. The success of Cleland and Crawford in fitting their data to the JLH model suggests that there are equal numbers of all levels in the neutron case. This equality would be expected if the levels are situated at individual vacancies and interstitials, but not if some are situated at individual, and others at associated, defects. This conclusion is consistent with our previous analysis, according to which we expect a greater ratio of individual to associated defects under neutron irradiation.

Further evidence for this assignment of levels to defects is based on the expectation that levels associated with individual defects should be present in all cases. Since the experiments indicate the levels cannot have the same apparent energy in all cases, it is natural to seek a rationalization in terms of clustering such as is given above. (We speak of apparent energy because a broadened level will not appear to be at its "center of gravity" in many of the experiments, such as those of Cleland and Crawford; the Fermi function acts as a weighting function tending to make the level appear closer to the Fermi level.)

[4] J. H. Crawford and J. N. Cleland, in *Progress in Semiconductors* (Heywood and Company, 1957), Vol. II, p. 96.

We conclude that the levels not found with neutron bombardment belong to associated defects, but at present there is no possibility of suggesting a detailed scheme.

In summary, despite the apparently conflicting and confusing experiments with deuterons and electrons, the general level scheme determined with neutrons is probably valid, though the numerical values of the energies are probably seriously affected by clustering. The fact that the low-temperature results with neutrons do not agree with the model need cause no serious lack of confidence as yet. These experiments are rather fragmentary and are beset with much greater difficulties than the room-temperature results. These include mobility variation under bombardment and the greater importance of photoconductivity due to the γ flux in the pile.[2]

II

In this section, we shall give an extremely qualitative treatment of the levels associated with vacancies and interstitials in the diamond structure. We think in terms of a tight-binding model using hybrid sp^3 orbitals for the electrons. We assume at the start that all these orbitals are orthogonal except for those pairs situated on nearest neighbors and directed at each other. Furthermore we assume that only these same pairs of orbitals have nonzero off-diagonal matrix elements of energy. In this case we can immediately set up the symmetric and antisymmetric combinations (the so-called bonding and antibonding orbitals) of each pair as a set of orthonormal localized orbitals (Löwdin functions). The bonding and antibonding orbitals will differ in the diagonal matrix element of energy by Δ. The bonding orbitals will be predominantly occupied.

When an interstitial atom is added to the crystal, it will be unable to form bonds; its electrons will in first approximation be in atomic orbitals rather than bonding orbitals. Thus their diagonal matrix element of energy will be roughly $\Delta/2$ above those of the valence band, and a similar amount below the conduction band. When an atom is removed, its four orbitals are eliminated and the orbitals on neighboring atoms will be unable to form the bonding combinations with it; one electron on each will therefore also be essentially in atomic orbitals of similar energy to those on interstitials.

In addition to Δ, another energy parameter is important. In order to form bonding orbitals the atoms must change from their normal s^2p^2 configuration to sp^3. This increases the energy of an atom, roughly by the difference in energy between s and p atomic orbitals, which we shall call δ. This change can occur only because $\frac{1}{2}\Delta$ is significantly larger than $\frac{1}{4}\delta$. When an atom has a neighbor removed, therefore, the electron in the affected orbital will be expected to revert toward a more s-like character, so that our estimate of the energy of this orbital becomes $(\frac{1}{2}\Delta-\alpha\delta)$ above the valence band where α is less than but not much less than 1. For an interstitial on the other hand, an electron removed or added

will be a p electron, so that the orbitals on the interstitial will be at $(\frac{1}{2}\Delta+\beta\delta)$ below the conduction band, where β is of the same order as α.

Let us now consider the situation when an extra electron is present in the crystal. From the previous paragraph, we see that its energy is lower when it is in one of the orbitals on an interstitial or neighboring a vacancy that if it is in an antibonding orbital elsewhere in the crystal. In particular, its diagonal matrix element of energy is lower at an interstitial by $(\frac{1}{2}\Delta-\beta\delta)$, at a vacancy by $(\frac{1}{2}\Delta+\alpha\delta)$.

Similarly, when a hole is present, its energy is lower by $(\frac{1}{2}\Delta+\beta\delta)$ when located at an interstitial; at a vacancy it is lower by $(\frac{1}{2}\Delta-\alpha\delta)$. In all cases, the hole or electron is attracted by the defect.

We have above described, not solved, a problem. The energy values given are diagonal matrix elements for an electron (or hole) located in a particular orbital. They are not energy values for stationary states. To determine the energy levels even for our simplified model would be very complicated. We shall content ourselves with the observation that this problem is similar to a still simpler one considered by Slater.[5] In this problem the only perturbation is in the diagonal matrix element of one orbital. The energy of the bound state is then given for not too large a perturbation, by

$$E\sim\frac{[V(0)-\gamma W]^2}{W}, \tag{1}$$

where $V(0)$ is the perturbation, W is a parameter characterizing the width of the band, and γ is a number of the order of 1. If $V(0)<\gamma W$, there is no bound state.

We believe that at least the following features of Slater's solution will be applicable to our problem. There will be a threshold value for the perturbing Hamiltonian below which no bound state will exist. This threshold will depend on the band width, which will also affect the binding energy in a manner similar to that of the denominator in (1).

We may now put these points together, finding the following results:

(1) The interstitial levels will be higher in the band than the corresponding vacancy levels; in other words, the vacancy level is deeper for the added electron while the interstitial level is deeper for the hole. This follows from the values for the perturbation given above in terms of Δ and δ.

(2) The levels will be asymmetrical in the gap, because the valence band is believed to be wider than the conduction band.[6] This implies that the hole levels associated with the valence band are closer to it than the electron levels are to the conduction band.

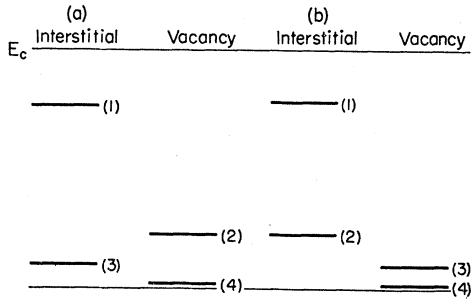

FIG. 2. Energy levels schemes proposed by (a) the author, and (b) James and Lark-Horovitz.

We are led to the assignment of the numbered levels shown in Fig. 2(a). On our model we could not predict whether levels (2) and (3) are as shown or reversed; this assignment has been made by a method used by Cleland and Crawford[2] and is based on the fact[2] that level (2) has a zero spin when vacant (occupied by a hole). This fact was determined from the statistical weights of the levels.

III

In this section, we shall describe the JLH model and compare it with our own.

James and Lark-Horovitz arrived at their model by considering a Ge crystal with one Ge^{4+} ion removed. They considered the possibility that instead of 4 localized states being split upward from the band there are only 3 or 2. Unable to make a theoretical preference for one of these, they chose the last, because of some indications that it fits the data better. Thus they concluded that an isolated vacancy has two tightly bound electrons but will attract two loosely bound holes, preserving neutrality. These holes are said to be attracted primarily by the Coulomb force. Similarly an interstitial is expected to have two tightly bound holes and two loosely bound electrons, the latter attracted primarily by the Coulomb force. The assignment of the numbered levels according to this model is shown in Fig. 2(b). Here again the assignment of levels (2) and (3) require the use of spin data and was made by Cleland and Crawford.[2]

From the above discussion of the JLH model Fig. 2(b), it follows that if only vacancies are present, they act as double acceptors, and interstitials as double donors. On the other hand, when the two types of defects are present in equal numbers, the loosely bound electrons on the interstitial recombine with the holes on the vacancies. The roles of the two defects are thus reversed. This is the normal situation in radiation damage.

We note that there are some distinct differences between the two models:

(1) In our model, each type of defect can act as either an acceptor or a donor, regardless of the presence of the other type.

[5] J. C. Slater, Technical Report No. 5, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished).

[6] See, for instance, F. Herman and J. Callaway, Phys. Rev. 89, 518 (1953). A more detailed picture may be found in G. Dresselhaus, thesis, University of California, 1955 (unpublished).

(2) There are no doubly charged states in our model.

(3) As a corollary, the two models predict different values of the charges of the centers for given Fermi levels.

(4) The ranges of Fermi level over which a given level can act as a minority carrier trap differ on the two models. For instance level (2) can act as a hole trap on our model for any value of the Fermi level above its own energy. In the JLH model, however, level (2) does not exist when level (1) is occupied.

All of these points may be susceptible to experimental check. We are aware of no definite evidence, but believe that some work by Shulman[7] on a hole trap in n-type Ge may be relevant to item (3). He observed a trap with a depth[8] of 0.25 ev in electron-bombarded Ge.

Naturally, we would hope that this trap can be identified with one of the levels in Fig. 1. We see that level (2) is the nearest one, and its value in electron bombarded Ge is close enough (0.23 ev) to 0.25 ev to make this identification reasonable, pending further evidence. According to the JLH model, this would be a positively charged level; according to ours, negatively charged.[9] Therefore, the trapping cross section would be different on the two models. The observed cross section is 3×10^{-15} cm^2. This lies between the typical values 10^{-13} cm^2 for a negatively charged trap[10] and 10^{-16} cm^2 for a neutral trap, and appears quite inconsistent with the typical value for 10^{-19} cm^2 for a positively charged trap. This fact tends to confirm our model. Indeed, it was inability to reconcile the JLH model to this information which originally led to the considerations of Sec. II.

Aside from possible experimental verification, we feel that our model has some theoretical preference over the JLH model. In the first place, it is qualitatively more definite. Whereas JLH could not make a theoretical choice between several alternatives, our reasoning though crude proceeds with no undetermined steps. JLH are also undoubtedly wrong in their belief that levels are hydrogenic, though this could not have been told when they wrote their paper, since the effective masses of electrons and holes were not then known. Finally, we believe that we have explained the asymmetrical distribution of levels. We also prefer a model which requires no doubly charged states, since crude estimates indicate that their energy would be too high.

The basic theoretical model of Sec. II should be applicable to other diamond-type structures, but at present work[11] has been done only on Si and it is still insufficient for comparison with the two models. The work of Longo suggests the possibility that there may be only one level to each defect, which is possible on our model if $V(0)$ is small enough in some cases, presumably those for which minus signs appear in Sec. II.

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[7] R. G. Shulman, Phys. Rev. **102**, 1451 (1956).

[8] Shulman gives a value of 0.25 ev determined from the slope of a logarithmic plot of decay time *vs* $1/T$, and a value of 0.30 ev obtained from the absolute value of the decay time. The former procedure seems to be more reliable.

[9] The conductivities of Shulman's samples indicate that the Fermi level is below level (1). For higher concentration, such that ζ is above level (1), this type would be impossible on the JLH model, as mentioned in item (4) above.

[10] W. Crawford Dunlap, in *Progress in Semiconductors* (Heywood and Company, 1957), Vol. 2.

[11] T. A. Longo, Ph.D. thesis, Purdue University, 1957 (unpublished); G. K. Wertheim, Phys. Rev. **105**, 1730 (1957).