PHYSICAL REVIEW VOLUME 115, NUMBER 5 SEPTEMBER 1, 1959

Hall Effect and Impurity Levels in Phosphorus-Doped Silicon

DONALD LONG AND JOHN MYERS
Honeywell Research Center, Hopkins, Minnesota

(Received April 13, 1959)

An experimental study has been made of the energy level structure of a phosphorus donor impurity in silicon, using Hall coefficient and Hall mobility measurements on six samples of widely varying impurity content and compensation. The main purpose was to test the Kohn-Luttinger theoretical model which predicts a splitting of the sixfold degenerate (excluding spin) ground "1*s*" level, with a single state being depressed in energy by between 0.009 and 0.015 ev relative to the remaining fivefold degenerate level. The splitting energy can be measured by comparing carrier concentration *vs* temperature curves corresponding to this energy level scheme with experimental curves derived from Hall data. The curves for our samples all agree well with the Kohn-Luttinger model for splitting energies of between 0.009 and 0.012 ev, in agreement with the theoretical prediction.

THIS paper is concerned with an experimental investigation of the energy level structure of group V donor impurities in silicon, made primarily to test the theoretical model proposed by Kohn and Luttinger.[1,2] This investigation is closely related to the study of ionized-impurity scattering reported in the preceding paper[3] (referred to hereinafter as LM1), and we have in fact used here the same Hall coefficient and Hall mobility data reported in LM1. Our specific interest has been to explore certain details of the donor energy level structure which are not amenable to investigation by other common experimental techniques. A preliminary report has already been given elsewhere.[4]

Kohn and Luttinger have calculated the type of energy level scheme to be expected for a group V donor in silicon, taking into account the known structure of the bottom edge of the conduction band.[1,2] They began with the well-known effective-mass equation, which permits the detailed motion of a nearly free electron in the lattice to be described by an effective mass different from the true electronic mass. The solutions of this equation give the energy levels of the ground and excited states. In analogy with the hydrogen atom, the ground state can be denoted by "1*s*" and the excited states by the other usual such symbols. However, in the case of the donor in silicon, the "1*s*" level is sixfold degenerate (excluding spin), because the wave function for this level is constructed from the Bloch functions of the six equivalent conduction band minima. This is the first of two important differences between the energy level scheme of an actual group V impurity in silicon and that of a true hydrogen-like atom. The second is associated with the ionization energy. The effective-mass theory predicts an ionization or ground-state energy of 0.029 ev for the well-established values of the electron effective mass in silicon; whereas, the observed ionization energy in phosphorus-doped silicon, for example, is about 0.044 ev.[2,3] Kohn and Luttinger have explained the discrepancy by a failure of the effective-mass theory for electron motion rather close to the donor ion; when the electron is moving in a tight orbit, the concept of an effective mass and its applicability tend to lose validity. Because the wave function for one of the six "1*s*" states has a nonzero, finite value at the position of the donor ion, it can be shown to be depressed in energy with respect to the other five "1*s*" states, which are relatively unaffected due to their zero wave functions at the donor ion. Thus, there should be a splitting of the "1*s*" level into a single state at ~0.044 ev below the conduction band edge, to agree with the observed ionization energy, and a fivefold degenerate level at an energy only slightly below that predicted by the effective mass theory. The resulting scheme is shown in Fig. 1. The "1*s*" splitting energy will be referred to as Δ in the remainder of the paper. We see that its value should lie between 0.009 and 0.015 ev.

The energies of the excited states, which all lie within about 0.011 ev of the band edge, have been measured by infrared absorption methods and are found generally to agree fairly well with the theoretical predictions.[2,5] Of course the excited states should be well described by the effective-mass theory; because of their large orbits, their energies are accurately calculable.

The upper, fivefold degenerate "1*s*" level has not to our knowledge previously been observed either directly or by its indirect effect on any experimental result. One would *not* ordinarily expect to observe an optically-induced transition between the two "1*s*" levels, because selection rules should prevent it.[5] On the other hand, there is nothing to prevent thermal excitation of electrons into the upper "1*s*" level, and so we should be able to detect its presence and measure Δ by means of an experiment which determines the distribution of a given number of electrons over the energy levels. The

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[1] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

[2] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, pp. 257–320.

[3] D. Long and J. Myers, preceding paper [Phys. Rev. **115**, 1107 (1959)].

[4] D. Long and J. Myers, Bull. Am. Phys. Soc. Ser. II, 4, 145 (1959).

[5] Picus, Burstein, and Henvis, J. Phys. Chem. Solids **1**, 75 (1956); H. J. Hrostowski and R. H. Kaiser, J. Phys. Chem. Solids **7**, 236 (1958).

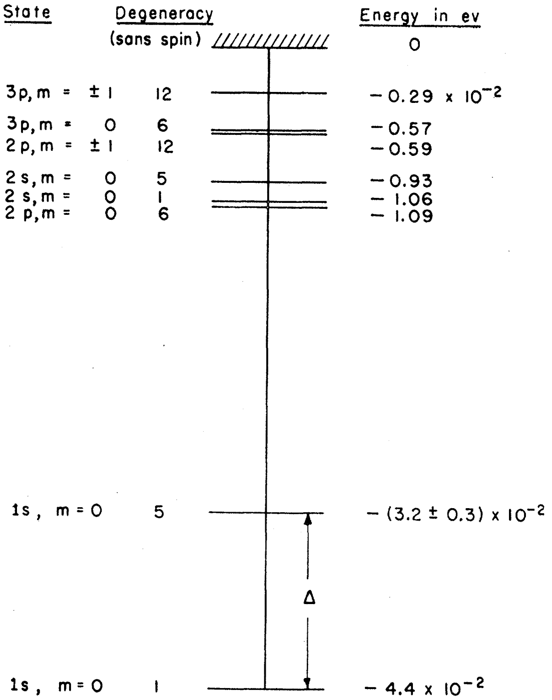

FIG. 1. Theoretical energy level spectrum for a phosphorus donor impurity in silicon (after Kohn and Luttinger).

practical way to do this is to obtain a curve of the temperature dependence of the concentration n of conduction electrons, as determined from Hall data, and then to correlate the shape of the curve with the existence and position of the upper "1s" level, since the fraction of the electrons which will be in the conduction band at a certain temperature is a function of the energies and degeneracies of all the levels available to them. The following statistical equation gives the dependence of n on the temperature T for the Kohn-Luttinger model for n-type silicon[3,6]:

$$\frac{n(n+N_A)}{(N_D-N_A)-n}=\frac{2.75\times10^{15}T^{\frac{3}{2}}e^{-\epsilon_g/kT}}{1+5e^{-\Delta/kT}+\sum_i g_i e^{-\Delta_i/kT}}.\qquad(1)$$

The g_i and Δ_i are the degeneracies and energies, respectively, of the various excited states. The other symbols in (1) are conventional and are defined in LM1. It can be seen in Eq. (1) that the existence of the upper "1s" level (and to a lesser extent also the excited states) makes the value of n at a particular temperature lower than if only the single state at energy ϵ_g were present.

We have already in LM1 described the iterative method which is used to derive the most nearly correct n *vs* T (or more exactly, $\ln n$ *vs* $1000/T$) curve for a sample of phosphorus-doped n-type silicon from Hall effect and Hall mobility data, and we have derived such curves from the data reported in LM1 for six samples of rather widely differing impurity content and compensation. These samples and their n *vs* T results are ideally suited to the present investigation also, and so we shall simply appropriate them for the present purposes. Reference should be made to LM1 for details of the experiments and the derivation of n *vs* T curves and for information about sample purity, etc. The most interesting portion of the $\ln n$ *vs* $1000/T$ curve for sample *SP1A*, which is of intermediate purity for the group of samples studied, is shown in Fig. 2. Arguments are given in LM1 which indicate how accurate one can expect such a curve to be.

Once the best possible $\ln n$ *vs* $1000/T$ curve has been obtained for a sample, it is a straightforward matter to find the value of Δ giving the best fit of Eq. (1) to it. This can be done conveniently from the following expression, which is simply Eq. (1) solved explicitly for Δ:

$$\Delta=kT\ln\left\{\frac{0.55\times10^{15}T^{\frac{3}{2}}e^{-\epsilon_g/kT}}{n(n+N_A)/[(N_D-N_A)-n]}-\tfrac{1}{5}\left(1+\sum_i g_i e^{-\Delta_i/kT}\right)\right\}^{-1}.\qquad(2)$$

Table I lists values of Δ calculated from Eq. (2) for each sample at several typical temperatures in the range where the upper "1s" level has the greatest influence on the n *vs* T behavior, but where the excited states are relatively unimportant. We see that the values of Δ all lie between 0.009 and 0.012 ev, and therefore within the theoretically predicted range. There is perhaps some indication of a slight decrease of Δ with decreasing temperature for several of the samples. This effect may be due to the further splitting of the upper

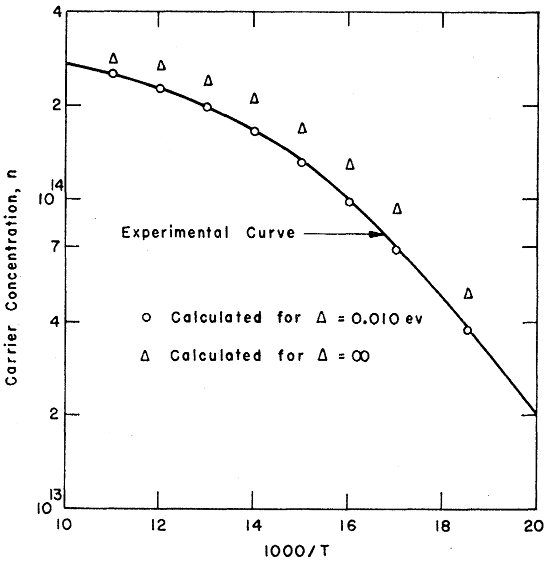

FIG. 2. Experimental carrier concentration *vs* temperature curve for sample *SP1A*, and points calculated from Eq. (1) for $\Delta=0.010$ ev and for $\Delta=\infty$.

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[6] E. H. Putley, Proc. Phys. Soc. (London) 72, 917 (1958).

"1*s*" level into threefold and twofold degenerate levels, with the threefold level lying lower, which has been predicted by Kohn and Luttinger,[1] but our inability to determine *n vs T* curves which we can be sure are exactly correct prevents us from making a *meaningful* resolution of this splitting from the experimental results. If a further splitting of this type really does exist, the values of Δ given here represent an average energy of the split levels.

Figure 2 shows that portion of the experimental ln*n vs* $1000/T$ curve for sample *SP*1*A* which is most sensitive to the existence of the upper "1*s*" level, as well as some representative points calculated from Eq. (1) for $\Delta=0.010$ ev to illustrate the nature of the fit of Eq. (1) to the experimental results. Some points for $\Delta=\infty$ are also shown to point up the effect of the upper "1*s*" level. The type of agreement of the experimental curve with the Kohn-Luttinger model shown in Fig. 2 is quite typical of that found for the other five samples also.

TABLE I. Values of Δ calculated from Eq. (2) for six phosphorus-doped silicon samples at temperatures where the upper "1*s*" level has the greatest influence.

Sample	Values of Δ, in ev $T_1=45$°K	$T_2=55$°K	$T_3=65$°K
*SP*6*A*	0.010	0.011	0.011
	$T_1=55$°K	$T_2=65$°K	$T_3=75$°K
*SP*4*A*	0.0095	0.011	0.012
*SP*1*A*	0.009	0.010	0.010
*SP*2*A*	0.009	0.010	0.010
*SM*2	0.010	0.010	0.011
*SM*3	0.010	0.011	0.011

The most important source of possible error in the results for Δ in Table I and Fig. 2 would seem to reside in the derivation of the *n vs T* curves from the Hall data; we have indicated in LM1 how the Hall factor *r* relating *n* to the measured Hall coefficient is somewhat sensitive to impurity concentrations, to how one calculates the ion scattering contribution to the mobility, and to several other such sources of uncertainty. It is possible, however, to become convinced that it really is not necessary to know the temperature dependence of the Hall factor for a sample very accurately, because Δ proves to be quite insensitive to it. All that *is* required is to know the dependence in only an approximate way, which we certainly do. As an example of the insensitivity of Δ, we give in Table II values of Δ for sample *SP*1*A* for a few of the successive approximations made in converging on the supposedly correct Hall factor behavior for this sample.[3] We see that even in the first approximation, where it was assumed that $r=1$ at all temperatures, Δ still lies between 0.010 and 0.013 ev. The values of Δ are not quite this insensitive to *r* for all the other samples at all temperatures, but these results do show that it is not necessary to know the Hall factor behavior very accurately to pin down Δ within rather narrow limits.

TABLE II. Values of Δ calculated from Eq. (2) for sample *SP*1*A* for a few of the successive approximations or iterations made in converging on the supposedly correct behavior of the Hall factor *r*.[a]

Approximation	Values of Δ, in ev at 55°K	at 65°K	at 75°K
First ($r=1$ at all temperatures)	0.010	0.011	0.013
Second	0.010	0.010	0.010
Final	0.009	0.010	0.010

[a] See reference 3.

There are several other sources of possible error which come to mind. It is conceivable that the electron effective mass parameters might change with increasing temperature from their values determined at 4°K by cyclotron resonance[7] or that the donor energy levels might be temperature dependent. If either effect were important, the 0.55×10^{15} factor in Eq. (2) could be changed considerably, thereby changing Δ. However, there is no evidence for either of these effects, and in fact Macfarlane and co-workers[8] have recently found that the mass is probably almost a constant over the temperature range in which we are interested. The actual energy level structure for the donor impurity may not be as nearly discrete as required by the model. This would be particularly true for large donor concentrations, but we have concentrated mostly on relatively pure samples.

It is our opinion that the experimental results and analysis used here are sufficiently precise to make the values of Δ quoted meaningful; that is, to establish Δ as lying between 0.009 and 0.012 ev. In reaching this conclusion, we have considered all the details and possible sources of error discussed in LM1. The best justification for it, however, is the consistency among the values of Δ calculated for the six samples studied; these samples cover a particularly wide range of impurity concentrations and compensation, leading to a variety of types of Hall factor *vs* temperature curves as well as variations in other properties and effects, and yet each sample gave essentially the same value of Δ.

In summary, we find from Hall experiments that the pronounced "1*s*" level splitting predicted by Kohn and Luttinger does exist for phosphorus donors in silicon and that its value lies within the 0.009 to 0.015 ev range predicted by theory. It would be interesting to make similar studies of other group V donors in silicon, particularly bismuth for which the splitting energy should be still larger.

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[7] See reference 3 for a listing of these values.

[8] Macfarlane, McLean, Quarrington, and Roberts, Phys. Rev. **111**, 1245 (1958).