increasing energy, observed in experimental deuteron-induced excitation curves: competition from reactions involving the emission of a second particle. The familiar $(d, 2n)$ is a special case of such reactions, in that the outgoing particles are not limited by the necessity of penetrating the Coulomb barrier and can therefore be produced with deuterons of moderate energies. The $(d; p, n)$ and $(d; n, p)$ reactions which must compete with the (d, p) and (d, n) would be difficult to observe, since they lead back to the target isotope and could be found by these techniques only where excited states of these isotopes exist. For light elements in general, where barriers are low for deuterons, the $(d; n, \alpha)$ and $(d; \alpha, n)$ reactions usually lead to stable isotopes. With the higher deuteron energies now becoming available, many more of these multiple disintegrations should be found.

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Thermal Ionization of Impurity Levels in Semi-Conductors†

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The probability of ionization of an impurity level by thermal agitation in a semi-conductor is estimated by the use of a simple Debye model. It is found that the probability of ionization by one phonon decreases exponentially with the depth of the impurity level below the conduction band, approaching zero as the energy separation becomes equal to $k\theta_D$. The probability of ionization by more than one quantum is also estimated by the use of an Einstein model. It appears that the probabilities so calculated may play an important role in determining the frequency dependence of the rectification efficiency in crystal rectifiers.

INTRODUCTION

THE electrical properties of many semi-conductors are determined primarily by the presence of impurities that introduce discrete electronic energy levels which lie between the empty conduction band of the semi-conductor and the next lowest lying filled electronic band. These discrete energy levels may act either as acceptor levels or as donator levels. In the first case, they lie near the top of the filled band, are empty at zero temperature, and can accept electrons from the filled band, thus producing "hole conduction." In the second case, the levels lie near the bottom of the empty band, are full at zero temperature, and can donate electrons to the empty band, thus augmenting the intrinsic electronic conduction. The two situations are represented schematically in Fig. 1 and Fig. 2, respectively. In the following discussion we shall consider only donator levels, which produce the so-called N-type semi-conductors, with the understanding that our conclusions are also applicable to acceptor levels forming P-type semi-conductors.

When a semi-conductor is placed in contact with a metal, a rectifying junction may be formed if the relative work functions of metal and semi-conductor are suitable. In the case of an N-type semi-conductor, the effective work function of the metal must be larger than that of the semi-conductor. Then the equilibrium situation near the junction is as represented schematically by the potential diagram of Fig. 3.[1] Practi-

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[1] F. Seitz and S. Pasternack, "The Principles of Crystal Rectifiers," NDRC Report No. 01-102, June 10, 1942.

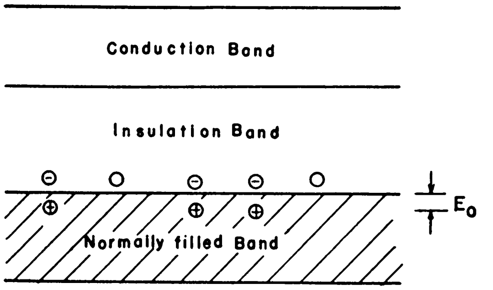

FIG. 1. Energy level diagram showing schematically the excitation of electrons from a normally filled band to acceptor levels producing hole conduction. E_0 represents the height of the acceptor levels above the normally filled band.

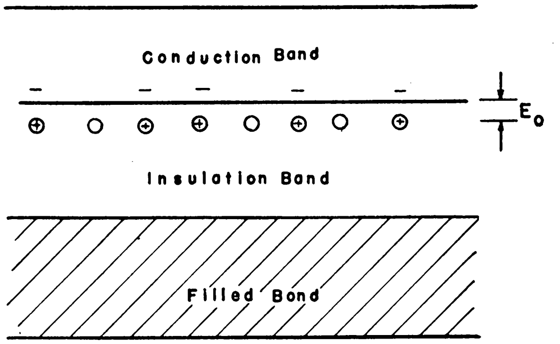

FIG. 2. Energy level diagram showing schematically the ionization of donator impurity levels to produce free electrons in the conduction band of a semi-conductor. E_0 represents the depth of the levels below the conduction band.

cally all of the donators lying more than thermal energy (kT) above the thermodynamic potential far from the junction (which is about midway between the donator levels and the bottom of the conduction band) will be ionized. This produces a net positive charge in the semi-conductor near the metal, and consequently a net negative charge in the metal on the other side of the potential barrier. Because of this double layer or potential step, the electron flow from semi-conductor to metal when the metal is made anodic by a given potential is greater than the reverse flow when the metal is made cathodic by the same amount. This results in a rectifying characteristic of the type shown in Fig. 4.

In addition to causing a net current through the junction, an applied voltage also changes the bound charge in the semi-conductor near the interface. Thus the amount of stored charge depends on the voltage, and the contact has some capacitative properties. The over-all electrical behavior of the rectifier may be represented approximately by the simple circuit of Fig. 5. It is evident that the capacity associated with the bound charge in the barrier layer will tend to short out the back resistance when the frequency becomes high enough that the impedance of C is comparable with R_b.[2] For high frequencies, this should cause the rectification efficiency to fall off as the inverse square of the frequency. Experimentally, however, in many rectifiers, the efficiency drops off much more slowly than this with increasing frequency. One possible explanation of this discrepancy lies in assuming that the circuit parameters of Fig. 5 are themselves functions of the frequency. The capacity C will be expected to decrease with increasing frequency if there is a time lag in ionization (and deionization) of the donator levels that is of the order of the period of the applied field. Such a lag can occur owing to the finite probability of ionization by thermal agitation of the lattice; an estimate of this probability is made in the following section.

THEORY

The transition probability per unit time for the excitation of electrons from donator levels is given by

$$w=(2\pi/\hbar)\,|V_{0K}|^2\rho_K, \tag{1}$$

where ρ_K, the energy density of states in the conduction band, is given by

$$\rho_K=4\pi\Omega mp/h^3. \tag{2}$$

m and p are the mass and momentum of the

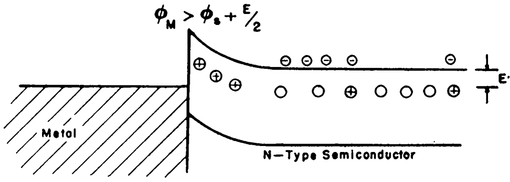

FIG. 3. Schematic diagram showing the relative energy levels in a metal and N-type semi-conductor. With no external applied field, the top of the Fermi distribution lies approximately half-way between the impurity levels and the conduction band of the semi-conductor.

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[2] H. A. Bethe, "Theory of High Frequency Rectification by Silicon Crystals," NDRC Report No. 43–11, October 29, 1942.

electron, respectively, and Ω is the volume of the crystal. V_{0K} is the matrix element

$$V_{0K}=\int\psi_0 V\psi_K{}^* d\tau \tag{3}$$

calculated in terms of normalized initial and final wave functions

$$\begin{aligned}\psi_0&=(1/(\pi a^3)^{\frac{1}{2}})e^{-r/a},\\ \psi_K&=(1/\Omega^{\frac{1}{2}})\exp(i\mathbf{K}\cdot\mathbf{r}).\end{aligned}\tag{4}$$

ψ_0 is taken for simplicity to be of hydrogenic form.

The perturbation V may be approximated as

$$V(\mathbf{r})=-\mathbf{R}_\sigma(\mathbf{r})\cdot\nabla V_0(\mathbf{r}),\tag{5}$$

where

$$\begin{aligned}V_0(\mathbf{r})&=-Ze^2\mathbf{r}/r^2,\\ \mathbf{R}_\sigma&=\boldsymbol{\varepsilon}_\sigma\exp(i\boldsymbol{\sigma}\cdot\mathbf{r}).\end{aligned}\tag{6}$$

Equations (5) and (6) may be interpreted as follows. The thermal agitation may be resolved into acoustic Debye waves which strain the lattice and alter the separation of electron and donator ion. The total strain will then involve a sum over the propagation vectors $\boldsymbol{\sigma}$ of the Debye waves. However, energy must be conserved between the phonons (Debye wave quanta) and the electrons, so that

$$h\nu_\sigma=\hbar^2K^2/2m+|E_0|,\quad E_0<0,\tag{7}$$

where ν_σ is the frequency of the Debye wave and E_0 the energy of the bound electron state.

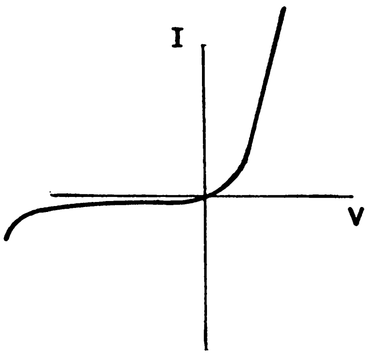

FIG. 4. Typical characteristic curve of a rectifying junction showing the dependence of current I on applied voltage V.

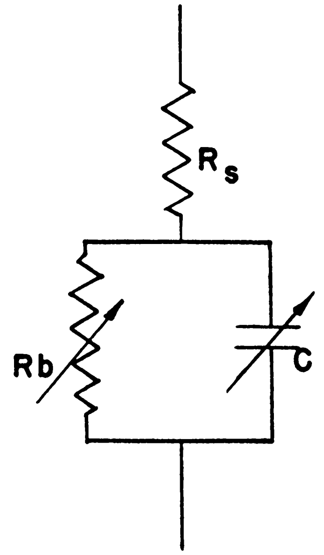

FIG. 5. Simple equivalent circuit of a rectifying contact. R_b and C, which are both functions of applied voltage, represent the resistance and capacitance of the barrier layer respectively, R_s is the bulk resistance of the semiconductor.

Equations (4)–(6) may be substituted into Eq. (3) and the integrals carried out to give

$$V_{0K}=4iaZe^2\left(\frac{\pi}{\Omega a^3}\right)^{\frac{1}{2}}\epsilon_\sigma\cos\theta_\sigma\left(\frac{\tan^{-1}aQ_\sigma-aQ_\sigma}{a^2Q_\sigma{}^2}\right),\tag{8}$$

where θ_σ is the angle between $\boldsymbol{\varepsilon}_\sigma$ and $\mathbf{Q}_\sigma\equiv\boldsymbol{\sigma}-\mathbf{k}$. For the situations of practical interest, σ, K, and $1/a$ are all of the same order of magnitude ($\sim10^7$ cm^{-1}). The quantity aQ_σ will be of the order of or less than unity, and a good enough approximation to Eq. (8) may be obtained by expanding the inverse tangent and keeping the first two terms, and replacing aQ_σ by aK. This gives for the square of the matrix element

$$|V_{0K}|^2\approx\frac{16\pi Z^2e^4aK^2}{9\Omega}\epsilon_\sigma{}^2\cos^2\theta_\sigma.\tag{9}$$

The amplitude of the Debye wave may be written

$$\epsilon_\sigma{}^2=\frac{h\nu_\sigma}{2\pi^2M\nu_\sigma{}^2(e^{h\nu_\sigma/kT}-1)}\tag{10}$$

where M is the mass of the donator atom. Since we have to integrate over the Debye spectrum, we need the number of modes between ν_σ and $\nu_\sigma+d\nu_\sigma$

$$f(\nu_\sigma)d\nu_\sigma=(3h^3\nu_\sigma{}^2/k^3\theta_D{}^3)d\nu_\sigma\tag{11}$$

where θ_D is the Debye temperature. Since the range of integration is small ($|E_0|$ is close to $k\theta_D$), the result for the total transition probability may be estimated as

$$w \approx \frac{114\pi^4 Z^2 e^4 a m^2 (2mkT)^{\frac{1}{2}}}{Mh^4} \frac{(\theta_D/T - C)}{(e^C - 1)C^{\frac{1}{2}}}, \qquad C = \frac{|E_0|}{kT}. \tag{12}$$

Typical numerical values for substitution in Eq. (12) are as follows: $\theta_D/T \cong 2$, $C \cong 3/2$, $Z \cong 0.1$, $a \cong 10^{-7}$ cm, $M = 27$ for aluminum impurity in a silicon semi-conductor. The small value of Z includes the effect of the dielectric constant (about 10) in reducing the single unbalanced charge of the aluminum ion; similarly a is larger than would be expected for a hydrogen atom by about a factor of 10. These values indicate that w is about 10^{10} sec.$^{-1}$, provided that $|E_0| < k\theta_D$.[3]

If $|E_0|$ exceeds $k\theta_D$, which seems unlikely on the basis of present information, then ionization involves the absorption of more than one phonon from the lattice vibrations. The order of magnitude of two or three phonon effects may be estimated by using the simpler Einstein model for the oscillations of the crystal lattice as follows. We assume that the atoms undergo a harmonic displacement from fixed lattice points given by

$$\mathbf{R} = \mathbf{R}_0 \sin\omega t, \tag{13}$$

which introduces a perturbation of the electron energy given by

$$V = \frac{Ze^2}{|\mathbf{r} - \mathbf{R}|} - \frac{Ze^2}{|\mathbf{r}|} = \frac{Ze^2}{r} \sum_{n=1}^{\infty} (R/r)^n P_n(\cos\theta'), \tag{14}$$

where θ' is the angle between $\mathbf{r}$ and $\mathbf{R}$, and $|R| \leqslant |r|$. Using the fact that $(Ka)^2 \ll 1$, one finds for the matrix element

$$V_{0K} = \frac{4\pi a^2 Ze^2}{(\pi a^3 \Omega)^{\frac{1}{2}}} \sum_{n=1}^{\infty} (iR_0K)^n \frac{2^n n!}{(2n+1)!} \times P_n(\cos\theta')(\sin\omega t)^n. \tag{15}$$

If we expand V_{0K} in a Fourier series, the first harmonic will be the matrix element for transitions from levels lying between 0 and $k\theta_E$, the second will correspond to transitions from levels lying between $k\theta_E$ and $2k\theta_E$, i.e., two phonon transitions, etc. Using the fact that $R_0K \ll 1$, one finds

$$\begin{aligned} {}^1V_{0K} &= \frac{4\pi a^2 Ze^2}{3(\pi a^3 \Omega)^{\frac{1}{2}}} (iR_0K) P_1(\cos\theta'), \\ {}^2V_{0K} &= \frac{4\pi a^2 Ze^2}{30(\pi a^3 \Omega)^{\frac{1}{2}}} (iR_0K)^2 P_2(\cos\theta'). \end{aligned} \tag{16}$$

etc.

From the foregoing equations, using the numerical value suggested above, one may show that each additional phonon absorbed reduces the transition probability by approximately a factor of 10^6.

It may readily be shown that the transition probability due to thermal radiation is of the order of 10^6 sec.$^{-1}$, and hence may be neglected in comparison with the probability of single phonon transitions.

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[3] We are indebted to Professor F. Seitz for informing us of the results of an independent estimate of the transition probability that is based on the Born-Oppenheimer molecular approximation. He obtained a numerical result of the same order of magnitude.