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Heat Treatment of Semi-Conductors and Contact Rectification*

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It is suggested that the heat treatment results in the formation of a layer low in impurity concentration near the surface of the semi-conductor. This is the result of a rapid evaporation of impurity atoms from the surface and a slower influx by diffusion from the interior. The conditions for the formation of this layer are discussed, and an expression for the ratio of the evaporation coefficient to the diffusion coefficient is derived. The effect of the depleted layer on the electrical characteristics of a semi-conductor-metal rectifying contact are calculated on the basis of the diode theory of rectification; and it is shown that the heat treatment results in increased back resistance and decreased contact capacity. The effect of these changes on the efficiency of rectification is discussed.

INTRODUCTION

THE preparation of semi-conductor-metal contact rectifiers usually involves the heating of the semi-conductor before the rectifier is assembled. In particular, in making silicon-tungsten point contact rectifiers, the silicon is heated at approximately 1000°C for about one hour. The silicon in these rectifiers has semi-conducting properties by virtue of the presence of impurities, small quantities of aluminum or boron, which are deliberately added to the original silicon melt.

We propose that one of the effects of the heating is to cause evaporation of the impurities from the surface of the semi-conductor. If the diffusion rate of the impurity in the bulk of the semi-conductor is slow enough, the decrease in impurity content near the surface will not be compensated by an influx of impurities from the bulk material. After some time, a layer low in impurity concentration will form near the surface of the semi-conductor. This change in impurity concentration near the surface, in turn, changes the electrical characteristics of a metal-semi-conductor contact.

The latest procedures of silicon preparation also involve polishing the surface and sometimes etching the surface. Further, the silicon is heated in air, and the resulting oxide layer is then dissolved away. These procedures undoubtedly change the surface and thus the character of the rectifying contact. These changes are hard to treat theoretically and are not understood, and we shall neglect them.

We shall treat only the simple case of heating in a vacuum, so as to avoid the complication introduced by the oxide surface layer. Heating in air probably produces effects of the same general nature as those that we discuss.

PRODUCTION OF A SURFACE LAYER DEPLETED OF IMPURITY ATOMS

We consider a semi-infinite, homogeneous, isotropic block of semi-conductor with its plane face at $x=0$, containing initially a uniform concentration N_0 of impurity atoms. The concentration of impurities in the semi-conductor at a distance x from the surface at a later time t is given by the solution of the diffusion equation

$$\mathfrak{D}\partial^2 N/\partial x^2 = \partial N/\partial t, \tag{1}$$

subject to the appropriate boundary conditions, where $\mathfrak{D}$ is the diffusion coefficient.

We assume that the rate of loss of impurity atoms per unit area from the surface is proportional to the surface concentration, i.e., equal to $kN(0, t)$, where we call k the evaporation coefficient. If the concentration of impurities outside the semi-conductor is maintained equal to zero, it follows from the equation of continuity that

$$-\mathfrak{D}(\partial N/\partial x)_{x=0}+kN(0, t)=0.$$

This is the first boundary condition. The other

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boundary conditions are clearly

$$N(x,0)=N_0,\quad x>0;$$
$$N(\infty,t)=N_0.$$

The solution of the analogous problem in heat flow (a semi-infinite body initially at uniform temperature losing heat by radiation into a region of zero temperature) is known,[1] so that by the proper substitution of variables, the solution of Eq. (1) is

$$N/N_0=F\{2^{-1}x(\mathfrak{D}t)^{-\frac{1}{2}}\}+[1-F\{2^{-1}x(\mathfrak{D}t)^{-\frac{1}{2}}+(\mathfrak{D}t)^{\frac{1}{2}}k\mathfrak{D}^{-1}\}]\times\exp(xk\mathfrak{D}^{-1}+\mathfrak{D}tk^2\mathfrak{D}^{-2}),$$

with

$$F\{u\}=2\pi^{-\frac{1}{2}}\int_0^u dy\cdot\exp(-y^2).$$

For large values of $(\mathfrak{D}tk^2\mathfrak{D}^{-2})$, this solution may be approximated by the simpler form

$$N/N_0=F\{2^{-1}\pi^{\frac{1}{2}}\alpha_0xk\mathfrak{D}^{-1}\}+[\exp(-4^{-1}\pi\alpha_0{}^2x^2k^2\mathfrak{D}^{-2})]\times[2^{-1}\pi\alpha_0k\mathfrak{D}^{-1}x+\alpha_0{}^{-1}]^{-1},\quad(2)$$

where

$$(N/N_0)_{x=0}=\alpha_0\equiv[(\pi\mathfrak{D}t)^{\frac{1}{2}}k\mathfrak{D}^{-1}]^{-1},$$

so that α_0 is the relative surface concentration. This approximation is valid in the limit that we may neglect $\alpha_0{}^3$ compared with α_0. Physically, we are interested only in the case of low surface concentration, so that Eq. (2) is the form of solution which is most useful.

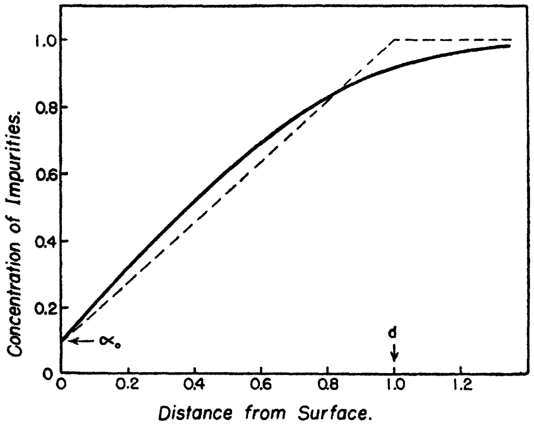

FIG. 1. The relative concentration of impurities is plotted as a function of the distance from the surface in units of the total thickness of the depleted layer. The dashed curve shows the linear approximation.

Substituting for x in Eq. (2) the value

$$d\equiv(\alpha_0k\mathfrak{D}^{-1})^{-1},$$

we obtain

$$(N/N_0)_{x=d}\simeq 0.9.$$

We call d the thickness of the depleted layer. Figure 1 shows a plot of N/N_0 as a function of x in units of d, for $\alpha_0=0.1$. We note that this curve may be roughly approximated by the linear relationship shown by the dotted curve.

If we require that $\alpha_0=0.1$, then for values of the thickness of the depleted layer $d\geqslant 10^{-6}$ cm, we obtain that $k/\mathfrak{D}\leqslant 10^7\ \mathrm{cm}^{-1}$. However, the smaller $k/\mathfrak{D}$, the longer the time it takes to realize a given α_0 and d. In the next section we discuss the factors which determine the magnitude of $k/\mathfrak{D}$.

RATIO OF EVAPORATION COEFFICIENT TO DIFFUSION COEFFICIENT

The diffusion coefficient may be expressed in terms of atomic parameters[2] as

$$\mathfrak{D}=a\delta^2\cdot\exp(-\epsilon'/KT),\quad(3)$$

where a is the "jumping frequency" of a substituted impurity atom in the bulk crystal lattice, δ is the distance between adjacent bulk atoms, ϵ' is the activation energy for diffusion, K is Boltzmann's constant, and T is the absolute temperature.

To derive an analogous expression for the evaporation coefficient we note that the rate at which impurity atoms leave the surface equals the product of the number of impurities on the surface and the probability per second that an atom will leave. We assume that the number of impurities on the surface is the number contained in the first atomic layer, and the probability that an atom will leave is given by

$$a\cdot\exp(-\epsilon''/KT),$$

where a is the same jumping frequency and ϵ'' is the activation energy for evaporation; thus

$$k=a\delta\cdot\exp(-\epsilon''/KT).\quad(4)$$

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[1] H. S. Carslaw, *Introduction to the Theory of Fourier Series and Integrals and the Theory of the Conduction of Heat* (The Macmillan Company, New York, 1906), pp. 245–247.

[2] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 494–496.

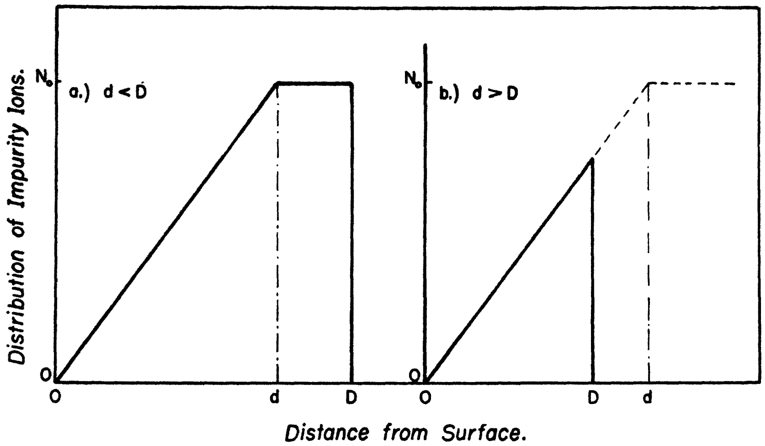

FIG. 2. The effective distribution of ions at the rectifying contact is shown for the two cases $d<D$ and $d>D$, where d is the thickness of the depleted layer. The potential goes to zero at D.

Combining Eqs. (3) and (4) we obtain

$$k/\mathfrak{D}=\delta^{-1}\cdot\exp\left[-(\epsilon''-\epsilon')/KT\right].$$

In most substances δ is of the order of a few Angstrom units, so that for $\epsilon''\simeq\epsilon'$, $k/\mathfrak{D}$ is of the order of 10^7 cm^{-1}. Since ϵ'' is probably greater than ϵ',[3] it is reasonable that $k/\mathfrak{D}\leqslant 10^7$ cm^{-1} and that a depleted layer thickness of $\geqslant 10^{-6}$ cm is readily attainable for a sufficient heating time.

EFFECT OF THE DEPLETED LAYER ON THE ELECTRICAL CHARACTERISTICS OF A RECTIFYING CONTACT

The theory of silicon-metal contact rectification for a uniform distribution of impurities was given by Bethe.[4] The impurity energy levels in silicon lie close enough to the conduction band for all the impurities to be ionized at room temperature. When a metal having a different work-function than the silicon is put in contact with the latter, a potential barrier is established at the contact, the voltage being equal to the contact potential difference at the surface and falling to zero at a distance D_0 inside the semiconductor. The distance at which the potential falls to zero is found by solving Poisson's equation for the electron potential V,

$$d^2V/dx^2=4\pi e^2(n_+-n_-)/\epsilon,$$

where e is the electronic charge, ϵ is the dielectric constant, and n_+ and n_- are, respectively, the density of positive and negative charges at x; subject to the boundary conditions $V=e\varphi$ at $x=0$, and $dV/dx=0$, $V=0$ at $x=D_0$, where φ is the potential at the contact. It is assumed that the density of electrons is zero and $n_+=N_0$ in the region where the potential is greater than zero ($x<D_0$) and the total charge density is zero for $x>D_0$. We obtain

$$D_0=(\epsilon\varphi/2\pi eN_0)^{\frac{1}{2}}.$$

To this potential we must add the potential due to the image force of the metal, which lowers the potential by an amount $-e^2/4\epsilon x$. This lowers the peak of the potential barrier approximately by

$$\Delta\varphi_0=(2e\varphi/\epsilon D_0)^{\frac{1}{2}}. \tag{5}$$

The position of the maximum of potential is also shifted into the semi-conductor by an amount

$$x_m=(eD_0/8\epsilon\varphi)^{\frac{1}{2}}.$$

Equation (5) is valid in the approximation that $(x_m/D_0)^2$ is negligible compared with (x_m/D_0).

If we assume that the electrons are not stopped by collisions in passing over the barrier (diode theory), we find the current density through the contact is

$$j=j_0\left[\exp -e(\varphi_0-\Delta\varphi_0)/KT\right]\left[(\exp e\varphi'/KT)-1\right],$$

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[3] J. Steigman, W. Schockley, and F. C. Nix, *Phys. Rev.* **56**, 13 (1939).

[4] Complete references will be found in the OSRD technical reports of the University of Pennsylvania: Div. 14 No. 282, May 29, 1944, and Div. 14 No. 304, August 3, 1944. Copies of these reports may be obtained from the Publications Board of the Department of Commerce, Washington, D. C.

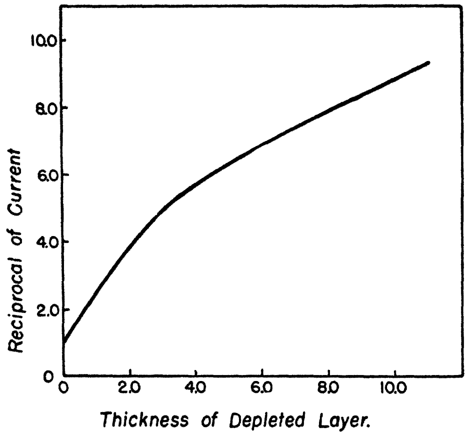

FIG. 3. The back current for an applied potential of -1.0 v is shown as a function of the thickness of the depleted layer in units of D_0. The current is in units of the current through a contact with no depleted layer.

where j_0 is the current density of electrons approaching the contact, φ_0 is the contact e.m.f., and φ' is the applied potential. The potential at the contact φ is the difference between φ_0 and φ' The current density is very small for negative applied voltages and increases rapidly with positive values of φ'. The effect of the tunneling of electrons through the barrier is neglected in the derivation of the expression for the current density.

To calculate the effect of the depletion of impurities on the electrical characteristics of the contact, we assume that the heat treatment results in a linear distribution of impurity atoms of the form

$$N=N_0x/d,\quad x\leqslant d;\quad N=N_0,\quad x>d;$$

where d is the thickness of the depleted layer (see Fig. 1). We neglect the concentration at the surface since this is small and only complicates our equations without adding to their significance. If D is now the distance at which the potential falls to zero, we must distinguish between two cases, $d<D$ and $d>D$. The effective distributions of impurity ions for these two cases are shown schematically in Fig. 2. The effective distribution of ions is zero at distances greater than D, because the ions are effectively neutralized by the conduction electrons of the semiconductor.

Solving Poisson's equation for these distributions of positive ions, subject again to the boundary conditions $V=e\varphi$ at $x=0$; $V=0$, $dV/dx=0$ at $x=D$, we obtain for the thickness of the potential barrier

$$\begin{aligned}&\text{(a)}\ D=(D_0^2+d^2/3)^{\frac{1}{2}}, && d<D,\\ &\text{(b)}\ D=(3D_0^2d/2)^{\frac{1}{3}}, && d>D.\end{aligned}\tag{6}$$

The depleted layer increases the thickness of the potential barrier. We note that $d=D$, when $d=(3/2)^{\frac{1}{2}}D_0$.

The increased thickness of the potential barrier decreases the amount that the top of the barrier is lowered by the image force. To the approximation that $(x_m/D)^2$ is negligible compared with (x_m/D), the height of the barrier is lowered by an amount

$$\begin{aligned}&\text{(a)}\ \Delta\varphi=\Delta\varphi_0[(1+d^2/3D_0^2)^{\frac{1}{2}}-d/2D_0]^{\frac{1}{2}}, && d<D,\\ &\text{(b)}\ \Delta\varphi=\Delta\varphi_0(2D_0/d)^{1/6}\cdot 3^{\frac{1}{2}}/2, && d>D,\end{aligned}$$

where $\Delta\varphi_0$ is given by Eq. (5). The reciprocal ratio of the current density through a contact with a depleted layer to the current density through a contact with no layer is

$$\exp\left[-e(\Delta\varphi_0-\Delta\varphi)/KT\right].$$

Figure 3 shows this ratio plotted as a function of the thickness of the depleted layer in units of D_0, where we have taken $N_0=5.0\cdot 10^{18}$ cm^{-3} (impurity content 0.01 percent), $\varphi_0=0.5$ v, $\varphi'=-1.0$ v, and $\epsilon=13$; this choice gives $\Delta\varphi_0=0.125$ v and $D_0=2.08\cdot 10^{-6}$ cm.

The effect of increasing the thickness of the depleted layer is to increase the resistance of the contact for negative applied voltages (back resistance).

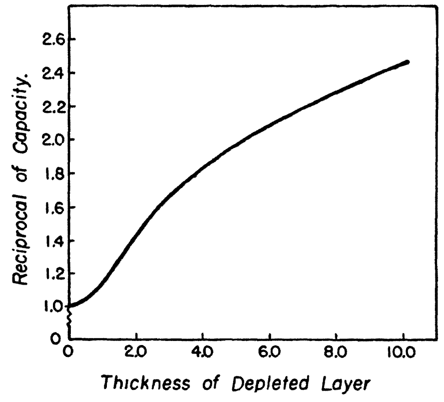

FIG. 4. The capacity in units of the capacity of the same contact with no depleted layer is shown as a function of the thickness of the depleted layer in units of D_0.

The depleted layer also changes the capacity of the contact. The capacity is determined by calculating the total charge in the barrier and then differentiating with respect to the applied voltage; it may be expressed by the usual formula

$$C=\epsilon A/4\pi D,$$

where A is the area of the contact and where now for D we must substitute the appropriate expression given by (6). Thus the effect of the depleted layer is to decrease the capacity of the contact; this is shown in Fig. 4.

Both these effects (the increase in back resistance and the decrease in capacity) contribute to improved rectifying performance at high frequencies. A model of a crystal rectifier is shown in Fig. 5. R is the resistance of the contact which varies rapidly with applied voltage, being very large for negative applied voltages and very small for positive voltages. C is the capacity of the contact which varies slowly with applied voltage. The quantity R_s is the resistance of the bulk of the semi-conductor. Bethe[4] has pointed out that in the forward direction R is very small, and the total impedance is R_s. In the back direction R is very large (in our case still larger), so that the total impedance is $R_s+(iC\omega)^{-1}$ where ω is the angular frequency of the applied voltage. Thus a decrease in capacity gives a larger ratio of back impedance to front impedance, thereby increasing the efficiency of rectification.

DISCUSSION

The neglect of the tunnel effect contribution to the current through the contact in the previous calculations does not affect the general conclusions. Courant[4] has shown that this effect may be regarded as producing a further decrease in the height of the potential barrier at the contact. The magnitude of the decrease can be of the same magnitude as the image force lowering of the potential barrier. The increased thickness of the potential barrier produced by a depleted layer will cause a decrease in the number of electrons tunneling through the barrier compared with the number tunneling through a normal barrier. Thus, the resistance of a contact with a depleted layer will be still larger than the resistance of a normal contact.

It is hard to say how changes in the surface properties of the semi-conductor affect the rectification characteristics. It is conceivable that polishing results in the production of a liquid-like layer near the surface. The impurities would probably diffuse faster in this layer than in the crystalline solid. Even if the layer were only 10^{-7} cm thick, it is believed that polishing distorts the lattice to a depth[5] as great as 10^{-4} cm, assuming no recrystallization upon heating. Hence the impurity diffusion rate may be a function of depth, increasing as the surface is approached. The thickness of the depleted layer would then depend on the nature of the polishing procedure. This effect has been observed in copper.[6] A polish layer also could change the work function of the surface by more strongly adsorbing gases.

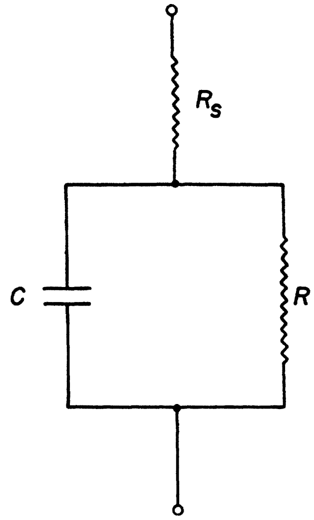

FIG. 5. The model of the crystal rectifier consists of a variable resistance R, a capacity C, and the resistance R_s of the bulk semi-conductor.

Considering these difficulties, all that we may reasonably conclude is that one of the functions of heating semi-conductors for use in contact rectifiers is to form a layer depleted of impurities near the surface, where contact is made. This

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[5] C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1943), p. 505.

[6] G. I. Finch, A. G. Quarrell, and J. S. Roebuck, Proc. Roy. Soc. **145**, 676 (1934).

layer increases the back resistance and decreases the capacity of the contact, improving the rectification efficiency. The quantitative results of these calculations have been used only to demonstrate the reasonableness of the assumptions and to illustrate the direction of the effects.

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On the Electronic Structure of the Nitrogen Molecule

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It is shown that the Lyman-Birge-Hopfield bands of nitrogen represent a forbidden $^1\Pi_g-{}^1\Sigma_g^+$ transition. A considerable difficulty in the interpretation of the electronic states of N_2 by electron configurations is thus removed. A revised electronic energy level diagram of N_2 is given.

The Lyman-Birge-Hopfield $(a-X)$ bands of nitrogen have been considered a $^1\Pi_u-{}^1\Sigma_g^+$ transition ever since it was established[1] that each band has a P, a Q, and an R branch. However, on this basis a serious difficulty arises in the interpretation of the upper state of the $a-X$ bands by means of electron configurations. The lower state (X) of these bands is the ground state of the N_2 molecule whose electron configuration is

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^4(\sigma_g2p)^2, \qquad (1)$$

where KK stands for the two K shells. The two lowest unoccupied orbitals are (π_g2p) and (σ_u2p), in this order, both of which are antibonding. Since, as shown by the N_2^+ spectrum, the orbitals (π_u2p) and (σ_g2p) have nearly the same energy, the lowest excited states of N_2 would be expected to belong to the following configurations:

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^4(\sigma_g2p)(\pi_g2p);\ {}^1\Pi_g,\ {}^3\Pi_g, \qquad (2)$$

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^3(\sigma_g2p)^2(\pi_g2p);\ {}^1\Sigma_u^+,\ {}^3\Sigma_u^+,\ {}^1\Delta_u,\ {}^3\Delta_u,\ {}^1\Sigma_u^-,\ {}^3\Sigma_u^-, \qquad (3)$$

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^4(\sigma_g2p)(\sigma_u2p);\ {}^1\Sigma_u^+,\ {}^3\Sigma_u^+, \qquad (4)$$

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^3(\sigma_g2p)^2(\sigma_u2p);\ {}^1\Pi_g,\ {}^3\Pi_g. \qquad (5)$$

They give rise to the states indicated at the right. Two of these, $^3\Sigma_u^+$ and $^3\Pi_g$, account readily for the two lowest observed triplet states $A\ {}^3\Sigma_u^+$ and $B\ {}^3\Pi_g$ of N_2 (compare the energy level diagram in Fig. 1) but a $^1\Pi_u$ state cannot be accounted for in this way. An electron configuration of higher energy would be required, which contradicts the fact that $a\ {}^1\Pi$ is a low, if not the lowest, excited singlet state.[1a]

This difficulty can now be resolved by a new interpretation of the Lyman-Birge-Hopfield bands made necessary by recent findings of new singlet band systems of nitrogen by Herman,[2] Gaydon,[3] and Worley.[4, 5]

As has been recognized by Herman, the upper state of the new singlet bands found by her is identical with the upper state of the ultraviolet emission bands $h-X$ found by Watson and Koontz[1] while their lower state is the upper

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[1] E. T. S. Appleyard, Phys. Rev. **41**, 254 (1932); W. W. Watson and P. G. Koontz, Phys. Rev. **46**, 32 (1934); J. W. T. Spinks, Can. J. Research **A20**, 1 (1942).

[1a] Compare R. S. Mulliken [Rev. Mod. Phys. **4**, 1 (1932)] and A. Recknagel [Zeits. f. Physik **87**, 375 (1934)] who have calculated the energies of the predicted low lying states. Both authors have emphasized the importance of the above mentioned difficulty.

[2] R. Herman, Comptes Rendus **217**, 141 (1943).

[3] A. G. Gaydon, Proc. Roy. Soc. **182**, 285 (1944).

[4] R. E. Worley, Phys. Rev. **64**, 207 (1943); **65**, 249 (1944).

[5] A. G. Gaydon and R. E. Worley, Nature **153**, 747 (1944).