Impurity Band in Semiconductors with Small Effective Mass*

Frank Stern and Robert M. Talley

United States Naval Ordnance Laboratory, White Oak, Maryland

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The energy levels of ordered impurities in semiconductors are formally equivalent to the energy levels of metallic hydrogen if a number of simplifying approximations are made. An approximate calculation of the energy states for the 1s band of metallic hydrogen is carried out for smaller lattice constants than those considered by Wigner and Huntington, or by Baltensperger. A simple transformation of the distance and energy scales converts the calculation for metallic hydrogen to one applying to impurities in a semiconductor, if values for the effective mass and the dielectric constant are given. Experimental results for the optical energy gap in InAs are reported as a function of impurity concentration. The effective mass required to fit the optical data for InSb published by other workers is about 0.03m, as compared to the value 0.013m found by cyclotron resonance measurements.

1. INTRODUCTION

A STRIKING phenomenon observed in inter-metallic semiconductors with small effective mass is the shift of the optical absorption edge to shorter wavelengths with increasing impurity concentration. This effect was first observed in indium antimonide by Tanenbaum and Briggs;[1] additional data for InSb have been reported by Hrostowski et al.[2] and by Breckenridge et al.[3] Data on the shift of the optical edge in indium arsenide are given in Sec. 3 of the present paper.

Burstein[4] proposed that the shift of the optical absorption edge is not related to a change in the band separation caused by the impurities, but rather to the fact that in impure samples the Fermi level lies well above the bottom of the conduction band. Thus, transitions to the filled levels near the bottom of the conduction band are improbable, and the absorption edge moves to higher energies.

One feature of Burstein's explanation which requires closer study is the distribution of energy levels in impure material which causes the Fermi level to rise as impurities are added. If all the impurity levels were below the bottom of the conduction band, the Fermi level could not rise sufficiently far to account quantitatively for the observed effect. In this paper, we will extend the ordinary hydrogenic model of impurities into the range of large impurity concentration, thus extending to smaller lattice constants the treatment of metallic hydrogen first carried out by Wigner and Huntington[5] and applied to semiconductors by Baltensperger.[6]

[1] M. Tanenbaum and H. B. Briggs, Phys. Rev. 91, 1561 (1953).
[2] Hrostowski, Wheatley, and Flood, Phys. Rev. 95, 1683 (1954).
[3] Breckenridge, Blunt, Hosler, Frederikse, Becker, and Oshinsky, Phys. Rev. 96, 571 (1954).
[4] E. Burstein, Phys. Rev. 93, 632 (1954).
[5] E. Wigner and H. B. Huntington, J. Chem. Phys. 3, 764 (1935).
[6] W. Baltensperger, Phil. Mag. 44, 1355 (1953); see also G. W. Castellan and F. Seitz, *Semiconducting Materials*, edited by H. K.

2. 1s BAND OF METALLIC HYDROGEN

The simple picture for explaining the ionization energy of dilute donor impurities in a semiconductor assumes that all but one of the electrons of the donor atom participates in the binding (or bonding) of the crystal, and that the remaining electron then sees the donor ion as a single positive charge. Thus, the donor ion and the extra electron look like a hydrogen atom; the energy required to remove the electron to a point far from the donor ion is given by the formula for the ionization energy of atomic hydrogen if we replace the free electron mass by m_c, the effective mass at the bottom of the conduction band, and take account of the fact that the dielectric constant κ of the semiconductor weakens the attraction between ion and electron. We then find for the ionization energy of a donor atom in a semiconductor:

$$E_D = \tfrac{1}{2}m_c(e^2/\kappa)^2\hbar^{-2}$$
$$= (m_c/m)\kappa^{-2}\,\mathrm{ry} = 13.60(m_c/m)\kappa^{-2}\,\mathrm{ev}, \quad (1)$$

where m is the free electron mass and m_c is the effective mass at the bottom of the conduction band.[7] This formula gives qualitative agreement with observed activation energies for impurities in semiconductors.

A direct extension of the picture which identifies isolated impurities with free hydrogen atoms is one which relates interacting impurities to solid hydrogen. The form of solid hydrogen which we consider is the metallic form first studied by Wigner and Huntington;[5] the restraining effect of the semiconductor lattice will keep the impurity atoms from clustering in the molecular phase, which is more stable than the metallic phase of hydrogen for large lattice constants. Our calculation is similar to the work of Baltensperger,[6] who applied the results to a discussion of impurity band conduction. Because of the very small effective mass of InAs and InSb, the overlap between donor electron orbits is much greater than in other known

Henisch (Academic Press, Inc., New York, 1951), p. 8; C. Erginsoy, Phys. Rev. 88, 893 (1952).
[7] A Rydberg (ry) is the ionization energy of atomic hydrogen for a nucleus of infinite mass. One ry equals 13.60 ev.

semiconductors; thus, the usual picture of impurity levels well separated from a conduction band will not hold here except for very low impurity concentrations. Our calculation extends the work of Baltensperger into this region of larger overlap between donor electrons.

Let us first list some of the approximations underlying this calculation:

(a) The electron sees the donor ion as a single positive charge; the interaction between electron and ion is $-e^2/\kappa r$ for all values of r.

(b) The interaction of the electron with the periodic potential of the semiconductor lattice is taken into account by assigning to the electron an effective mass m_c.

(c) This effective mass is isotropic.

(d) The impurity ions form an ordered array of high symmetry.

(e) The zero level of energy is identified with the energy of the bottom of the conduction band in pure material.

(f) No electrons are thermally excited from the highest filled band to the lowest empty band, and the impurities are uncompensated.

The Schrödinger equation for the motion of an electron in the neighborhood of a donor ion in a semiconductor is, on the basis of our assumptions:

$$(\hbar^2/2m_c)(d^2P_l/dr^2)$$
$$-[(\hbar^2/2m_c)l(l+1)r^{-2}-(e^2/\kappa r)-E]P_l=0, \quad (2)$$

where P_l is r times the radial part of the wave function belonging to angular momentum l. We put:

$$r=(\kappa m/m_c)x, \quad E=(m_c/m\kappa^2)\epsilon. \quad (3)$$

If we use Bohr radii as units of distance and Rydbergs as energy units we can write:

$$(d^2P_l/dx^2)+[(2/x)+\epsilon-l(l+1)x^{-2}]P_l(x)=0. \quad (4)$$

The energy ϵ_B for the $1s$ wave function with propagation vector $k=0$ is found from the usual Wigner-Seitz boundary condition that the radial derivative of the wave function vanish at the surface of the unit sphere surrounding each ion. Our boundary condition is:

$$\{d[x^{-1}P_0(x)]/dx\}x_s=0 \quad \text{for} \quad \epsilon=\epsilon_B, \quad (5)$$

where x_s is the radius of the unit sphere; see Eqs. (18) and (19) for expressions relating x_s to the impurity concentration.

The solution of Eq. (4) with the boundary condition given by Eq. (5) will give us ϵ_B, the energy of the bottom of the $1s$ band, as a function of x_s. To find the energy levels for electrons with propagation vectors different from zero, we use a method developed by Bardeen. We assume that in the lower part of the band the energy is given approximately by

$$\epsilon(k)=\epsilon_B+\alpha k^2. \quad (6)$$

In other words, the $1s$ band of metallic hydrogen is

assumed to be parabolic in shape, with an effective mass α^{-1}. Then the density of states (including a factor two for spin) is given by:

$$\rho(\epsilon)=\alpha^{-\frac{3}{2}}(\epsilon-\epsilon_B)^{\frac{1}{2}}/2\pi^2 \quad \text{Bohr radii}^{-3} \text{ ry}^{-1}. \quad (7)$$

There is one orbital state in the $1s$ band for each atom; each of these states may be occupied by two electrons with oppositely directed spin orientation. We find for the width of the filled portion of the $1s$ band:

$$w=(9\pi/4)^{\frac{2}{3}}\alpha x_s^{-2}=3.6832\alpha x_s^{-2}. \quad (8)$$

Bardeen's formula[8] for α is:

$$\alpha=\frac{x_s^3[P_0(x_s)]^2\{d[x^{-1}P_1(x)]/dx\}x_s}{3P_1(x_s)\int_0^{x_s}[P_0(x)]^2dx}. \quad (9)$$

This method of finding α is different from the one used by Baltensperger.[6] He found the energy of the top of the band from the boundary condition $P_l(x)=0$, and used the band width to find the effective mass. Bardeen's method is likely to be more accurate since it is valid for the region near the bottom of the band where the parabolic approximation holds best. A perturbation theory expression for α developed by Wigner and Seitz[9] shows that α will be less than or equal to one if all the perturbing levels lie above the level in question. Thus $\alpha\leq1$ for the $1s$ band, while Baltensperger finds values between 1 and 1.7 for $x_s<2$. On the other hand, Baltensperger's method gives a quick estimate for the width of a band, and can give such an estimate even for p bands and bands of higher angular momentum, where the parabolic approximation of Eq. (6) is no longer applicable.

The solution of the reduced Schrödinger equation, Eq. (4), which vanishes at the origin is given for negative values of ϵ by Whittaker and Watson[10] in the form:

$$P_l(x)\sim M_{n,\,l+\frac{1}{2}}(2x/n)\sim x^{l+1}e^{-x/n}$$

$$\times\left\{1+\sum_{i=1}^{\infty}\frac{(1+l-n)(2+l-n)\cdots(i+l-n)}{i!(2l+2)(2l+3)\cdots(2l+i+1)}(2x/n)^i\right\},$$

$$\hspace{11cm} (10)$$

where

$$n=(-\epsilon)^{-\frac{1}{2}}. \quad (11)$$

It is most convenient to choose a value for ϵ, say $\epsilon=\epsilon_B$, evaluate $P_0(x)$ by using this value, and then find the value of x for which the boundary condition of Eq. (5) is satisfied. Using this value of x_s, we then calculate α using Eq. (9). A separate power series is

[8] J. Bardeen, J. Chem. Phys. 6, 367 (1938).
[9] E. Wigner and F. Seitz, Phys. Rev. 46, 509 (1934); see F. Seitz, Modern Theory of Solids (McGraw-Hill Book Company, Inc., New York, 1940), pp. 352-3.
[10] E. T. Whittaker and G. N. Watson, Modern Analysis (Cambridge University Press, Cambridge, 1950), fourth edition, Sec. 16.1.

TABLE I. Calculated points for metallic hydrogen.[a]

x_s	ϵ_B(ry)	α	$\psi(x_s)/\psi(0)$
0.03003	−100	1.0000	0.985
0.06765	−44.44	1.0000	0.967
0.12049	−25	0.9999	0.941
0.27258	−11.11	0.9995	0.870
0.7726	−4	0.995$_4$	0.665
1.580	−2.041	0.963	0.410

[a] x_s is the radius of a sphere whose volume is the reciprocal of the concentration; it is given in units of the Bohr radius. ϵ_B is the energy of the bottom of the $1s$ band relative to the energy of an electron at rest far from the crystal. α^{-1} is the effective mass near the bottom of the $1s$ band. The last column gives the ratio of the value of the $1s$ wave function at the edge of the cell to its value at the center.

derived, using Eq. (10), for each of the factors needed to evaluate Eq. (9). For the values of ϵ_B which we consider, i.e., $\epsilon_B < -2$, the power series converge quite rapidly and an accuracy of 0.1% is attained if ten terms in the power series are used.

The power series solution of Eq. (4) given above is useful for finding the wave function for the bottom of the $1s$ band. We will list here a number of solutions valid for other ranges of ϵ. When $-1 < \epsilon < 0$, the expansion given by Kuhn[11] is convenient. For $\epsilon = 0$, Eq. (4) has the solution:

$$P_l(x) \sim (8x)^{\frac{1}{2}} J_{2l+1}((8x)^{\frac{1}{2}}),$$ (12)

where J_{2l+1} is a Bessel function of order $2l+1$. When $\epsilon > 0$, we can use tables of Coulomb wave functions[12] which cover the range $0 \leq x \leq 5$. Finally, if $\epsilon^{-1} \sim 0$, we have:

$$P_l(x) \sim (x\sqrt{\epsilon})^{\frac{1}{2}} J_{l+\frac{1}{2}}(x\sqrt{\epsilon}).$$ (13)

We list in Table I the results of our calculation for ϵ_B and for α as functions of x_s. We used empirical fits for ϵ_B and α as functions of x_s to draw up the more complete list of values given in Table II. The entries in this table are given as functions of x_s^{-3}, since this quantity is proportional to the density of metallic hydrogen—and to the concentration of impurities in a semiconductor. The proportionality factor is given in Eq. (19). In Table II, we list ϵ_B, α, and f, where f is the position of the Fermi level at absolute zero and is given by:

$$f = \epsilon_B + w.$$ (14)

The approximate empirical expressions we used in calculating the entries for Table II are:

$$x_s = -(3/\epsilon_B)[1 - (1/10\epsilon_B) + (1/15\epsilon_B^2) - (1/20\epsilon_B^3) + \cdots],$$ (15)

$$\alpha^{-1} = 1 + 0.006x_s^2 + 0.001x_s^3 + 0.002x_s^5.$$ (16)

These expressions are good to within about 0.1% for x_s in the range covered by our calculations, i.e., $0.03 < x_s < 1.58$.

[11] T. S. Kuhn, Quart. Appl. Math. 9, 1 (1951).
[12] Tables of Coulomb Wave Functions, U. S. National Bureau of Standards Applied Mathematics Series (U. S. Government Printing Office, Washington, D. C., 1952), Vol. 17.

We can qualitatively characterize our results for the $1s$ band of metallic hydrogen by saying that for the range of lattice constants covered in our calculation the effective mass is slightly larger than the free electron mass. For small lattice constants, the energy of the bottom of the band is given approximately by $-3/x_s$, and the width of the band by $3.68/x_s^2$. As the lattice constant decreases, the Fermi level rises much more rapidly than the bottom of the band falls. It is this fact which is responsible for the shift of the absorption edge to shorter wavelengths with increasing impurity concentration in semiconductors with small effective mass.

We have calculated the energy of the bottom of the $2s$ and $2p$ bands, with the boundary condition used by Baltensperger,[6] i.e., vanishing derivative at the edge of the cell. (Note that the bottom of the $2p$ band will not be at $k=0$, but at the edge of the Brillouin zone along the cubic axes.) Baltensperger found that in the range of lattice constants covered in his calculation the $2s$ band was always well above the top of the $1s$ band, while the bottom of the $2p$ band crossed the top of the $1s$ band for $x_s \sim 2$. We have verified that for smaller lattice constants the $2s$ band remains well separated from the $1s$ band; the bottom of the $2p$ band remains below the top of the $1s$ band for lattice constants smaller than the crossover value. However, the bottom of the $2p$ band never falls below the energy level at which the $1s$ band is half-filled. In other words, the density of states below the Fermi level at absolute zero is the density of states in the $1s$ band alone, with no other band contributing.

Application to Semiconductors

Our calculation to this point, as summarized in Table II, refers directly only to metallic hydrogen. We can easily convert the results so that they apply to impurities in semiconductors. The conversion factor for the energy scale, as in Eq. (3) is:

$$E_B/\epsilon_B = F/f = 13.60(m_c/m)\kappa^{-2}.$$ (17)

TABLE II. $1s$ band in metallic hydrogen.[a]

x_s^{-3}	f(ry)	α	ϵ_B(ry)
36 930	3984	1.0000	−100
15 940	2257	1.0000	−75.6
7630	1369	1.0000	−59.2
3230	761	1.0000	−44.4
1521	452.5	1.0000	−34.6
571.6	228.7	0.9999	−25
246.1	125.8	0.9998	−18.9
117.4	73.5	0.9997	−14.79
49.38	38.44	0.9995	−11.11
16.31	15.95	0.9990	−7.72
6.36	6.94	0.998$_0$	−5.67
2.168	2.14	0.995$_4$	−4.00
0.690	0.06	0.987	−2.78
0.253	−0.62	0.963	−2.041

[a] f is the Fermi level at absolute zero, i.e. the energy at which the $1s$ band is half filled. The other quantities are defined as in Table I. See Eqs. (17) and (19) to apply these numbers to impurities in semiconductors.

Here the units are electron volts for the quantities referring to the semiconductor (E_B, F) and Rydbergs for the quantities referring to metallic hydrogen (ϵ_B, f). E_B and F give the energy of the bottom of the $1s$ impurity band and the energy of the Fermi level at absolute zero, respectively, relative to the energy of the bottom of the conduction band in pure material.

To relate x_s to the impurity concentration we note that the radius r_s of the cell surrounding each impurity atom is given by:

$$4\pi r_s^3/3 = N_D^{-1}, \qquad (18)$$

where N_D is the donor concentration. If we use Eq. (3), we find

$$x_s^{-3} = 6.2064 \times 10^{-25} (\kappa m/m_c)^3 N_D, \qquad (19)$$

where x_s is given in Bohr radii and N_D in cm^{-3}. Using Eqs. (17) and (19), with suitable values for the dielectric constant and the effective mass, we can convert the entries of Table II into graphs showing the dependence of the Fermi level on impurity concentration.

3. COMPARISON WITH EXPERIMENT

The experiment to which the foregoing calculations most closely apply is the dependence of the optical energy gap on impurity concentration. The experiments give ΔE, the difference between the optical energy gap in an impure sample and the gap in a pure sample. From the theory one can determine the position of the Fermi level, given κ and m_c. The shift of the edge is related to the Fermi level by the equation,

$$\Delta E = [1 + (m_c/m_v)](F - \gamma kT), \qquad (20)$$

where m_v is the effective mass near the top of the valence band. Equation (20) is similar to an equation given by Burstein,[4] who used $\gamma = 4$. In general, γ will depend both on the value of F and on α_E, the value of absorption constant used to define the edge. For sufficiently low values of α_E, γ will increase continuously from zero as the Fermi level rises. Also, γ will decrease as α_E increases. This explains why the National Bureau of Standards[3] points $(\alpha_E \sim 10^2)$ in Fig. 2 lie below the Bell Telephone Laboratory[2] points $(\alpha_E \sim 10^3)$.

TABLE III. Experimental results for indium arsenide.[a]

Sample	$N_D - N_A$ (cm^{-3})	Optical gap (ev)	Doping agent
9	5×10^{16}	0.30$_7$	none
8	2×10^{17}	0.32$_5$	none
15	1×10^{18}	0.35	Se
25	3×10^{18}	0.36$_5$	Se
27a	3.3×10^{18}	0.40	Se
12	6×10^{18}	0.44$_6$	Se
28a	7.7×10^{18}	0.46	Se
24	1.8×10^{19}	0.47$_5$	Se
29	2.1×10^{19}	0.57	Se
11	-7×10^{17}	0.29$_5$	Cd

[a] $N_D - N_A$ was determined from the saturation value of the Hall constant at low temperatures. The optical gap given here is the room temperature value, for an absorption constant of 30 cm^{-1}.
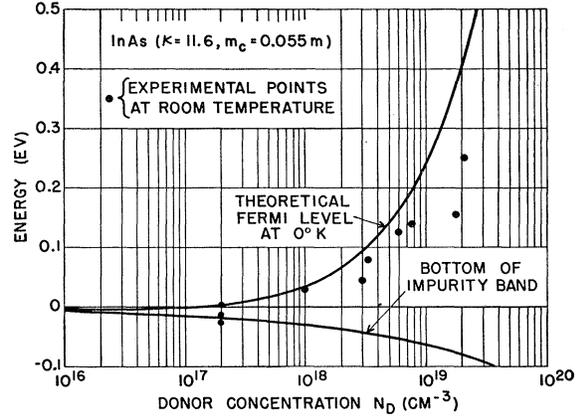

FIG. 1. The top curve shows the theoretical Fermi level at absolute zero for InAs as a function of donor impurity concentration; the bottom curve shows the energy of the bottom of the $1s$ impurity band. Both are given relative to the energy of the bottom of the conduction band in pure InAs. κ is the dielectric constant, m_c is the effective mass at the bottom of the conduction band, and m is the free electron mass. The points are our experimental results for the shift of the optical energy gap with impurity concentration.

In comparing ΔE and F for InAs and InSb, we have neglected the term (m_c/m_v) in Eq. (20), since no data for m_v are available. Thus our value for m_c will be too low by perhaps 10%, which is within the uncertainty in m_c. For a different method of analyzing the optical data, see the paper of Kaiser and Fan.[13]

Experimental Results for InAs

The results of our determination of the optical energy gap as a function of impurity concentration in indium arsenide are summarized in Table III. The samples were prepared in evacuated sealed Vycor containers, as described previously.[14] The optical samples were about 1 mm thick, with ground and polished surfaces. Large cleavage faces are not obtained with this material. The transmission samples are poly-crystalline, but in most cases they contain only a few crystals. Two transmission curves have been previously published.[14]

In order to make our determination of the optical absorption edge independent of sample thickness, we calculated the absorption constant as a function of energy, assuming 50% reflection loss. The absorption gap, or edge, was defined as the energy for which the absorption constant is 30 cm^{-1}. This was a convenient value because of the thickness of our samples, but has no other special significance. Lacking data for a very pure sample, we estimate that the absorption edge (at 30 cm^{-1}) for pure InAs at room temperature would be 0.32 ev.

Our results for the shift of the absorption edge with impurity concentration are given by the points of Fig. 1. For comparison we draw a curve for the Fermi

[13] W. Kaiser and H. Y. Fan, Phys. Rev. 98, 966 (1955).
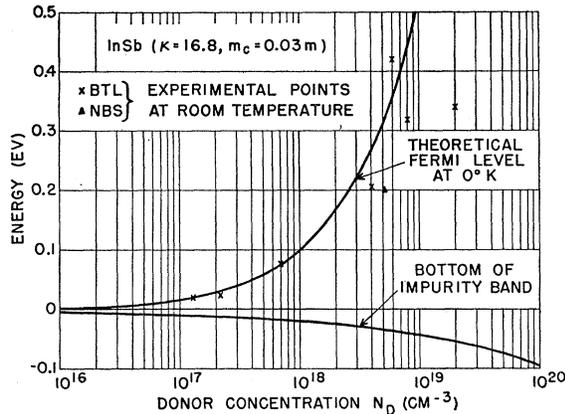[14] R. M. Talley and D. P. Enright, Phys. Rev. 95, 1092 (1954).

FIG. 2. Comparison of theory and experiment for InSb. The curves and symbols are defined as in Fig. 1. The points marked BTL and NBS come from references 2 and 3, respectively.

level at absolute zero based on Table II, using[15] 11.6 as the value of the dielectric constant. We have used $m_c=0.055m$ for the conduction band effective mass; a smaller value would raise the curve showing the position of the Fermi level, while a larger value would lower it. In view of the considerations mentioned above, the optical edge will lie somewhat below the Fermi level; the theoretical curve for $m_c=0.055m$, therefore, agrees approximately with the experimental points. We have also drawn the curve for E_B, the energy of the bottom of the $1s$ band; this curve is quite insensitive to the value of effective mass used.

An interesting effect is observed in the three samples in Fig. 1 drawn for a donor concentration of 2×10^{17}. These samples were prepared from arsenic of about the same purity, and are assumed to have about the same donor concentration. They correspond to samples 8, 9, and 11 of Table III, with sample 8, which is assumed to be nearly uncompensated, having the biggest optical gap. Sample 9, which we assume to be partially compensated although no impurities were purposely added, has a smaller gap. Sample 11 was purposely doped with Cd, and was p-type; it has the smallest gap of the three. We can explain this behavior by saying that the three samples represent different stages of the emptying of the $1s$ impurity band, with the electrons being drained off to acceptor atoms. This could account for the observations, but a theoretical study of the dependence of impurity band energy levels on degree of compensation is needed, as well as further experimental study of compensated samples.

InSb

In Fig. 2, we show a theoretical curve for the Fermi level at absolute zero and experimental points for the shift of the optical energy gap as a function of impurity concentration for InSb. The experimental points are taken from data of Hrostowski et al.[2] and Breckenridge

[15] F. Oswald and R. Schade, Z. Naturforsch. 9a, 611 (1954).

et al.,[3] marked BTL and NBS, respectively. The BTL points correspond to various absorption constants of the order of 10^3 cm^{-1}; the NBS points are in the 10^2 cm^{-1} range. The theoretical curve is calculated using a dielectric constant of[15] 16.8 and an effective mass for the conduction band of $0.03m$.

4. DISCUSSION

A quantitative check of the value of effective mass required to fit the experimental results for the shift of the optical absorption edge as a function of impurity concentration is possible for InSb, where the effective mass in the conduction band has been measured by cyclotron resonance. The value found by Dresselhaus et al.[16] is $(0.013\pm0.001)m$. This is to be compared with the value $0.03m$, which gives approximate agreement between the theoretical Fermi level and the optical points. One way to explain the discrepancy would be to assume that there is more than one minimum in the conduction band. There would then be a g-fold multiplicity in the impurity band, where g is the number of minima in the conduction band. This has been discussed in connection with impurity states in silicon and germanium by Kittel and Mitchell[17] and by Kohn and Luttinger.[18] The approximate effect on our results would be to decrease the effective mass required to explain the optical data by a factor $g^{\frac{2}{3}}$, since the optical effective mass is essentially a density-of-states mass. The cyclotron resonance mass would still refer only to a single minimum.

A second effect which acts to improve the agreement between the cyclotron resonance effective mass and the optical data as interpreted by our theory is the lowering of the energy levels which results from the fact that in the neighborhood of the donor ion the dielectric constant of the lattice is no longer effective in reducing the Coulomb attraction between ion and electron. This effect is, in part, responsible for the differences between the ionization energies of different impurities in germanium, and in silicon. A quantitative treatment would require a calculation similar to the one described by Kohn and Luttinger.[18] If this effect were appreciable one would expect the shift of the optical absorption edge to be measurably different for different impurities in the same column of the periodic table, e.g., for S and Se or Te in InAs.

The most serious objection to a calculation like ours is its neglect of randomness. The work of James and Ginzbarg[19] and of Aigrain and Jancovici[20] has shown that when impurities are randomly distributed, there will be a tail in the density of states at both edges of

[16] Dresselhaus, Kip, Kittel, and Wagoner, Phys. Rev. 98, 556 (1955).
[17] C. Kittel and A. H. Mitchell, Phys. Rev. 96, 1488 (1954).
[18] W. Kohn and J. M. Luttinger, Phys. Rev. 97, 883 (1955); 98, 915 (1955).
[19] H. M. James and A. S. Ginzbarg, J. Phys. Chem. 57, 840 (1953).
[20] P. Aigrain, Physica 20, 978 (1954).

the band. What influence this will have on our results remains to be determined.

5. ACKNOWLEDGMENTS

Detection of Vacancies Created by X-Rays in Sodium Chloride

H. W. ETZEL
United States Naval Research Laboratory, Washington, D. C.
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The creation of vacancies in sodium chloride by x-rays is detected using optical techniques. The F-band absorption produced by ultraviolet irradiation is measured and the band is then optically bleached. The crystal is then x-rayed and optically bleached. The crystal is again subjected to the same ultraviolet radiation as it received prior to x-raying, and the optical absorption of the F-band is remeasured. It is found that the sensitivity of a single crystal of NaCl to ultraviolet radiation is enhanced by a factor of 100 after it has been exposed to 40-kvp x-rays at 13 milliamperes for 30 minutes. Experiments are also performed to determine the stability at room temperature of the excess vacancies under visible and ultraviolet radiation.

INTRODUCTION

THE generally accepted model for the F-center in the alkali halides is that it consists of an electron trapped at a negative-ion vacancy in the lattice. This model of the F-center was tested experimentally by Estermann, Leivo, and Stern.[1] It had been determined[1] that the F-band which is observed in various alkali halides is greater than that which would be expected on the basis of the number of vacancies in the crystal before prolonged x-ray irradiation. If this model is valid then the dimensions of the crystal should change under or after such irradiation. This change was detected by Estermann, Leivo, and Stern who measured the decrease in density of single crystals of KCl after x-ray irradiation. More recently the increase in the dimensions of alkali halide crystals under irradiation has been measured by Sakaguchi and Suita[2] using an electrical technique. Their experiment had been carried out in air and it has since been repeated by Lin and Russell[3] in an inert atmosphere, thereby ruling out any surface effects due to atmospheric contamination. The work of Estermann, Leivo, and Stern did not show definitely that the decrease in density observed was not in part due to a change in the lattice parameter. Recently, Berry,[4] using an x-ray diffraction technique, has shown that the contribution to the increase in volume due to an increase in lattice parameter is negligible. The present work is not intended to substantiate the F-center model further, but to show that the creation of vacancies by x-rays can be detected by using simple optical measurements.

EXPERIMENTAL DETAILS

The crystals used in this experiment were grown by the Kyropoulos technique using sodium chloride which had been treated with dithizone to remove any heavy metal impurities. The $\frac{1}{4}$ in.$\times\frac{1}{4}$ in. plates were cleaved to 0.008 in.$\pm$0.001 in. in thickness to insure the usefulness of the data on a comparative basis even if the F-band produced by the x-rays was not uniform throughout the crystal.

The ultraviolet source was an Allen hydrogen-arc lamp with a lithium fluoride window. The x-ray machine used was operated at 40 kvp and 13 milliamperes and
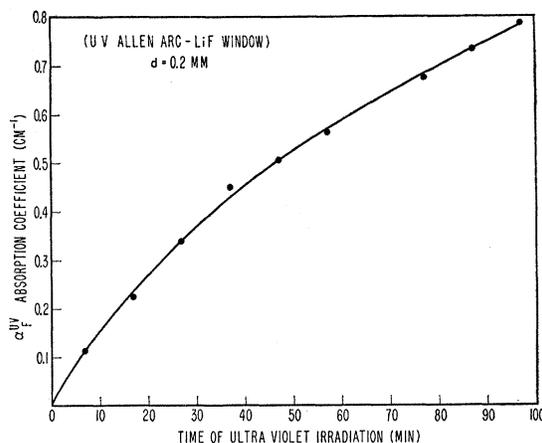
[1] Estermann, Leivo, and Stern, Phys. Rev. 75, 627 (1949).
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FIG. 1. The growth of the F-band in NaCl during ultraviolet irradiation at room temperature. Measured at $\lambda = 4650$ A.