ON IMPURITY BANDS IN SEMI-CONDUCTORS.

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Summary.

The interaction between the impurity centers in a semi-conductor widens their energy level into an impurity band. A theoretical investigation of the form of this band is carried out, assuming a random distribution of impurity centers in the semi-conductor. At the bottom of the band, the density of levels increases as the square root of the energy, as usual, but, due to the random distribution of centers, there is an infinite exponential tail toward high energies. This form of band is used, as an application, to explain experimental data on abnormal electrical conductivities at low temperatures, quasi-metallic degeneracy, and abnormal electronic specific heats at low temperatures.

I- Introduction.

When the impurity concentration of an impurity semi-conductor is sufficiently low, one gets fair to good results by treating each center as isolated, neglecting the interactions between the centers. It is well known that, for higher concentrations, this approximation is no longer valid. The most striking effect is an apparent lowering of the energy of activation of the impurities, the properties of the semi-conductor approaching those of a metal: this is quasi-metallic degeneracy. Even at lower impurity concentrations, it was possible to point out possible direct transitions of an electron from an impurity center to another, without going through the conduction band. Finally, the electronic specific heat of impurities may exhibit abnormally

From a theoretical point of view, one must expect that, in the same way as the interaction of the atoms in a pure solid widens their energy levels into bands, the interaction of the impurity centers will widen the impurity level into an impurity band. The degeneracy will occur when there is no longer any important gap between the impurity band and the conduction band. The electrons may move in the impurity band, giving rise to electrical conductivity, even at temperatures at which no electrons are in the conduction band. The electrons thermally excited inside the impurity band will give rise to an electronic specific heat.

A quantitative discussion of these effects requires a calculation of the form of the band, i.e. the density of levels inside the band, versus the energy. Calculations on this subject were previously carried out by several authors, always assuming a regular distribution of impurity centers at the nodes of a periodic lattice, for the sake of simplicity. The aim of this paper is to present a calculation on the assumption of a random distribution of the impurity centers in the semiconductor. This more physical assumption leads to an entirely different form of band, if compared to the previous ones, the impurity band in the random case having an infinite exponentially decreasing tail toward high energies. Thus, the disorder of the centers widens the band.

5. Esternmann and Friedberg, Contributions électroniques à la chaleur spécifique du semi-conducteur germanium, Compte rendu de la deuxième réunion de Chimie-Physique (2-7 Juin 1952, Paris).
We limit ourselves to the study of the band originating with the ground states of the isolated impurity centers, first for the sake of simplicity, and second because the excited levels are much nearer to the conduction band and they will soon merge with the conduction band.

Thus, we shall carry out the calculation of the form of the impurity band, and apply the results to interpretations of data on electrical conductivity, degeneracy, electronic specific heat.

II. Wave functions and energies.

All calculations will be made about n-type impurity centers, but all that follows is immediately transposable for p-type centers.

A well known approximation, originating with Mott, makes it possible to calculate the properties of isolated impurity centers in semi-conductors. In this approximation, which will be used throughout this paper, each center is taken to be equivalent to a fixed charge +e, with a bound electron, while the semi-conductor lattice is replaced by a continuous medium of dielectric constant \( \varepsilon \).

All calculations will refer to a cube of semi-conductor, of volume \( V \), at the face of which periodic boundary conditions will apply. This will be called the fundamental cube. In the end, \( V \) will be made to go to infinity.

Now the problem of finding the distribution of energy levels on the impurity band for a semi-conductor with many interacting centers can be formulated in Fock's approximation as that of finding the eigenvalues of an operator

\[
H_F = -\left( \frac{e^2}{2m} \right) \Delta + W + R + U, \quad (1)
\]

\[ \Delta \text{ is the laplacian operator.} \]

\[ W \text{ is the potential due to the impurity centers, located at points spaced at random with a density of } N \text{ per unit volume. Letting } \mathbf{x}_n \text{ be the coordinates of the } m^{th} \text{ center,} \]

\[ W = -\left(\frac{e^2}{\kappa}\right) \sum_n \left( \frac{1}{|\mathbf{x} - \mathbf{x}_n|} \right). \quad (2) \]

\[ U \text{ is the potential due to all the electrons bound to the centers.} \]

\[ R \text{ is the exchange energy.} \]

We will not take \( R \) into account explicitly. However, neglecting completely the exchange energy would yield erroneous results even in the case of infinitely spaced centers. It is well known that, in this case, the \( R \) terms cancel part of the \( U \) terms, leaving only that part of the interelectronic energy which is necessary to compensate the infinite space charge of the remote centers by an equal and opposite, uniformly distributed space charge. As usual in discussing narrow bands, we will assume this cancellation still takes place for finite densities of centers, even though this is known to be only a rough approximation. Indeed, although a Heitler-London type of approximation would yield better results as far as the total energy of the system is concerned, than the "extended wave functions", the latter, analogous to the Hund-Julliken-Bloch wave functions, are the only ones with which it is possible to calculate the distribution of energy levels. As a result, what follows can only be considered as a procedure to get the trend of the phenomenon, and as an order of magnitude calculation, though much more precise than previous works in which the randomly placed centers were replaced by a regular distribution, at the nodes of a cubic lattice for example.

The approximated Hamiltonian to be used is thus:

\[ H = -\left(\frac{\hbar^2}{2m}\right)\Delta - \left(\frac{e^2}{\kappa}\right) \sum_n \left( \frac{1}{|\mathbf{x} - \mathbf{x}_n|} \right) + U' \quad (3) \]

The eigenvalue \( \varepsilon_k \) of the equation obeyed by the \( k^{th} \) eigenfunction \( \psi_k \) of the energy,

\[ H \psi_k = \varepsilon_k \psi_k \]

is to be found by a variational method. This fairly simple, because it is known that for the range of impurity concentrations of interest, the eigenfunctions can be approximated very well by

$$\psi_k = \sum_n c_k n u_n (\mathbf{r} - \mathbf{r}_n) \tag{5}$$

where $u_n (\mathbf{r} - \mathbf{r}_n)$ is the wave function relating to the $n$th isolated center in the ground state:

$$u_n (\mathbf{r} - \mathbf{r}_n) = (i \gamma a_o \mathbf{k})^{-3/2} \exp \left(-|\mathbf{r} - \mathbf{r}_n|/a_o \mathbf{k}\right) \tag{6}$$

$a_o$ being the Bohr radius of the hydrogen atom in vacuum, $a = a_o \mathbf{k}$ the Bohr radius of the hydrogenoid impurity center.

The coefficients $c_k n$ depend on the state $k$ (increasing with energy) and on the impurity center $n$. In the case of the regular lattice, Bloch's theorem makes it possible to write down $c_k n$ directly. No such theorem exists in this case, and this is why the authors had to look for an approximate for a random distribution.

To begin with, it will be convenient to re-formulate equation (6) in the following manner:

$$\psi_k = \sum_n b_k (\mathbf{r}_n) c_0 n u_n \tag{7}$$

where $u_n$ stands for $u (\mathbf{r} - \mathbf{r}_n)$. This brings out the coefficients $c_0 n$ for the ground state, according to the equation (5). Furthermore

$$b_k (\mathbf{r}_n) = c_k n / c_0 n$$

$b_k (\mathbf{r}_n)$ has been written as a function of the space point $\mathbf{r}_n$, rather than its coefficient attached to the $n$th center. Of course, the function $b_k (\mathbf{r}_n)$ is only defined at the points $\mathbf{r}_n$, but, at least for small values of $k$ (for lying levels), $b_k (\mathbf{r}_n)$ will vary slowly with $\mathbf{r}_n$, and thus it will be possible to find a smooth function of $\mathbf{r}_n$ which will take the right value at each point $\mathbf{r}_n$.

Let it be remarked that all the $c_0 n$ have the same sign, since $\Psi_0 (\mathbf{r})$ has no nodes, while $\Psi_1, \Psi_2, \Psi_3, \ldots$ have $1, 2, 3, \ldots$ nodal surfaces. So $b_0 (\mathbf{r})$ has no nodes.
\(b_0(x) \leq 1\), while \(b_1(x), b_2(x), b_3(x), \ldots\) have 1, 2, 3, \ldots nodal surfaces. It is obvious that the quantity \(b_k(x)\) is to be regarded as perfectly defined, to an arbitrary multiplicative factor of unity modulus, even though we might find some mathematical complexities in writing down its expression. Also, as long as \(k\) is small, \(b_k(x)\) is a very slowly varying function, keeping a nearly constant value over regions in space which contain many centers. But, it is considered self-evident that all the physical quantities referring to such a portion of space which includes many centers are completely defined by the data of the density of the centers \(N\), and the fact that these are randomly spaced. More precisely, if one considers a space region of volume \(V\), each physical quantity referring to this region will be defined to a relative precision of order \((NV)^{-1/2}\), which is very small if \(V\) is large enough. In the case of the quantity \(b_k(x)\) (\(k\) small), this means that it can depend on the space point \(x\) only through the density of centers at that point. Since this density is constant, the operator for \(b_k(x)\) commutes with translations in space, so that one can write down directly:

\[
b_k(x) = \rho_k \exp(2\pi i k \cdot r_x)
\]

where \(k\) is an arbitrary vector, and \(\rho_k\) a normalisation factor. This is true to a relative precision of order \((k/\sqrt{N V})^{1/2}\).

If periodic boundary conditions are imposed at the edges of the fundamental cube, then \(k\) has to terminate at one of the nodes of a regular cubic lattice in \(k\) space; the vector \(k\) may then be used to classify levels in place of the scalar index \(k\).

Thus, for small \(k\), the set of functions

\[
\phi_k(x) = \rho_k \sum_n \exp(2\pi i k \cdot r_n) c_n u_k(x)
\]

are expected to coincide closely with the functions \(\psi_k(x)\). In the Appendix, the quantity

\[
E_k = \langle \phi_k | H | \phi_k \rangle
\]

will be evaluated, \(\phi_k\) being supposed normalised to the fundamental cube. In fact, \(E_k\) is not the true energy, as long as the \(\phi_k\)'s are not the true wave functions, for greater \(k\). However, the calculation of \(E_k\) is useful
not only as a first approximation of the energy for the small \( k \), but also as an intermediate step for the calculation of the energy \( E_k \) for all \( k \). Since \( E_k \) is expected to depend somewhat on the exact position of the centers, only the average of the right-hand member of (11) over all possible distributions of centers has been calculated.

It is worth remarking immediately that \( \psi_k(\mathbf{r}) \) does not fulfill exactly, even when \( k \) is small, one of the essential requirements of \( \psi_j(\mathbf{r}) \). Namely, it is not orthogonal to the \( \psi \) functions of lower order. For example \( \psi_j \) will not, in general, be orthogonal to \( \psi_0 \). Rather, if both are normalised over the fundamental cube their scalar product \( \langle \psi_j | \psi_0 \rangle \) will have a root mean square expectation value (over all possible distributions of centers) of \( N^{-1/2} \). That is,

\[
\left( \frac{\langle \psi_j | \psi_j \rangle^2}{N} \right) = (N/V)^{-1} \quad \text{if} \quad k \neq l \tag{12}
\]

(as can easily be shown by considering the \( \psi_k \) as unit vectors in Hilbert space, in which they will be oriented at random. The left-hand side of (12) is then the mean square value of a director cosine of an unit vector, in a \( NV \) dimensional space, which obviously is \( N/V \) since all the squared director cosines add up to unity).

Thus a better set of wave functions than the \( \psi_k \) would be:

1) \( \psi_0 = \psi_1 \)

2) The projection of \( \psi_1 \) on the subspace, in Hilbert space, which is orthogonal to \( \psi_0 \). This projection is the vector in this subspace which differs least from \( \psi_1 \), so that it should be very nearly equal to \( \psi_1 \).

3) The next wave function will be, in turn, the projection of \( \psi_2 \) on the subspace orthogonal to \( \psi_0 \) and \( \psi_1 \).

etc... etc...

The above procedure is exactly equivalent to Schmidt's orthogonalisation method, whereby one sets

\[
\psi_k = A_k \psi_k + \sum_{\rho=0}^{p-k-1} x_{k\rho} \psi_\rho . \tag{12}
\]
\( \lambda_k \) can be chosen a real number. The \( \lambda_k \)'s and \( \omega_{kp} \)'s can be calculated from orthogonality and normalisation conditions.

1) \[ \langle \psi_k | \psi_p \rangle = 0, \quad k > p \] (13)
yields \[ A_k \langle \psi_k | \psi_p \rangle + \alpha_{kp} = 0 \] (14)
that is \[ \alpha_{kp} = -A_k \beta_{kp} \] (15)
where \[ \beta_{kp} = \langle \psi_k | \psi_p \rangle \] (16)

2) \[ \langle \psi_k | \psi_k \rangle = 1 \] (17)
yields \[ A_k^2 + \sum_{p=0}^{p=k-1} |\alpha_{kp}|^2 + A_k \sum_{p=0}^{p=k-1} \alpha_{kp}^* \langle \psi_p \psi_k \rangle + A_k \sum_{p=0}^{p=k-1} \alpha_{kp} \langle \psi_p \psi_k \rangle = 1 \] (18)

Using equations (14), (15), (16), and the hermitian relation
\[ \langle \psi_p | \psi_k \rangle = \langle \psi_k | \psi_p \rangle^* = \beta_{kp}^* \] (19)
(18) yields
\[ A_k^2 = (1 - \sum_{p=0}^{p=k-1} |\beta_{kp}|^2)^{-1} \] (20)

(14), (16), and (20) yield \( \lambda_k \) and \( \omega_{kp} \) as functions of the \( \beta_{kp} \)'s, which are unknown at present. But a fortunate circumstance exists, which makes it possible to calculate the energy

\[ \varepsilon_k = \langle \psi_k | H | \psi_k \rangle \] (21)
without actually knowing the value of \( \beta_{kp} \), namely using (12) and (21):
\[ \varepsilon_k = A_k^2 \langle \psi_k | H | \psi_k \rangle + A_k \sum_{p=0}^{p=k-1} \alpha_{kp}^* \langle \psi_k | H | \psi_p \rangle + A_k \sum_{p=0}^{p=k-1} \alpha_{kp} \langle \psi_p | H | \psi_k \rangle + \sum_{p=0}^{p=k-1} |\beta_{kp}|^2 \varepsilon_p \] (22)
The first term in (22) is given by (12). The third term can be rewritten

\[ A_k \sum_{\ell \in \ell_0} C_{\ell} \langle \Psi_k | H | \Psi_p \rangle^* \tag{24} \]

(24) and the second term of (22) can be evaluated, using the relation

\[ H | \Psi_p \rangle = E_p | \Psi_p \rangle \tag{25} \]

since \( | \Psi_p \rangle \) is assumed to be a very good approximation to the actual \( p \)th wave function. Thus

\[ \langle \phi_k | H | \phi_p \rangle = E_p \langle \phi_k | \phi_p \rangle = E_p | \beta_{kp} \rangle \tag{26} \]

and, using (20), (24) and (26), (22) may be written

\[ E_k = \frac{E_p - \sum_{p=0}^{p=k} | \beta_{kp} |^2 E_p}{1 - \sum_{p=0}^{p=k} | \beta_{kp} |^2} \tag{27} \]

The relation only involves \( E_k \) and quantities like

\[ \sum_{p=0}^{p=k-1} | \beta_{kp} |^2 \tag{28} \]

The \( | \beta_{kp} |^2 \)'s are unknown for any one distribution of the centers, but their average over all distributions are easy to calculate. As far as \( E_k \) is concerned, it is the same for all distributions, but a set of measure zero. Thus, it is equal to its average over all distributions. Furthermore, the number of terms in each summation (28) can be made to go to infinity by taking a large enough fundamental cube at the limits of which periodic boundary conditions are imposed. Thus, (28) can be replaced by its average value, to which it will converge with certainty as the fundamental cube size is increased. In the limit,

\[ E_k = \frac{\langle E_k \rangle_{AV} - \int \langle | \beta_{kp} |^2 \rangle_{AV} \, d\tau_p}{1 - \int \langle | \beta_{kp} |^2 \rangle_{AV} \, d\tau_p} \tag{29} \]

where \( d\tau_p \) is the volume element of \( p \) space.

The same reasoning that was applied for obtaining (12) can be applied to the evaluation of \( | \beta_{kp} |^2 \), since, if \( \phi_k \) is placed at random in Hilbert space with respect to \( \psi_p \) ( \( p < k \)), the same will be true of \( \phi_k \) and \( \psi_p \).
where $\Psi$ is a linear combination of $\varphi_j (j \leq \nu)$, the coefficients of which do not involve $\varphi_j$. We must assume however, that the process of orthogonalisation does not introduce correlations between the $\Psi_K$. Thus

$$\left< |\beta_{kp} |^2 \right>_{Av} = \left< NV \right>^{-1} \quad \text{(30)}$$

Since there is no preferred orientation, the constant energy surfaces in $\kappa$ space are spheres centered on the origin.

Thus the number of terms in (28) is \((4\pi/3)N |K| \) \^3

$$\sum_{p=0}^{2N+k-1} \left< |\beta_{kp} |^2 \right>_{Av} = \left(4\pi/3N\right) |K| \^3 \quad \text{(31)}$$

Putting

$$u = \left(4\pi/3N\right) |K| \^3 \quad \text{(32)}$$

one gets from (29):

$$\varepsilon_k = \frac{\left< E_k \right>_{Av} - \int u(k) d\varepsilon_p du(k)}{1 - u(k)} \quad \text{(33)}$$

Multiplying through by \(1-u\) and differentiating (33) with respect to \(u\),

$$\left(1-u\right) \frac{d\varepsilon_k}{du} - \varepsilon_k = \frac{d\left< E_k \right>_{Av}}{du} - \varepsilon_k \quad \text{(34)}$$

Thus, putting \(\left< E_0 \right>_{Av} = \varepsilon_0\),

$$\varepsilon_k = \varepsilon_0 + \int_0^u \frac{d\left< E_p \right>_{Av}}{1-u^p} \quad \text{(35)}$$

which is the fundamental result of this theoretical work.

III EXPLICIT CALCULATIONS OF THE
FORM OF THE IMPURITY BAND

It is shown in the Appendix (with some approximations) that, for the range of $\kappa$ values of interest,

$$0 < u < 1 \quad \text{or} \quad 0 < |K| < \left(3\pi/4N\right)^{1/3}$$
one has

\[ \langle E_k \rangle_{AV} = \varepsilon_o + A |k|^2 + \cdots, \tag{36} \]

where all further terms are negligibly small. \( A \) is proportionnal to \( N \). Thus

\[ \varepsilon_k = \varepsilon_o + \int_0^{\ell} \frac{d \langle E \rangle_{AV}}{d \ell} \frac{1}{1 - u(\ell)} d \ell \]

\[ = \varepsilon_o + 2A \int_0^{|k|} \frac{1}{1 - (4\pi/3N)|k|^3} d |k| \tag{37} \]

For simplicity one sets

\[ t^3 = \left( \frac{4\pi}{3N} \right) |k|^3 \tag{38} \]

Thus

\[ \varepsilon_k = \varepsilon_o + B \int_0^t \frac{3s ds}{1 - s^3} \]

\[ = \varepsilon_o + B \left( \log \frac{(1 - t^3)^{1/2}}{(1 - t)^{3/2}} - \sqrt{3} t \tan^{-1} \frac{2t + 1}{\sqrt{3}} + \frac{n\sqrt{3}}{6} \right) \tag{39} \]

The density of levels per unit volume per unit energy is given by

\[ n(\varepsilon) = 2N \frac{du}{d\varepsilon} = 2N (d\varepsilon/dt) t \frac{du}{dt} \]

Using (38) and (39)

\[ n(\varepsilon) = \left( \frac{2N}{B} \right) t (1 - t^3) \tag{40} \]

The fact that each energy level may be occupied by two electrons of opposite spins has been taken into account.

(39) and (40) together define parametrically the \( n(\varepsilon) \) versus \( \varepsilon \) curve II (Fig. 1). Thus, this curve gives the form of the impurity band. Of course, the exponential tail must meet the conduction band at the higher energies with the conduction band. The value

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11. Our results give a high energies the same exponential decreasing of the level density as in a previous work on a linear disordered lattice, the given energies of which were calculated in an entirely different way. We are indebted to Professor James for the private communication of this result.
of A given in the appendix (A13) yields

\[ B \approx 6,100 \varepsilon_i (N_a^3)^{5/3} \]  
(41)

and

\[ \varepsilon_s = -\varepsilon_i \left(1 + 64 \pi N_a^3 \right) \]  
(42)

\( \varepsilon_i \) being the activation energy of an isolated impurity center.

Of special interest for what follows is the density of levels \( n(\varepsilon_s) \) at the Fermi level \( \varepsilon_F \) at the absolute zero, i.e., at the half full band point, \( \nu = 1/2 \)

\[ n(\varepsilon_F) = \left(2N_\nu B \right) 2^{-4/3} = 0.733(N/B) \]  
(43)

We consider the band only as half filled because of the open degeneracy. Of course, it is well known that the spin degeneracy cannot be observed for infinitely remote centers: there is room on each impurity center only for one electron, but in this latter case our approximation of "extended wave functions" is clearly bad. As the concentration of impurities reaches values which make it possible to observe the impurity band, it becomes possible to use "extended wave functions", for which we may admit "spin degeneracy."

IV APPLICATIONS AND EXPERIMENTAL VERIFICATION

1. Electrical conductivity in the impurity band.

The impurity band is only half filled (the presence of some additional impurities of p type may even diminish the filling), or, at any rate, is not completely filled, and consequently there exists an electrical mobility of the electrons in this band, even at 0°K. This effect was experimentally observed by Hung and Gliessmann 2,3. But we could not get, at this time, a quantitative calculation of these mobilities.

However, we could roughly estimate the percentage of impurities which gives rise to quasi-metallic degeneracy of the semi-conductor. We assume that degeneracy occurs when, let us say, 10% of the impurity band levels have fallen into the conduction band, so that there is no longer an important gap between impurity and ordinary conduction levels. Thus, the conduction band occurs for \( \nu \approx 0.9 \). This means that
\[ \varepsilon(u=0.9) = 0. \] According to (39) and to Fig. 1,

\[ \varepsilon(u=0.9) - \varepsilon_0 \approx 3B \]

Thus

\[ \varepsilon_s \left(1 + \epsilon_{\pi} N \alpha^2 \right) \sim 3 \times 6.14 \times 10^{-3} \varepsilon_s \left( N \alpha^2 \right)^{5/3} \]

One finds degeneracy for impurity concentration greater than \( N \alpha \sim (1/600) \). Experimental results of Pearson and Bardeen yield a value of the order of \( N \alpha \sim (1/500) \), in very good agreement with our rather rough evaluation.

2. Electronic specific heat in the impurity band

One often observes electronic specific heats at very low temperatures, much too great to be explained by the few electrons which could be in the conduction band at these temperatures. But, if the impurity band has a certain width, we can explain this specific heat by a thermal excitation of the electrons inside the impurity band. We shall analyse two experimental data on this subject.

a) Very impure germanium

Measurements of specific heat were made on germanium by Estermann at 24°, but the specimens used were much too impure to allow our approximation to be used. However, we are able to give a qualitative justification of the experimental results.

We shall see in the Appendix that the development (36) is no longer valid for high impurity concentrations. It must be replaced by a more complicated form which yields a curve \( \langle E \rangle \) versus \( |k| \) of the form represented on Fig. 2. The state \( k=0 \) is no longer the ground state, but the latter corresponds to a value \( |k| \neq 0 \). We must build new functions \( \psi_k \) from the \( \phi_{k} \)'s, mixing up for \( \langle E \rangle \) and for \( f \langle |k| \rangle \) and for \( f \langle |k| \rangle \).

This procedure would give a band of the form drawn in Fig. 3. The first peak contains about 30% of the levels.

At 0°K, the Fermi-level, which is at 50% of the levels, is in the second peak. The excitation of the electrons inside this peak yields an electronic specific heat about 0°K. At higher temperatures, the Fermi level slides down into the first peak, and one gets a peak of specific heat.
These specific heat anomalies were experimentally observed about 0° K and 75° K.

b) Rather pure silicon

A more reliable calculation may be made on a specimen of siliconium experimentally studied by Keesom and Pearman, this latter specimen being pure enough to be treated semi-quantitatively by our method. The specimen had \(10^{18}\) impurity centers per cm\(^3\). The electronic specific heat between 1°K and 4°K was experimentally found 3.1 \(10^{-5}\) T joules/degree-mole, value 100 times too great to be explained by the free carriers.

We attribute this specific heat to electrons in the impurity band. The density of levels at the Fermi level is given by (43). Thus the specific heat per cm\(^3\) is

\[
\gamma = \left( \frac{2}{\pi} \right) \left( \frac{T}{3} \right) \frac{n(\epsilon)}{\epsilon^2} = \left( \frac{2}{\pi} \right) \left( \frac{T}{3} \right) \frac{n(\epsilon)}{\epsilon^2 (N_a)}
\]

where \(\epsilon\) is the constant of Boltzmann. With the experimental data above, we find the theoretical value 15.10 \(-^3\) T joules/degree-mole, only differing by a factor 3 from the experimental result. The agreement must be considered as very good, according to the great uncertainty (20%) of the latter intervening to the 5th power.

V. APPENDIX

1. Calculation of the functions \(\psi_k(x)\)

We are only able to choose for \(\psi(x)\) a mean value on all possible distributions of centers, by setting all the coefficients \(C_n\) equal. This is, of course, only an approximation. However, such a \(\psi(x)\) is not a bad ground function, if the impurity density is not too high, as is shown by the fact that the energy \(E_0\) found \(\psi_0(x) = \psi_0^k(x)\) will be smaller than the energy \(E_k\) found for all the other functions \(\psi_k(x)\) that we shall calculate hereafter.

Thus, we set

\[
\psi_0(x) = \sum_n u(x - x_n)
\]

and consequently

\[
\psi_k(x) = \rho_k \sum_n \exp(2\pi i k x_n) u(x - x_n) \tag{A1}
\]

We shall now calculate the coefficients \( c_{oo} \) and \( \varphi_k \) to get \( \varphi_k (x) \) normalised in the fundamental cube. We shall choose \( c_{oo} \) and the \( \varphi_k \)'s as real. We have of course \( p_0 = 1 \). Anyways

\[
\langle \varphi_k (x) | \varphi_k (x) \rangle = p_k^2 c_{oo} \sum_n \sum_m \exp \left[ 2\pi i k (x - x_m) \right] \langle u_n | u_m \rangle = 1 \quad (A2)
\]

Thus,

\[
\langle u_n | u_m \rangle = (4\pi)^{-2} \int \exp \left( -\frac{1}{2} \frac{|x - x_n|}{a} \right) \exp \left( -\frac{1}{2} \frac{|x - x_m|}{a} \right) dx
\]

\[
= \frac{1}{(1 + (|x_m - x_n|/a)^2 + (1/3)(|x_m - x_n|/a)^4)} \exp \left( -\frac{1}{2} \frac{|x_m - x_n|}{a} \right) \quad (A3)
\]

(In (A3) and all similar integrals on decreasing exponentials, we may take the volume integral over all space instead of over the fundamental cube). Using (A2) and (A3), replacing the summation in (A2) by an integral, and carrying apart the term \( m=n \), we get

\[
p_k c_{oo} = \left\{ N \left[ 1 + 64 \pi N^2 \left( 1 + \frac{1}{2} (|k|^2)^{-4} \right) \right] \right\}^{-1/2} \quad (A4)
\]

(A1) and (A4) determine the functions \( \varphi_k (x) \).

2. Calculation of \( \langle E_k \rangle_n \).

According to (11) and (A1),

\[
E_k = p_k^2 c_{oo} \sum_n \sum_m \exp \left[ 2\pi i k (x_n - x_m) \right] \langle u_n | H | u_m \rangle \quad (A5)
\]

\( \langle u_n | H | u_m \rangle \) only depends on the difference \( |x_n - x_m| \); replacing the summation in (A5) by an integral, and carrying apart the term \( m=n \), we get

\[
\langle E_k \rangle_n = N p_k^2 c_{oo} \left[ \langle u_o | H | u_o \rangle + \int \exp \left( 2\pi i k (x_m - x_n) \right) \langle u_o | H | u_m \rangle dx_m \right] \quad (A6)
\]

Using (3) we find

\[
\langle u_o | H | u_m \rangle = \langle u_o | \left( \frac{p_0^2}{2m} \right) \Delta - \frac{e^2}{\kappa |x - x_m|} \right] u_m \rangle
\]

\[
+ (\delta_{om} - 1) \langle u_o \bigg| \frac{e^2}{\kappa |x_n|} \bigg| u_m \rangle + \langle u_o \bigg| \sum_{n \neq 0} \frac{e^2}{\kappa |x_n - x_m|} + U' \bigg| u_m \rangle \quad (A7)
\]

where \( \delta_{om} \) is the Kronecker symbol.
The first term of (A7) contains the Hamiltonian of an isolated center. Thus,
\[ \left[ -\frac{\hbar^2}{2m} \Delta - \frac{e^2}{\kappa |\mathbf{r} - \mathbf{r}_m|} \right] \psi_m = -\varepsilon_m \psi_m , \]
setting \( \varepsilon_m = -\frac{e^2}{2\kappa a} \). Thus, the first term of (A7) becomes:
\[ -\varepsilon_m \langle u_o | u_m \rangle \] (A8)

The second term of (A7) may be thoroughly calculated:
\[ \langle u_o | \frac{e^2}{\kappa |\mathbf{r} - \mathbf{r}_m|} | u_m \rangle = (\pi a^3)^{-1} \int \exp \left( -\frac{1}{\kappa} |\mathbf{r} - \mathbf{r}_m| \right) \exp \left( -\frac{1}{\kappa} |\mathbf{r} - \mathbf{r}_m| / a \right) d\tau \]
\[ = 2 \varepsilon_m \left( 1 + \frac{1}{\kappa} |\mathbf{r}_m| / a \right) \exp \left( -\frac{1}{\kappa} |\mathbf{r}_m| / a \right) \] (A9)

The third term of (A8) is zero, cancelling exactly the long range potential \( e^2 / (\kappa |\mathbf{r} - \mathbf{r}_m|) \) where \( n \neq 0 \) and \( n \neq m \).

Using (A3), (A8) and (A9) we get
\[ \langle u_o | H | u_m \rangle = -\varepsilon_m \left( 3 - 2 \delta_{om} + \frac{1}{3} |\mathbf{r}_m| / a + \frac{1}{3} |\mathbf{r}_m|^2 / 3a \right) \exp \left( -\frac{1}{\kappa} |\mathbf{r}_m| / a \right) \] (A10)

Carrying (A10) in (A6), performing the integral, and using (A4), we get
\[ \langle E_{H} \rangle_{av} = -\varepsilon_m \left[ 1 + 128 \pi N a^3 \left( 1 + 2 \pi \frac{1}{a} |k|^2 \right) \left( 1 + 4 \pi \frac{1}{a} |k|^2 \right) \right]^{\frac{1}{2}} \]
\[ \times \left[ 1 + 64 \pi N a^3 \left( 1 + 4 \pi \frac{1}{a} |k|^2 \right) \right]^{-1} \] (A11)

We limit ourselves to the case where \( Na^3 \gg 1 \). We may then approximate (A11) by
\[ \langle E_{H} \rangle_{av} = -\varepsilon_m \left[ 1 + 64 \pi N a^3 \left( 1 + 4 \pi \frac{1}{a} |k|^2 \right) \right]^{-\frac{1}{2}} \]

Taking into account of the fact that the maximum value of \( k \) is \( (3N/4\pi)^{\frac{1}{3}} \), we note that \( a^2 \kappa^2 \) is of the order of \( Na^3 \)^{\frac{2}{3}} \) and we consider that \( 4 \pi a^2 |k|^2 \ll 1 \). Thus, we may write
\[ \langle E_k \rangle_v = -\varepsilon_i \left[ 1 + 6' \pi N a^2 (1 - 2 r^2 \varepsilon_i^2) \right] \quad (A.12) \]

(A12) has effectively the form (36) with

\[ \varepsilon_0 = -\varepsilon_i \left( 1 + 6' \pi N a^4 \right) \quad A = 768 \pi^4 \varepsilon_i N a^5 \quad (A13) \]

(33) and (34) together with (A13) yield

\[ B = 128 \times 6^{2/3} \pi^{5/3} (N a^3)^{5/3} \approx 6,100 (N a^3)^{5/3} \]

as indicated in (41).