Electronic Specific Heats of Dilute Solid Solutions

H. Jones*

Department of Physics, Oklahoma State University, Stillwater, Oklahoma

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The partition function of an electron gas in the presence of scattering centers, such as exist in a dilute solution, is obtained by using the method first introduced by Matsubara. It is shown that the electronic specific heat at low temperatures, in such a case, contains a term arising from virtual electron scattering. If the Fermi limit in the pure metal lies just beyond a sharp peak in the density-of-states curve, this term increases the specific heat. Comparison with the observations by Rayne on the dilute solid solutions of zinc and germanium in copper indicate that the effect discussed is probably the explanation of the observed initial increase in the low-temperature specific heat at small concentrations.

1. INTRODUCTION

THE electronic properties of disordered alloys are difficult to analyze because there are no simple quantum numbers in terms of which the single-electron wave functions can be described. Equilibrium properties, however, are fully determined when the partition function is known, and this can be obtained as the trace of an operator with respect to any complete orthonormal set of total wave functions. For dilute solid solutions the Slater determinants of the Bloch functions of the pure metal form an obvious choice for such a set. In this representation, the wave function of the ground state of the alloy is not a single Slater determinant, as in the Hartree-Fock approximation for a pure metal, but an infinite series of such determinants. The first member of the series corresponds to the ground state of the pure metal, and the other members to various excited states. In wave-vector k space the alloy has not therefore a sharply defined Fermi surface in its ground state but one which is broadened by the effect of virtual electron scattering. There must, of course, always be a precisely defined Fermi limit in terms of the true one-electron states of the alloy but these are not representable in k space. When the solute concentration is a few percent, the broadening of the Fermi surface of the ground state will be large compared to the thermal broadening in the pure metal at low temperatures.

If the density of states in the pure metal has special features lying just below the Fermi limit, these will not affect the low-temperature electronic specific heat of the pure metal, but they will affect that of the dilute alloy if the ground-state broadening, just referred to, is large enough to include these features. This appears to be exactly the situation which exists in copper and its solid solutions. In pure copper it is believed that the Fermi limit lies just beyond the peak of the density-of-states curve. Hence, in dilute solid solutions, the influence of this peak may be felt on the equilibrium properties and, in particular, on the low-temperature electronic specific heat. It will be shown that in such a case it leads to a slight increase in the specific heat even when the electron concentration remains constant. This increase is closely related to the residual electrical resistance and is determined by the matrix elements of the scattering potential.

2. PERTURBATION EXPANSION OF THE PARTITION FUNCTION

The partition function is obtained as a particularly simple example of the method introduced by Matsubara[1] and developed by Thouless.[2] Let H denote the complete Hamiltonian, N the number of electrons in a volume v, $\beta = 1/kT$, and $\alpha = \mu\beta$. If μ denotes the partial potential α is the activity. The grand partition function Z is given by the trace of ψ, where

$$\psi = e^{\alpha N - \beta H}, \tag{1}$$

and

$$Z = \mathrm{Tr}\psi = \sum_n \langle n | e^{\alpha N - \beta H} | n \rangle. \tag{2}$$

The wave functions $|n\rangle$, which are used for the evaluation of the trace are Slater determinants of Bloch functions including the spin factor and relating to the pure metal.

To simplify the notation let

$$H - \mu N = H_0 + V(\mathbf{r}), \tag{3}$$

where H_0 is the Hamiltonian of the pure metal minus μN, and $V(\mathbf{r})$ is the potential energy of an electron due to the randomly distributed impurity atoms. $V(\mathbf{r})$ is therefore the difference between the potential in the solid solution and that in the pure metal.

The interaction representation is defined by

$$\psi_I = e^{H_0\beta}\psi, \tag{4}$$

and if we write

$$H_1(u) = e^{H_0 u}V(\mathbf{r})e^{-H_0 u}, \tag{5}$$

or in terms of the creation and annihilation operators, $\tilde{C}_k(u)$, $C_k(u)$,

$$H_1(u) = \sum_{k,l}\langle k | V | l \rangle \tilde{C}_k(u)C_l(u), \tag{6}$$

then

$$\partial\psi_I/\partial\beta = -H_1(\beta)\psi_I, \tag{7}$$

[1] T. Matsubara, Progr. Theoret. Phys. (Kyoto) 14, 351 (1955).
[2] D. J. Thouless, Phys. Rev. 107, 1162 (1957); *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

* On leave of absence from Imperial College, London, England.

which may be solved by iteration as follows:

$$\psi_I = 1 - \int_0^\beta du_1 H_1(u_1) + \int_0^\beta du_1 \int_0^{u_1} du_2 H_1(u_1) H_1(u_2)$$

$$- \int_0^\beta du_1 \int_0^{u_2} du_2 \int_0^{u_2} du_3 H_1(u_1) H_1(u_2) H_1(u_3) + \text{etc.},$$

$$\tag{8}$$

where

$$\beta > u_1 > u_2 > u_3 \cdots .$$

The above solution not only satisfies (7) but also the boundary condition, $\psi_I = 1$, when $\beta = 0$.

From (4) and (2) it follows that, with ψ_I as given by (8),

$$\frac{Z}{Z_0} = \frac{\sum_n \langle n | e^{-H_0\beta} \psi_I | n \rangle}{\sum_n \langle n | e^{-H_0\beta} | n \rangle}, \tag{9}$$

where Z_0 is the partition function relating to the pure metal. The terms of the sum (8) can be evaluated in a manner exactly analogous to that used for the determination of the energy of the ground state in the many-body problem.

Writing

$$H_0 = \sum_k (\epsilon_k - \mu) C_k^+ C_k,$$

it follows from relations similar to (5), and applicable to any operator, that

$$\begin{aligned} C_k(u) &= C_k e^{-(\epsilon_k - \mu) u}, \\ \tilde{C}_k(u) &= C_k^+ e^{(\epsilon_k - \mu) u}. \end{aligned} \tag{10}$$

An essential feature of Matsubara's method (cf. Ref. 2) lies in the following definition of the normal product which ensures that its trace in (9) vanishes:

$$N[C_k^+ C_k] = (1 - f_k) C_k^+ C_k - f_k C_k C_k^+. \tag{11}$$

For example, the contribution to Z/Z_0 of any normal product occurring in (8) is given by

$$(1/Z_0) \sum \langle n | e^{-H_0\beta} N[C_k^+ C_k] | n \rangle$$

$$= (1/Z_0) \sum \langle n | e^{-H_0\beta} \{ (1 - f_k) C_k^+ C_k - f_k C_k C_k^+ \} | n \rangle, \tag{12}$$

which is zero, if

$$(1/Z_0) \sum \langle n | e^{-H_0\beta} C_k^+ C_k | n \rangle = f_k,$$

and

$$(1/Z_0) \sum \langle n | e^{-H_0\beta} C_k C_k^+ | n \rangle = 1 - f_k. \tag{13}$$

The number f_k, defined by (13), is just the occupation number for the state k, i.e.,

$$f_k = \{ 1 + e^{\beta(\epsilon_k - \mu)} \}^{-1}. \tag{14}$$

The contractions then introduce factors f_k or $1 - f_k$ as indicated below. Using the linked-graph theorem, the result to second order can be given in the following form.

$$\ln(Z/Z_0) = \ln(\sum \text{all graphs}) = \sum (\text{linked graphs})$$

$$= -\beta \sum_k V_{kk} f_k + \beta \sum_{k,l} |\langle k | V | l \rangle|^2$$

$$\times [f_k(1 - f_l)/(\epsilon_l - \epsilon_k)] + \text{etc.} \tag{15}$$
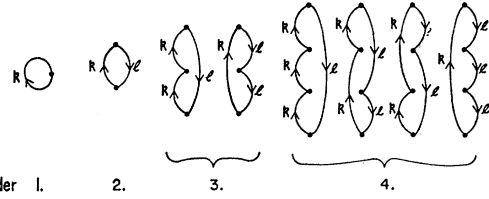

Order 1. 2. 3. 4.

FIG. 1. Diagrams for the perturbation series of the partition function involving only two wave vectors.

The second-order term in (15) diverges logarithmically near the Fermi limit, and it is therefore necessary to make a partial summation over all orders of (8) in which only two wave vectors, k and l, are involved. If we represent the vertices by points with the values of u increasing upwards, the graphs of the terms to be summed are as shown in Fig. 1.

When the operators are u ordered as in (8), it follows from (13) that an upward line corresponds to $C_k C_k^+$ and gives a factor $1 - f_k$ and a downward line to $C_l^+ C_l$ which gives a factor f_l. The energy denominators for all these particular graphs are powers of $\epsilon_l - \epsilon_k$ and the matrix elements at the vertices either V_{kl}, V_{lk}, V_{kk}, or V_{ll}. [Henceforth we use this abreviated notation rather than that of (15).] It is now easy to see that the above sequence of graphs gives the following contribution to $\ln(Z/Z_0)$.

$$-\beta \sum_k V_{kk} f_k + \beta \sum_{k,l} \frac{|V_{kl}|^2 f_k(1 - f_l)}{\epsilon_l - \epsilon_k}$$

$$\times \left\{ 1 - \left[\frac{V_{kk} f_k + V_{ll}(1 - f_l)}{\epsilon_l - \epsilon_k} \right] + [\quad]^2 - [\quad]^3 + \cdots \right\}$$

$$= -\beta \sum_k V_{kk} f_k + \beta \sum_{k,l} \frac{|V_{kl}|^2 f_k(1 - f_l)}{\epsilon_l - \epsilon_k + \{ V_{kk} f_k + V_{ll}(1 - f_l) \}}, \tag{16}$$

which remains finite at the Fermi limit. It may be noted that the lower limits of the integrals in (8) (i.e., the zeros) give no contribution because factors like $e^{(\epsilon_k - \epsilon_l)\beta}$, etc., combine with f_k and f_l in such a way as to lead to exact cancellation. There are, of course, many other terms in the expansion of ψ_I, but all will involve higher powers of the nondiagonal matrix elements V_{kl}, and will therefore be neglected in the present approximate considerations.

The range of ϵ_k and ϵ_l (now written for convenience as ϵ and η, respectively) over which the summand of the second sum of (16) differs appreciably from zero is shown in Fig. 2.

Since all quantities in (16) apart from V_{kl} depend only on the energies of the states k and l, the first step in the summation is to average $|V_{kl}|^2$ over all relative directions θ of the vectors k and l, and to assume that the result depends only on ϵ and η. This assumption is correct if the matrix elements are calculated with
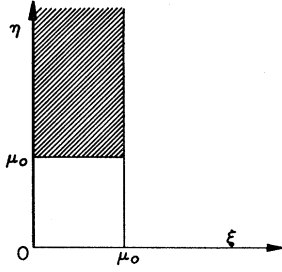
Fig. 2. Range of integration for the second-order correction to the partition function.

respect to free-electron wave functions. It will be assumed, therefore, that

$$\frac{1}{2}\int_0^\pi |V_{kl}|^2 \sin\theta d\theta = K(\epsilon,\eta) = K(\eta,\epsilon). \quad (17)$$

To simplify the calculations the following assumptions and approximations are also made: (i) that in the demoninator of (16) f_k and f_l may be replaced by their values at absolute zero, (ii) V_{kk} is independent of k and equal to a constant V. Hence, if $N(\epsilon)$ denotes the density of states, the sum (16) may be written as an integral as follows:

$$\int\int \frac{N(\epsilon)N(\eta)K(\epsilon,\eta)}{\eta-\epsilon+2V}f(\epsilon)[1-f(\eta)]d\epsilon d\eta$$

$$=\int_0^{\mu_0} d\epsilon \int_{\mu_0}^\infty d\eta \frac{N(\epsilon)N(\eta)K(\epsilon,\eta)}{\eta-\epsilon+2V}$$

$$+\int_{\mu_0}^\infty d\eta \int_0^\infty d\epsilon \frac{N(\epsilon)N(\eta)K(\epsilon,\eta)}{\eta-\epsilon+2V}\phi(\epsilon)$$

$$-\int_0^{\mu_0} d\epsilon \int_0^\infty d\eta \frac{N(\epsilon)N(\eta)K(\epsilon,\eta)}{\eta-\epsilon+2V}\phi(\eta), \quad (18)$$

where

$$\phi(\epsilon)=\begin{cases} \{1+e^{\beta(\epsilon-\mu)}\}^{-1}, & \epsilon>\mu_0 \\ -\{1+e^{-\beta(\epsilon-\mu)}\}^{-1}, & \epsilon<\mu_0, \end{cases} \quad (19)$$

and the second and third integrals are taken along the boundary of the shaded region of Fig. 2. The term arising from the immediate neighborhood of (μ_0,μ_0) has been omitted as negligible compared with the others. In the last integral the symbols ϵ and η may be interchanged; and therefore, if

$$g(\epsilon)=\int_0^{\mu_0} \frac{N(\eta)K(\epsilon,\eta)}{\epsilon-\eta+2V}d\eta+\int_{\mu_0}^\infty \frac{N(\eta)K(\epsilon,\eta)}{\epsilon-\eta-2V}d\eta, \quad (20)$$

the whole of the second sum of (16) may be written

$$-\beta E_2-\beta\int_0^\infty N(\epsilon)g(\epsilon)\phi(\epsilon)d\epsilon, \quad (21)$$

where E_2 is the second-order energy due to the perturba-

tion and is independent of temperature. If E_1 denotes the energy correction in the first order, then

$$\ln Z = \ln Z_0-\beta(E_1+E_2)-\beta\int_0^\infty N(\epsilon)g(\epsilon)\phi(\epsilon)d\epsilon. \quad (22)$$

The last term of (22) can be written

$$-\beta\int_0^\infty N(\epsilon)g(\epsilon)\phi(\epsilon)d\epsilon$$

$$=\beta\int_0^\mu \frac{N(\epsilon)g(\epsilon)d\epsilon}{1+e^{-\beta(\epsilon-\mu)}}-\beta\int_\mu^\infty \frac{N(\epsilon)g(\epsilon)d\epsilon}{1+e^{\beta(\epsilon-\mu)}}. \quad (23)$$

Let $x=\beta(\epsilon-\mu)$, then

$$\beta\int_0^\infty N(\epsilon)g(\epsilon)\phi(\epsilon)d\epsilon=\int_0^\infty \frac{dx}{1+e^x}\Big[N\Big(\mu+\frac{x}{\beta}\Big)g\Big(\mu+\frac{x}{\beta}\Big)$$

$$-N\Big(\mu-\frac{x}{\beta}\Big)g\Big(\mu-\frac{x}{\beta}\Big)\Big], \quad (24)$$

in which the usual approximation has been made of replacing the lower limit $-\beta\mu$ by $-\infty$ in one integral.

The partition function for the pure metal is well known and may be expressed

$$\ln Z_0=\beta\{\mu n(\mu)-E(\mu)\}+\frac{1}{\beta}\int_0^\infty \ln(1+e^{-x})$$

$$\times\Big[N\Big(\mu+\frac{x}{\beta}\Big)+N\Big(\mu-\frac{x}{\beta}\Big)\Big]dx, \quad (25)$$

where

$$n(\mu)=\int_0^\mu N(\epsilon)d\epsilon, \quad \text{and} \quad E(\mu)=\int_0^\mu N(\epsilon)\epsilon d\epsilon, \quad (26)$$

are both functions of temperature through their dependence on μ. On substituting (24) and (25) into (22) it follows that for low temperatures,

$$\ln Z=\alpha n(\mu)-\beta[E(\mu)+E_1+E_2]$$

$$+\frac{\pi^2}{6\beta}\Big\{N(\mu)-\Big[\frac{d}{d\epsilon}N(\epsilon)g(\epsilon)\Big]_\mu\Big\}. \quad (27)$$

It may be noted that $N(\mu)$ is the density of states including the factor 2 which arises as a consequence of each state being doubly occupied by electrons of opposite spins.

The properties of an assembly consisting of a fixed number of electrons are obtained by using the relation,

$$(\partial \ln Z/\partial\alpha)_\beta=\bar n, \quad (28)$$

to determine μ when $\bar n$ is constant. The energy is then given by

$$-(\partial \ln Z/\partial\beta)_\alpha=\bar E. \quad (29)$$

The specific heat of the system C_v (it has been assumed throughout that the volume is constant) is given by

$$C_v = -\frac{\beta^2}{k}\left(\frac{\partial \bar{E}}{\partial \beta}\right)_{\hbar} = \gamma T. \tag{30}$$

Although γ may readily be evaluated, it is sufficient for the present purpose to note that

$$\gamma = \gamma_0\left\{1 - \frac{1}{N(\mu)}\left[\frac{d}{d\epsilon}N(\epsilon)g(\epsilon)\right]_\mu\right\}, \tag{31}$$

where γ_0 refers to the pure metal.

3. EVALUATION OF MATRIX ELEMENTS

It will be assumed that the potential $V(\mathbf{r})$ arises from ν screened unit positive charges randomly distributed through the volume v which contains N electrons and the same number of lattice sites. The solute concentration is therefore given by $c = \nu/N$. Hence

$$V(\mathbf{r}) = -e^2 \sum_i \exp\{-\alpha|\mathbf{r}-\mathbf{R}_i|\}/|\mathbf{r}-\mathbf{R}_i|, \tag{32}$$

where $\mathbf{R}_i$ denotes the position of the solute atoms, and α is the reciprocal of the screening length.

If in order to estimate the magnitude of V_{kl} we use free-electron wave functions defined by

$$\psi_{\mathbf{k}} = \frac{1}{\sqrt{v}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{33}$$

the following well-known result is readily obtained.

$$V_{kl} = -\frac{4\pi e^2}{v}\frac{1}{|\mathbf{k}-\mathbf{l}|^2+\alpha^2}\sum_i e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_i}. \tag{34}$$

As a result of the random nature of the distribution of solute atoms,

$$|V_{kl}|^2 = \left(\frac{4\pi e^2}{v}\right)^2\frac{\nu}{(|\mathbf{k}-\mathbf{l}|^2+\alpha^2)^2}. \tag{35}$$

The average of this expression over all directions of $\mathbf{l}$ relative to $\mathbf{k}$ depends only on k^2 and l^2 and therefore is in accordance with assumption (17).

In order to simulate the effect of the peak in the density of states of copper just below the Fermi limit and at the same time enable the integrals to be evaluated without too much difficulty we adopt the following model.

$$N(\eta) = N_0 + Np\delta(\eta-\epsilon_1), \quad \epsilon_1 < \mu_0, \tag{36}$$

where N_0 is a constant. Here p is a fraction of order 10^{-1}. It is further assumed that $K(\mu,\eta) \to 0$ for large values of η as would be the case with (35). Substituting (36) into (20) gives

$$g(\epsilon) = \int_0^{\mu_0}\frac{N_0K(\epsilon,\eta)}{\epsilon-\eta+2V}d\eta + \int_{\mu_0}^\infty\frac{N_0K(\epsilon,\eta)}{\epsilon-\eta-2V}d\eta$$
$$+ \frac{NpK(\epsilon,\epsilon_1)}{\epsilon-\epsilon_1+2V}. \tag{37}$$

When $\epsilon \simeq \mu_0$ it will be seen that the first two integrals are of opposite sign and tend to cancel each other, and their contribution to $g'(\mu)$ will not be considered further. The third term represents the effect of the peak in $N(\epsilon)$ and its variation with ϵ results mainly from the denominator. Hence a reasonable approximation is

$$g'(\mu) = -NpK(\mu,\epsilon_1)/(\mu-\epsilon_1+2V)^2, \text{ and } N'(\mu)=0. \tag{38}$$

Thus

$$\gamma = \gamma_0\left\{1 + \frac{K(\mu,\epsilon_1)Np}{(\mu-\epsilon_1+2V)^2}\right\}. \tag{39}$$

To estimate the additional term in γ we use (35) and (17) and find

$$\frac{K(\mu,\mu)Np}{\mu^2} = \frac{(4\pi e^2)^2}{\Omega^2}\left(\frac{\hbar}{2m}\right)^2\frac{p}{\mu^2(w^2+4w\mu)}\left(\frac{\nu}{N}\right), \tag{40}$$

where Ω is the atomic volume which may be written $\Omega = \frac{4}{3}\pi r_s^3$, and $w = (\hbar^2/2m)\alpha^2$. Hence using the free-electron approximation to determine μ_0 and writing for simplicity, $w = \mu$,

$$\frac{K(\mu,\mu)Np}{\mu^2} = \frac{p}{5}\left(\frac{256}{4\pi^4}\right)^{1/3}\frac{(e^2/r_s)^2}{\mu^2}c, \tag{41}$$

which gives finally, neglecting $2V$ compared with $\mu-\epsilon_1$,

$$\gamma = \gamma_0\left\{1 + \frac{0.13p}{(1-\epsilon_1/\mu)^2}\frac{(e^2/r_s)^2}{\mu^2}c\right\}. \tag{42}$$

Suppose the ratio of the two energies is unity, that ϵ_1 lies $\frac{1}{10}$ of μ_0 below the Fermi limit, and that $p \simeq 10^{-1}$, i.e., one-tenth of the electrons lie under the effective part of the peak. These rough estimates which seem reasonable enough then give $\gamma = \gamma_0(1+c)$, where c is the concentration expressed as a fraction.

4. RELATION TO RESIDUAL RESISTIVITY

Imagine a hole to exist in the Fermi distribution at absolute zero in the neighborhood of ϵ_1. Elastic scattering due to impurities will result in a finite lifetime τ of any particular state k of this hole. This lifetime will be approximately equal to the relaxation time for impurity resistivity. Each level therefore will have a width of order $\hbar/\tau$. The delta function of (36) is therefore effectively replaced by a function of width $\hbar/\tau$, and if $\mu-\epsilon$, is small part of the tail will overlap the Fermi limit and give a contribution to the linear electronic specific heat. This argument can be made semiquantitative as follows. The linewidth at ϵ may be written

$$\frac{\hbar/\tau}{\pi\{(\epsilon-\eta)^2+(\hbar/\tau)^2\}}, \tag{43}$$

and hence if the density of states in the pure metal is

$N_0(\eta)$ in the solid solution it is

$$N(\epsilon)=\int_0^\infty \frac{N_0(\eta)\hbar/\tau}{\pi\{(\epsilon-\eta)^2+(\hbar/\tau)^2\}}d\eta. \tag{44}$$

For the model in which the density-of-states $N_0(\eta)$ is as given by (36) it follows that

$$N(\mu)=N_0+\frac{(\hbar/\tau)Np}{\pi\{(\mu-\epsilon_1)^2+(\hbar/\tau)^2\}}. \tag{45}$$

Hence when $\hbar/\tau\ll\mu-\epsilon_1$, which implies that the correction is small and corresponds to a second-order effect,

$$N(\mu)=N_0+\frac{Np(\hbar/\tau)}{\pi\mu^2(1-\epsilon_1/\mu)^2} \tag{46}$$

and

$$\gamma=\gamma_0\left\{1+\frac{p(\hbar/\tau)}{\pi\mu(1-\epsilon_1/\mu)^2}\right\}, \tag{47}$$

where the approximation $N_0\mu\simeq N$ has been used. The relaxation time is given by the well-known formula,

$$\frac{\hbar}{\tau}=\frac{mkv}{2\pi\hbar^2}\int_0^\pi |V_{kl}|^2(1-\cos\theta)\sin\theta d\theta, \tag{48}$$

where $v=\Omega N$ is the volume which contains ν impurities and with respect to which the electronic wave functions are normalized. If we define half of the integral as $K'(\mu,\mu)$, then a simple calculation shows that

$$\hbar/\tau=3\pi NK'/2\mu, \tag{49}$$

and

$$\gamma=\gamma_0\{1+[3K'Np/2(\mu-\epsilon_1)^2]\}, \tag{50}$$

which is similar to (39) apart from the numerical factor $3/2$, the neglect of $2V$ in the denominator and the different definitions of K and K'. Both derivations show that the addition to the electronic specific heat is proportional to the residual resistivity.

5. COMPARISON WITH EXPERIMENTAL RESULTS

The electronic specific heats of dilute solid solutions of Zn and Ge in Cu have been measured by Rayne[3] and by Veal and Rayne.[4] It is found that initially for small concentrations of the solute γ increases in both cases. Since the Fermi limit lies beyond the peak of the density of states a simple theory would suggest a decrease of γ due to the increase of the electron concentration. This decrease is easily calculated and is indicated by Veal and Rayne. If we attribute the difference between the observed increase and the expected decrease to virtual electron scattering and express the results for the initial slopes by giving the values of b in $\gamma/\gamma_0=1+bc$, where c is the fractional concentration, then for Zn we find $b=1.4$ and for Ge, $b=5.8$. Equation (42) appears therefore to give values of b of roughly the right magnitude. Moreover, as might be expected, Ge with the greater scattering power has the higher value.

There are other examples where the observed electronic specific heat is larger than would be anticipated from a simple band model. For example, Keesom and Kurrelmeyer[5] find for a copper-nickel alloy containing approximately 20 at.% Ni, a γ value which is 1.56 times as great as the γ value for pure Cu. Conventional theory visualizes the d band as just filled in $Cu_{60}Ni_{40}$. At 80% Cu the Fermi limit will be beyond the point where $N(\epsilon)$ rises steeply due to the d levels. A similar situation to that discussed in the preceding theory therefore exists and may perhaps be explained in the same way. The measurements of Hoare and his collaborators[6,7] on Ag-Pd and Au-Pt point in the same direction.

[3] J. A. Rayne, Phys. Rev. 108, 22 (1957).
[4] B. W. Veal and J. A. Rayne, Phys. Rev. 130, 2156 (1963).
[5] W. K. Keesom and B. Kurrelmeyer, Physica 7, 1003 (1940).
[6] F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) A240, 42 (1957).
[7] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) A257, 250 (1960).