Perturbation of the Electronic Specific Heat Due to Magnetic Impurities*

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The s–d exchange model used successfully by Kondo to explain the resistance minimum in dilute magnetic alloys is employed to calculate the change in the electronic specific heat. For an unmagnetized system, the first anomalous effects, which depend on the sharpness of the Fermi surface, occur in third-order perturbation theory. The perturbation expansion for the thermodynamic potential is used to calculate the equilibrium properties of the system. The temperature and impurity-concentration dependence of the anomalous term in the specific heat is found to be $cT \ln T$. The magnitude of the coefficient of this term is too small to render it observable in metals.

INTRODUCTION

IN a recent paper, Kondo[1] has used the interactions of electrons with magnetic impurities to explain the resistance minimum found in a number of dilute magnetic alloys. Singular Fermi-surface effects first appear in third-order perturbation for the scattering probability of the electrons. Kondo chose the s–d exchange model introduced and used by Zener,[2] Kasuya,[3] and Yosida,[4] and showed that the scattering probability was logarithmically singular as the temperature approached zero, for electron energies close to the Fermi energy, in accord with the experimental data.

There are several transport phenomena which will be affected by the logarithmic singularity in the electron lifetime. However, there is another class of phenomena which will be more sensitive to the shift in the electron density of states at the Fermi surface. Two such examples are the electronic specific heat and tunneling. In this paper we calculate the shift of the specific heat to third order in the s–d exchange integral. No singular effects due to the sharpness of the Fermi surface arise in second order. In Sec. 1 we calculate the shift of the thermodynamic potential, assuming the temperature to be high enough so that the system will not be magnetically ordered, and the spin states to be degenerate.

The second-order correction to the specific heat is calculated in Sec. 2. Only a small correction to the density of states occurs in this order. An approximation to the correct noninteracting distribution function is made in the Appendix. In Sec. 4, using this simplified distribution function, we calculate the third-order correction to the specific heat. The new term which appears varies as $cT \ln T$, where c is the impurity concentration and T the temperature. The coefficient of this term is such as to make it unobservable in metals.

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).
[2] C. Zener, Phys. Rev. **81**, 440 (1951).
[3] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956).
[4] K. Yosida, Phys. Rev. **106**, 893 (1957); **107**, 396 (1957).

1. Shift of the Thermodynamic Potential

In this section we calculate the thermodynamic potential to third order in the coupling constant. The Hamiltonian we choose is identical with that given by Kondo.[1] The Hamiltonian for noninteracting electrons is

$$H_0 = \sum_{k,\sigma} \epsilon(k) c_{k,\sigma}^* c_{k,\sigma}, \tag{1.1}$$

where the noninteracting electron spectrum is taken to be ($\hbar = 1$)

$$\epsilon(k) = k^2/2m.$$

The various magnetic states of the impurities are taken to be degenerate, when the crystal field splitting etc. is neglected. The interaction term is

$$H' = -\frac{J}{N} \sum_{n,k,k'} e^{i(k-k')\cdot R_n} \big[(c_{k'\uparrow}^* c_{k\uparrow} - c_{k'\downarrow}^* c_{k\downarrow}) S_{nz} + c_{k'\uparrow}^* c_{k\downarrow} S_{n-} + c_{k'\downarrow}^* c_{k\uparrow} S_{n+} \big]. \tag{1.2}$$

The system has N atoms in it. R_n is the position vector and S_n the spin operator of the nth impurity atom. S_{n+} and S_{n-} are the usual spin-raising and lowering operators.

$$S_{n\pm} \equiv S_{nx} \pm i S_{ny}.$$

As Kondo points out, J, the value of the direct exchange interaction between the localized and conduction electrons, can be either positive or negative.

Bloch and DeDominicis[5] have shown that the shift of the thermodynamic potential may be obtained from the linked diagram expansion for the ground-state energy. It is obtained by associating the appropriate unperturbed distribution functions with the particle and hole lines of the diagrams. The ground-state energy shift to third order is given by

$$\Delta U = \langle 0|H'|0 \rangle + \sum_i \frac{\langle 0|H'|i \rangle \langle i|H'|0 \rangle}{E_0 - E_i}$$

$$+ \sum_{i,j} \frac{\langle 0|H'|i \rangle \langle i|H'|j \rangle \langle j|H'|0 \rangle}{(E_0 - E_i)(E_0 - E_j)}, \tag{1.3}$$

[5] C. Bloch and C. DeDominicis, Nucl. Phys. **7**, 459 (1958).

where $|0\rangle$ represents the ground state, a filled Fermi sea, and E_0 is its energy in the presence of the Hamiltonian H_0. The kets $|i\rangle$ and $|j\rangle$ are excited-state configurations with E_i and E_j the energies of those particular configurations. Since H' has no diagonal matrix elements in the unmagnetized state, there is no contribution to the first-order shift in energy.

The diagrams corresponding to the four terms of the second-order shift in energy are shown in Fig. 1. Figure 1(d) shows the time-reversed diagram of Fig. 1(c). By applying the designation time reversal to a diagram, we mean that the direction of the arrows on the lines are reversed, interchanging particles and holes. In writing the single-particle distribution functions in the expressions for the shift of the thermodynamic potential, we will not distinguish between the spin up $f_\uparrow$ and the spin down $f_\downarrow$ distribution functions. In the unmagnetized state, both distribution functions are identical. The second-order shift in the thermodynamic potential is

$$\Delta\Omega^{(2)} = -\frac{J^2}{N^2}\sum_{n,k,k'}\frac{(1-f')f}{\epsilon'-\epsilon}$$
$$\times[2M_n^2+(S+M_n)(S-M_n+1)$$
$$+(S-M_n)(S+M_n+1)]. \quad (1.4)$$

The primes on the distribution functions and single-particle energies indicate to which momentum they refer: $f\equiv f(k)$, $f'\equiv f(k')$, etc., M_n is the z component of the spin of the nth atom, and S is its maximum value.

The first term in the bracket is the contribution of Figs. 1(a) and (b), the second term is that of 1(c) and the last comes from 1(d).

There are 16 diagrams which contribute to the third-order shift in energy. Eight of these are shown in Fig. 2. The other eight are the time-reversed diagrams of those shown in Fig. 2. We have not included some of those terms which vanish in the unmagnetized state, i.e., terms which involve impurities at different sites. The contribution of each of the diagrams can be written down quite directly. The only point which perhaps should be mentioned is the sign of the product of matrix elements which arises when contractions are made in the matrix elements. Because of the contractions made, all the terms shown in Fig. 2 have the same positive sign. We illustrate by extracting the combination of electron operators which leads to Fig. 2(a).

$$\langle 0|c_{k\uparrow}^*c_{k''\uparrow}c_{k''\uparrow}^*c_{k'\uparrow}c_{k'\uparrow}^*c_{k\uparrow}|0\rangle=f_\uparrow(1-f_\uparrow')(1-f_{\uparrow''}).$$

In contrast, all the time-reversed diagrams have matrix elements which lead to a negative sign when the electron contractions are made. As an example, let us consider the time-reversed diagram to Fig. 2(a). The electron operators enter the matrix element as

$$\langle 0|c_{k''\uparrow}^*c_{k\uparrow}c_{k'\uparrow}^*c_{k''\uparrow}c_{k\uparrow}^*c_{k'\uparrow}|0\rangle=-(1-f_\uparrow)f_\uparrow'f_\uparrow''.$$

Since one of the contractions must be made by bringing an electron operator past another single electron operator with which it anticommutes, the result is always negative. The third-order shift in thermodynamic potential is

$$\Delta\Omega^{(3)} = -\left(\frac{J}{N}\right)^3\sum\left(\frac{f(1-f')(1-f'')}{(\epsilon'-\epsilon)(\epsilon''-\epsilon)}+\frac{(1-f)f'f''}{(\epsilon-\epsilon')(\epsilon-\epsilon'')}\right)$$
$$\times[M_n^3-(M_n+1)(S-M_n)(S+M_n+1)+M_n(S-M_n)(S+M_n+1)+M_n(S-M_n)(S+M_n+1)$$
$$+(M_n-1)(S+M_n)(S-M_n+1)-M_n^3-M_n(S+M_n)(S-M_n+1)-M_n(S+M_n)(S-M_n+1)]. \quad (1.5)$$

The first of the two terms in the first bracket is the contribution of the diagrams shown in Fig. 2, the second is of the contribution of the time-reversed diagrams. The diagrams of Fig. 2 are given in an order which corresponds to that of the terms in (1.5). The total Ω up to third order is the sum of (1.4) and (1.5) added to the contribution of the unperturbed term

$$\Omega=\Omega^{(0)}-2\frac{J^2}{N^2}S(S+1)\sum\frac{(1-f')f}{\epsilon'-\epsilon}+2\frac{J^3}{N^3}S(S+1)$$
$$\times\sum\left[\frac{f(1-f')(1-f'')}{(\epsilon'-\epsilon)(\epsilon''-\epsilon)}+\frac{(1-f)f'f''}{(\epsilon-\epsilon')(\epsilon-\epsilon'')}\right]. \quad (1.6)$$

We do not retain those terms which vanish in the unmagnetized state, i.e., those proportional to an odd power of M_n.

2. Second-Order Correction to the Specific Heat

The second-order shift in the specific heat can be calculated directly from (1.6), since the entropy is given by

$$S=-\partial\Omega/\partial T. \quad (2.1)$$

The specific heat is then

$$C=T(\partial S/\partial T)=-T(\partial^2\Omega/\partial T^2). \quad (2.2)$$

Since several of the integrals as written in (1.6) are divergent, we should mention some salient points about the coupling function J. The exchange integrals which occur are actually functions of the momenta summed over. For example, in the second-order term of (1.6) we should have $J^2(k,k')$. As Kasuya[3] points out, J can be approximated as a function of the magnitude of the vector difference $|k-k'|$, by a function which is con-
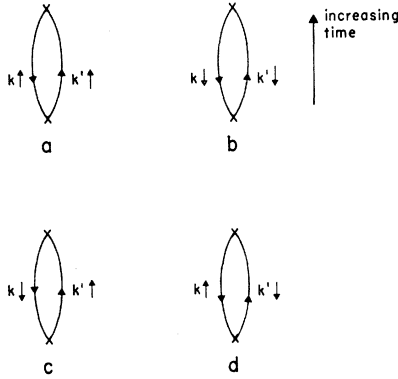
FIG. 1. Second-order diagrams for the normal-state energy. The values of the momentum and spin are indicated alongside the particle and hole lines.
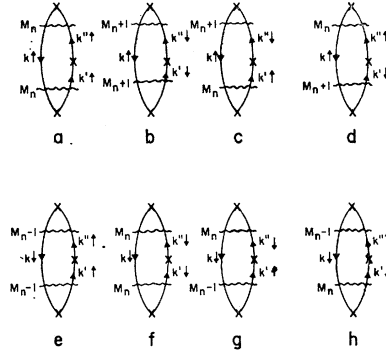

FIG. 2. Fourth-order diagrams for the normal-state energy. The values next to the wavy lines indicate the z component of the impurity spin in the intermediate states.

stant out to the first reciprocal lattice vector and then drops rapidly to zero. Since we are interested only in the Fermi-surface effects which may give rise to logarithmic singularities, we will take $J(\mathbf{k},\mathbf{k}')$ to be a constant for energies $\epsilon(\mathbf{k})$ and $\epsilon(\mathbf{k}')$ less than an energy M greater than the Fermi energy. That is,

$$J(\mathbf{k},\mathbf{k}')=J \quad \text{for} \quad 0<\epsilon(\mathbf{k})<M+\mu_0, \; 0<\epsilon(\mathbf{k}')<M+\mu_0$$
$$=0 \quad \text{otherwise}, \tag{2.3}$$

where μ_0 is the Fermi energy at zero temperature. This

approximation will certainly give Fermi-surface effects correctly, but contributions which depend on regions far from the Fermi surface will be only roughly approximated. The second-order shift in entropy is

$$\Delta S^{(2)} = -\partial \Delta \Omega^{(2)}/\partial T$$
$$= 2\frac{J^2}{N}cS(S+1)\sum_{\mathbf{k},\mathbf{k}'} \frac{1}{\epsilon'-\epsilon}\frac{\partial f}{\partial T}, \tag{2.4}$$

where c is the impurity concentration. We convert the sums in (2.4) to principal value integrals.

$$\sum_{k,k'} \frac{1}{\epsilon'-\epsilon}\frac{\partial f}{\partial T} = \left(\frac{(2m)^{3/2}V}{4\pi^2}\right)^2 \int_0^{M+\mu_0} d\epsilon\; \epsilon^{1/2}\frac{\partial f}{\partial T}P\int_0^{M+\mu_0} d\epsilon'\frac{\epsilon'^{1/2}}{\epsilon'-\epsilon}$$

$$= \frac{(N(0)V)^2}{\mu_0}\int_0^{M+\mu_0} d\epsilon\; \epsilon^{1/2}\frac{\partial f}{\partial T}\left[2(\mu_0+M)^{1/2}-\epsilon^{1/2}\ln\left|\frac{\epsilon^{1/2}+(\mu_0+M)^{1/2}}{\epsilon^{1/2}-(\mu_0+M)^{1/2}}\right|\right]. \tag{2.5}$$

We have introduced the energy density of states for electrons of one spin at the Fermi surface

$$N(0)=(2m)^{3/2}\mu_0^{1/2}/(2\pi)^2. \tag{2.6}$$

We can see from (2.5) that there are no singular effects in second order from the sharpness of the Fermi surface. The derivative of the Fermi function f will put ϵ at the Fermi surface. The integrand is then perfectly regular. We may use the usual techniques to obtain the leading term of the specific heat, keeping only the terms of (2.5) linear in the temperature. In calculating $\partial\Omega/\partial T$, the chemical potential is held fixed. In fact, it is unnecessary to retain the temperature-dependent terms of the chemical potential which appear in the Fermi function. When we define a new variable of integration in (2.5)

$$x=(\epsilon-\mu_0)/kT,$$

the integral becomes

$$\sum_{k,k'} \frac{1}{\epsilon'-\epsilon}\frac{\partial f}{\partial T}=\frac{-(N(0)V)^2}{\mu_0}k\int_{-\mu_0/kT}^{M/kT} dx\frac{\partial f}{\partial x}x(\mu_0+kTx)^{1/2}\left[2(\mu_0+M)^{1/2}-(\mu_0+kTx)^{1/2}\ln\left|\frac{(\mu_0+M)^{1/2}+(\mu_0+kTx)^{1/2}}{(\mu_0+M)^{1/2}-(\mu_0+kTx)^{1/2}}\right|\right]$$

$$= \frac{-(N(0)V)^2}{\mu_0^{3/2}}k^2T\left[(\mu_0+M)^{1/2}\left(\frac{M-\mu_0}{M}\right)-\mu_0^{1/2}\ln\left|\frac{(\mu_0+M)^{1/2}+\mu_0^{1/2}}{(\mu_0+M)^{1/2}-\mu_0^{1/2}}\right|\right]\int_{-\infty}^{\infty} dx\; x^2\frac{\partial f}{\partial x}+O\left(\left(\frac{kT}{\mu_0}\right)^2\right)$$

$$= -\pi^2(N(0)V)^2k^2Ta/3\mu_0, \tag{2.7}$$

where we have denoted the constant

$$a = -\left(1+\frac{M}{\mu_0}\right)^{1/2}\frac{M-\mu_0}{M}+\ln\left|\frac{(\mu_0+M)^{1/2}+\mu_0^{1/2}}{(\mu_0+M)^{1/2}-\mu_0^{1/2}}\right|.$$

For a cutoff M taken of the order of magnitude of the Fermi energy, a is of the order of magnitude of one. The second-order shift in specific heat is obtained by using (2.2), (2.4), (2.7):

$$\Delta C^{(2)} = -(2\pi^2/3)(J^2/N)acS(S+1)[(N(0)V)^2/\mu_0]k^2T,$$

or equivalently

$$\Delta C^{(2)}/C_0 = \Delta C^{(2)}/\tfrac{2}{3}\pi^2 N(0)Vk^2T$$
$$= -\tfrac{3}{4}(J^2/\mu_0^2)aczS(S+1), \quad (2.8)$$

where C_0 is the free-electron contribution to the specific heat. The expression for the chemical potential at zero temperature

$$\mu_0 = (1/2m)(3\pi^2\rho)^{2/3}, \quad (2.9)$$

is used in (2.8) to eliminate the number density of electrons

$$\rho = zN/V. \quad (2.10)$$

3. Third-Order Correction to the Specific Heat

In the following calculation of third-order effects, we will only be interested in those leading terms involving logarithmic singularities. We will not retain those terms which only shift the linear term of the specific heat. The third-order shift in the thermodynamic potential is included in (1.6).

$$\Delta\Omega^{(3)} = 2\frac{J^3}{N^2}cS(S+1)\sum_{k,k',k''}\frac{f-2ff'+f'f''}{(\epsilon'-\epsilon)(\epsilon''-\epsilon)}, \quad (3.1)$$

where we have summed over the impurity sites. To find which of the terms of (3.1) can give singular effects we can take the zero-temperature limit. In this case

$$f(\epsilon) = 1: \quad \epsilon < \mu_0$$
$$= 0: \quad \epsilon > \mu_0.$$

Both the first and the third terms can be seen to have finite principal-value integrals. The only end points of those integrals where the denominator vanishes is at zero energy. The zero phase space available there eliminates that as a possible singular contribution. Only the second term of (3.1) gives rise to a singular effect.

$$\Delta\Omega^{(3)} \approx -4\frac{J^3}{N^2}cS(S+1)\sum\frac{ff'}{(\epsilon'-\epsilon)(\epsilon''-\epsilon)}. \quad (3.2)$$

At zero temperature the singularity arises since the denominator vanishes when both ϵ and ϵ' are at their Fermi-energy end points. In (3.2) the integration over ϵ'' will be restricted by the coupling function J. The resulting value of the integral will depend explicitly on the functional dependence of J on ϵ''. Since the actual behavior of J is not well known we will, for simplicity, choose the model given in (2.3). The result we will obtain could then vary by as much as an order of magnitude for different models. The singular term of (3.2) will depend on the behavior of the Fermi function near the Fermi energy. Replacing the Fermi function by an approximate single-particle distribution function will not alter our limit of accuracy at this stage. However, it will have the advantage of affording an analytic rather than numerical evaluation. In the Appendix we obtain the distribution function we will use in calculating (3.2).

The integral over k'' is identical with that performed in (2.5)

$$h(\epsilon) = \sum_{k''}(\epsilon''-\epsilon)^{-1} = N(0)V\mu_0^{-1/2}\int_0^{M+\mu_0}d\epsilon''\,\epsilon''^{1/2}(\epsilon''-\epsilon)^{-1}$$

$$= 2N(0)V\mu_0^{-1/2}\left[(\mu_0+M)^{1/2}-\frac{\epsilon^{1/2}}{2}\ln\left|\frac{(\mu_0+M)^{1/2}+\epsilon^{1/2}}{(\mu_0+M)^{1/2}-\epsilon^{1/2}}\right|\right]. \quad (3.3)$$

Using (A14) we may perform the integral over k'

$$g(\epsilon) = \sum_{k'}f'(\epsilon'-\epsilon)^{-1}$$

$$= -2N(0)V\left[\frac{\bar\epsilon}{2\mu_0}-\frac{1}{2}+\left(\frac{\epsilon}{\mu_0}\right)^{1/2}\ln(\epsilon^{1/2}+(\mu_0-\xi/2)^{1/2})+\frac{1}{\xi}\left(\frac{\epsilon}{\mu_0}\right)^{1/2}\left(\frac{\xi}{2}-\bar\epsilon\right)\ln\left|\frac{\epsilon^{1/2}+(\mu_0+\xi/2)^{1/2}}{\epsilon^{1/2}+(\mu_0-\xi/2)^{1/2}}\right|\right.$$

$$\left.+\frac{1}{2\xi}\left(\frac{\epsilon}{\mu_0}\right)^{1/2}\left(\bar\epsilon-\frac{\xi}{2}\right)\ln\left|\bar\epsilon-\frac{\xi}{2}\right|-\frac{1}{2\xi}\left(\frac{\epsilon}{\mu_0}\right)^{1/2}\left(\bar\epsilon+\frac{\xi}{2}\right)\ln\left|\bar\epsilon+\frac{\xi}{2}\right|+O\left(\left(\frac{\xi}{\mu_0}\right)^2\right)\right]. \quad (3.4)$$

The integral in (3.2) can now be expressed as

$$I=\sum \frac{ff'}{(\epsilon'-\epsilon)(\epsilon''-\epsilon)}=N(0)V\mu_0^{-1/2}\int_0^\infty d\epsilon \ \epsilon^{1/2}f(\epsilon)g(\epsilon)h(\epsilon)$$

$$=N(0)V\mu_0^{-1/2}\left[\int_{-\mu}^{-\frac{1}{2}\xi} d\tilde{\epsilon} \ \epsilon^{1/2}g(\epsilon)h(\epsilon)+\int_{-\frac{1}{2}\xi}^{+\frac{1}{2}\xi} d\tilde{\epsilon} \ \epsilon^{1/2}\left(\frac{1}{2}-\frac{\tilde{\epsilon}}{\xi}\right)g(\epsilon)h(\epsilon)\right]. \quad (3.5)$$

The part of I arising from the sharpness of the Fermi surface may be extracted by rewriting (3.5) as

$$I=N(0)V\mu_0^{-1/2}\left[\int_{-\mu}^{0} d\tilde{\epsilon} \ \epsilon^{1/2}g(\epsilon)h(\epsilon)-\int_{-\frac{1}{2}\xi}^{0} d\tilde{\epsilon} \ \epsilon^{1/2}\left(\frac{1}{2}+\frac{\tilde{\epsilon}}{\xi}\right)g(\epsilon)h(\epsilon)+\int_0^{\frac{1}{2}\xi} d\tilde{\epsilon} \ \epsilon^{1/2}\left(\frac{1}{2}-\frac{\tilde{\epsilon}}{\xi}\right)g(\epsilon)h(\epsilon)\right]. \quad (3.6)$$

We may take the limit of ξ or the temperature going to zero in the first term of (3.6) without obtaining any singular term.

$$\lim_{\xi\to 0} g(\epsilon)=N(0)V\left[2-2\left(\frac{\epsilon}{\mu_0}\right)^{1/2}\ln(\epsilon^{1/2}+\mu_0^{1/2})\right.$$

$$\left.+\left(\frac{\epsilon}{\mu_0}\right)^{1/2}\ln(\epsilon-\mu_0)\right].$$

In the other two terms of (3.6) we make the change of variables $x=\tilde{\epsilon}/\xi$. When we expand the integrand for small ξ/μ_0 the singular term comes from g

$$g\approx -N(0)V[\tfrac{1}{2}(x\xi/\mu_0)\ln(\mu_0/\xi)+\ln(\mu_0/\xi)].$$

The most singular term of the integral is

$$I=+\tfrac{1}{16}(N(0)V)^3b(\xi^2/\mu_0)\ln(\mu_0/\xi)$$
$$+O[(\xi^3/\mu_0^2)\ln(\mu_0/\xi)], \quad (3.7)$$

where we have defined

$$b=\ln\left|\frac{(\mu_0+M)^{1/2}+\mu_0^{1/2}}{(\mu_0+M)^{1/2}-\mu_0^{1/2}}\right|$$
$$-\tfrac{2}{3}(2-(\mu_0/M))(1+(M/\mu_0))^{1/2}. \quad (3.8)$$

The value of b depends on the model we have chosen for J. For the cutoff M equal to μ_0, b is of the order of magnitude of one. Using (A9), (2.6), (2.9), (2.10), (3,2), and (3.7), we obtain the shift of the thermodynamic potential

$$\Delta\Omega^{(3)}=-(81/16)(J/\mu_0)^3z^2cS(S+1)$$
$$\times N(0)Vbk^2T^2\ln(\mu_0/6kT). \quad (3.9)$$

The most singular contribution to the third-order shift in entropy is

$$\Delta S^{(3)}=+(81/8)(J/\mu_0)^3z^2cS(S+1)$$
$$\times N(0)Vbk^2T\ln(\mu_0/6kT). \quad (3.10)$$

The corresponding singular part of the specific heat may be compared to the specific heat of the free electrons (A11)

$$\Delta C^{(3)}/C_0=(27/16)(J/\mu_0)^3z^2c$$
$$\times S(S+1)b\ln(\mu_0/6kT). \quad (3.11)$$

Although the temperature dependence of (3.11), $\ln T$, is very interesting, there is little hope of observing the effect experimentally in those metals which show a resistance minimum. In this case perturbation theory works too well. The coefficient of the log term is of the order of

$$(J/\mu_0)^3c\approx (0.02)^3(10^{-3})\approx 10^{-8}.$$

We use the concentration $c=10^{-3}$ because when impurity concentrations are much greater than this, magnetic ordering has started at the temperatures of the resistance minimum.[6] Since there is a very large contribution to the specific heat from the magnetic ordering itself, the contribution (3.11) will be overwhelmed before we get to temperatures at which these electron-scattering effects can give rise to a shift of as much as one part in a million.

CONCLUSIONS AND DISCUSSION

The mechanism through which magnetic impurities give rise to observable anomalies in transport properties may also be used to calculate anomalous equilibrium properties. In transport properties the s-d exchange interaction perturbs the electron lifetime in a singular way. This mechanism leads to the same type of singular behavior of the electron density of states close to the Fermi surface. In order to obtain singular effects on either property, the impurity spin states must be degenerate and the Fermi surface sharp. Magnetic fields quench the singular behavior. When the splitting of the spin states is of the order of the temperature times Boltzmann's constant, a logarithmic behavior is completely quenched.

The perturbation of the electron's equilibrium properties due to magnetic impurities is too small to be observable. It is simple to understand why a perturbation can observably affect transport properties and leave equilibrium properties essentially unaltered. As the temperature goes to zero, the major mechanism for high temperature resistivity, scattering from phonons, vanishes rapidly and a small temperature-independent residual resistance from impurities combines with a small but effective term which varies logarithmically

[6] M. P. Sarachik, Phys. Rev. 137, A659 (1965).

with the temperature. In the case of equilibrium properties such as the specific heat, the perturbation is of the density of states at the Fermi surface which does not vanish at zero temperature. The fact that we are doing perturbation theory in a very small quantity J/μ_0 makes the third-order singular term unobservable in the case of metals. Stated in another way, for transport coefficients we are perturbing from zero, for equilibrium properties we are perturbing from one.

Although this calculation does not predict an observable specific-heat excess due to magnetic impurities above their ordering temperature, such an excess is in fact observed. Experiments by Frank, Manchester, and Martin[7] on dilute systems of Cu-Fe show that although the excess resistivity can be well described by a $\ln T$ term down to about 5°K indicating negligible internal magnetic fields, there is an excess specific heat of the same order of magnitude as the electronic specific heat. The excess is fitted quite accurately by a function of the form

$$\Delta C \propto cT \ln^2 T$$

down to about 1°K. The order of magnitude of the effect shows that one will have to go outside the realm of perturbation theory in order to explain this interesting anomaly.

In recent papers, Suhl[8] and Kondo[9] have shown that an infinite summation of terms replaces the logarithmic singularity in the scattering probability by a resonant scattering away from the Fermi surface. When $|J/\mu| \times \ln(\mu/kT) \ll 1$, the lowest order logarithmic term occurring in perturbation theory gives the dominant behavior of the resistivity. The temperatures at which the anomalous behavior in the specific heat occur are sufficiently high for perturbation theory to be an adequate representation of the infinite summation. However, as we have shown the s-d exchange used as a perturbation does not explain the experimental results.

ACKNOWLEDGMENTS

APPENDIX

Approximate Single-Particle Distribution Function

As mentioned in Sec. 3, if we were to use the true Fermi distribution function in (1.6), the integrals would be extremely difficult. We will use a much simpler form for the distribution, which has the same general properties as the true one and can be expected to give the Fermi-surface effects correctly. The functional form we choose for the distribution function is

$$f(\epsilon) = 1: \qquad 0 < \epsilon < \alpha\xi - \xi,$$

$$= \alpha - \frac{\epsilon}{\xi}: \quad \alpha\xi - \xi < \epsilon < \alpha\xi, \qquad (A1)$$

$$= 0: \qquad \alpha\xi < \epsilon.$$

The form chosen in (A1) is similar to the choice made by Koppe[10] and Wolfarth[11] in calculations of the effect of exchange on the specific heat with Coulomb interactions present.

First we determine the condition on α which ensures the constancy of the number of electrons

$$zN = \sum_{k,\sigma} f = \frac{(2m)^{3/2}}{2\pi^2} V \int d\epsilon\, \epsilon^{1/2} f(\epsilon)$$

$$= [(2m)^{3/2}/2\pi^2] V(\alpha\xi)^{3/2}$$

$$\times [\tfrac{2}{3} - \tfrac{1}{2}(\xi/\alpha\xi) + \tfrac{1}{12}(\xi/\alpha\xi)^2 + \cdots]. \quad (A2)$$

We may solve (A2) iteratively for $\alpha\xi$, using (2.9) and (2.10).

$$\alpha\xi = \mu_0 + \tfrac{1}{2}\xi - (1/48)(\xi^2/\mu_0) + O(\xi^3/\mu_0^2). \quad (A3)$$

Since the width of the Fermi surface ξ is proportional to kT, we neglect terms of order $\xi(\xi/\mu_0)^2$ in (A3).

The thermodynamic potential of the noninteracting system is

$$\Omega^{(0)} = 2 \sum_p (\epsilon_p - \mu) f_p$$

$$+ 2kT \sum_p [f_p \ln f_p + (1 - f_p) \ln(1 - f_p)]. \quad (A4)$$

The distribution function (3.1) depends upon two parameters. One of them α was determined in (A3) by fixing the density of the system. The second ξ will be chosen by minimizing $\Omega^{(0)}$. The first term of (A4) is the energy of the noninteracting electrons

$$U^{(0)} = 2 \sum_p \epsilon_p f_p = \tfrac{4}{5} N(0) V \mu_0^2$$

$$+ \tfrac{1}{12} N(0) V \xi^2 + O(\xi^3/\mu_0), \quad (A5)$$

where we have used the distribution function (A1), the expansion (A3) for $\alpha\xi$ and introduced the density of states $N(0)$ given in (2.6). The entropy of the system enters $\Omega^{(0)}$,

$$S = -2k \sum_p [f_p \ln f_p + (1 - f_p) \ln(1 - f_p)]$$

$$= kN(0) V\xi + O(\xi^3/\mu_0^2), \quad (A6)$$

[7] J. P. Frank, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) A263, 494 (1961).
[8] H. Suhl, Phys. Rev. 138, A515 (1965).
[9] J. Kondo (to be published).
[10] H. Koppe, Z. Naturforsch. 2a, 429 (1947).
[11] E. Wolfarth, Phil. Mag. 41, 534 (1950).

using the distribution function (A1). The thermo-dynamic potential of the noninteracting system is then

$$\Omega^{(0)} = \tfrac{4}{5}N(0)V\mu_0^2 + \tfrac{1}{12}N(0)V\xi^2 - \mu z N - N(0)V\xi kT. \quad (A7)$$

The minimum $\Omega^{(0)}$ is at that value of ξ for which

$$\partial\Omega^{(0)}/\partial\xi = 0, \quad (A8)$$

namely,

$$\xi_0 = 6kT. \quad (A9)$$

The specific heat

$$C = T(\partial S/\partial T) \quad (A10)$$

may be calculated from the expression (A6) obtained for the entropy. The result is

$$C_0/V = 6N(0)k^2T. \quad (A11)$$

We now can see the damage done by our choice of the distribution function. The exact result for the term in the free-electron specific heat linear in temperature is[12]

$$C_0/V = \tfrac{2}{3}\pi^2 N(0)k^2T. \quad (A12)$$

Thus our crude form for the distribution function re-

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[12] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 150.

places π^2 by 3^2. This approximation is certainly sufficient for our purposes.

We can rewrite the distribution function (A1) using (A3) and the energy variable measured relative to the Fermi energy:

$$\bar{\epsilon} = \epsilon - \mu_0 + (1/48)(\xi^2/\mu_0) = \epsilon - \mu, \quad (A13)$$

$$f(\bar{\epsilon}) = 1: \qquad -\mu_0 + (1/48)(\xi^2/\mu_0) < \bar{\epsilon} < -\tfrac{1}{2}\xi,$$

$$= \tfrac{1}{2} - \frac{\epsilon}{\xi}: \quad -\tfrac{1}{2}\xi < \bar{\epsilon} < \tfrac{1}{2}\xi,$$

$$= 0: \qquad \tfrac{1}{2}\xi < \bar{\epsilon}. \quad (A14)$$

From (A9), (A13), and (A14), we may obtain the dependence of the Fermi energy on temperature for the noninteracting system

$$\mu = \mu_0[1 - (1/48)(\xi_0^2/\mu_0^2)] = \mu_0[1 - \tfrac{3}{4}(kT/\mu_0)^2]. \quad (A15)$$

Once again we may compare with the exact result[13]

$$\mu = \mu_0[1 - (\pi^2/12)(kT/\mu_0)^2] \quad (A16)$$

and find that π^2 has been replaced by 3^2.

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[13] F. Seitz, Ref. 12, p. 149.

Specific Heat of Alpha-Manganese at Liquid-Helium Temperatures†

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The heat capacities of two independently prepared specimens of α-Mn have been measured between 1.75 and 4.2°K. The coefficient of the contribution linear in T is found to be $(30.6\pm1.5)\times10^{-4}$ cal/mole(°K)^2. This value is in reasonable agreement with that determined by Booth, Hoare, and Murphy from measurements made in the liquid-hydrogen range.

INTRODUCTION

PUBLISHED reports[1–6] of measurements of the heat capacity of α-manganese at low temperatures have

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[1] G. L. Booth, F. E. Hoare, and B. T. Murphy, Proc. Phys. Soc. (London) **B68**, 830 (1955).

[2] L. D. Armstrong and H. Grayson-Smith, Can. J. Phys. **A27**, 9 (1945).

[3] R. G. Elson, H. Grayson-Smith, and J. O. Wilhelm, Can. J. Res. **A18**, 83 (1940).

[4] N. M. Woolcott, *Proceedings of the Conference on Physics of Low Temperatures, Paris, 1955* (Centre Nationale de la Recherche Scientifique, and UNESCO, Paris, 1956), p. 286.

[5] C. H. Shomate, J. Chem. Phys. **13**, 326 (1945).

[6] K. K. Kelley, J. Am. Chem. Soc. **61**, 203 (1939).

yielded conflicting values for the electronic heat capacity and the Debye theta. It now appears that at least some of the discrepancies are attributable to the contamination of α-Mn with other phases.[1] The present work[7] is a report of the helium-temperature heat capacities of two separate specimens prepared independently by different procedures and known to be in the alpha phase. The two results agree and are consistent with the heat-capacity data of Booth, Hoare, and Murphy,[1] obtained between 11 and 20°K using Mn specimens of known crystal structure.