

However,

$$\left(\frac{\partial M}{\partial T}\right)_{H_e} = -\frac{(\partial H_e/\partial T)_M}{(\partial H_e/\partial M)_T} = -\frac{(\partial H/\partial T)_M}{(\partial H/\partial M)_T + \bar{D}}, \quad (\text{A10})$$

where the second equality utilizes (2.6). Finally, the Maxwell relation<sup>4</sup>

$$(\partial S/\partial M)_T = -(\partial H/\partial T)_M \quad (\text{A11})$$

completes the derivation.

In computing  $C_e$  it is convenient, given  $H_e$ , to first choose  $M$ , then evaluate  $x = \tau M^{-2}$  by combining (2.6) and (A1), and express the right-hand side of (A7) in terms of  $x$  and  $M$ . If  $\bar{D} = D/V$  is set equal to zero in (A7),  $C_e$  is identical to  $C_H$ .

It is clear from (A4) that  $T^{-1}C_M$  satisfies a "scaling" relation. The same is true of  $T^{-1}C_H$ . It can, in fact, easily be shown that

$$T^{-1}C_H = C_0(T) + f(\tau|H|^{-2/3}) - \lambda \ln|H| \quad (\text{A12})$$

for an appropriate function  $f(x)$  and constant  $\lambda$ .

## Numerical Study of the $t$ Matrix in the Kondo Problem\*

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A numerical study of the Kondo problem is presented. The calculations are based on the Suhl-Abrikosov-Nagaoka integral equation for the scattering amplitude  $t(\omega, T)$  of the  $s$ - $d$  exchange Hamiltonian. Use is made of the exact analytic solution first given in detail by Zittartz and Müller-Hartmann. It is shown that, because of the resonance in  $\text{Im}t(\omega, T)$  which occurs at the Fermi energy ( $\omega = 0$ ) at low temperatures, the tunneling density of states of a dilute paramagnetic alloy is very slightly reduced at zero bias voltage. There is, however, a possibility of detecting this change by studying the derivative of the conductance. The details of the Zittartz-Müller-Hartmann expression are found to be unimportant for the low-temperature behavior of the transport coefficients with the exception of the thermoelectric power. A reinvestigation of the thermoelectric power shows that some care is necessary in the evaluation of the integrals  $K_n = \int_{-\infty}^{\infty} d\omega \omega^n n_0(\omega) \tau(\omega, T) \partial f / \partial \omega$ , because of the strong  $\omega$  dependence of the electronic lifetime  $\tau(\omega, T) \propto [\text{Im}t(\omega, T)]^{-1}$  at low temperatures. While the transport coefficients reflect the behavior of the scattering amplitude in a small energy interval about the Fermi energy, the specific-heat anomaly is found to be related to the temperature derivative of  $t(\omega, T)$  at large values of the energy variable  $\omega$  comparable to the bandwidth. We point out that the quasiparticle approximation is not valid for electrons interacting with impurity spins due to the rapid variation of  $t(\omega, T)$  near the Fermi energy.

### I. INTRODUCTION

IN this paper, we study numerically the low-temperature anomalies of dilute magnetic alloys. The  $s$ - $d$  exchange model (or Kondo Hamiltonian) is widely accepted as a reasonable description of the interaction between conduction electrons and the localized magnetic moments of the impurity ions. This model Hamiltonian consists of a simple contact interaction between the impurity spin  $\mathbf{S}_j^{\text{imp}}$  and the electron spin density at the position of the impurity:

$$H_{sd} = H_{\text{kin}} - \frac{J}{N} \sum_j \mathbf{S}_j^{\text{imp}} \cdot \mathbf{s}^{\text{el}}(\mathbf{R}_j). \quad (1.1)$$

Here  $H_{\text{kin}}$  is the kinetic energy of the noninteracting

electron system,  $N$  is the number of atomic cells, and  $J$  is the coupling constant. We shall consider only the case of antiferromagnetic coupling ( $J > 0$ ).

In the course of explaining the resistance minimum of dilute magnetic alloys on the basis of the  $s$ - $d$  exchange Hamiltonian, Kondo<sup>1</sup> discovered that in perturbation theory the one-electron scattering amplitude has a logarithmic singularity at small temperatures and energies. Various nonperturbational methods<sup>2-7</sup> have since been developed to explain quantitatively the anomalous behavior of the physical properties of dilute magnetic alloys. Of particular interest to us are the methods of

<sup>1</sup> J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32**, 37 (1964).

<sup>2</sup> H. Suhl, *Phys. Rev.* **138**, A515 (1965); **141**, 483 (1966); *Physics* **2**, 39 (1965).

<sup>3</sup> A. A. Abrikosov, *Physics* **2**, 5 (1965).

<sup>4</sup> Y. Nagaoka, *Phys. Rev.* **138**, A1112 (1965); *Progr. Theoret. Phys. (Kyoto)* **36**, 875 (1966).

<sup>5</sup> J. Appelbaum and J. Kondo, *Phys. Rev. Letters* **19**, 906 (1967); *Phys. Rev.* **170**, 542 (1968).

<sup>6</sup> K. Yosida, *Phys. Rev.* **147**, 223 (1966); *Progr. Theoret. Phys. (Kyoto)* **36**, 875 (1966).

<sup>7</sup> A. Okiji, *Progr. Theoret. Phys. (Kyoto)* **36**, 712 (1966).

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Suhl,<sup>2</sup> Abrikosov,<sup>3</sup> and Nagaoka.<sup>4</sup> Suhl applied dispersion relation techniques to the *s-d* scattering problem and obtained a set of two coupled nonsingular integral equations for the non-spin-flip and the spin-flip parts of the electron scattering amplitude. Essentially the same equations were obtained by Abrikosov, who used a graphical technique to sum up the most singular terms in the perturbation series for the scattering amplitude. The complete equivalence of the Suhl and Abrikosov methods has been proved by several authors.<sup>8,9</sup> Nagaoka considered the hierarchy of equations of motion starting with the equation of motion for the one-electron Green's functions. He decoupled the higher-order Green's function so that a closed set of equations for the first two Green's functions was obtained. Later on, Falk and Fowler<sup>10</sup> and, independently, Hamann<sup>11</sup> showed that Nagaoka's equations could be cast into the form of a single nonlinear singular integral equation for the non-spin-flip scattering amplitude. The solution of this integral equation is due to Hamann,<sup>11</sup> Bloomfield and Hamann,<sup>12</sup> and Zittartz and Müller-Hartmann (ZMH).<sup>13</sup> Hamann, as well as Hamann and Bloomfield, truncated the integral equation by neglecting the regular contributions to the kernel as small compared to the singular ones. Their solutions for the *t* matrix are accurate for small energies and thus quite sufficient to explain the anomalies in those physical quantities which only depend on the scattering amplitude for small values of the energy. The exact solution of Hamann's integral equation is due to ZMH.

In Sec. II we discuss the relation between the *t* matrix and the one-electron spectral density and the density of states. In Sec. III, we present the results of a detailed numerical study of the ZMH analytic expression for the scattering amplitude. Section IV is devoted to the question as to how far the details of this expression are of importance in the computation of measurable physical quantities.

## II. SPECTRAL DENSITY AND DENSITY OF STATES

The spectral density of one-electron states in an alloy is given by

$$\rho_{\text{alloy}}(\mathbf{k}, \omega) = \frac{1}{\pi} \frac{-\text{Im}\Sigma(\mathbf{k}, \omega)}{[\omega - \epsilon_{\mathbf{k}} - \text{Re}\Sigma(\mathbf{k}, \omega)]^2 + [\text{Im}\Sigma(\mathbf{k}, \omega)]^2}. \quad (2.1)$$

Here  $\epsilon_{\mathbf{k}}$  is the kinetic energy of our electron with momentum  $\mathbf{k}$ . The effect of interactions on the spectral

density is entirely contained in the self-energy function  $\Sigma(\mathbf{k}, \omega)$  which, in general, may be split into three contributions:

$$\Sigma(\mathbf{k}, \omega) = \Sigma_{\text{el-el}}(\mathbf{k}, \omega) + \Sigma_{\text{el-ph}}(\mathbf{k}, \omega) + \Sigma_{\text{el-imp}}(\mathbf{k}, \omega). \quad (2.2)$$

We shall neglect the first two terms which result from electron-electron and electron-phonon interactions since they are also present in the pure host material. In so doing, we assume that  $\Sigma_{\text{el-el}}$  and  $\Sigma_{\text{el-ph}}$  are the same for the pure host material and for the alloy. This assumption is quite generally made for low concentration of impurities although it is hard to justify rigorously. One may incorporate the real parts of the first two terms on the right-hand side of (2.2) by interpreting  $\epsilon_{\mathbf{k}}$  to be the renormalized electronic energy. Near the Fermi surface, such effects may be simply expressed in terms of an effective mass  $m^*$ , i.e.,  $\epsilon_{\mathbf{k}} = k^2/2m^*$ .

To lowest order in the impurity concentration,  $\Sigma_{\text{el-imp}}$  is given by

$$\Sigma_{\text{el-imp}}(\mathbf{k}, \omega) = n_i t_{\mathbf{k}\mathbf{k}}(\omega), \quad (2.3)$$

where  $n_i$  is the impurity concentration and  $t_{\mathbf{k}\mathbf{k}}(\omega)$  is the one-electron non-spin-flip forward-scattering amplitude. Since the interaction which we are considering is a contact interaction, the scattering amplitude and hence the self-energy are independent of the momentum  $\mathbf{k}$  of the electron

$$t_{\mathbf{k}\mathbf{k}}(\omega) \equiv t(\omega), \quad \Sigma_{\text{el-imp}}(\mathbf{k}, \omega) \equiv \Sigma(\omega). \quad (2.4)$$

This fact makes it especially easy to compute the density of states of the alloy. In terms of the spectral density, the density of states can be written as

$$n(\omega) = n_0(\omega) + \frac{1}{N} \sum_{\mathbf{k}} \rho_{\text{alloy}}(\mathbf{k}, \omega) = n_0(\omega) + \int d\epsilon_{\mathbf{k}} n_0(\epsilon_{\mathbf{k}}) \rho_{\text{alloy}}(\mathbf{k}, \omega), \quad (2.5)$$

where  $n_0(\epsilon_{\mathbf{k}})$  is the density of states of the host metal. We choose  $n_0(\epsilon_{\mathbf{k}})$  to be a Lorentzian, namely,

$$n_0(\epsilon_{\mathbf{k}}) = \bar{n}_0 D^2 / (\epsilon_{\mathbf{k}}^2 + D^2). \quad (2.6)$$

The reason for this choice is that the ZMH solution for the *t* matrix, which we shall use in our later work, is also based on this bare density-of-states function.  $\bar{n}_0 \equiv n_0(\epsilon_{\mathbf{k}} = 0)$  is the density of states at the Fermi energy (all energies are measured relative to the Fermi energy  $\epsilon_F$ ). From the exact sum rule,

$$\int_{-\infty}^{\infty} n_0(\epsilon_{\mathbf{k}}) d\epsilon_{\mathbf{k}} = 1,$$

we see that

$$\bar{n}_0 = 1/\pi D \quad (2.7)$$

in the case of the Lorentzian band model.<sup>14</sup>

<sup>14</sup>  $\bar{n}_0$  is the density of states per unit cell. To obtain the total density of states, one has to multiply by the number of atoms in the system.

<sup>8</sup> S. D. Silverstein and C. B. Duke, Phys. Rev. **161**, 456 (1967).

<sup>9</sup> H. Keiter, Z. Physik **214**, 22 (1968).

<sup>10</sup> D. S. Falk and M. Fowler, Phys. Rev. **158**, 567 (1967).

<sup>11</sup> D. R. Hamann, Phys. Rev. **158**, 570 (1967).

<sup>12</sup> P. E. Bloomfield and D. R. Hamann, Phys. Rev. **164**, 856 (1967).

<sup>13</sup> J. Zittartz and E. Müller-Hartmann, Z. Physik **212**, 380 (1968).

Using (2.3), (2.4), and (2.6) in the evaluation of (2.5), one finds that the change in the density of states is given by

$$\begin{aligned} \Delta n(\omega, T) &\equiv n(\omega, T) - n_0(\omega) \\ &= n_i n_0^2(\omega) \left[ 2 \frac{\omega}{D} \operatorname{Re} t_{\text{ret}}(\omega, T) \right. \\ &\quad \left. + \left( 1 - \frac{\omega^2}{D^2} \right) \operatorname{Im} t_{\text{ret}}(\omega, T) \right], \end{aligned} \quad (2.8)$$

where  $t_{\text{ret}}(\omega, T)$  is the retarded forward-scattering amplitude. For energies well within the band ( $|\omega| \ll D$ ), this result simplifies to

$$\Delta n(\omega) = n_i n_0^2 \operatorname{Im} t_{\text{ret}}(\omega, T). \quad (2.9)$$

It is well known that the imaginary part of the scattering amplitude is bounded by the unitarity limit

$$-\operatorname{Im} t_{\text{ret}}(\omega, T) \leq 1/\pi \bar{n}_0, \quad (2.10)$$

and hence we see that<sup>15</sup>

$$\left| \frac{\Delta n(\omega, T)}{\bar{n}_0} \right| \leq r_i. \quad (2.11)$$

The relative change in the density of states is less than the concentration of impurities. For values of the concentration of the order of  $10^{-3}$  which are common for dilute magnetic alloys, it would therefore be difficult to observe  $\Delta n(\omega)/\bar{n}_0$  in a tunneling experiment. However, one might try to do experiments with magnetic impurity concentration of order  $10^{-2}$  as long as one has a sufficient concentration of nonmagnetic impurities which would destroy the long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) polarization effects that induce impurity spin-impurity spin coupling. Moreover, there might be a chance of observing the derivative ( $d/d\omega$ )  $\Delta n(\omega, T)$ , which is large because of the rapid variation of  $\Delta n(\omega)$  with energy.<sup>16</sup> We shall come back to this point in Sec. IV A.

### III. NUMERICAL RESULTS FOR NON-SPIN-FLIP t MATRIX

In this section we shall discuss the results for the scattering amplitude  $t_{\text{ret}}(\omega, T)$  which we have obtained by evaluating numerically the analytic expression for  $t(\omega, T)$  as given by ZMH.<sup>17</sup> It is evident from Sec. II that this provides all the information needed to determine the one-particle excitation spectrum as well as the density-of-states function.

<sup>15</sup> A. Griffin, in *Lectures Notes of McGill Summer School on Superconductivity*, edited by P. R. Wallace (Gordon and Breach, Science Publishers, Inc., New York, to be published).

<sup>16</sup> This was suggested by A. Griffin.

<sup>17</sup> A similar analysis of Bloomfield-Hamann solution for  $t(\omega, T)$  is contained in a recent paper by B. N. Ganguly and C. S. Shastry, *Phys. Rev.* (to be published).

ZMH were able to obtain an exact solution of the approximate Suhl-Abrikosov-Nagaoka integral equation for  $t(\omega, T)$  under the assumption that the density-of-states function of the pure metal is a Lorentzian [see Eq. (2.6)]. For convenience, we state their solution for  $t_{\text{ret}}(\omega, T)$  here<sup>18</sup>

$$t_{\text{ret}}(\omega, T) = \frac{1}{2\pi i n_0(\omega)} \left( 1 - \frac{X(\omega, T)}{[K(\omega, T)]^{1/2}} e^{i\theta(\omega, T)} \right). \quad (3.1)$$

The functions  $X(\omega, T)$  and  $K(\omega, T)$  are defined as follows:

$$X(\omega, T) \equiv 1 - (\pi\gamma)^2 \rho_0(\omega) \left[ \frac{1}{4} S(S+1) + A(T) \right] + \gamma \rho_0(\omega)$$

$$\times \left[ \psi \left( \frac{1}{2} + \frac{\beta D}{2\pi} \right) - \psi \left( \frac{1}{2} - i \frac{\beta \omega}{2\pi} \right) \right], \quad (3.2a)$$

$$\rho_0(\omega) = D^2 / (\omega^2 + D^2), \quad (3.2b)$$

$$K(\omega, T) \equiv |X(\omega, T)|^2 + [\pi\gamma\rho_0(\omega)]^2 S(S+1). \quad (3.3)$$

Here  $\psi(z)$  denotes the digamma function and  $\gamma \equiv J\bar{n}_0$  is a dimensionless coupling constant which is assumed to be much smaller than unity. The function  $\theta(\omega, T)$ , which we will henceforth refer to as the phase, is given by a principal-value integral

$$\theta(\omega, T) \equiv -P \int_{-\infty}^{\infty} \frac{\ln K(\omega', T)}{\omega' - \omega} d\omega'. \quad (3.4)$$

The function  $A(T)$  which enters  $K(\omega, T)$  via  $X(\omega, T)$  has to be determined self-consistently from

$$A(T) = \frac{1}{2i\pi\gamma} \int_{-\infty}^{\infty} d\omega (\tanh \frac{1}{2}\beta\omega) \frac{\omega - 2iD}{(\omega - iD)^2} t_{\text{ret}}(-\omega). \quad (3.5a)$$

For convenience, we shall use the alternative condition obtained by ZMH to determine  $A(T)$ ,

$$M_0(A, T) \equiv \int_{-\infty}^{\infty} \ln K(\omega, T) d\omega = 0. \quad (3.5b)$$

The physical meaning of  $A(T)$  becomes apparent from the exact result

$$A(T) = (2\pi D |\gamma|)^{-1} (\Delta E_{\text{kin}} - E_{\text{int}}), \quad (3.6)$$

which relates it to the difference between the incremental kinetic energy of the electrons,

$$\Delta E_{\text{kin}} = E_{\text{kin}}^{\text{alloy}} - E_{\text{kin}}^{\text{host metal}},$$

and to the interaction energy.

The following general features of  $t_{\text{ret}}(0, T)$  follow immediately from (3.1):

<sup>18</sup>  $t_{\text{ret}}$  as given here differs from the corresponding quantity in the paper of ZMH by a factor of  $J$ , i.e.,  $t_{\text{ret}}(\omega, T) = J t_{\text{ret}}^{\text{ZMH}}(\omega, T)$ .

(a) If the density-of-state function of the host material  $n_0(\omega)$  is an even function of  $\omega$ , then

$$\text{Im}t_{\text{ret}}(\omega, T) = \text{Im}t_{\text{ret}}(-\omega, T), \quad (3.7a)$$

$$\text{Re}t_{\text{ret}}(\omega, T) = -\text{Re}t_{\text{ret}}(-\omega, T). \quad (3.7b)$$

This applies, of course, to our case since  $n_0(\omega)$  is a Lorentzian.

(b)  $\text{Im}t_{\text{ret}}(\omega, T) \leq 0$  for all  $\omega$  and  $T$ .

(c) Making use of the asymptotic form of the function  $X(\omega, T)$  for  $T=0$ , namely,

$$\lim_{T \rightarrow 0} X(\omega, T) = 1 - (\pi\gamma)^2 \rho_0(\omega) \left[ \frac{1}{4} S(S+1) + A \right] + \gamma \rho_0(\omega) (\ln |D/\omega| + i \frac{1}{2} \pi \text{sgn} \omega)$$

and of the fact that

$$\theta(\omega=0, T) = 0, \quad (3.8)$$

one can easily prove the inequality

$$-\text{Im}t_{\text{ret}}(\omega, T) \leq -\text{Im}t_{\text{ret}}(0, 0) = \pi^{-1} (\text{unitarity limit}). \quad (3.9)$$

Furthermore, for arbitrary temperature,  $X(\omega=0, T)$  takes the simple form

$$X(\omega=0, T) = -\gamma \ln(T/T_K), \quad (3.10)$$

where the Kondo temperature  $T_K$  is defined by

$$T_K = (\bar{D}/k_B) \exp\left(\frac{1}{\gamma}\{1 - (\pi\gamma)^2 [\frac{1}{4} S(S+1) + A]\}\right), \quad (3.11)$$

with

$$\bar{D} = (2/\pi) D \exp(\gamma_{\text{Euler}}) = 1.13D.$$

Here,  $A(T)$  is treated as a temperature-independent constant for reasons which will become clear later on. Because of (3.8), using (3.10), we find that

$$t_{\text{ret}}(\omega=0, T) = \frac{1}{2i\pi\bar{n}_0} \left( 1 - \frac{\ln(T/T_K)}{[\ln(T/T_K)]^2 + \pi^2 S(S+1)} \right)^{1/2}. \quad (3.12)$$

The remarkable feature of this simple formula is that the right-hand side depends on the coupling constant only through the ratio  $\tau \equiv T/T_K$ . Thus  $T_K$  completely determines the temperature scale on which  $t_{\text{ret}}(\omega=0, T)$  varies.

(d) A more general statement can be made in the weak coupling limit ( $|\gamma| \rightarrow 0$ ). It has been shown by Müller-Hartmann<sup>19</sup> (MH) that, in this limit, the scattering amplitude approaches a function which is independent of the coupling constant  $\gamma$ . This obtains for fixed values of the dimensionless temperature  $\tau$  and the dimensionless energy variable  $\epsilon \equiv \omega/k_B T_K$ . Moreover, this function does not depend on the specific form of the

<sup>19</sup> E. Müller-Hartmann, Z. Physik. **223**, 267 (1969).

density-of-states function of the host metal  $n_0(\omega)$ . In mathematical terms, if we define

$$Y(\epsilon, \tau) \equiv \lim_{\gamma \rightarrow 0} [-(1/\gamma)X(\omega, T)] = \ln \tau + \psi\left(\frac{1}{2} - i\epsilon/2\pi\tau\right) - \psi\left(\frac{1}{2}\right), \quad (3.13)$$

then  $t_{\text{ret}}(\epsilon, \tau)$  is given by

$$t_{\text{ret}}^{(0)}(\omega, \tau) = \lim_{\gamma \rightarrow 0} t_{\text{ret}}(\omega, T) = \frac{1}{2i\pi\bar{n}_0} \left( 1 - \frac{Y(\epsilon, \tau)}{[K_y(\epsilon, \tau)]^{1/2}} e^{i\theta_y(\epsilon, \tau)} \right), \quad (3.14)$$

where

$$K_y(\epsilon, \tau) = |Y(\epsilon, \tau)|^2 + \pi^2 S(S+1) \quad (3.15)$$

and

$$\theta_y(\epsilon, \tau) = \frac{1}{2\pi} P \int_{-\infty}^{\infty} d\epsilon' \frac{\ln K_y(\epsilon', \tau)}{\epsilon' - \epsilon}. \quad (3.16)$$

The right-hand side of (3.14) is evidently independent of the coupling constant  $\gamma$  and of the density-of-state function of the host metal  $n_0(\omega)$ . The important question of how well this simple limiting expression for  $t_{\text{ret}}(\epsilon, \tau)$  approximates the scattering amplitude for finite but small values of  $\gamma$  will be answered by our numerical results.

The analytic expression for the scattering amplitude is complicated a great deal by the presence of the unimodular factor  $e^{i\theta}$  in the expression for  $t_{\text{ret}}(\omega, T)$  and by the fact that the function  $X(\omega, T)$  depends on the function  $A(T)$  which has to be determined self-consistently from Eq. (3.5). Neither  $\theta(\omega, T)$  nor  $A(T)$  can be expressed by simple analytic functions.

In deriving (3.11), we have treated  $A(T)$  as a constant. This is justifiable since, as was pointed out by ZMH, the over-all magnitude of  $A(T)$  is small, being of the order of the coupling constant  $\gamma$ . Thus for small enough  $\gamma$ ,  $A$  can be neglected relative to the term  $\frac{1}{4} S(S+1)$  in (3.11). For small  $\gamma$ , one can obtain an asymptotic expansion for  $A$  by expanding the integrand in the Eq. (3.5b) in powers of  $\gamma$ . This yields

$$A(T) = -\frac{3}{8} \gamma S(S+1) [1 + O(T/D)] + O(\gamma^2). \quad (3.17)$$

For  $T=0$ , this expansion has been derived by ZMH. As one can see, the temperature dependence of the lowest-order contribution for  $A(T)$  is negligible for all physically reasonable temperatures.

The results of the numerical calculation of Eq. (3.5b) agree qualitatively with the expansion (3.17). To obtain the values of  $A(T)$  listed in Table I, we computed the integral

$$M_0(A, T) = \int_{-\infty}^{\infty} d\omega \ln K(\omega, T) \quad (3.18)$$

for specific values of  $A$ . To find  $A$ , we then determined graphically the zero of  $M_0(A, T)$  as a function of  $A$ .

TABLE I. The values of  $A$  obtained for two different values of the reduced coupling constant  $\gamma$ . See Eqs. (3.17) and (3.18) in text.

$\gamma$	$A$
-0.08	0.031
-0.11	0.050

Within the numerical precision of this procedure, we could not detect any temperature variation in  $A$  over a temperature interval of 100°K.

Let us note here, that, as far as the scattering amplitude is concerned,  $A(T)$  is of no importance. In contrast, however, it turns out that  $A(T)$  is crucial for the calculation of the specific heat of dilute magnetic alloys.

To compute  $\theta(\omega, T)$  numerically, we use the expression

$$\theta(\omega, T) = -P \int_{-\infty}^{\infty} d\omega' \frac{\omega}{\omega'^2 - \omega^2} \ln \left( \frac{K(\omega', T)}{K(\omega, T)} \right), \quad (3.19)$$

which is identical to (3.4) since

$$P \int_{-\infty}^{\infty} d\omega' \frac{\omega}{\omega'^2 - \omega^2} \equiv 0$$

and

$$K(\omega', T) = K(-\omega', T).$$

It is obvious that the integral in (3.19) is easier to handle in a numerical integration than the integral in (3.4). The convergence of the latter depends on the delicate compensation of the contributions from large positive and large negative values of the integration variable  $\omega'$ .

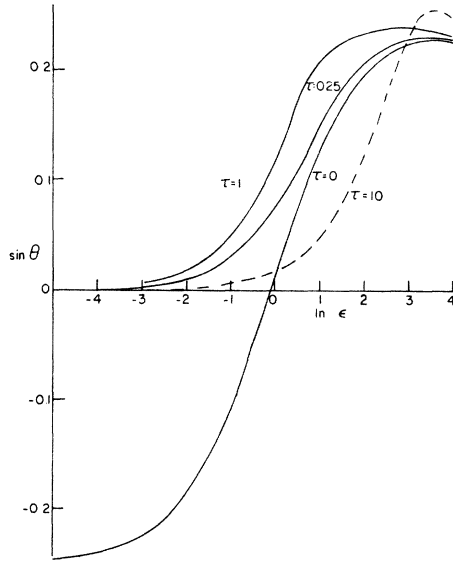


FIG. 1.  $\sin\theta$  is plotted as a function of  $\ln\epsilon = \ln(\omega/T_K)$  for four values of the dimensionless temperature  $\tau = T/T_K$ . See Eq. (3.4) in the text. We have taken  $\gamma = -0.11$  which corresponds to  $T_K = 9.84^\circ\text{K}$ . Subsequent figures involve the same dimensionless variables and the same value of  $\gamma$ .

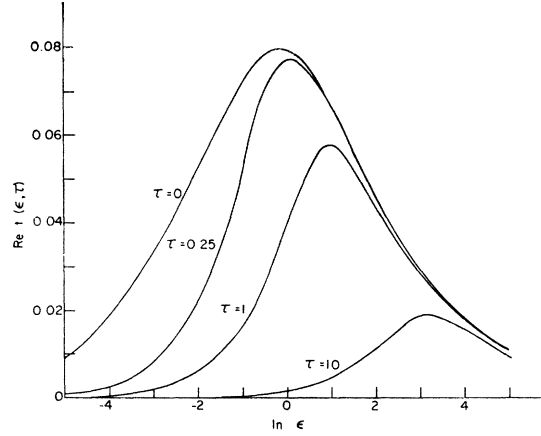


FIG. 2. The real part of the scattering amplitude is shown as a function of  $\ln\epsilon$ . The unimodular factor  $e^{i\theta}$  is included in the computation of these curves. See Eq. (3.20).

In Fig. 1 we have plotted  $\sin\theta(\epsilon, \tau)$  as a function of  $\epsilon$  for four different values of the dimensionless temperature  $\tau$ . The dimensionless coupling constant  $\gamma$  was chosen to be  $\gamma = -0.11$ . The curves for finite values of  $\tau$  and the one for  $\tau = 0$  differ qualitatively. For the values of  $\tau \neq 0$  for which we have computed  $\theta(\epsilon, \tau)$ , it approaches zero smoothly from above as  $\epsilon$  goes to zero. In contrast to that, it appears that  $\theta(\epsilon, \tau = 0)$  goes to zero with a large negative slope if  $\epsilon$  goes to zero. We have not been able to do the numerical integration of (3.19) for values of  $\epsilon$  which are small enough so that the increase of  $\theta(\epsilon, \tau = 0)$  becomes visible. The evaluation of (3.19) for small values of  $\omega$  at  $T = 0$  is difficult since  $K(\omega', T = 0)$  has a logarithmic singularity at  $\omega' = 0$ .

It is easy to see that  $\theta_y(\epsilon, \tau)$  defined in (3.16) is obtained from (3.19) if the Lorentzian  $\rho_0(\omega)$  which occurs in the function  $K(\omega, T)$  [see (3.2) and (3.3)] is replaced by unity. We have done this and found that the values of  $\theta_y(\epsilon, \tau)$  so obtained do not deviate significantly from those of  $\theta(\epsilon, \tau)$ . We conclude that  $\theta_y(\epsilon, \tau)$  is a very good approximation to  $\theta(\epsilon, \tau)$  for values of  $|\gamma|$  as large as 0.11.

Figures 2 and 3 show the results of the numerical evaluation of

$$\text{Re}l_{\text{ret}}(\omega, T) = -\frac{1}{2\pi n_0(\omega)} K^{-1/2}(\omega, T) [\text{Re}X(\omega, T) \sin\theta(\omega, T) + \frac{1}{2}\pi\gamma\rho_0(\omega) \tanh\frac{1}{2}\beta\omega \cos\theta(\omega, T)] \quad (3.20)$$

and

$$\text{Im}l_{\text{ret}}(\omega, T) = -\frac{1}{2\pi n_0(\omega)} \{1 - K^{-1/2}(\omega, T) \times [\text{Re}X(\omega, T) \sin\theta(\omega, T) + \frac{1}{2}\pi\gamma\rho_0(\omega) \times \tanh\frac{1}{2}\beta\omega \sin\theta(\omega, T)]\}. \quad (3.21)$$

[To obtain these expressions for  $\text{Re}$ ,  $\text{Im}l_{\text{ret}}$ , we have used (3.2a) and the mathematical identity  $\text{Im}\psi(\frac{1}{2} - ix)$

$= -\frac{1}{2}\pi \tanh\pi x$ ].  $\text{Re}t_{\text{ret}}$  and  $\text{Im}t_{\text{ret}}$  are plotted as functions of the dimensionless energy variable  $\epsilon$  for various values of the dimensionless temperature  $\tau$ . The results are independent of the coupling constant  $|\gamma|$  for values of  $|\gamma|$  as large as 0.11. The resonance peak in the  $\text{Im}t_{\text{ret}}(\epsilon, \tau)$  gets sharper with decreasing  $\tau$ , and its maximum value approaches the unitarity limit [ $\text{Im}t_{\text{ret}}(0, 0) = -1/\pi$ ] as  $\tau$  goes to zero. At  $T=0$ , the resonance peak (which has a horizontal tangent at  $\epsilon=0$  for all finite temperatures) degenerates into a cusp with an undefined derivative at  $\epsilon=0$ :

$$\lim_{\epsilon \rightarrow \pm 0} \frac{\partial}{\partial \epsilon} \text{Im}t_{\text{ret}}(\epsilon, \tau=0) = \pm \infty. \quad (3.22)$$

This behavior can be derived from the following asymptotic expression for  $t_{\text{ret}}(\epsilon, \tau=0)$ , given by MH:

$$\text{Im}t_{\text{ret}}(\epsilon, \tau=0) = -\frac{1}{2\pi\tilde{n}_0} \left[ 2 + \frac{\pi^2 S(S+1)}{2 \ln^2 \epsilon} + O\left(\frac{1}{\ln^3 |\epsilon|}\right) \right], \quad \epsilon \rightarrow 0. \quad (3.23)$$

The singularity of  $\text{Im}t_{\text{ret}}(\epsilon, \tau=0)$  at  $\epsilon=0$  is reflected in  $\text{Re}t_{\text{ret}}(\epsilon, \tau=0)$  by an infinite derivative at  $\epsilon=0$ .

To give a quantitative picture of the influence of the unimodular factor  $e^{i\theta}$  on  $\text{Re}t_{\text{ret}}$  and  $\text{Im}t_{\text{ret}}$ , we compare these functions in Figs. 4 and 5 to the real and imaginary parts of the function

$$t_{\text{ret}}^{\theta=0}(\omega, T) \equiv [2\pi i n_0(\omega)]^{-1} \times [1 - K^{-1/2}(\omega, T)X(\omega, T)], \quad (3.24)$$

which is obtained from (3.1) if the unimodular factor is replaced by unity. We should emphasize that, at  $\tau=0$ , the imaginary part of the function defined in (3.24) has the same asymptotic behavior for small  $\epsilon$  as the imaginary part of the exact ZMH solution (3.23). As the graphs show, the imaginary parts of  $t_{\text{ret}}^{\theta=0}$  and of the exact solution (3.1) differ considerably only for  $\epsilon > 1$ .

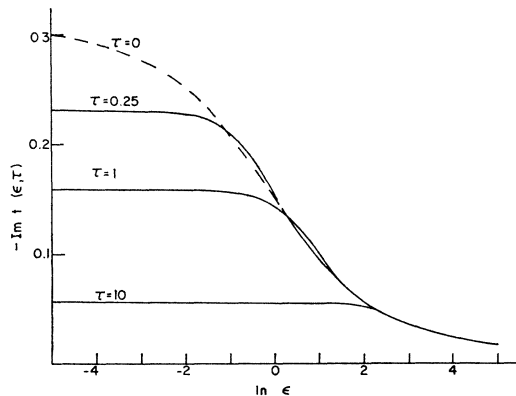


FIG. 3. The imaginary part of the scattering amplitude is shown as a function of  $\ln \epsilon$ . The unimodular factor  $e^{i\theta}$  is included in the computation of these curves. See Eq. (3.21).

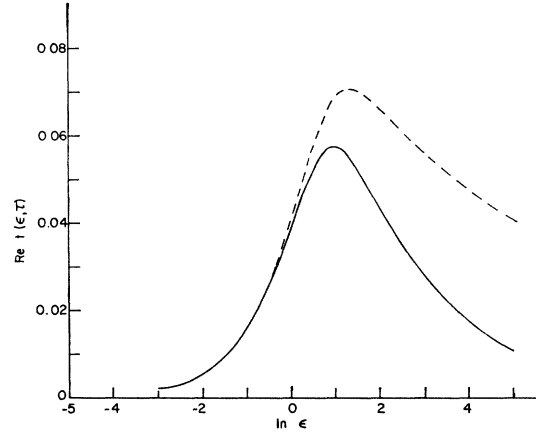


FIG. 4. Comparison of  $\text{Re}t_{\text{ret}}(\epsilon, \tau)$  with  $\text{Re}t_{\text{ret}}^{\theta=0}(\epsilon, \tau)$  for  $\tau=1$ . The dashed curve represents  $\text{Re}t_{\text{ret}}^{\theta=0}(\epsilon, \tau)$ . See Eq. (2.34).

For  $\tau=1$  the real parts of these two functions are also in fairly good agreement as long as  $\epsilon < 1$ . In view of the behavior of  $\theta(\epsilon, \tau=0)$  it is not surprising that, for  $\tau=0$ , the real parts of  $t_{\text{ret}}^{\theta=0}$  and of the exact solution differ both for  $\epsilon < 1$  and for  $\epsilon > 1$ . Nevertheless, the approximation (3.24) which has a relatively simple analytic structure may be useful for the computation of low-temperature transport properties which only depend on the value of  $\text{Im}t_{\text{ret}}(\epsilon, \tau)$  at small values of  $\epsilon$ .

#### IV. PHYSICAL QUANTITIES DIRECTLY RELATED TO THE SCATTERING AMPLITUDE

Having worked out quantitatively the details of ZMH's expression for the non-spin-flip scattering amplitude in Kondo's model, we now turn to the question of how much of the detailed structure is reflected in measurable physical quantities.

##### A. Tunneling Density of States

Since there is no way of measuring the spectral function  $\rho^{\text{alloy}}(\omega, k)$  directly, the most detailed information about the scattering amplitude that one could hope to obtain would come from a tunneling experiment. The quantity which one probes in a tunneling experiment is the density-of-state function  $n(\omega)$ . Let us, for simplicity, assume that the tunneling diode has the following structure: a pure metal on one side of an oxide layer and a dilute paramagnetic alloy of the same metal on the other side of the oxide layer. No paramagnetic ions will be assumed to be in the oxide layer itself. The conductance of such a diode can be expressed as

$$\begin{aligned} G(V) &= dI(V)/dV \\ &= 4\pi e \langle |T|^2 \rangle \frac{d}{dV} \int_{-\infty}^{\infty} d\omega n^{\text{metal}}(\omega) n^{\text{alloy}}(\omega + eV) \\ &\quad \times [f(\omega) - f(\omega + eV)]. \quad (4.1) \end{aligned}$$

Here  $4\pi\langle|T|^2\rangle$  is the average tunneling probability and  $V$  is the applied voltage [ $f(\omega)$  is the Fermi function].  $n^{\text{metal}}(\omega)$  and  $n^{\text{alloy}}(\omega)$  are the density-of-state functions of the pure metal and of the alloy, respectively. For small voltages ( $eV \ll \epsilon_F$ ),  $n^{\text{metal}}(\omega)$  can be treated as a constant. Using the expression (2.8) for the difference between the density of states of the alloy and that of the pure metal, one obtains for the relative change of conductance  $\Delta G(V) \equiv [G(V) - G(V=0)]/G(V=0)$  at zero temperature,

$$\Delta G(V) = \frac{\pi \bar{n}_0 n_i [\text{Im}t_{\text{ret}}(eV) - \text{Im}t_{\text{ret}}(0)]}{1 + \pi \bar{n}_0 n_i \text{Im}t_{\text{ret}}(0)} \simeq \pi \bar{n}_0 n_i [\text{Im}t_{\text{ret}}(eV) - \text{Im}t_{\text{ret}}(0)],$$

for  $n_i \ll 1$  (4.2)

where  $\bar{n}_0$  denotes the density of states of the pure metal. Since the impurity concentration in dilute magnetic alloys is usually small,  $n_i \simeq 10^{-3}$  or less,  $\Delta G(V)$  is a small quantity. However, for small temperatures it varies very rapidly with  $V$ . For example, at zero temperature it follows from (3.25) that

$$\frac{d}{d\omega} \text{Im}t_{\text{ret}}(\omega) \sim \frac{\pi S(S+1)}{2\bar{n}_0} \frac{1}{\omega \ln^3 \omega}, \quad \omega \rightarrow 0. \quad (4.3)$$

Thus at zero temperature the derivative of  $\Delta G(V)$  with respect to  $V$  becomes infinite as  $V$  approaches zero. For finite temperatures (but  $T \ll T_K$ ), the derivative remains finite even for  $V=0$ . The maximum value of  $d[\Delta G(V)]/dV$  occurs at  $V \sim T_K$  and is of the order  $n_i (T \ln T/T_K)^{-1}$ , so that one has to go to very low temperatures if one wants to make  $d[\Delta G(V)]/dV$  large. Nevertheless, it might be possible to detect the rapid variation of  $\Delta G(V)$  experimentally. This would, at least, give some information about the width of the resonance in the scattering amplitude.

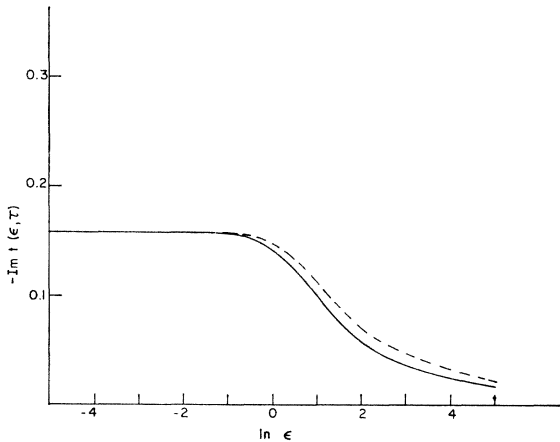


FIG. 5. Comparison of  $\text{Im}t_{\text{ret}}(\epsilon, \tau)$  with  $\text{Im}t_{\text{ret}}^{\theta=0}(\epsilon, \tau)$  for  $\tau=1$ . The dashed curve represents  $\text{Im}t_{\text{ret}}^{\theta=0}(\epsilon, \tau)$ . See Eq. (3.24).

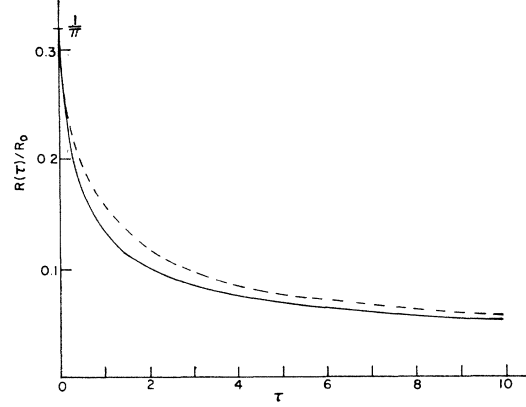


FIG. 6. Resistivity ratio  $R(\tau)/R_0$  (where  $R_0 \equiv -3Jn_i/\bar{n}_0 e^2 v_F^2$ ) is plotted as a function of  $\tau$ . The dashed curve represents the result of the approximation (4.6) in which  $R(\tau)/R_0 = -\text{Im}t_{\text{ret}}(\epsilon=0, \tau)$ . The solid curve represents  $R/R_0 = -J\bar{n}_0 v_F^2/2n_i K_0$ , where  $K_0$  is computed numerically according to Eq. (4.4).

The large anomalies in the conductance of tunneling diodes containing magnetic impurities<sup>20,21</sup> certainly cannot be explained by the change in the bulk density of states of the alloy. Other mechanisms such as scattering from impurities located inside the oxide layer are probably responsible for these effects.<sup>22</sup>

## B. Transport Properties

While a tunneling experiment, in principle, enables one to measure the density of states and hence the scattering amplitude at arbitrarily high energies, the transport coefficients depend on  $\text{Im}t_{\text{ret}}(\omega, T)$  for small values of the energy only. In general, the transport coefficients can be expressed in terms of the following integrals<sup>23</sup>:

$$K_n = - \int_{-\infty}^{\infty} d\omega v^2(\omega) \omega^n \tau_i(\omega, T) \frac{\partial f}{\partial \omega} n_0(\omega), \quad (4.4)$$

where  $n_0(\omega)$  denotes the density of states of the pure host metal as before and  $v(\omega)$  is the speed of an electron with energy  $\omega$ .

The electronic lifetime due to impurity scattering is given by the imaginary part of the scattering amplitude,

$$\tau_i^{-1}(\omega, T) = -2n_i \text{Im}t_{\text{ret}}(\omega, T). \quad (4.5)$$

Since  $\partial f(\epsilon)/\partial \epsilon$  is sharply peaked at  $\epsilon=0$ , the main contribution to the integral (4.4) comes from a narrow region around  $\epsilon=0$ . This suggests the following well-known approximation for these integrals

$$K_n \simeq \frac{\bar{n}_0 v_F^2}{2n_i \text{Im}t_{\text{ret}}(0, T)} \int_{-\infty}^{\infty} d\omega \omega^n \frac{\partial f}{\partial \omega}, \quad (4.6)$$

<sup>20</sup> A. F. G. Wyatt, Phys. Rev. Letters **13**, 401 (1964).

<sup>21</sup> J. M. Rowell and L. Y. L. Shen, Phys. Rev. Letters **17**, 15 (1966).

<sup>22</sup> J. Solyom and A. Zawadowski, Phys. Status Solidi **25**, 473 (1968).

where  $v_F$  is the Fermi velocity. This approximation is not too good, however, since at low temperature  $\text{Im}t_{\text{ret}}(\omega, T)$  is itself a rapidly varying function of  $\epsilon$ .<sup>24,25</sup> We have illustrated this in Fig. 6 using the example of the electrical resistance which is proportional to  $K_0$ . For other transport coefficients which involve integrals  $K_n$  with  $n > 0$ , such as the thermal conductivity, the approximation (4.6) is even worse. On the other hand, computation of the resistivity shows that, to a very good approximation,  $\text{Im}t_{\text{ret}}(\omega, T)$  may be replaced by  $\text{Im}t_{\text{ret}}^{\theta=0}(\omega, T)$  [see (3.27)]. We infer from this that no conclusion about the detailed structure of  $t_{\text{ret}}(\omega, T)$  can be easily drawn from a comparison of the experimental data for the transport coefficients and the theoretical expressions.

So far, we have completely neglected the normal potential scattering arising from the impurity ions. If one intends to compare the theoretical expressions for the transport coefficients with experimental results, this has certainly to be taken into account. As we shall show in some detail, the anomalous low-temperature maximum in the thermoelectric power cannot be understood even qualitatively if the scattering of the electrons from the electrostatic impurity potential is neglected.<sup>26,27</sup>

In terms of the integrals  $K_n$ , the thermoelectric power  $Q(T)$  can be expressed as

$$Q(T) = (1/eT)K_1/K_0. \quad (4.7)$$

For a band which is described by a Lorentzian density-of-state function of width  $2D$ , we find the following dispersion of the electrons for energies near the Fermi energy ( $\omega \ll D$ ):

$$v(\omega) = v_F(1 + \bar{v}\omega/D). \quad (4.8)$$

Here  $\bar{v}$  is a constant of the order of unity. As a direct consequence of the symmetry (3.7a) of  $\text{Im}t_{\text{ret}}(\omega, T)$ ,

it follows that at low temperatures

$$K_1 = O(T/D).$$

Thus  $Q(T)$  becomes small of the order  $1/D$  and independent of the temperature in contradiction to the experimental observations.<sup>28</sup> However, the symmetry (3.7a) is removed if the ordinary potential scattering is taken into account in addition to the exchange scattering.

Assuming that the electrostatic potential  $V(r)$  of the impurity can be approximated by a contact potential  $V\delta(r)$ , one can write the scattering amplitude with the inclusion of potential scattering in the form<sup>29,30</sup>

$$t_{J+V}(\omega, T) = t_V + e^{2i\delta_V} t_{\tilde{J}}(\omega, T), \quad (4.9)$$

where

$$t_V = (2i\pi\bar{n}_0)^{-1}(1 - e^{2i\delta_V}) \quad (4.10)$$

is the scattering amplitude of the electrostatic potential alone,  $\delta_V$  being the phase shift associated with it.  $\tilde{J}$  is an effective coupling constant given by

$$\tilde{J} = J \cos^2 \delta_V. \quad (4.11)$$

The expression (4.9) was derived from a more general expression for  $t_{J+V}$  developed by Schotte<sup>29</sup> under the assumption that  $\omega \ll D$  so that the band structure of the host metal is unimportant. For the computation of the integrals  $K_1$  and  $K_0$ , one needs the electronic lifetime

$$\begin{aligned} \tau_i(\omega, T) &= (2n_i)^{-1} [\text{Im}t_{J+V}(\omega, T)]^{-1} \\ &= -[2n_i]^{-1} [(2\pi\bar{n}_0)^{-1}(\cos 2\delta_V - 1) + \cos 2\delta_V \\ &\quad \times \text{Im}t_{\tilde{J}}(\omega, T) + 2 \sin 2\delta_V \text{Re}t_{\tilde{J}}(\omega, T)]^{-1}. \end{aligned} \quad (4.12)$$

For the range of energy  $|\omega| \lesssim k_B T$  for which we need  $\tau_i(\omega)$ , the phase shift of the electrostatic potential can be treated as a constant. Then  $t_{\tilde{J}}(\omega, T)$  has the same symmetry properties as  $t_{\text{ret}}(\omega, T)$ .  $\tau_i(\omega)$  can be written as the sum of an even and an odd function

$$\tau_i(\omega, T) = \tau_{i,\text{even}}(\omega, T) + \tau_{i,\text{odd}}(\omega, T),$$

where

$$\tau_{i,\text{even}}(\omega) = \frac{1}{2\bar{n}_i} \frac{(2\pi\bar{n}_0)^{-1}(\cos 2\delta_V - 1) + \cos 2\delta_V \text{Im}t_{\tilde{J}}}{[(2\pi\bar{n}_0)^{-1}(\cos 2\delta_V - 1) + \cos 2\delta_V \text{Im}t_{\tilde{J}}]^2 - [\sin 2\delta_V \text{Re}t_{\tilde{J}}]^2}, \quad (4.13)$$

$$\tau_{i,\text{odd}}(\omega) = \frac{1}{2n_i} \frac{-\sin 2\delta_V \text{Re}t_{\tilde{J}}(\omega, T)}{[(2\pi\bar{n}_0)^{-1}(\cos 2\delta_V - 1) + \cos 2\delta_V \text{Im}t_{\tilde{J}}]^2 - [\sin 2\delta_V \text{Re}t_{\tilde{J}}]^2}. \quad (4.14)$$

<sup>23</sup> See, e.g., J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 384.

<sup>24</sup> It should be emphasized that, while the approximation (4.6) for  $K_n$  is inaccurate because of the rapid variation of  $\text{Im}t_{\text{ret}}(\omega, T)$ , the usual expressions for the transport coefficients involving the integrals  $K_n$  (see Ref. 23) are still exact in spite of the strong  $\omega$  dependence of  $\text{Im}t_{\text{ret}}(\omega, T)$ .

<sup>25</sup> K. K. Murata and J. W. Wilkins, in *Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, 1968*, edited by J. F. Allan, G. M. Finlayson and D. M. McCall. (University of St. Andrews Printing Department, St. Andrews, Scotland, 1969), p. 1242.

<sup>26</sup> J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **34**, 372 (1965).

<sup>27</sup> K. Fischer, *Phys. Rev.* **158**, 613 (1967).

<sup>28</sup> D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, *Proc. Roy. Soc. (London)* **A266**, 161 (1962).

<sup>29</sup> K. D. Schotte, *Z. Physik* **212**, 467 (1968).

<sup>30</sup> Y. Nagaoka, *Progr. Theoret. Phys. (Kyoto)* **39**, 533 (1968).



We note that  $\tau_{\text{even}}$  enters in  $K_0$ , while  $\tau_{\text{odd}}$  determines  $K_1$ . We also recall that the integral  $K_0$  gives the conductivity. In the approximation (4.6), we obtain

$$K_0 \simeq -\frac{\bar{n}_0 v_F^2}{2n_i} \left( \frac{1}{2\pi\bar{n}_0} (\cos 2\delta_V - 1) + \cos 2\delta_V \text{Im} \mathcal{I}(\omega=0) \right)^{-1}. \quad (4.15)$$

Using (3.12), we can write this as

$$K_0 \simeq -\frac{\pi \bar{n}_0^2 v_F^2}{n_i} \left( 1 - \cos 2\delta_V \frac{\ln \tau}{[\ln^2 \tau + \pi^2 S(S+1)]^{1/2}} \right)^{-1}. \quad (4.16)$$

In the same approximation,  $K_1$  can be reduced to

$$K_1 \simeq -\frac{\pi \bar{n}_0^2 v_F^2}{n_i} \sin 2\delta_V \left( 1 - \cos 2\delta_V \frac{\ln \tau}{[\ln^2 \tau + \pi^2 S(S+1)]^{1/2}} \right)^{-2} [\ln^2 \tau + \pi^2 S(S+1)]^{-1/2} \int \frac{d\omega}{4k_B T} \omega \cosh^{-2} \left( \frac{\omega}{2k_B T} \right) \times (1/|\gamma|) [\text{Re} X(\omega, T) \sin \theta(\omega, T) + \text{Im} X(\omega, T) \cos \theta(\omega, T)]. \quad (4.17)$$

The integral still can not be evaluated exactly and so, as a further approximation, we set

$$\theta(\omega, T) \equiv 0, \quad (4.18)$$

which means that we adopt the approximation (3.24) for the real part of  $t_{\text{ret}}(\omega, T)$ . We are aware of the fact that this might not be a good approximation for very low temperature, where, as shown in Fig. 5,  $\theta(\omega, T)$  becomes important in determining  $\text{Re} t_{\text{ret}}(\omega, T)$ . As we shall see, the approximation (4.18) becomes also invalid at high temperatures, where perturbation theory is applicable. For temperatures of the order of the Kondo temperature, however, the approximation should not be too bad. Using (4.18), we find from (4.17) that

$$K_1 \simeq \frac{n_i}{2\bar{n}_0^2 v_F^2} k_B T \frac{\sin 2\delta_V}{[\ln^2 \tau + \pi^2 S(S+1)]^{1/2}} \quad (4.19)$$

and hence

$$Q(\tau) = -(\pi k_B / 2e) \sin 2\delta_V q(\tau), \quad (4.20)$$

where

$$q(\tau) \equiv \{[\ln^2 \tau + \pi^2 S(S+1)]^{1/2} - \cos 2\delta_V \ln \tau\}^{-1}. \quad (4.21)$$

$q(\tau)$  is plotted in Fig. 7 as a function of  $\tau$ . From (4.19), one can see that the sign and the magnitude of the thermoelectric power depend on the sign and the magnitude of the phase shift  $\delta_V$  through the factor  $\sin 2\delta_V$ . The same dependence of  $Q(\tau)$  on  $\delta_V$  was found by Fischer,<sup>27</sup> who calculated the thermoelectric power in perturbation theory. In the high- and low-temperature limits ( $|\ln \tau| \gg 1$ ),  $Q(\tau)$  reduces to

$$Q(\tau) \sim -(\pi k_B / 2e) \sin 2\delta_V (\ln \tau)^{-1}. \quad (4.22)$$

In the high-temperature limit, (4.22) should agree with the perturbative expression for  $Q(\tau)$  obtained

by Fischer<sup>27</sup> and Kondo.<sup>31</sup> By expanding

$$(\ln \tau)^{-1} \simeq -\frac{\gamma}{1 - \gamma \ln(T/D)}$$

in powers of  $\gamma$ , we find, in this limit,

$$Q_{\text{pert}}(\tau) = (\pi \gamma k_B / 2e) \sin 2\delta_V [1 + \gamma \ln(T/D)]. \quad (4.23)$$

In contrast to this, Fischer and Kondo found

$$Q_{\text{pert}}(\tau) \propto \gamma^3.$$

This failure of (4.22) to reproduce the correct perturbative result for  $Q(\tau)$  is due to the approximation (4.19).

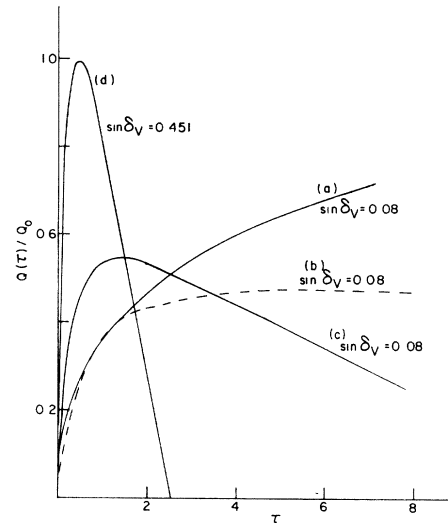


FIG. 7. Thermoelectric power ratio  $Q(\tau)/Q_0$  [where  $Q_0 \equiv -(\pi k_B / 2e) \sin 2\delta_V$ ] is shown as a function of  $\tau$ . Curves (a) and (b) corresponds to the approximation in Eq. (4.20) and Maki's result given by Eq. (4.26), respectively. Curves (c) and (d) are obtained by computing  $K_0$  and  $K_1$  numerically.

<sup>31</sup> J. Kondo, Progr. Theoret. Phys. (Kyoto) **40**, 695 (1968).

In the limits  $\ln\tau \rightarrow \pm\infty$ , the integrals  $K_0$  and  $K_1$  can be evaluated exactly. The results are given in Appendix A [(A14) and (A15)]. Using these expressions, one obtains the following exact asymptotic expressions for the thermoelectric power:

$$Q(\tau) = \frac{\pi k_B}{2e} \frac{\sin 2\delta_V}{1 + \cos 2\delta_V} \frac{\pi^2 S(S+1)}{|\ln\tau|^3} \times \left[ 1 + \frac{\cos 2\delta_V}{1 + \cos 2\delta_V} \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right], \quad \tau \rightarrow 0 \quad (4.24)$$

and

$$Q(\tau) = \frac{\pi k_B}{2e} \frac{\sin 2\delta_V}{1 - \cos 2\delta_V} \frac{\pi^2 S(S+1)}{|\ln\tau|^3} \times \left[ 1 - \frac{\cos 2\delta_V}{1 - \cos 2\delta_V} \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right], \quad \tau \rightarrow \infty. \quad (4.25)$$

Since

$$|\ln\tau|^{-3} = |\gamma|^{-3} \{1 + O[\gamma \ln(T/D)]\},$$

the high-temperature expansion of  $Q(\tau)$  clearly agrees with perturbation theory. We note that the asymptotic expansion (4.25) is meaningful only if

$$\frac{\cos 2\delta_V}{1 - \cos 2\delta_V} \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} \ll 1.$$

For small values of the phase shift  $\delta_V$ , this requires very large values of  $\tau$ .

In a very recent publication, using the solution of Hamann and Bloomfield for the scattering amplitude and making the same approximation that led us to (4.20), Maki<sup>32</sup> obtained the following expression for the thermoelectric power<sup>33</sup>:

$$Q_{\text{Maki}}(\tau) = \frac{\pi k_B}{2e} \frac{\sin 2\delta_V}{[\ln^2 \tau + \pi^2 \delta(S+1)]^{1/2} - \cos 2\delta_V \ln \tau} \times \frac{\pi^2 S(S+1)}{\ln^2 \tau + \pi^2 S(S+1)}. \quad (4.26)$$

In the two limits  $\ln\tau \rightarrow \pm\infty$ , this expression agrees with the exact expansions (4.24) and (4.25). For temperatures such that

$$\ln^2 \tau \lesssim \pi^2 S(S+1),$$

the factor

$$\pi^2 S(S+1) / [\ln^2 \tau + \pi^2 S(S+1)]$$

by which Maki's expression differs from our approximate result (4.20) is nearly unity. In particular, at the

Kondo temperature the expressions (4.20) and (4.26) are identical. We have plotted the functions (4.20) and (4.26) in Fig. 7. Experimentally, a fairly sharp extremum of the thermoelectric power is observed near the Kondo temperature.<sup>28,34</sup> It is evident that the functions (4.20) and (4.26) *do not* exhibit this extremum. In order to avoid the approximation (4.6), we have evaluated numerically the integrals  $K_0$  and  $K_1$  in (4.7), using the complete expressions  $t\bar{\gamma}$  for two values of the phase shift due to normal potential scattering,  $\sin\delta_V = 0.08$  and  $0.45$ . These results are included in Fig. 7. It can be seen that  $Q(\tau)$  is very sensitive to the phase shift considered.  $|Q(\tau)|$  attains a maximum near  $T_K$  and decreases at higher temperatures. These features are in agreement with experiment and with earlier numerical calculations by Suhl and Wong.<sup>35</sup>

We should note that the thermoelectric power we have computed is independent of the impurity concentration. The impurity concentration is a multiplicative factor in both  $K_0$  and  $K_1$ , and consequently cancels out. However, at temperatures higher than the Kondo temperature, the scattering of electrons from phonons becomes comparable to, and possibly more important than scattering from impurities. Consequently, the integrals  $K_1$  and  $K_0$  in (4.7) have to be computed with the total electronic lifetime

$$1/\tau_{\text{tot}} = 1/\tau_i + 1/\tau_{\text{ph}} \quad (4.27)$$

rather than  $\tau_i$  from (4.12) alone. Since  $\tau_{\text{ph}}(\tau_i)$  is independent (dependent) on the impurity concentration, the resultant thermoelectric power will depend on the impurity concentration in general. In the limits, however,

$$1/\tau_i \gg 1/\tau_{\text{ph}} \quad (4.28a)$$

and

$$1/\tau_{\text{ph}} \gg 1/\tau_i. \quad (4.28b)$$

$Q(\tau)$  will become concentration independent. The former situation is realized at temperatures  $\tau \lesssim 1$ . The latter condition holds true already for temperatures much less than the Debye temperature and, in this case, the thermoelectric power approaches that of a pure metal,  $Q_{\text{metal}}$ .  $Q_{\text{metal}}$  is usually at least an order of magnitude smaller than that of the alloy near the Kondo temperature.

In summarizing the discussion of the transport coefficients, one can say that they do not provide information about the detailed structure of the Kondo resonance as it was worked out in Sec. III. Just as in the case of the density of states, the best one can hope for is some information about the width of the resonance. In addition, we have seen that measurements of the thermoelectric power allow one to indirectly draw some conclusions about the electrostatic potential associated with a paramagnetic impurity in a metal.

<sup>32</sup> K. Maki, Progr. Theoret. Phys. (Kyoto) **41**, 586 (1969).

<sup>33</sup> The negative sign in Maki's expression is erroneous (private communication).

<sup>34</sup> M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. **40**, 380 (1968).

<sup>35</sup> H. Suhl and D. Wong, Physics **3**, 17 (1967).

### C. de Haas-van Alphen Effect

Several authors<sup>36,37</sup> have interpreted the observed field and temperature dependence of the damping of the de Haas-van Alphen oscillations in dilute magnetic alloys in terms of the electronic lifetime  $\tau(\omega, T)$  [see (4.5)]. Their approach was to take Dingle's<sup>38</sup> expression for the periodic part of the free energy of the alloy in an external magnetic field and to replace the electronic lifetime  $\tau$ , which in Dingle's paper is treated as a constant, by the energy- and temperature-dependent lifetime that results from the  $s$ - $d$  exchange interaction. The effect of the magnetic field on the  $s$ - $d$  scattering amplitude is neglected, however.

We feel that such a procedure is not firmly based on theoretical arguments. A rederivation of Dingle's expression for the periodic part of the free energy by Brailsford<sup>39</sup> shows that it is not necessary to assume that the electronic lifetime is a constant. The electronic excitation spectrum however, must have the characteristic features of a quasiparticle spectrum, i.e., near the Fermi energy, the electronic self-energy  $\Sigma(\omega)$  must be a slowly varying function of  $\omega$ . As we have shown in Secs. II and III of this paper, this is not the case for the Kondo model.  $\Sigma(\omega)$  is a rapidly varying function of  $\omega$  near  $\omega = 0$  and the quasiparticle picture does not apply. Furthermore, it is questionable whether it is a good approximation to neglect the influence of the magnetic field on the  $s$ - $d$  scattering mechanism. The magnetic fields applied in the experiments which are reported in Refs. 36 and 37 range 2–5 kOe and the temperatures at which the measurements were carried out range 1–5°K, so that for the extreme values  $T = 1^\circ\text{K}$  and  $H = 5$  kOe we have

$$\mu_B H \simeq \frac{1}{2} k_B T.$$

Thus, in this case, the magnetic energy is of the same order of magnitude as the thermal energy and certainly not negligible.

It appears that a more careful theoretical consideration of these points is necessary before conclusions about the scattering mechanism can be drawn from the observed field- and temperature-dependent damping of the de Haas-van Alphen oscillations in dilute magnetic alloys.

### D. Specific Heat

It has been shown by several authors<sup>12,13,40</sup> that the anomaly in the electronic specific heat which is observed in dilute magnetic alloys can be attributed to the resonant scattering of the electrons from magnetic impurities. In terms of the change in the density of states  $\Delta n(\omega)$  discussed in Sec. II, the incremental

specific heat can be expressed by the well-known exact formula

$$\Delta C(T) = \frac{\partial}{\partial T} \int_{-\infty}^{\infty} \Delta n(\omega, T) \omega f(\omega) d\omega, \quad (4.29)$$

where the integral represents the incremental internal energy of the system due to the interaction with impurities. It is suggestive to split  $\Delta C(T)$  in the following two contributions:

$$\Delta C_n(T) = \int_{-\infty}^{\infty} d\omega \Delta n(\omega, T) \omega \frac{\partial f}{\partial \omega}, \quad (4.30)$$

$$\Delta C_a(T) = \int_{-\infty}^{\infty} d\omega \left( \frac{\partial}{\partial T} \Delta n(\omega, T) \right) \omega f(\omega). \quad (4.31)$$

Henceforth we shall call  $\Delta C_n$  and  $\Delta C_a$  the normal and the anomalous contribution to the specific heat. We recall that for an electron gas interacting with normal nonmagnetic impurities the change in the density of states  $\Delta n(\omega, T)$  is temperature-independent, so that there is no contribution to the specific heat from the derivative of  $\Delta n(\omega, T)$  with respect to the temperature.

In what follows we shall examine  $\Delta C_n(T)$  and  $\Delta C_a(T)$ , given by (4.30) and (4.31), using the expression (2.8) for  $\Delta n(\omega, T)$ . ZMH and Brenig and Götze<sup>40</sup> developed an elegant way of singling out the important contribution to the specific heat. They were able to relate the internal energy of the system to the coefficients of the asymptotic expansion of  $t_{\text{ret}}(\omega, T)$  for large  $\omega$ . Nevertheless, we find it worthwhile to discuss the integrals (4.30) and (4.31) directly. We will show that, in contrast to all other quantities which we have discussed so far in this section, the specific heat depends crucially on the presence of the unimodular factor  $e^{i\theta}$  and on the temperature dependence of the function  $A(T)$  in the ZMH expression for the scattering amplitude  $t_{\text{ret}}(\omega, T)$ .

Let us first consider the normal contribution to the specific heat. Because of the factor  $\partial f / \partial T$  in the integrand of (4.30),  $\Delta n(\omega, T)$  is only needed in the energy interval  $|\omega| \lesssim k_B T$ . Thus it is sufficient to work with the approximate expression (2.9) for  $\Delta n(\omega, T)$ , with the result

$$\Delta C_n(T) = n_i \bar{n}_0^2 \int d\omega \omega \text{Im} t_{\text{ret}}(\omega) \frac{\partial f}{\partial T}. \quad (4.32)$$

Introducing the dimensionless variables  $\epsilon$  and  $\tau$  again, we can write this as

$$\Delta C_n(T) = n_i \bar{n}_0^2 k_B T_K \int d\epsilon \epsilon \text{Im} t_{\text{ret}}(\epsilon, \tau) \frac{\partial f(\epsilon, \tau)}{\partial \tau}, \quad (4.33)$$

where

$$f(\epsilon, \tau) \equiv [\exp(\epsilon/\tau) + 1]^{-1}.$$

With (2.10), we then can give the following estimate for  $\Delta C_n(\tau)$

$$\begin{aligned} \Delta C_n(\tau) &\leq \frac{1}{3} n_i \bar{n}_0 k_B^2 T_K \tau \\ &\leq n_i n_0 k_B^2 T. \end{aligned} \quad (4.34)$$

<sup>36</sup> E. B. Paton and W. B. Muir, Phys. Rev. Letters **20**, 732 (1968).

<sup>37</sup> H. Nagasawa, Solid State Commun. **7**, 259 (1969).

<sup>38</sup> R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 517 (1952).

<sup>39</sup> A. D. Brailsford, Phys. Rev. **149**, 456 (1966).

<sup>40</sup> W. Brenig and W. Götze, Z. Physik. **217**, 188 (1968).

Thus  $\Delta C_n(\tau)$  goes to zero at least as fast as  $T$ . Compared to the specific heat of the free-electron gas

$$C_{\text{free el}} = \frac{1}{3}n_0k_B^2T.$$

$\Delta C_n$  is small because of the concentration factor  $n_i$ . It is possible to separate  $\Delta C_n$  from the measured total specific heat of the alloy but this is not very interesting.

At this point, it is necessary to define more precisely what type of contribution to the specific heat we consider to be typical for the Kondo effect. Looking at the first line of (4.34), we see that, for fixed  $\tau$ ,  $\Delta C_n$  vanishes in the limit  $\gamma \rightarrow 0$ . In contrast to this, there are quantities which, in the same limiting process, remain finite. An example of this is the thermoelectric power as given by Eq. (4.18). As was pointed out by MH, the latter type of behavior is typical for physical quantities which show Kondo anomalies. It may, in fact, be used to characterize a Kondo anomaly in any physical quantity.

Following ZMH, we shall now search for a contribution to  $\Delta C_a$  which remains finite in the limiting process described above and disregard all contributions which vanish like  $\Delta C_n$  in the limit  $\gamma \rightarrow 0$ . Using the expression (2.8) for  $\Delta n(\omega, T)$ , we have

$$\begin{aligned} \Delta C_a(T) &= n_i \bar{n}_0^2 \int_{-\infty}^{\infty} d\omega \omega \rho^2(\omega) \left[ \frac{2\omega}{D} \left( \frac{\partial}{\partial T} \text{Re} t_{\text{ret}}(\omega, T) \right) \right. \\ &\quad \left. + \left( 1 - \frac{\omega^2}{D^2} \right) \left( \frac{\partial}{\partial T} \text{Im} t_{\text{ret}}(\omega, T) \right) \right] f(\omega), \\ &\equiv n_i (I^{\text{Re}} + I^{\text{Im}}). \end{aligned} \quad (4.35)$$

As we show in Appendix B, the contribution from the second term in the integrand vanishes as  $\gamma$  goes to zero. The important anomalous contribution comes from the first term. Since the first term contains a factor  $(\omega/D)$ , this means that the anomalous contribution arises from the behavior of  $\text{Re} t_{\text{ret}}(\omega, T)$  at energies of the order of  $D$  and is not directly related to the resonance structure in  $t_{\text{ret}}(\omega, T)$ . The latter is confined to the energy region  $|\omega| \lesssim K_B T_K$ . As the calculations in Appendix B show, the part of  $\Delta C_a$  which remains finite (in the limit  $\gamma \rightarrow 0$ ) is proportional to the derivative of  $A(T)$  with respect to  $T$

$$\Delta C_a(T) = n_i \pi \gamma^2 D (\partial A / \partial T). \quad (4.36)$$

This clearly indicates the importance of the function  $A(T)$  in the ZMH forward-scattering amplitude. The fact that we did not find any temperature variation in  $A(T)$  in our numerical calculation of  $A(T)$  does not mean that  $\Delta C_a(T)$  as given by (4.36) is small. The large factor  $D$  makes up for the smallness of  $\partial A / \partial T$  which, as Eq. (B20) shows, is of the order  $D^{-1}$ . The derivation of (4.36) in Appendix B also shows clearly that, as was first pointed out by Hamann and Bloomfield, the presence of the unimodular factor in the exact solution

is closely related to the occurrence of an anomalous contribution to the specific heat.

From the expression (B20) for  $(\pi\gamma)^2 D \partial A / \partial T$ , Eq. (4.36) may be written in the form

$$\Delta C_a(\tau) = \frac{n_i k_B}{2\pi^2} \int_{-\infty}^{\infty} d\epsilon \frac{(\partial / \partial \tau) |Y(\epsilon, \tau)|^2}{|Y(\epsilon, \tau)|^2 + \pi^2 S(S+1)}. \quad (4.37)$$

This agrees with the results found by ZMH as well as by Brenig and Götze.  $\Delta C_a(\tau)$  is evidently independent of the coupling constant.

Integrating  $\Delta C_a(\tau)$  with respect to temperature, we can find that portion of the total internal energy the temperature variation of which is responsible for the occurrence of the anomalous contribution to the specific heat

$$\begin{aligned} E_a(T_0) &= \int_0^{T_0} \Delta C_a(\tau) dT \\ &= T_K \int_0^{T_0} \Delta C_a(\tau) d\tau. \end{aligned} \quad (4.38)$$

The integral in (4.30) is a dimensionless quantity of the order of unity. Thus the magnitude of  $E_{\text{anom}}(T_0)$  is governed by  $k_B T_K = D e^{1/\gamma}$ . On the other hand, there are certainly perturbative contributions to the total internal energy which are of the order  $\gamma^2 D$ . For small  $\gamma$ , these are much larger than  $E_{\text{anom}}(T_0)$ . Any attempt to first compute the total internal energy of the system and to obtain the specific heat by differentiating the result with respect to temperature appears to be hopeless.

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## APPENDIX A

Introducing the variable  $x = \frac{1}{2}\beta\omega$ , we can write the integrals  $K_n$  in the form

$$K_n = \frac{1}{2} v_F^2 \bar{n}_0 \left( \frac{2}{\beta} \right)^n \int_{-\infty}^{\infty} dx x^n \tau_i(x, \tau) \cosh^{-2} x. \quad (A1)$$

Here we have assumed that  $v(\omega)$  and  $n_0(\omega)$  can be treated as constants and have replaced them by their values at the Fermi energy. Because of the factor  $\cosh^{-2} x$  in the integrand of (A1), the electron lifetime  $\tau_i$  is important in the interval  $|x| \lesssim 1$  only. To obtain the asymptotic behavior of  $K_0$  and  $K_1$  in the limits  $\ln \tau \rightarrow \pm \infty$ , it is therefore sufficient to derive an asymptotic expansion for  $\tau_i$  which holds for all  $x$  such

that  $|x| \lesssim 1$ . The most convenient starting point for such an expansion is the following expression for the scattering amplitude which can be derived from (3.1) by a mathematical transformation (see MH)

$$t_{\text{ret}}(x, \tau) = (2i\pi\bar{n}_0)^{-1} [1 - s(x, \tau)]. \quad (\text{A2})$$

where

$$s(x, \tau) = \frac{|Y(\epsilon, \tau)|}{[|Y(\epsilon, \tau)|^2 + \pi^2 S(S+1)]^{1/2}} \frac{x - ix_0}{x + ix_0} \times \exp \left[ \frac{i}{2\pi} P \int_{-\infty}^{\infty} \frac{dx'}{x - x'} \ln \left( \frac{|Y(x', \tau)|^2}{|Y(x', \tau)|^2 + \pi^2 S(S+1)} \right) \right], \quad (\text{A3})$$

in which

$$Y(x, \tau) = \ln \tau + g(x), \quad g(x) = \psi(\frac{1}{2} - ix/\pi) - \psi(\frac{1}{2}) \quad (\text{A4})$$

is the dimensionless function defined in (3.12). Here  $ix_0$  is the solution of the equation

$$Y(x, \tau) = 0, \quad \tau < 1 \quad (\text{A5})$$

and it is zero otherwise. It is easy to verify that in the limit of  $\tau$  going to zero

$$x_0(\tau) = 1/\tau + O(\tau). \quad (\text{A6})$$

The following two asymptotic expressions are immediate consequences of (A4) and (A6)

$$\frac{Y(x, \tau)}{[|Y(x, \tau)|^2 + \pi^2 S(S+1)]^{1/2}} \frac{x - ix_0}{x + ix_0} = - \left[ 1 - \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right] [1 + 2ix\tau - O(x^2\tau^2)], \quad \tau \rightarrow 0 \quad (\text{A7})$$

$$\frac{Y(x, \tau)}{[|Y(x, \tau)|^2 + \pi^2 S(S+1)]^{1/2}} \frac{x - ix_0}{x + ix_0} = 1 - \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right), \quad \tau \rightarrow \infty. \quad (\text{A8})$$

The principal-value integral in the argument of the exponential in (A3) can be expanded as follows:

$$P \int_{-\infty}^{\infty} \ln \left( \frac{|Y(x', \tau)|^2}{|Y(x', \tau)|^2 + \pi^2 S(S+1)} \right) \frac{dx'}{x - x'} = -\pi^2 \frac{\pi^2 S(S+1)}{\ln^3 \tau} \tanh x + O\left(\frac{1}{\ln^4 \tau}\right), \quad \ln \tau \rightarrow \pm \infty. \quad (\text{A9})$$

To obtain this expansion, we have made use of the analyticity of  $g(x)$  in the upper half of the complex  $x$  plane. Combining the results (A7)–(A9), we find the following asymptotic expansions for  $\text{Re}t_{\text{ret}}$  and  $\text{Im}t_{\text{ret}}$ :

$$\text{Re}t_{\text{ret}}(x, \tau) = \frac{1}{2\pi\bar{n}_0} \frac{\pi^2 S(S+1)}{|\ln \tau|^3} \left[ 1 - \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right] \frac{1}{2} \pi \tanh x, \quad \ln \tau \rightarrow \pm \infty \quad (\text{A10})$$

$$\text{Im}t_{\text{ret}}(x, \tau) = -\frac{1}{2\pi\bar{n}_0} \begin{cases} \left[ 2 - \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right], & \tau \rightarrow 0 \\ \left[ \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} - O\left(\frac{1}{\ln^3 \tau}\right) \right], & \tau \rightarrow \infty \end{cases}. \quad (\text{A11})$$

Inserting these expansions into (4.13) and (4.14), we obtain asymptotic expansions for the even and odd parts of the electronic lifetime

$$\tau_{i, \text{even}} = \frac{\pi\bar{n}_0}{n_i} \begin{cases} \frac{1}{1 + \cos 2\delta_V} \left[ 1 + \frac{\cos 2\delta_V}{1 + \cos 2\delta_V} \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right], & \tau \rightarrow 0 \\ \frac{1}{1 - \cos 2\delta_V} \left[ 1 - \frac{\cos 2\delta_V}{1 - \cos 2\delta_V} \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right], & \tau \rightarrow \infty \end{cases}, \quad (\text{A12})$$

$$\tau_{i, \text{odd}} = \frac{n_i}{\pi\bar{n}_0} \sin 2\delta_V \frac{\pi^2 S(S+1)}{|\ln \tau|^3} \frac{1}{2} \pi \tanh x \tau_{i, \text{even}}, \quad \ln \tau \rightarrow \pm \infty. \quad (\text{A13})$$

In (A13) the appropriate asymptotic expressions for  $\tau_{i, \text{even}}$  given in (A12) have to be inserted. Finally, we obtain

for  $K_0$  and  $K_1$ ,

$$K_0 = \pi v_F^2 \frac{\bar{n}_0^2}{n_i} \begin{cases} \frac{1}{1 + \cos 2\delta_V} \left[ 1 + \frac{\cos 2\delta_V}{1 + \cos 2\delta_V} \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right], & \tau \rightarrow 0 \\ \frac{1}{1 - \cos 2\delta_V} \left[ 1 - \frac{\cos 2\delta_V}{1 - \cos 2\delta_V} \frac{\pi^2 S(S+1)}{2 \ln^2 \tau} + O\left(\frac{1}{\ln^3 \tau}\right) \right], & \tau \rightarrow \infty \end{cases}, \quad (\text{A14})$$

$$K_1 = \frac{1}{2} \pi k_B T \frac{n_i}{v_F^2 \bar{n}_0^2} \sin 2\delta_V \frac{\pi^2 S(S+1)}{|\ln \tau|^3} \left( 1 - \frac{1}{2} \frac{\pi^2 S(S+1)}{\ln^2 \tau} \right) K_0^2, \quad \ln \tau \rightarrow \pm \infty. \quad (\text{A15})$$

### APPENDIX B

To evaluate the anomalous part of the specific heat given by (4.35), we must compute two integrals. To begin with, we consider the integral

$$I^{1m} \equiv \bar{n}_0^2 \int_{-\infty}^{\infty} d\omega \omega \rho^2(\omega) \left( 1 - \frac{\omega^2}{D^2} \right) \times \frac{\partial}{\partial T} \text{Im} t_{\text{ret}}(\omega, T) f(\omega). \quad (\text{B1})$$

Taking the temperature derivative of  $\text{Im} t_{\text{ret}}(\omega, T)$  as given by (3.4), one gets a variety of terms. It is convenient to regroup them in the following way:

$$I^{1m} = I_1^{1m} + I_2^{1m} + I_3^{1m}, \quad (\text{B2})$$

where

$$I_1^{1m} = -\frac{\bar{n}_0}{2\pi} \int_{-\infty}^{\infty} d\omega \omega \rho(\omega) \left( 1 - \frac{\omega^2}{D^2} \right) K^{-1/2} \times \left\{ \left[ \left( 1 - \frac{(\text{Re}X)^2}{K} \right) \cos \theta + \frac{\text{Re}X \text{Im}X}{K} \sin \theta \right] \frac{\partial X}{\partial T} \Big|_A - \left[ \frac{\text{Im}X \text{Re}X}{K} \cos \theta + \left( 1 - \frac{(\text{Im}X)^2}{K} \right) \sin \theta \right] \times \text{Im} \frac{\partial X}{\partial T} \right\} f(\omega). \quad (\text{B3})$$

The symbol  $\partial X / \partial T|_A$  means that  $A$  is considered as a constant in the differentiation,

$$I_2^{1m} = -\frac{\bar{n}_0}{2\pi} (\pi\gamma)^2 \frac{\partial A}{\partial T} \int_{-\infty}^{\infty} d\omega \omega \rho^2(\omega) K^{-1/2} \times \left[ \left( 1 - \frac{(\text{Re}X)^2}{K} \right) \cos \theta + \frac{\text{Re}X \text{Im}X}{K} \sin \theta \right] f(\omega) \quad (\text{B4})$$

$$|I_1^{1m}| \equiv \frac{\bar{n}_0}{2\pi} \left| \int_{-\infty}^{\infty} d\omega \omega \rho(\omega) \left( 1 - \frac{\omega^2}{D^2} \right) \left[ \left( 1 - \frac{(\text{Re}X)^2}{K} \right) \cos \theta + \frac{\text{Re}X \text{Im}X}{K} \sin \theta \right] \text{Re} \frac{\partial X}{\partial T} \Big|_A f(\omega) \right| \leq c \frac{\bar{n}_0}{2\pi} \left[ \int_0^{\omega_c} d\omega \omega \left| K^{-1/2} \text{Re} \frac{\partial X}{\partial T} \Big|_A \right| + \int_{\omega_c}^{\infty} d\omega \omega \left| K^{-1/2} \text{Re} \frac{\partial X}{\partial T} \Big|_A (\gamma \rho(\omega) + \gamma^2 \rho^2(\omega)) \right| \right]. \quad (\text{B11})$$

and

$$I_3^{1m} = -\frac{\bar{n}_0}{2\pi} \int_{-\infty}^{\infty} d\omega \omega \rho(\omega) \left( 1 - \frac{\omega^2}{D^2} \right) \frac{\text{Im}(X e^{i\theta})}{K^{1/2}} \times \left( \frac{\partial \theta}{\partial T} \Big|_A + \frac{\partial A}{\partial T} \frac{\partial \theta}{\partial A} \right) f(\omega). \quad (\text{B5})$$

We shall show that these integrals vanish in the limit  $\gamma \rightarrow 0$  at any fixed value of  $\tau$ , which is less than a certain upper limit (see B7). Starting with  $I_1^{1m}$ , we first notice that

$$\partial \text{Im} X(\omega, T) / \partial T = \gamma \frac{1}{2} \pi (\partial / \partial T) \tanh \frac{1}{2} \beta \omega \quad (\text{B6})$$

decays exponentially for  $|\omega| \gg k_B T$ . Using this, one can easily show that the third term in the integrand of  $I_1^{1m}$  behaves like  $\Delta C_n$  as a function of temperature (see main text). It is therefore negligible. To estimate the other two terms, we need upper bounds for the functions  $|( \text{Re}X )^2 / K - 1|$  and  $|(\text{Re}X)(\text{Im}X) / K|$ . We adopt the procedure of ZMH and limit the temperature by

$$k_B T \leq D^\alpha (k_B T_K)^{1-\alpha} \quad (0 < \alpha < \frac{1}{2}). \quad (\text{B7})$$

Then we consider these functions in two intervals, namely,  $|\omega| \leq \omega_c$  and  $|\omega| > \omega_c$ , where

$$\omega_c = D^{(1-\alpha)} (k_B T_K)^\alpha. \quad (\text{B8})$$

Omitting the details, we merely state the upper bounds that we have found.

(i)  $|\omega| \leq \omega_c$ :

$$|(\text{Re}X)^2 / K - 1| \leq 1, \quad (\text{B9a})$$

$$|\text{Re}X \text{Im}X / K| \leq c. \quad (\text{B9b})$$

(ii)  $|\omega| > \omega_c$ :

$$|(\text{Re}X)^2 / K - 1| \leq c \gamma^2 \rho^2(\omega), \quad (\text{B10a})$$

$$|\text{Re}X \text{Im}X / K| \leq c |\gamma| \rho. \quad (\text{B10b})$$

In these estimates,  $c$  is a constant of order unity which is independent of  $\gamma$ . Using these bounds, we have

Now

$$K^{-1/2}(\omega) \leq 1/|\gamma|, \quad \omega \leq \omega_c \quad (\text{B12a})$$

$$K^{-1/2}(\omega) \leq c, \quad \omega > \omega_c. \quad (\text{B12b})$$

Furthermore, using the asymptotic expansion for  $\psi(\frac{1}{2}+z)$  and  $d[\psi(\frac{1}{2}+z)]/dz$ , one finds the following bounds for  $\text{Re}(\partial X/\partial T|_A)$  (see Ref. 13, Appendix C).

(i)  $\omega \leq \omega_c$ :

$$\left| \frac{\partial \text{Re}X}{\partial T} \Big|_A \right| \leq \gamma \frac{1}{T} \left[ \left| 1 - \frac{\beta\omega}{2\pi} \frac{d}{d(\beta\omega/2\pi)} \text{Re}\psi\left(\frac{1}{2} - i\frac{\beta\omega}{2\pi}\right) \right| + \frac{1}{12} \left(\frac{2\pi}{\beta D}\right)^2 \right]. \quad (\text{B13a})$$

(ii)  $\omega > \omega_c$ :

$$\left| \frac{\partial \text{Re}X}{\partial T} \Big|_A \right| \leq \frac{1}{6} \frac{|\gamma| \rho(\omega)}{T} \left(\frac{2\pi}{\beta D}\right)^2. \quad (\text{B13b})$$

Using (B12a), we obtain

$$\int_0^{\omega_c} d\omega \omega \left| K^{-1/2} \frac{\partial \text{Re}X}{\partial T} \Big|_A \right| \leq c_1 k_B^2 \tau T_K \times \left[ |\ln \tau| + \ln\left(\frac{D}{k_B T_K}\right) + \left(\frac{k_B T_K}{D}\right)^{2\alpha} + c_2 \right], \quad (\text{B14a})$$

and from (B12b) and (B13b),

$$\int_{\omega_c}^{\infty} d\omega \omega \left| K^{-1/2} \text{Re} \frac{\partial X}{\partial T} \Big|_A \right| |\gamma \rho(\omega) + \gamma^2 \rho^2(\omega)| \leq c k_B^2 \tau T_K |\gamma|^2 (1 + |\gamma|). \quad (\text{B14b})$$

Since  $n_0 = \pi/D$ , it follows that

$$|\bar{I}_1^{1m}| = c_1 k_B \tau \frac{k_B T_K}{D} \left( |\ln \tau| + \ln \frac{D}{k_B T_K} + c_2 + |\gamma|^2 + |\gamma|^3 \right). \quad (\text{B15})$$

In the limit  $|\gamma| \rightarrow 0$ ,  $\tau$  fixed, this vanishes obviously.  $\bar{I}_1^{1m}$  differs from  $I_1^{1m}$  by their term in the integrand of  $I_1^{1m}$  which we have already shown to be negligible. Thus (B15) completes the proof that  $I_1^{1m}$  does not contain a Kondo-type anomalous term.

To estimate the integral  $I_2^{1m}$ , we make use of the bounds (B9a)–(B10b), (B12a) and (B12b). We obtain

$$|I_2^{1m}| \leq c(\bar{n}_0/2\pi)(\pi\gamma)^2(\partial A/\partial T) \times [\omega_c^2/|\gamma| + |\gamma|D^2(1+|\gamma|)]. \quad (\text{B16})$$

To obtain  $\partial A/\partial T$ , we differentiate the condition (3.5b) and solve for  $\partial A/\partial T$ . This yields

$$(\pi\gamma)^2 \frac{\partial A}{\partial T} = \int_{-\infty}^{\infty} d\omega \frac{1}{K(\omega, T)} \left[ \text{Re} \left( X \frac{\partial X}{\partial T} \right) + \text{Im} \left( X \frac{\partial X}{\partial T} \right) \right] / \int_{-\infty}^{\infty} d\omega \rho(\omega) \frac{\text{Re}X(\omega, T)}{K(\omega, T)}. \quad (\text{B17})$$

The integrals involved in this expression have been estimated in Ref. 13, Appendix C. Neglecting terms which vanish in the limit  $\gamma \rightarrow 0$ , one finds

$$(\pi\gamma)^2 \frac{\partial A}{\partial T} = \frac{k_B}{2\pi D} \int_{-\infty}^{\infty} d\epsilon \frac{(\partial/\partial\tau) |Y(\epsilon, \tau)|^2}{|Y(\epsilon, \tau)|^2 + \pi^2 S(S+1)}, \quad (\text{B18})$$

where  $y(\epsilon, \tau)$  is the dimensionless function defined in (3.12). Evidently  $(\pi\gamma)^2 \partial A/\partial T$  remains finite in the limit  $\gamma \rightarrow 0$  at fixed  $\tau$ . From (B17) and (B18), it follows that its magnitude is of order  $1/D$ . Therefore

$$\lim_{|\gamma| \rightarrow 0} I_2^{1m} \leq \lim_{|\gamma| \rightarrow 0} c(\pi\gamma)^2 \left( \frac{1}{|\gamma|(\beta k D)^{2\alpha}} + |\gamma| + |\gamma|^2 \right) = 0. \quad (\text{B19})$$

Using the definition (3.4) for  $\theta$ , the integral  $I_3^{1m}$  can be written

$$I_3^{1m} = \frac{\bar{n}_0}{2\pi} \int_{-\infty}^{\infty} d\omega \omega \rho(\omega) \left( 1 - \frac{\omega^2}{D^2} \right) \frac{\text{Im}(X e^{i\theta})}{K^{1/2}} f(\omega) \frac{P}{2\pi} \times \int_{-\infty}^{\infty} \frac{d\omega'}{\omega - \omega'} \left( \frac{\partial \ln K(\omega', T)}{\partial T} \Big|_A + \frac{\partial A}{\partial T} \frac{\partial \ln K(\omega', T)}{\partial A} \right). \quad (\text{B20})$$

With the help of the condition (3.5b), we have

$$I_3^{1m} = \bar{n}_0 \int_{-\infty}^{\infty} d\omega \rho^2(\omega) \left( 1 - \frac{\omega^2}{D^2} \right) \text{Re}l_{\text{ret}}(\omega, T) F(\omega, T), \quad (\text{B21})$$

where

$$F(\omega, T) = \frac{P}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega'}{\omega' - \omega} \left( \frac{\partial \ln K(\omega', T)}{\partial T} \Big|_A + \frac{\partial A}{\partial T} \frac{\partial \ln K(\omega', T)}{\partial A} \right). \quad (\text{B22})$$

We obtain the estimate for  $I_3^{1m}$

$$|I_3^{1m}| \leq \bar{n}_0 F_{\max} \int_0^{\infty} d\omega \rho(\omega) |\text{Re}l_{\text{ret}}(\omega, T)|, \quad (\text{B23})$$

where  $F_{\max}$  is the maximum value of  $F(\omega, T)$  for all  $\omega$  and for  $k_B T \leq D^\alpha (k_B T_K/D)^{(1-\alpha)}$ . Without going into the details, we state that

$$\int_0^{\infty} d\omega \rho(\omega) |\text{Re}l(\omega, T)| \leq c_1 k_B T_K + c_2 D |\gamma|, \quad (\text{B24})$$

where the first term arises from the resonance in  $l_{\text{ret}}(\omega, T)$  near  $\omega=0$  and the second term is the contribution to the integral from large values of  $\omega$ . Since  $F_{\max}$  remains finite as  $\gamma$  approaches zero, it follows that

$$\lim_{|\gamma| \rightarrow 0} |I_3^{1m}| = 0. \quad (\text{B25})$$

Thus we have shown that the integrals  $I_1^{Im}$ ,  $I_2^{Im}$ , and  $I_3^{Im}$ , and hence  $I^{Im}$ , vanish in the limit  $|\gamma| \rightarrow 0$ , with  $\tau$  fixed.

We now turn to the evaluation of the other integral in (4.35)

$$I^{Re} \equiv 2\bar{n}_0^2 \int_{-\infty}^{\infty} d\omega \omega \frac{\omega}{D} \rho^2(\omega) \left( \frac{\partial}{\partial T} \text{Re}l_{\text{ret}}(\omega, T) \right) f(\omega). \quad (B26)$$

We again regroup the various terms that arise from performing the differentiation in the integrand in three integrals just as in the case of  $I^{Im}$

$$I^{Re} = I_1^{Re} + I_2^{Re} + I_3^{Re}, \quad (B27)$$

where

$$I_1^{Re} \equiv -\frac{\bar{n}_0}{\pi} \int_{-\infty}^{\infty} d\omega \omega \frac{\omega}{D} \rho(\omega) \times \text{Im} \left[ \frac{\partial X}{\partial T} \Big|_A \left( \frac{\partial}{\partial X} \frac{X}{\sqrt{K}} \right) e^{i\theta} \right] f(\omega), \quad (B28)$$

where

$$I_{31}^{Re} \equiv -\frac{\bar{n}_0}{\pi^2} \int_{-\infty}^{\infty} d\omega \frac{\omega}{D} \rho(\omega) [1 + 2\pi n_0(\omega) \text{Im}l_{\text{ret}}(\omega, T)] f(\omega) P \int_{-\infty}^{\infty} d\omega' \frac{\omega'}{\omega' - \omega} \frac{\text{Re}[X(\omega', T)(\partial/\partial T)X(\omega', T)]}{K(\omega', T)} \quad (B32)$$

and

$$I_{32}^{Re} \equiv -\frac{\bar{n}_0}{\pi} \int_{-\infty}^{\infty} d\omega \frac{\omega}{D} \rho(\omega) [1 + 2\pi \rho(\omega) \text{Im}l_{\text{ret}}(\omega, T)] f(\omega) \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\omega'}{\omega' - \omega} (\pi\gamma)^2 \frac{\partial A}{\partial T} \rho(\omega') \frac{\text{Re}X(\omega', T)}{K(\omega', T)}. \quad (B33)$$

The integral  $I_{31}^{Re}$  can again be shown to vanish in the limit  $\gamma \rightarrow 0$  with  $\tau$  fixed. The important contribution to  $I_3^{Re}$ , and hence to  $I^{Re}$ , comes from  $I_{32}^{Re}$  which can be written

$$I_{32}^{Re} = \frac{\bar{n}_0}{\pi} (\pi\gamma)^2 \frac{\partial A}{\partial T} \left[ \int_{-\infty}^{\infty} d\omega \frac{\omega}{D} f(\omega) \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\omega'}{\omega' - \omega} \rho(\omega') + \int_{-\infty}^{\infty} d\omega \frac{\omega}{D} \rho(\omega) f(\omega) \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\omega'}{\omega' - \omega} \rho(\omega') \left( \frac{\text{Re}X(\omega', T)}{K(\omega', T)} - 1 \right) + 2\pi \int_{-\infty}^{\infty} d\omega \frac{\omega}{D} \rho^2(\omega) \text{Im}l_{\text{ret}}(\omega, T) f(\omega) \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\omega'}{\omega' - \omega} \frac{\text{Re}X(\omega', T)}{K(\omega', T)} \right]. \quad (B34)$$

The first integral in the square brackets can be calculated by elementary methods

$$\int_{-\infty}^{\infty} d\omega \frac{\omega}{D} \rho(\omega) f(\omega) \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\omega'}{\omega' - \omega} \rho(\omega') = \pi D^2 \left[ 1 + O\left(\frac{T^2}{D^2}\right) \right]. \quad (B35)$$

The second and third integral can again be shown to vanish in the limit  $|\gamma| \rightarrow 0$  so that for  $|\gamma| \ll 1$  and  $T \ll D$

$$I^{Re} \simeq I_{32}^{Re} \simeq \bar{n}_0 D^2 (\pi\gamma)^2 \partial A / \partial T. \quad (B36)$$

The significance of this expression is discussed in the main text.

$$I_2^{Re} \equiv -\frac{\bar{n}_0}{\pi} \int_{-\infty}^{\infty} d\omega \omega \frac{\omega}{D} \rho(\omega) \times \text{Im} \left[ e^{i\theta} \left( \frac{\partial}{\partial(\pi^2 \gamma^2 A)} \frac{X}{\sqrt{K}} \right) \right] f(\omega), \quad (B29)$$

and

$$I_3^{Re} \equiv -\frac{\bar{n}_0}{\pi} \int_{-\infty}^{\infty} d\omega \omega \frac{\omega}{D} \rho(\omega) \times \frac{\text{Re}(X e^{i\theta})}{\sqrt{K}} \left( \frac{\partial \theta}{\partial T} \Big|_A + \frac{\partial A}{\partial T} \frac{\partial \theta}{\partial A} \right) f(\omega). \quad (B30)$$

The integrals  $I_1^{Re}$  and  $I_2^{Re}$  can be shown to vanish in the limit  $|\gamma| \rightarrow 0$  with  $\tau$  fixed by the same methods that were used to show that  $I_1^{Im}$  and  $I_2^{Im}$  vanish in this limit.

Using (3.1), we can write  $I_3^{Re}$  as

$$I_3^{Re} = I_{31}^{Re} + I_{32}^{Re}, \quad (B31)$$