Theory of Low-Temperature Resistance Anomalies in Dilute Alloys

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By means of a generalization of the Wick contraction procedure to the case of a localized spin, it is shown that the perturbation series for scattering of a conduction electron at zero temperature on a localized magnetic impurity in a metal may be generally resummed so as to express it in terms of the solution of a Slater-Koster model with a spin-dependent and strongly energy-dependent effective potential. A perturbation expansion of the effective potential provides a systematic approximation to the scattering cross section which does not suffer from the divergence found by Kondo. The results of computations of resistivity and thermopower based on this perturbation approximation and using a simple model for the conduction-electron density of states are reported, leading to a possible interpretation of the resistance anomaly in rhodium-based alloys.

1. INTRODUCTION AND DISCUSSION

THE discovery by Kondo[1] of the logarithmically divergent behavior of the second Born approximation to the scattering amplitude of conduction electrons on a magnetic impurity in a metal has recently led a number of people[2–4] to investigate how this divergence would become modified in nonperturbational treatments.

In this paper the results of an investigation of the general properties of this scattering amplitude based on study of the perturbation series to all orders in the interaction between the noninteracting Fermi gas of electrons and a single, localized, magnetic impurity are reported. The principal result is a proof that, at zero temperature, the perturbation series can generally be resummed to express the scattering of a single electron in the presence of the Fermi sea in terms of a spin- and energy-dependent effective potential for a single electron interacting, independently of the Fermi sea, with the center. A systematic perturbation expansion of the effective potential in powers of the coupling constant is derived. The main advantage of this expansion, as compared to the perturbation expansion of the scattering amplitude used by Kondo,[1] is that although the terms in the expansion of the effective potential still contain divergences, these no longer result in a divergence in the cross section, which is therefore shown to be an artificial consequence of Kondo's original approximation.

The approach used depends on a method of evaluation of time-ordered products of localized spin operators. Although Wick's theorem in its usual form cannot be used, it is shown that it is nevertheless possible to define propagators for the spin variables. This leads to a physical interpretation of the Kondo phenomenon as a self-energy effect resulting from spontaneous excitation of electron-hole pairs by spin fluctuations. A key property is, then, that since, in the absence of a magnetic field, the spins have zero excitation frequency, the excitation of electron-hole pairs near the Fermi surface will not require any extra spin excitation energy, and so will lead to the divergence. The point of this remark is that the degeneracy of an impurity spin is a general property of a magnetized local state in the absence of a magnetic field, so that although in reality such states are not completely localized and resonate with band electrons,[5] this spread will not destroy the magnetic degeneracy, so that the Kondo phenomenon may be expected to persist even for partly delocalized spins.

At this point, a comment on the relation of the present approach to that of other authors: Abrikosov,[4] using a different method of evaluating time-ordered products of spin operators, has summed a subseries of contributions to the scattering amplitude, containing dominant divergences. In terms of the resummation procedure of the present paper, such a subseries would also contribute an infinite subseries of terms to the effective potential. In the present paper, the effective potential has only been studied to second order in the coupling constant, so that no further conclusions can be drawn about the nature of resonance obtained by Abrikosov or that of the analogous complex pole and conjectured instability of the system discussed by Suhl[2,6] and by Nagaoka.[3]

However, the relatively simple nondiverging perturbation approximation to the scattering amplitude obtained by our method does allow extension of the original Kondo study to two further problems of physical interest. This is done in the remainder of the paper where results of computations of thermopower, and of resistivity in a partly filled band situation, based on this approximation, are reported.

The first conclusion from these computations, is a qualitative confirmation of recent calculations by Kondo[7] on the giant thermopower. Excitation of electron-hole pairs by a conduction-electron scattering on an isolated magnetic impurity atom, leads to inelastic contributions to the cross section, expressed, in the language of the present paper, through the fact that the effective potential is now complex. It turns out that

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).
[2] H. Suhl, Phys. Rev. **138**, A515 (1965).
[3] Y. Nagaoka, Phys. Rev. **138**, A1112 (1965).
[4] A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **48**, 990 (1965) [English transl.: Soviet Phys.—JETP **21**, 660 (1965)]; Physics **2**, 5 (1965).
[5] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[6] H. Suhl, Phys. Rev. **141**, 483 (1966).
[7] J. Kondo, Progr. Theoret. Phys. (Kyoto) **34**, 372 (1965).

these inelastic processes are not symmetric about the Fermi level, so that carriers in the region of kT below the Fermi level scatter more strongly than those in the region of kT above the Fermi level. This provides a detailed mechanism for the origin of the negative thermopower, originally conjectured by Korringa and Gerritsen[8] to arise on this basis using a phenomenological model. However, the calculations of the present paper are only qualitative, as an ansatz has had to be made in extending the zero-temperature formula for the cross section to calculate the transport properties at finite temperatures. The effects of magnetic ordering fields on the thermopower have not been considered.

The second conclusion from the computations concerns the appearance of a resonance in the scattering under conditions of fairly strong coupling and partly filled conduction band. These results suggest a qualitative interpretation of the observed resistivity decrease of Rh alloys[9] as resulting from a resonance in the scattering of d-band electrons, with resonance energy above the region of observation. Such an interpretation would also provide an understanding of the low magnetoresistance of these alloys compared with that of alloys of the **Cu** Mn type.

2. FEYNMAN DIAGRAMS FOR LOCALIZED SPINS

We consider the one-electron Green's function, at zero temperature, for a system of independent fermions interacting with a randomly placed set of localized impurity spins via a spin-dependent interaction. We make the assumption that, in the limit of low impurity concentration, interference effects for electron interaction with two or more impurities at a time may be neglected as far as electrical resistance is concerned, so that the average of the Green's function over the ensemble of random impurity positions will be expressed in terms of an average electron self-energy equal to the impurity concentration c_0 ($=N_0/N$ where N_0 is the number of impurity atoms and N the number of matrix atoms) times the analytically continued forward scattering amplitude for the electron scattering on a single impurity. This will be derived from the one-electron Green's function evaluated for an interaction with a single impurity. The unperturbed Hamiltonian is

$$H_0=\sum_{\mathrm{p},\sigma}\epsilon_{\mathrm{p}}a_{\mathrm{p},\sigma}{}^{\dagger}a_{\mathrm{p},\sigma}, \tag{1}$$

where a, $a^{\dagger}$ satisfy the anticommutation rule $\{a_{\mathrm{p},\sigma},a_{\mathrm{p}',\sigma'}{}^{\dagger}\}=\delta_{\mathrm{p},\mathrm{p}'}\delta_{\sigma,\sigma'}$. The interaction Hamiltonian is[10]

$$H_1=J\mathbf{S}\cdot\sum_{\mu,\mu'}\alpha_{0,\mu}{}^{\dagger}\boldsymbol{\sigma}_{\mu\mu'}\alpha_{0,\mu'}, \tag{2}$$

where $\alpha_{0,\mu}$ is the Wannier destruction spinor operator for an electron at site zero, spinor suffix μ,

$$\alpha_{0,\mu}=(1/\sqrt{N})\textstyle\sum_{\mathrm{p}}a_{\mathrm{p},\mu}, \tag{3}$$

$\boldsymbol{\sigma}_{\mu\mu'}$ are the spin-$\frac{1}{2}$ Pauli matrices ($\boldsymbol{\sigma}^2=\frac{3}{4}$) and $\mathbf{S}$ are the operators for the impurity spin satisfying the usual commutation rules

$$[S_i,S_j]=i\epsilon_{ijk}S_k. \tag{4}$$

This one-impurity Green's function may now be expanded in powers of (2) using the Feynman-Dyson expansion

$$G_{\mu\nu}(t-t')=i\langle T\{\tilde{\alpha}_{0,\mu}(t)\tilde{\alpha}_{0,\nu}{}^{\dagger}(t')\}\rangle, \tag{5}$$

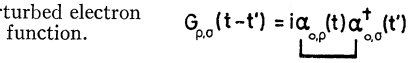
$$=\left\langle T\left\{\exp\int_{-\infty}^{\infty}-iH_1(t)\,dt\right\}\right\rangle_0^{-1}\sum_n\frac{(-i)^n}{n!}$$

$$\times\int_{-\infty}^{\infty}dt_1\cdots dt_n\langle T\{\alpha_{0,\mu}(t)H_1(t_1)\cdots$$

$$\times H_1(t_n)\alpha_{0,\nu}{}^{\dagger}(t')\}\rangle_0, \tag{6}$$

where the brackets $\langle\ \rangle_0$ include an average over the impurity spin states (in zero magnetic field this is just a normalized trace) and $\tilde{\alpha}_{0\mu}(t)$ are Heisenberg operators. Now the expectations of the interaction representation $\alpha_{0,\mu}(t)$ operators may be evaluated immediately, using Wick's theorem, in terms of the contractions represented in Fig. 1,

FIG. 1. Unperturbed electron Green's function.



where

$$G_{\rho,\sigma}{}^0(t-t')=i\delta_{\rho\sigma}(1/N)\textstyle\sum_{\mathrm{p}}e^{-i\epsilon_{\mathrm{p}}(t-t')}$$

$$\times\{f^+(\epsilon_{\mathrm{p}})\theta(t-t')-f^-(\epsilon_{\mathrm{p}})\theta(t'-t)\}, \tag{7}$$

where $\theta(t)=1$ for $t>0$ and 0 for $t<0$, ϵ_{p} are the unperturbed electron-band energies and $f^+(\epsilon)=1$ for $\epsilon>\epsilon_F$ and 0 for $\epsilon<\epsilon_F$ (and vice versa for f^-). In the absence of external magnetic fields, ϵ_{p} are independent of the spin state of the electron, so that $G_{\rho,\sigma}{}^0$ becomes independent of ρ, σ and the spinor suffixes may be dropped. Because of the δ-function range of interaction all momentum sums separate completely as in the original Slater-Koster model. The result of this process may be represented by a diagram in which directed lines represent the G^0's and at each vertex a scalar product of $\mathbf{S}$ and a Pauli matrix occurs (Fig. 2). Because the $G_{\rho\sigma}{}^0$ are diagonal in the spin suffixes, the order of multiplication of the Pauli matrices is dictated by following the order

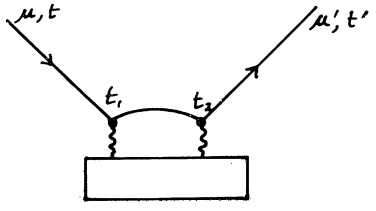


FIG. 2. Second-order contribution to one-electron Green's function.

[8] J. Korringa and A. N. Gerritsen, Physica **19**, 457 (1953).

[9] B. R. Coles, Phys. Letters **8**, 243 (1964). A similar resistivity decrease has also been observed for **Rh** Mn [B. R. Coles (private communication)].

[10] The J defined here is related to Kondo's (Ref. 1) coupling constant J_K by $J=-2J_K$.

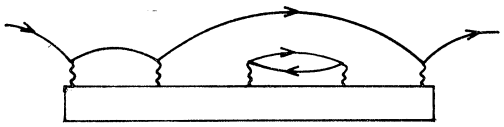


FIG. 3. Higher order contribution to one-electron Green's function.

of the arrows on any linked electron line. For instance, the contribution to (6) resulting from the diagram of Fig. (2) is

$$\frac{(-J)^2}{2!}\int_{-\infty}^{\infty} dt_1 dt_2 G^0(t-t_1)G^0(t_1-t_2)G^0(t_2-t') \times \mathrm{Tr}_s\{T\{\boldsymbol{\sigma}_{\mu\mu_1}\cdot\mathbf{S}(t_1)\boldsymbol{\sigma}_{\mu_1\mu}\cdot\mathbf{S}(t_2)\}\}. \quad (8)$$

While for the contraction of Fig. 3 we obtain the contribution to (6) of an appropriate product of electron propagators G^0 multiplied by

$$\sum_{\mu_1\mu_2}\{T\{\boldsymbol{\sigma}_{\mu\mu_1}\cdot\mathbf{S}(t_1)\boldsymbol{\sigma}_{\mu_1\mu_2}\cdot\mathbf{S}(t_2) \times\sum_{\mu_3\mu_4}(\boldsymbol{\sigma}_{\mu_4\mu_3}\cdot\mathbf{S}(t_3)\boldsymbol{\sigma}_{\mu_3\mu_4}\cdot\mathbf{S}(t_4))\boldsymbol{\sigma}_{\mu_2\mu}\cdot\mathbf{S}(t_5)\}\}, \quad (9)$$

where the time dependence $\mathbf{S}(t)$ serves only to label the order induced in the operators by the original T product in (6). The spinor products may be rewritten without spinor suffixes using a direct-matrix-product notation. For instance (9) becomes

$$\mathrm{Tr}_s\{T\{\boldsymbol{\sigma}_1\cdot\mathbf{S}(t_1)\boldsymbol{\sigma}_1\cdot\mathbf{S}(t_2)\ \mathrm{Tr}_{\sigma_2}(\boldsymbol{\sigma}_2\cdot\mathbf{S}(t_3)\boldsymbol{\sigma}_2\cdot\mathbf{S}(t_4)) \times\boldsymbol{\sigma}_1\cdot\mathbf{S}(t_5)\}\}. \quad (10)$$

Here the suffixes, 1, and 2 on the $\boldsymbol{\sigma}$'s denote that the matrix product of all $\boldsymbol{\sigma}_1$'s is to be taken, and also the independent matrix product of the $\boldsymbol{\sigma}_2$'s.

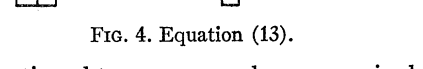
We now introduce a term "structure" to different classes of contractions of electron operators which may occur in a perturbation term with a given number of vertices. To each partition of a term with n vertices into a set of n_0, $n_1\cdots n_r$ subsets of vertices in which n_0 vertices are contracted to the ingoing and outgoing electrons and each of the remaining sets $n_1\cdots n_r$ are contracted to form r distinct closed loops we associate a class of diagrams said to be of the same structure, which we will denote by a symbol Γ. Then for a given time ordering of the n vertices there will be $s_\Gamma = n!/\prod_{l=1}^{r} n_l \prod_{i=1}^{n} \nu_i!$ [where ν_i is the number of closed loops with i vertices $(0!=1)$] ways of contracting the electron operators to produce a diagram of chosen structure, i.e., this will be the number of diagrams in the given structure class. The spin-operator factors [as in (10)] occurring for the members of a given structure class will however have the $\boldsymbol{\sigma}$ matrices multiplied in different orders. By relabeling the time variables, we can fix on a definite order of multiplication of the σ's as represented by a chosen drawing of the diagram, and include all the other contractions leading to diagrams of the same structure by reordering the operators. The resulting contribution to (6) from a diagram of structure Γ will have the form, including a factor (-1) for each closed loop,

$$(-1)^{n+r}J^n s_\Gamma \int_{-\infty}^{\infty} dt_1\cdots dt_n \prod G^0(t_i-t_j) \times\langle T_s\{\Pi\boldsymbol{\sigma}_i\cdot\mathbf{S}(t_{im})\}\rangle_0, \quad (11)$$

where the necessary traces over the σ's belonging to closed loops are implied and T_s denotes boson-like time ordering with respect to the S operators only:

$$T_s(S(t_1)S(t_2)) = +S(t_2)S(t_1) \quad \text{for} \quad t_2>t_1. \quad (12)$$

The main step in this paper is the following procedure to disentangle commuting contributions to the time-ordered product of S operators in (11). As stated above, the order of multiplication of the σ's is fixed by the chosen drawing of a diagram of given structure. We define that time ordering of the S operators which is the same as a chosen order of operation of the σ operators as the normal form for the class Γ of diagrams of given structure. This is denoted by $\{:S_{i_1}(t_1)\cdots S_{i_n}(t_n):\}_\Gamma$. (Here $i_1\cdots i_n$ are Cartesian suffixes.) Any other time ordering of the S operators may be reordered to the normal form by using the commutation rules (4). In doing this there will appear a sum of terms involving first and higher order commutators of the S operators. These may be separated out recursively as contractions of various orders (denoted by link symbols). If we abbreviate $S_{i_m}(t_m)$ by S_m then we obtain for second- and third-order contractions the expressions given in Eq. (13) (Fig. 4). This procedure



(13)

FIG. 4. Equation (13).

may be continued to as many orders as required. (Note that the choice of the normal form as corresponding to a chosen order of multiplication of the σ matrices is merely imposed for the later convenience of handling of the σ matrices. In fact any arbitrary order would be as good as far as the S operators are concerned.) Because the contractions are still operators, the normal product with contractions requires further definition. We define the order in which contracted operators are to be taken in a normal product with contractions to be that corresponding to the order in which the first line of the link symbol for each contraction group occurs, reading from right to left, when the operators themselves are written in the normal order for the class Γ. (An uncontracted vertex counts as a first-order link symbol.) For example the normal product given in Fig. 5(a) is to be evaluated as the expression given in Fig. 5(b).

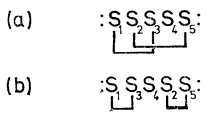


FIG. 5. Illustration of convention given in text for evaluating a normal product with contractions.

In this way the product of operators for arbitrary time ordering can be re-expressed as a sum of time-independent products, corresponding to the normal products with contractions, of time-dependent operators resulting from the contraction procedure. For example, for the second- and third-order contractions corresponding to the normal forms

$$\begin{aligned} :S_1S_2: &= S_1S_2, \\ :S_1S_2S_3: &= S_1S_2S_3, \end{aligned} \tag{14}$$

we find the expressions given in Eq. (15) (Fig. 6).

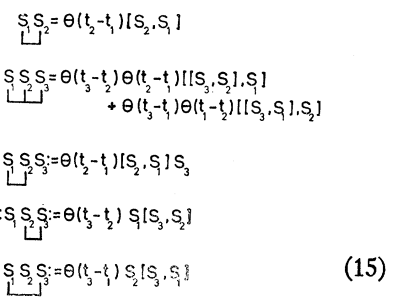


FIG. 6. Equation (15).

(15)

By this means the T product in (11) may be re-expressed as the sum of all possible normal products with contractions.[11] These may conveniently be represented by means of diagrams of the Feynman type in which, however, the spin-contraction lines do not represent c numbers but operator products. Possible such terms corresponding to the class in Fig. (3) are shown in Fig. (7).

3. THE EFFECTIVE POTENTIAL

Using the expansion of the T products developed in Sec. 2, the contributions to the single impurity scattering Green's function are represented by a set of Feynman-type diagrams derived from the electron

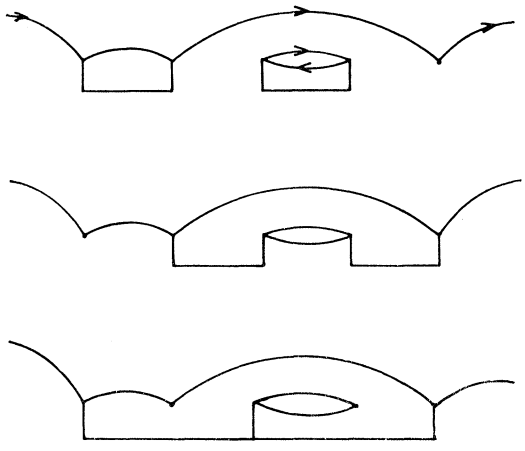


FIG. 7. In this figure an unlinked vertex represents an uncontracted term $\boldsymbol{\sigma}\cdot\mathbf{S}$ (contraction of order one) in the normal product.

[11] The content of the usual Wick theorem is that in the case of bosons all contractions higher than the second are zero.

diagrams of different structures by performing the contraction procedure on the spin operators. The resulting diagrams consist of one-electron irreducible parts strung together with G^0 functions, together with disconnected parts. The disconnected parts are those pieces of the diagram which have no electron or hole lines connecting them to the rest of the diagram, and which also have no contraction links crossing contraction links from another part of the diagram. (This last is necessary since the contracted operators do not commute.)

For the problem of the present paper (i.e., only a *single* localized spin), there now appears a further simplifying feature which is that, as a result of the rotational invariance of H_1, Eq. (2), and the traces over the closed-loop spin matrices, the contributions to a normal product corresponding to a disconnected part can depend on the operators $\mathbf{S}$ only through $\mathbf{S}^2$, hence will be c numbers. For similar reasons the one-electron irreducible parts are diagonalized by the spin eigenstates of the combined spin j_z for a *single* electron spin coupled to the impurity spin

$$\mathbf{j}=\boldsymbol{\sigma}+\mathbf{S} \tag{16}$$

and depend only on j and not on m_j. Because of the c-number character of the disconnected part contributions we expect that the sum of these contributions cancels the normalizing factor $\left\langle T\left\{\exp-\int_{-\infty}^{\infty} iH_1(t)\,dt\right\}\right\rangle_0$ in (6) in the usual way. The spin average over the connected parts may then be replaced by the weighted mean of the two j eigenvalues, $j=S\pm\frac{1}{2}$ for the single electron entering the definition of $G^0(5)$ coupled to the impurity spin. Finally, if we denote by $V_{\text{eff}}{}^j(t-t')$ the j eigenvalue of the contributions from the sum of all possible one-electron irreducible parts, and its Fourier transform by $V_{\text{eff}}{}^j(\omega)$ then the total single-impurity one-electron Green's function (5) may be written as

$$G(\omega)=\sum_j w_j \frac{G^0(\omega)}{1+G^0(\omega)V_{\text{eff}}{}^j(\omega)}, \tag{17}$$

where

$$w_j=(2j+1)/2(2s+1) \tag{18}$$

and $G^0(\omega)$ is the Fourier transform of (7)

$$G^0(\omega)=I(\omega)+i(f^+(\omega)-f^-(\omega))\Gamma(\omega), \tag{19}$$

with

$$\begin{aligned} I(\omega) &= N^{-1}\textstyle\sum_{\mathbf{p}} (\mathcal{P}/(\epsilon_{\mathbf{p}}-\omega)), \\ \Gamma(\omega) &= N^{-1}\textstyle\sum_{\mathbf{p}} \pi\delta(\epsilon_{\mathbf{p}}-\omega). \end{aligned} \tag{20}$$

Note that Eq. (17) is the Green's function for scattering on a single impurity. If the one-electron irreducible parts are denoted by a circle [Fig. 4(a)] then the single impurity character of G is emphasized by drawing dotted lines to denote momentum transfer to the impurity atom [Fig. 8(b)]. On making an ensemble average over impurity positions,[12] only forward scat-

[12] S. F. Edwards, Phil. Mag. 3, 1020 (1958).

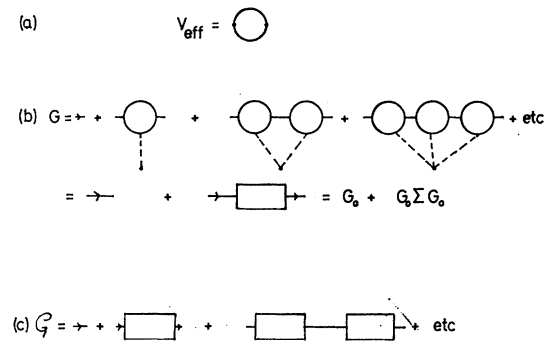


FIG. 8. Construction of the many-impurity Green's function $\mathcal{G}$ in the low-concentration limit in terms of the one-impurity self-energy diagrams Σ which are in turn constructed from the effective potential V_{eff}. [The dotted lines denote momentum transfer to the impurity (see text).]

tering contributions to the total, many-impurity, one-electron Green's function, denoted by $\mathcal{G}_p(\omega)$, will survive. In the low-concentration limit discussed in Sec. 2, $\mathcal{G}$ will result by stringing together one-atom scattering, contributions [Fig. 8(c)]

$$\mathcal{G}_p(\omega)=(\epsilon_p-\omega-c_0\sum(\omega))^{-1}, \tag{21}$$

where $\sum$ follows from (17) as

$$\sum(\omega)=G^{0-1}[GG^{0-1}-1]$$
$$=\sum_j w_j\frac{V_{\text{eff}}{}^j(\omega)}{1+G^0(\omega)V_{\text{eff}}{}^j(\omega)}. \tag{22}$$

Finally, in the limit $c_0\to 0$, the quasiparticle lifetime follows from (21) as

$$1/\tau_p=-c_0\,\text{Im}\sum(\epsilon_p). \tag{23}$$

In the case that the original impurity interaction is not spin-dependent, all except the lowest order irreducible diagrams disappear and (23) reduces, using (19) to

$$[1/\tau_p]_{\text{spin-independent}}=c_0(f_p{}^+-f_p{}^-)|A|^2\Gamma(\epsilon_p), \tag{24}$$

where

$$A=V/(1+G^0V) \tag{25}$$

which is the usual answer for a Slater-Koster potential of strength V. This is therefore a proof that exclusion principle effects cancel to all orders for a spin-independent potential. (Kondo showed this to third order.[13])

4. APPROXIMATE CALCULATION OF THE ELECTRICAL RESISTIVITY AND THERMOPOWER

In this section we discuss qualitative features of the quasiparticle lifetime, (23) by using (22) and expanding $V_{\text{eff}}{}^j$ in powers of J. Although terms in this expansion will still contain the Kondo divergence, the effect of the resummation is to remove this from the scattering amplitude, so that in this form, perturbation theory gives physically reasonable results. We use it to investigate qualitative features of the model. (An unphysical singularity does, however, occur off the real axis for $J_K>0$ as discussed in the Appendix.)

From (15) we have for the first and second perturbations to V_{eff} (see Fig. 9)

$$[V_{\text{eff}}{}^j(t-t')]_1=\delta(t-t')J\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j,$$
$$[V_{\text{eff}}{}^j(t-t')]_2=-J^2G^0(t-t')\langle\textstyle\sum_{\alpha\beta}\sigma_\alpha\sigma_\beta[S_\beta,S_\alpha]\rangle_j \tag{26}$$
$$=-J^2G^0(t-t')\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j$$

with Fourier transforms [using (7)]

$$[V_{\text{eff}}{}^j(\omega)]_1=J\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j,$$
$$[V_{\text{eff}}{}^j(\omega)]_2=-J^2\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j g(\omega), \tag{27}$$

where

$$g(\omega)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}d\omega' G^0(\omega-\omega')\frac{1}{\omega'-i\epsilon} \tag{28}$$

$$=\frac{1}{N}\sum_{\mathbf{p}}\frac{f^-(\epsilon_p)}{\epsilon_p-\omega+i\epsilon}=g_R(\omega)-if^-(\omega)\Gamma(\omega). \tag{29}$$

In (28) appears the characteristic zero-frequency pole for the spin propagator mentioned in Sec. 1, which has the additional feature of picking out only a negative time, i.e., electron-hole pair, contribution to V_{eff}. The iteration of this term in the scattering amplitude via (22) suggests, by analogy with electron-phonon interaction, that the Kondo effect should be interpreted as resulting from this interaction with a "spring" of zero restoring force[14] rather than directly as a Pauli principle exclusion effect of the type originally proposed by Cooper[15] for superconductivity. Using (27), (23), and (22) we recover Kondo's original expression (retaining only logarithmically diverging terms) by expanding $1/\tau$

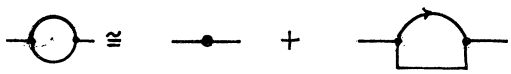


FIG. 9. First- and second-order contributions to the effective potential V_{eff}.

[13] This must happen, of course, as one can first solve the Schrödinger equation for a single electron scattering on the impurity, then fill up the modified Fermi sea without altering the scattering wave functions.

[14] Appearance of the spin propagator in (22) also allows us to estimate the effect of paramagnetic polarization of the electron gas on the spin response leading to the Kondo effect. The main point here is that although this polarization damps the spin response it does not remove the spin degeneracy, so that the zero-frequency pole persists even for a damped spin. The qualitative effect of electron-hole pairs on the spin propagator is to replace $1/(\omega-i\epsilon)$ by $1/[\omega(1+i\gamma)-i\epsilon]$ where, to lowest perturbation order $\gamma\propto(J/\epsilon_F)^2$. This seems likely to be true generally, as γ measures the ratio of the spin resonance linewidth to frequency. This should remain finite as the applied field tends to zero. (The author is grateful to Professor M. H. Cohen for questioning this point.)

[15] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

to third order in J

$$1/\tau \cong c_0(f^+(\omega)-f^-(\omega))\Gamma(\omega) \times (J^2-J^3\mathcal{G}(\omega))\sum_j w_j\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j^2. \quad (30)$$

Using (18) and

$$\begin{aligned}\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j &= \tfrac{1}{2}S \quad \text{for} \quad j=S+\tfrac{1}{2}\\ &= -\tfrac{1}{2}(S+1) \quad \text{for} \quad j=S-\tfrac{1}{2}\end{aligned} \quad (31)$$

we have

$$\sum_j w_j\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j^2 = \tfrac{1}{4}S(S+1) \quad (32)$$

so that (30) agrees with Kondo's expression.[16] (We have not included a spin-independent part in the interactions.) We proceed to use the perturbation approximation (27)

$$V_{\text{eff}}{}^j=[V_{\text{eff}}{}^j]_1+[V_{\text{eff}}{}^j]_2=\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j(J-J^2\mathcal{G}(\omega)) \quad (33)$$

as a basis for a nonperturbative computation of the electrical resistivity and thermopower.

A problem which arises at this point is that the effective potential and hence the lifetime at given electron energy ω will be strongly temperature-dependent since the divergence of (29) as ω approaches ϵ_F results from the sharpness of the Fermi distribution $f^-(\omega)$ leading to the logarithmic divergence of $\mathcal{G}_R(\omega)$ which becomes smeared out as the temperature increases. One cannot therefore use the zero-temperature cross section to calculate scattering at finite temperatures. The best way to proceed would be a recalculation of the self-energy using finite-temperature Green's functions. We believe that the treatment of Sec. 3 can be generalized to work at finite temperatures, but for the purposes of the present paper, a qualitative estimate of the scattering is made by assuming that the main effect of temperature will be to replace the step function f^- of Eq. (6) by the Fermi distribution (and similarly for f^+ using $f^+=1-f^-$). (This will have the advantage of joining smoothly on to the approximation at $T=0$.) Equation (29) then becomes

$$\mathcal{G}(T,\omega)=N^{-1}\sum_{\mathbf{p}}(\mathcal{P}f(\epsilon_{\mathbf{p}})/(\epsilon_{\mathbf{p}}-\omega))-if(\omega)\Gamma(\omega), \quad (34)$$

where

$$f(\omega)=1/(e^{\beta(\omega-\epsilon_F)}+1).$$

For calculation of the electrical resistivity we further require, not the quasiparticle relaxation rate but, by analogy with the case of an energy-independent potential, the difference of "particle" and "hole" relaxation rates.[17] An estimate of this is made by noticing that in the spin-independent case the current relaxation rate $1/\tau_{\text{res}}$ is obtained from the quasiparticle relaxation rate $1/\tau_{\mathbf{p}}$ by dropping the factor (f^+-f^-) in (24). We therefore make a crude ansatz at this point and set

$$1/\tau_{\text{res}}=\sum_j w_j|A_j(\omega)|^2\Gamma(\omega), \quad (35)$$

where

$$A_j(\omega)=\frac{V_{\text{eff}}{}^j(\omega)}{1+(I(\omega)+i\Gamma(\omega))V_{\text{eff}}{}^j(\omega)}, \quad (36)$$

where I and Γ are given in (20) and V_{eff} is obtained by inserting (34) in (33). Formula (35) was used to calculate the electrical resistivity (in arbitrary units) by means of

$$\rho(T)=\left[\tfrac{1}{3}v_F{}^2\int d\omega-\frac{\partial f}{\partial\omega}\tau_{\text{res}}(T,\omega)\right]^{-1} \quad (37)$$

and the thermopower[18] via[19]

$$S(T)=-\frac{1}{eT}\left[\tfrac{1}{3}V_F{}^2\int d\omega(\epsilon_F-\omega)\tau_{\text{res}}(T,\omega)\frac{\partial f}{\partial\omega}\right]\rho(T). \quad (38)$$

For the computations a simple parabolic density-of-states model[20]

$$N^{-1}\sum_{\mathbf{p}}\delta(\epsilon_{\mathbf{p}}-\omega)=(4\rho_0/\epsilon_B)((\omega/\epsilon_B)(1-\omega/\epsilon_B)) \quad (39)$$

was used. (ϵ_B = band width.) ρ_0 is determined (assuming one electron per atom) by the normalization

$$N^{-1}\sum_{|p|<p_F}1=1. \quad (40)$$

For a half-filled band, $I(\omega)$ in (20) is zero [in noble-metal-based alloys, the band is not symmetric, but one

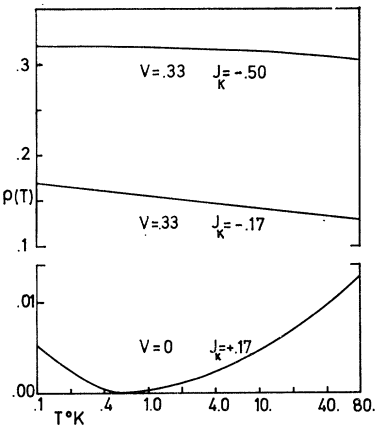


FIG. 10. Resistivity (arbitrary units) against temperature for a half-filled band situation (bandwidth was taken to be 10.0 eV, Fermi energy 5.0 eV), calculated using the second-order approximation to V_{eff} of Eq. (33), to which a spin-independent potential $2V$ has been added. J_K is Kondo's coupling constant.[10]

[16] In making the comparison, Kondo's definition of the coupling constant[10] must be used.

[17] A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinsky, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963), p. 334. In the present case of a δ-function interaction the $(\cos\theta-1)$ term in the Boltzmann integral averages to (-1).

[18] N. F. Mott and H. Jones, *The Theory of Metals and Alloys* (Oxford University Press, London, 1936), 1st ed., p. 310.

[19] The approximate formula for $S(T)$ in terms of the logarithmic derivative of the cross section at the Fermi surface cannot be applied in the present case owing to the rapid variation with energy [c.f. A. R. de Vroomen and M. L. Potters, Physica **27**, 1083 (1961)].

[20] A. M. Clogston, Phys. Rev. **125**, 439 (1962).

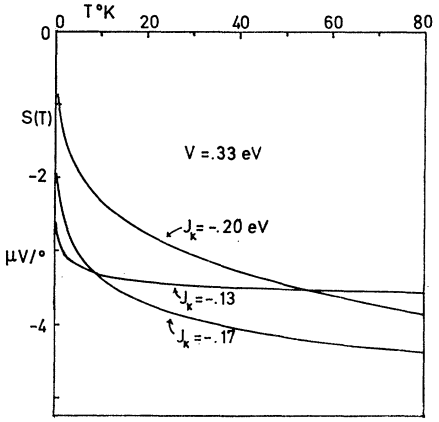


FIG. 11. Thermopowers calculated with the approximation and band parameters used for Fig. 6. (No magnetic-ordering field effects have been included.) As J increases relative to V, the effect of the log term shows up as a suppression of the thermopower at low temperatures, together with an over-all negative increase of thermopower.

would still expect $I(\omega)$ to be small] and as $V_{\text{eff}}(\omega)$ increases at low temperatures, the effect is to saturate the resistivity, flattening off the rise proportional to $\ln T$ which was found by Kondo from (30). The results of numerical integration on the IBM 7090 at Imperial College are shown in Fig. (10). The principal conclusion to be drawn from these results is that the region of validity of Kondo's perturbation estimate (30) is restricted to $|J_K| \lesssim 0.2$ eV in the temperature range of observation. However, for negative J_K[10] and a half-full band the linear dependence on $\ln T$ persists even for fairly large values of J_K. For positive J_K there appears a cancellation between the perturbation terms $[V_{\text{eff}}]_1$ and $[V_{\text{eff}}]_2$ indicating that this approximation is bad in this region. (See also the Appendix.) But the indication remains that the decrease of $\rho(T)$ as $T \to 0$ predicted by the perturbation formula (30) for $J_K > 0$ will probably not persist in a more exact theory, for $J_K \gtrsim 0.2$ eV. We conclude from this that the observation of increasing $\rho(T)$ for all known dilute magnetic alloys of the type with transition-metal impurities in Cu, Au (half-filled band situation) cannot be taken as conclusive evidence for $J_K < 0$.

Results for the thermopower are probably much more sensitive to the brutal use of the ansatz (35), (36) than the resistivity case. As mentioned in the Introduction, the scattering is no longer elastic for the spin-dependent case, as may be seen from the $if\Gamma$ contribution to $[V_{\text{eff}}{}^i]_2$ appearing via (34). The present approximations are in fact equivalent to Kondo's[7] up to fourth order in J; as in the present treatment, he also uses a quasielastic formula of the type of (35) to calculate the scattering cross section. This approximation probably excludes some inelastic (pair production) contributions. The results of the computation for thermopower are shown in Fig. 11 for a variety of J values. The effects of adding a spin-independent term V to the effective potential is also shown. Owing to the saturation effects of the denominator in (36) mentioned above, a larger ratio J/V is needed to obtain a given resistance rise at low temperature than that needed by Kondo using his perturbation approximation. Although the magnetic-field effects considered by Kondo[7] have not been included, the thermopower predicted still tends to fall off at low temperatures due to the increase of the logarithmic part of the cross section over the inelastic part which gives the large, fairly temperature-independent part at higher temperatures.

5. APPLICATION TO TRANSITION-METAL-BASED ALLOYS

In the case of transition-metal-based alloys it is probable[21] that $s \to d$ scattering provides an important contribution to the resistivity. This means that the coupling of the d electrons to the impurity spin should be taken into account in determining this transition rate. We simulate this qualitatively by lowering (or raising) the Fermi level in the above one-band model. The immediate physical result is to increase $I(\omega)$ and reduce $\Gamma(\omega)$ in (20). As $I(\omega)$ increases, the fact that $V_{\text{eff}}(\omega)$ may become large as ω approaches ϵ_F can lead to a zero for the real part of the denominator of (36) for scattering energies near the Fermi surface. This leads to a very sharp resonance in the scattering amplitude at these energies. This resonance is completely different from the usual Friedel virtual bound state for scattering from nonmagnetic impurities, described by (25), for which V does not vary with energy. Here the resonance width would be measured in electron volts. In the present magnetic case, however, the resonance is a result of the fact that the effective potential itself is becoming large in the region of the Fermi surface. The width of the resulting resonance now depends exponentially on the coupling constant J but at any rate is very sharp, to be measured in 10^{-4} eV units. Since V_{eff} has opposite sign for $S+\frac{1}{2}$ and $S-\frac{1}{2}$ in the approximation of Eq. (33) the resonance could occur for either sign of J within this approximation.

The main point of the present section is the observation that as the Fermi level is lowered or raised in the band, the position of the resonance may move into the energy range of carriers in the usual temperature range of observation (≈ 1 to 50°K). This is to be contrasted with noble metal situations where, if a resonance does occur, it is at energies corresponding to extremely low temperatures. (This situation appears to be the case for the resonances discussed by Suhl[6] and Abrikosov[4] which are somewhat different in origin from the present one. (See remarks in Sec. 1.) We further observe that, whatever the approximation used, V_{eff} is likely to increase at low energies, since for ω large compared to ϵ_F, the perturbation approximation for $V_{\text{eff}}(\omega)$ is good, and this shows V_{eff} increasing as $\omega \to \epsilon_F$. Hence it seems likely

[21] See Ref. 18, p. 267.

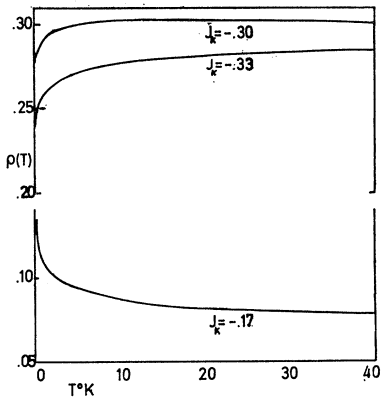


FIG. 12. Resistivity (arbitrary units) for a partly filled band situation. Fermi level was taken at 1.0 eV for bandwidth 10.0 eV [using the parabolic density-of-states model (39)]. As J increases the resonance moves exponentially fast through the temperature range of observation.

that the existence of the resonance does not depend too strongly on the present perturbation approximation.

In order to check that the resonance could appear in the physical range of temperatures, the approximation of Eq. (35) using (33) for V_{eff} has been run on the computer using values of I and Γ corresponding to a partly filled band. The results are shown in Fig. (12) plotted on a linear scale. Owing to the logarithmic dependence of V_{eff} on energy, the resonance is very distorted in shape. We propose that the observed resistance anomaly in dilute alloys **Rh**-Fe and **Rh**-Mn may be interpreted as a resonance of this type, although the scale of the observed resistivity decrease is larger than that in the present approximation. (This decrease depends on the ratio I/Γ and is sensitive to details of the band structure.) The absence of resistance anomaly in dilute **Pd** Fe alloys,[22] above the ordering temperature could be similarly interpreted as a case with both J and I/Γ very large.

This interpretation is also in qualitative agreement with the observed low magnetoresistance in **Rh**-Fe compared with that of **Au**-Fe. The detailed effects of the magnetic field will depend on the g factor of the impurity state; however, its qualitative effect is to reduce the log term, $I_R(\omega)$ in V_{eff},[23] since, if ω_0 is the energy required to alter the magnetic quantum number of **S** by a unit, (29) becomes modified to

$$\frac{1}{N}\sum_{\mathbf{p}}\frac{f(\epsilon_{\mathbf{p}})}{(\epsilon_{\mathbf{p}}-\omega_0)-\omega+i\epsilon}.$$

The resulting change in V_{eff} leads to a change in $\sum(\omega)$ of

$$\delta\sum(\omega)=\sum_j w_j\delta V_{\text{eff}}{}^j/(1+G^0V_{\text{eff}}{}^j)^2. \quad (41)$$

[22] B. R. Coles, J. H. Waszink, and J. Loram, *Proceedings of the International Conference on Magnetism, Nottingham* (Institute of Physics and the Physical Society, London, 1965), p. 165.

[23] N. Mikoshiba and K. Yoshiro, J. Phys. Soc. Japan. **19**, 2346 (1964).

It follows that for small J, the change in resistivity due to a magnetic field will be proportional to the resulting change in V_{eff}, while for large J, the change in $\sum$ and hence in $1/\tau$ will be strongly suppressed by the large denominator in (41).

ACKNOWLEDGMENTS

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APPENDIX: STABILITY OF THE APPROXIMATION OF SEC. 4

The resummation procedure of Sec. 3 leading to V_{eff} removes Kondo's singularity in the scattering amplitude, but there is still the possibility that approximations to the resulting self-energy function $\sum(\omega)$ (22) may lead to unphysical singularities off the real ω axis. Singularities of this type were found by Suhl[2,6] in his calculation of the scattering amplitude. The correct analytic behavior of the one-particle Green's function (21) will be guaranteed at $T=0$ in the limit $c_0\to 0$ provided the quasiparticle lifetime has the correct sign

$$1/\tau=-c_0\,\mathrm{Im}\sum(\omega)>0 \quad \text{for} \quad \omega>\epsilon_F$$
$$<0 \quad \text{for} \quad \omega<\epsilon_F. \quad (A1)$$

We discuss this for the approximation (33) to $V_{\text{eff}}{}^i$. We have

$$1/\tau=c_0\sum_j W_j\{(f^+-f^-)\Gamma|V_{\text{eff}}{}^j|^2 - \mathrm{Im}V_{\text{eff}}{}^j\}/|1+G^0V_{\text{eff}}|^2. \quad (A2)$$

For $\omega>\epsilon_F$, $\mathrm{Im}V_{\text{eff}}$ is zero, from (33, 29) so that $1/\tau>0$. For $\omega<\epsilon_F$ however, $\mathrm{Im}V_{\text{eff}}{}^i$ can take either sign depending on $j=S\pm\frac{1}{2}$ so that we must consider the relative magnitudes of the two terms in the numerator of (A2). We have for $\omega<\epsilon_F$

$$-\Gamma|V_{\text{eff}}{}^i|^2-\mathrm{Im}V_{\text{eff}}{}^i=-\Gamma J^2\langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j{}^2|1-J\mathcal{g}|^2 - \langle\boldsymbol{\sigma}\cdot\mathbf{S}\rangle_j\Gamma J^2. \quad (A3)$$

Hence this has the correct sign (<0) provided

$$|1-J\mathcal{g}|^2>1/S. \quad (A4)$$

This will always hold for $J>0(J_K<0)$ since $\mathcal{g}_R(\omega)<0$. But for negative $J(J_K>0)$ there will be a small region of energies ω over which the real part of $V_{\text{eff}}{}^i$ is small, in which the unphysical sign for $1/\tau$ occurs. As noted in Sec. 4, this is also the region where the perturbation approximation is badly wrong, so that an improved approximation to V_{eff} should really be used in this region.