already exist in the use of de Haas-van Alphen[29] and cyclotron resonance[30] techniques, transport property measurements might better be used for tests of transport theories for cases in which the shapes of the energy surfaces are already known.

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[29] For a review, see D. Shoenberg, in *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 226.

[30] For a review, see B. Lax, Revs. Modern Phys. **30**, 122 (1958).

V. ACKNOWLEDGMENTS

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Impurity Scattering in Superconductors

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With the Bardeen-Cooper-Schrieffer theory as a starting point, perturbation theory is used to determine the reduction in superconducting transition temperature due to scattering by impurities dissolved in the superconductor. Two cases are discussed: scattering due to a localized exchange interaction between the spins of the conduction electrons and impurity spins, and purely orbital scattering by nonmagnetic impurities. In the former case good quantitative agreement with observations is obtained. In the latter case numerical agreement is less good, but the qualitative feature, that the initial reduction in T_c is a universal function of residual resistivity is made evident. It is further shown that indiscriminate application of perturbation theory of B.C.S. states leads to the wrong result in predicting the transition temperature, if the transition is of second order.

1. INTRODUCTION

It has been known for some time that the addition of impurities to a superconductor can have a major effect on its transition temperature.[1,2] The difficulty in the interpretation of most such results is that the impurities will change several characteristics of the material at the same time, and it is not always clear which change is the most important. Thus, if host and solute atoms have different numbers of valence electrons, there may be a modification in the electron concentration upon which, according to the current theory,[3] the criterion for superconductivity sensitively depends. Alternatively, there might be a change in the effective electron-electron interaction due to the solute, and this interaction enters current theory in a similarly critical way. Finally at the larger concentrations, there might be some upset in the phonon spectrum.

To overcome such objections, and at the same time to investigate relationships between superconductivity and ferromagnetism, Matthias and co-workers[4] studied solutions of the various rare earths in lanthanum. The rare earths differ from lanthanum only in the number of inner-shell, *f*, electrons. Hence changes in the conduction-electron density should be minimal in this case. Also the field near an impurity should not be too different from that near a lanthanum atom. No very large, purely orbital, scattering effects are therefore to be expected.

Yet it turned out that the reduction in transition temperature was surprisingly large: just over one atomic percent of gadolinium reduced it almost to zero. Furthermore the reduction depended more nearly on the spin, rather than on the magnetic moment, of the solute, being largest by far for gadolinium, which has the largest spin ($S=\frac{7}{2}$) and much smaller for holmium and dysprosium whose ions have the largest magnetic moments. (We assume here that the rare earths are present in their trivalent form, the outer electrons having joined the sea of conduction electrons.) This led Herring[5] to suggest that an exchange interaction between the conduction electrons and the *f*-shell spins is responsible for the reduction in transition temperature, and his rough estimate showed that with an exchange constant of about 0.2 volt one would indeed obtain the observed reduction in T_c. Part of this paper is concerned with a calculation of this effect. That the magnetic dipole fields of the solute ions are too weak to account for the observations is demonstrated in Appendix I.

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[1] Lynton, Serin, and Zucker, J. Phys. Chem. Solids **3**, 165 (1957).

[2] B. Serin, International Conference on Electronic Properties of Metals at Low Temperatures, Geneva, 1958 (unpublished).

[3] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957). Hereafter referred to as B.C.S.

[4] Matthias, Suhl, and Corenzwit, Phys. Rev. Letters **1**, 93 (1958).

[5] C. Herring, Kamerlingh Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958 [Suppl. Physica **24**, (September, 1958)].

Other experiments, by Lynton, Serin, and Zucker[1] and by Serin, Lynton, and Chanin,[2] using nonmagnetic impurities, yielded results amenable to a similar interpretation for sufficiently small impurity concentrations. They found that their initial reduction in T_c seemed to be a universal function of the residual resistance of the specimen, rather than of the particular impurity introduced. However, as the concentration increased, other effects rapidly became dominant. The critical concentration above which this occurred was extremely small ($<0.1\%$). Thus this case is not as unequivocally related to scattering as the spin exchange mechanism. In either case a reduction of the transition temperature can come about in the manner already outlined by Herring.[5] In second-order perturbation theory, the free energies of both the normal and the superconducting state are depressed; however, the decrease is slightly greater for the normal than for the superconducting state. Consequently the transition from the superconducting to the normal state will occur at a lower temperature than in the absence of impurities. The perturbation causes an electron to be scattered from one plane-wave state to another (with or without possible spin reversal according to whether the interaction is spin dependent or not). In second order each such scattering contributes to the lowering of the free energy an amount depending on the reciprocal difference between the energies of the final and initial momentum states. For electrons whose initial and final energies are remote from the Fermi energy, this contribution is about the same in the normal and superconducting states; but when both initial and final states are within a neighborhood ϵ_0 of the Fermi surface (where ϵ_0 is the energy gap of the B.C.S. theory) the reduction of the free energy is greater for the normal state. The reason is that in the normal condition, the energy denominator can go to zero; in the superconducting state it cannot become smaller than $2\epsilon_0$. When only one or other of the initial or final states falls within the gap region no simple estimate of this kind is possible; and a detailed analysis becomes necessary.

Though such a procedure seems perfectly straightforward, it is subject to a serious weakness. Let $\xi = N_I/N$ be the impurity concentration. One might suppose that, in order to relate the value of ξ required to reduce the transition temperature from T_c to T_c^*, one may simply calculate the free energies, $F_n(T_c^*) - \xi\delta F_n(T_c^*)$ of the normal, and $F_s(T_c^*) - \xi\delta F_s(T_c^*)$ of the superconducting state, and equate the two,[6] giving

$$\xi = \frac{F_n(T_c^*) - F_s(T_c^*)}{\delta F_n(T_c^*) - \delta F_s(T_c^*)}.$$

If to evaluate $\delta F_s(T)$ in this formula one uses a set of states appropriate to the unperturbed sample, featuring the energy gap at temperature T_c^* of the pure sample; that is to say, if one follows the perturbation theory of the B.C.S. paper to the letter, this formula fails to predict the linear behavior observed for the initial decline of T_c *versus* ξ in the case of nonmagnetic scattering. In fact for both exchange and nonmagnetic scattering it predicts $dT/d\xi \rightarrow 0$ as $\xi \rightarrow 0$, contrary to reference 1. The reason for this difficulty could be the following: If we take the view that the impure superconductor behaves in essentially the same way as a pure superconductor, then its energy gap must go to zero at T_c^*. Thus, arbitrarily close to T_c^*, the actual state of the medium is one with an arbitrarily small energy gap. To reach this state from the unperturbed state of the pure sample, which at T_c^* has a finite energy gap, would require carrying perturbation theory to extremely high order, certainly higher than second. There are two ways out of this dilemma. One is to revert to a very much earlier point in superconductivity theory, and to determine what effect the impurities have on the electron-phonon interaction which, in turn, leads to a modification in the effective electron-electron interaction.[7] Thereby one will arrive at the correctly modified energy gap, and hence at the new transition temperature. This approach will form the subject of a later communication. The other way out is that taken by Herring in his original calculation. The essence of this view is to calculate the change in transition temperature "from a safe distance," assuming the impure substance to obey the law of corresponding states. This law gives a universal proportionality between the energy gap *at absolute zero*, and the transition temperature. Let us assume that ξ is not sufficient to reduce T_c to zero. Then we may calculate the difference in the free energy shifts *at absolute zero* for the impure and pure sample on the one hand by perturbation theory (which at $T=0$ should now be more reliable), and on the other hand by a rigorous theory. This would give [see B.C.S. Eq. (2.42)]

$$-\xi[\delta F_n(0) - \delta F_s(0)] = \tfrac{1}{2}[\epsilon_0^2(\xi,0) - \epsilon_0^2(0,0)]N(0),$$

where $N(0)$ is the number of states per unit energy range near the Fermi surface, and $\epsilon_0(\xi,0)$ the energy gap which a rigorous theory would predict at concentration ξ and temperature zero. More generally, we may imagine that we start with a sample at concentration ξ,

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[6] That the shift in the free energies is linear in the concentration for small concentration will become apparent later, but is in any case obvious on general grounds.

[7] This modification is not to be confused with the *additional* effective electron-electron interaction via virtual excited states of the scatterers. For scatterers that are assumed structureless such virtual states do not exist at all, and so no extra electron interaction can arise. This is presumably the case for nonmagnetic scattering. In the case of exchange scattering it is true that the ionic spins have different states; however, a further requirement for electron interaction via these is that they be nondegenerate in energy. For gadolinium in lanthanum, different spin states differ only very slightly in energy as the result of weak spin-orbit plus crystal field effects, and the extra electron interaction is therefore quite negligible. For other rare earths, with nonzero orbital angular momentum, it may be slightly greater; however, the continuity of the data with those for gadolinium suggest that there, too, the effect can be neglected.

with energy gap $\epsilon_0(\xi,0)$ and add a small concentration $d\xi$. Then the analog of the last equation is

$$-d\xi[\delta F_n(\xi,0)-\delta F_s(\xi,0)]=\epsilon_0(\xi,0)N(0)d\epsilon_0,$$

or

$$\frac{d\epsilon_0}{d\xi}=-\frac{\delta F_n(\xi,0)-\delta F_s(\xi,0)}{N(0)\epsilon_0(\xi,0)},$$

which is a differential equation for $\epsilon_0(\xi,0)$, and thus, by the law of corresponding states, for $T_c^*(\xi)$. Since δF_n, on the right-hand side is not explicitly dependent on concentration, while δF_s depends on it only through ϵ_0, this equation is readily integrated. For exchange scattering, the right-hand side is independent of ϵ_0, so that a linear relation between T_c^* and ξ is obtained. For the nonmagnetic case, too, T_c^* *versus* ξ is initially linear, but T_c^* approaches zero with steadily diminishing slope.

To summarize, if the perturbation is of a kind that brings about a first-order phase change, with the energy gap remaining finite at the transition, the perturbation theory as given by B.C.S. may safely be applied right up to $T=T_c^*$. But when the perturbation changes T_c without changing the order of the transition, that is to say when ϵ_0 goes to zero at T_c^*, one cannot apply it directly near T_c^*. Then one must either recalculate the interaction in the presence of the perturbation or use a special artifice like the above. In this paper we shall first calculate the various F's at arbitrary temperature T (since this is no harder than at $T=0$) and demonstrate in a little more detail why this leads the trouble near T_c^*. Finally we set $T=0$, and use the law of corresponding states to determine T_c^* on the assumption that $\epsilon_0(T_c^*)=0$.

Present evidence, in reference 4 and in another paper being submitted for publication, somewhat favors the view that the gap is finite at T_c^* in the magnetic case. $dT^*/d\xi$ seems to increase as $T\to 0$, and by and large the T^* *versus* ξ curves have a tandency to convexity. Evidence in the nonmagnetic case[1] favors the view that the gap vanishes at T_c^*.

2. THE UNPERTURBED HAMILTONIAN

In calculating the free energies to second order in the impurity perturbation, we make the assumption that the scatterer does not upset either the normal or superconducting states in any qualitative way. This assumption is reasonable if the concentration of impurities is not too high, and if the scatterers are "structureless," that is to say if they are not capable of changing to states of different energy by interaction with the electrons. If they can change state, a more detailed treatment than the one presented here is required.

Although the second-order calculation just indicated could be carried out using the prescription for the formation of matrix elements given in the paper[3] of Bardeen, Cooper, and Schrieffer, we shall find it more convenient to use the formalism developed by Bogoliubov[8] and Valatin.[9] In the language of these authors the reduced B.C.S. Hamiltonian [B.C.S., Eq. (2.14)], which in the notation of B.C.S. reads

$$\begin{aligned}\mathcal{H}^0=\sum \epsilon_{\mathbf{k}}(c_{\mathbf{k}\uparrow}{}^*c_{\mathbf{k}\uparrow}+c_{\mathbf{k}\downarrow}{}^*c_{\mathbf{k}\downarrow})\\ -\sum V_{\mathbf{k}\mathbf{k}'}c_{\mathbf{k}'\uparrow}{}^*c_{-\mathbf{k}'\downarrow}{}^*c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow},\end{aligned}\tag{1}$$

(with $\epsilon_{\mathbf{k}}$ measured from the Fermi surface), is "diagonalized" as follows: The c^* and c are replaced by new fermion creation and destruction operators d^* and d through the transformations

$$\begin{aligned}c_{\mathbf{k}\uparrow}&=\cos(\theta_{\mathbf{k}}/2)d_{k\uparrow}+\sin(\theta_{\mathbf{k}}/2)d_{-k\downarrow}{}^*,\\ c_{\mathbf{k}\downarrow}&=\cos(\theta_{\mathbf{k}}/2)d_{\mathbf{k}\downarrow}-\sin(\theta_{\mathbf{k}}/2)d_{-\mathbf{k}\uparrow}{}^*.\end{aligned}\tag{2}$$

The $\theta_{\mathbf{k}}$'s are disposable constants which are determined by substituting (2) into (1), and equating to zero the coefficient of the term $(d_{\mathbf{k}\uparrow}{}^*d_{-\mathbf{k}\downarrow}{}^*+d_{-\mathbf{k}\downarrow}d_{\mathbf{k}\uparrow})$. The remaining terms then have a form diagonal in $d_{k\uparrow}{}^*d_{k\uparrow}$ etc. The kinetic energy part of $\mathcal{H}^0$ will make a purely numerical contribution to the coefficient of $(d_{\mathbf{k}\uparrow}{}^*d_{-\mathbf{k}\downarrow}{}^*+d_{-\mathbf{k}\downarrow}d_{\mathbf{k}\uparrow})$; on the other hand the interaction energy will also make contributions of the form $d_{\mathbf{k}}{}^*d_{\mathbf{k}}$, which must be replaced by their average values at the temperature in question. The equation for $\theta_{\mathbf{k}}$ finally obtained is

$$\epsilon_{\mathbf{k}}\tan\theta_{\mathbf{k}}=\tfrac{1}{2}\sum V_{\mathbf{k}\mathbf{k}'}\sin\theta_{\mathbf{k}'}(1-d_{\mathbf{k}'\uparrow}{}^*d_{\mathbf{k}'\uparrow}-d_{\mathbf{k}'\downarrow}{}^*d_{\mathbf{k}'\downarrow}).$$

A comparison with B.C.S. [Eqs. (3.22) through (3.25)] shows that the $h_{\mathbf{k}}$ of that paper correspond to the $\sin^2(\theta_{\mathbf{k}}/2)$, and that $2f_{\mathbf{k}}$ corresponds to the thermal average of $d_{\mathbf{k}\uparrow}{}^*d_{\mathbf{k}\uparrow}+d_{\mathbf{k}\downarrow}{}^*d_{\mathbf{k}\downarrow}$. Taking $V_{\mathbf{k}\mathbf{k}'}=V$ to be constant in the interval $|\epsilon_{\mathbf{k}}|<\hbar\omega$, $|\epsilon_{\mathbf{k}'}|<\hbar\omega$ and zero elsewhere, one obtains the solution

$$\begin{aligned}\sin\theta_{\mathbf{k}}&=\frac{\epsilon_0(\mathbf{k})}{[\epsilon_{\mathbf{k}}{}^2+\epsilon_0{}^2(\mathbf{k})]^{\frac{1}{2}}},\quad |\epsilon_{\mathbf{k}}|<\hbar\omega\\ &=0\text{ (elsewhere)},\end{aligned}\tag{3}$$

where the energy gap $\epsilon_0(\mathbf{k})$ is constant, $=\epsilon_0$, when $|\epsilon_{\mathbf{k}}|<\hbar\omega$, and zero elsewhere. [In these inequalities $\hbar\omega$ stands for some typical phonon energy (see B.C.S.).] ϵ_0 is the solution of the equation

$$1=\frac{V}{2}\sum_{|\epsilon_k|<\hbar\omega}\frac{1-2f_{\mathbf{k}}}{[\epsilon_k{}^2+\epsilon_0{}^2(\mathbf{k})]^{\frac{1}{2}}}.$$

The transformed Hamiltonian now takes the form

$$\begin{aligned}\mathcal{H}^0=\text{zero-point terms}+\sum E_{\mathbf{k}}(d_{\mathbf{k}\uparrow}{}^*d_{\mathbf{k}\uparrow}+d_{\mathbf{k}\downarrow}{}^*d_{\mathbf{k}\downarrow})\\ +\text{terms of fourth order in the } d\text{'s},\end{aligned}\tag{4}$$

where

$$E_k=[\epsilon_{\mathbf{k}}{}^2+\epsilon_0{}^2(\mathbf{k})]^{\frac{1}{2}}.\tag{5}$$

Here, we need not concern ourselves with the zero-point

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[8] N. N. Bogoliubov, J. Exptl. Theoret. Phys. U.S.S.R. **34**, 65 (1958).

[9] J. G. Valatin, Nuovo cimento **7**, 843 (1958).

terms, since they are involved only in the evaluation of the unperturbed state of the medium. The fourth-order terms are neglected since they only cause zero-point motions about states of the quadratic part of the Hamiltonian, which lead to a negligible correction of their energies.

Thus, for our purposes, we may take the unperturbed Hamiltonian in the form

$$\mathcal{H}^0=\sum E_{\mathrm{k}}(d_{\mathrm{k}\uparrow}{}^*d_{\mathrm{k}\uparrow}+d_{\mathrm{k}\downarrow}{}^*d_{\mathrm{k}\downarrow}), \tag{6}$$

and the mean value of the occupation number $n_{\mathrm{k}}=d_{\mathrm{k}}{}^*d_{\mathrm{k}}$ at temperature T is given by the Fermi function

$$f_{\mathrm{k}}=\frac{1}{e^{E_{\mathrm{k}}/kT}+1}.$$

3. CALCULATION OF THE FREE ENERGIES IN THE PRESENCE OF EXCHANGE SCATTERING

The Hamiltonian (6) must now be supplemented by a perturbation appropriate to exchange scattering. If it is assumed that the exchange interaction between conduction electrons and impurity spins is strictly localized to a very small region around the impurity, the perturbing Hamiltonian takes the form

$$\mathcal{H}'=J\Omega_0\sum_i\int\delta(\mathbf{r}-\mathbf{R}_i)\mathbf{S}_i\cdot\mathbf{s}(\mathbf{r})dv, \tag{7}$$

where Ω_0 is the volume occupied by the ionic spin $\mathbf{S}_i$, and $\mathbf{s}(\mathbf{r})$ the conduction-electron spin density at $\mathbf{r}$. In second quantized form this becomes

$$\mathcal{H}'=\frac{J}{2}\frac{1}{N}\sum_{\mathrm{p,q}}[S_{\mathrm{p-q}}{}^+c_{\mathrm{p}\downarrow}{}^*c_{\mathrm{q}\uparrow}+S_{\mathrm{p-q}}{}^-c_{\mathrm{q}\uparrow}{}^*c_{\mathrm{p}\downarrow}+S_{\mathrm{p-q}}{}^z(c_{\mathrm{p}\uparrow}{}^*c_{\mathrm{q}\uparrow}-c_{\mathrm{p}\downarrow}{}^*c_{\mathrm{q}\downarrow})],$$

with

$$S_{\mathrm{p}}{}^+=\sum S_i{}^+e^{-i\mathbf{p}\cdot\mathbf{R}_i}\text{ etc.} \tag{8}$$

It has been supposed, in deriving (8) from (7) that the basis functions are plane-wave states (normalized to the total volume Ω), $(1/\Omega^{\frac{1}{2}})e^{i\mathbf{p}\cdot\mathbf{r}}$, and that $\Omega/\Omega_0=N$ the total number of atoms in the sample.

The transformation (2) changes this into

$$\begin{aligned}\mathcal{H}^1=\frac{J}{2N}\sum\{&S_{\mathrm{p-q}}{}^+[\alpha_{\mathrm{pq}}d_{\mathrm{p}\downarrow}{}^*d_{\mathrm{q}\uparrow}\\&+\tfrac{1}{2}\beta_{\mathrm{pq}}(d_{\mathrm{p}\downarrow}{}^*d_{-\mathrm{q}\downarrow}{}^*+d_{-\mathrm{p}\uparrow}d_{\mathrm{q}})_{\uparrow}]+\text{comp. conj.}\\&+S_{\mathrm{p-q}}{}^z[\alpha_{\mathrm{pq}}(d_{\mathrm{p}\uparrow}{}^*d_{\mathrm{q}\uparrow}-d_{\mathrm{p}\downarrow}{}^*d_{\mathrm{q}\downarrow})\\&+\beta_{\mathrm{pq}}(d_{\mathrm{p}\uparrow}{}^*d_{-\mathrm{q}\downarrow}{}^*-d_{-\mathrm{p}\downarrow}d_{\mathrm{q}\uparrow})]\},\end{aligned} \tag{9}$$

where

$$\alpha_{\mathrm{pq}}=\cos[(\theta_{\mathrm{q}}-\theta_{\mathrm{p}})/2]\quad\beta_{\mathrm{pq}}=\sin[(\theta_{\mathrm{q}}-\theta_{\mathrm{p}})/2]. \tag{10}$$

Our object is to determine the temperature at which the free energy of the normal state becomes equal to that of the superconducting state, in the face of perturbation (9). This could, of course, be accomplished by expanding the free energy, $F=-kT\ln\operatorname{Tr}\exp[-(\mathcal{H}^0+\mathcal{H}^1)/kT]$ in a power series in $\mathcal{H}^1$, taking note of the noncommutativity of $\mathcal{H}^0$ and $\mathcal{H}^1$, and using a representation in which the d^*d are diagonal for evaluating the trace. However, this denies one the possibility of examining the reasons for the qualitative failure of such a procedure as mentioned in the introduction. An alternative procedure, which leaves this possibility open, is to find a canonical transformation of $\mathcal{H}^0+\mathcal{H}^1$, which eliminates $\mathcal{H}^1$ to the first order. The new Hamiltonian then consists of $\mathcal{H}^0$ plus a second-order correction. The nonrandom part of this correction, which arises from excitation of an electron by a given spin and de-excitation of the electron by the same spin makes a nonvanishing contribution to the free energy. The part involving excitation by a given spin and de-excitation by another spin leaves one with an effective spin-spin interaction of the type examined by many investigators[10–12] for the normal metal, which, of course, has its analog in the superconductor.

Following this procedure, we seek a transformation function such that the new Hamiltonian

$$\mathcal{H}_{\mathrm{new}}=\exp(-i\mathcal{S})(\mathcal{H}^0+\mathcal{H}^1)\exp(i\mathcal{S}) \tag{11}$$

no longer contains terms of first order in J. The new eigenfunctions will be related to the original ones by

$$\psi_{\mathrm{new}}=\exp(-i\mathcal{S})\psi_{\mathrm{old}},$$

$\mathcal{S}$ itself will be small, of the same order as $\mathcal{H}^1$. Expanding the exponentials to second order, we obtain

$$\mathcal{H}_{\mathrm{new}}=\mathcal{H}^0+\mathcal{H}^1+i[\mathcal{H}^0,\mathcal{S}]+\{i[\mathcal{H}^1,\mathcal{S}]-\tfrac{1}{2}[[\mathcal{H}^0,\mathcal{S}],\mathcal{S}]\}.$$

If $\mathcal{S}$ is determined in such a way that

$$\mathcal{H}^1=-i(\mathcal{H}^0,\mathcal{S}), \tag{12}$$

then the new Hamiltonian, correct to second order, is

$$\mathcal{H}_{\mathrm{new}}=\mathcal{H}^0+\tfrac{1}{2}(\mathcal{H}^1,\mathcal{S}). \tag{13}$$

It is readily verified that, with $\mathcal{H}^1$ of the form (9),

$$\begin{aligned}\mathcal{S}=i\frac{J}{N}\sum_{\mathrm{pq}}\{&S_{\mathrm{p-q}}{}^+[f_{\mathrm{pq}}d_{\mathrm{p}\downarrow}{}^*d_{\mathrm{q}\uparrow}\\&+\tfrac{1}{2}g_{\mathrm{pq}}(d_{\mathrm{p}}{}^*{}_{\downarrow}d_{-\mathrm{q}\downarrow}{}^*-d_{-\mathrm{p}\uparrow}d_{\mathrm{q}\uparrow})]-\text{comp. conj.}\\&+S_{\mathrm{p-q}}{}^z[f_{\mathrm{pq}}(d_{\mathrm{q}\uparrow}{}^*d_{\mathrm{q}\uparrow}-d_{\mathrm{p}\downarrow}{}^*d_{\mathrm{q}\downarrow})\\&+g_{pq}(d_{\mathrm{p}}{}^*{}_{\uparrow}d_{-\mathrm{q}\downarrow}{}^*+d_{-\mathrm{p}\downarrow}d_{\mathrm{q}\uparrow})]\},\end{aligned} \tag{14}$$

provided the unperturbed Hamiltonian contains no spin-dependent terms whatever. Here

$$f_{\mathrm{pq}}=\alpha_{\mathrm{pq}}/(E_{\mathrm{p}}-E_{\mathrm{q}}),\quad g_{\mathrm{pq}}=\beta_{\mathrm{pq}}/(E_{\mathrm{p}}+E_{\mathrm{q}}).$$

(We note at this point that it will not be necessary to

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[10] H. Fröhlich and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A175**, 382 (1940).

[11] M. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

[12] K. Yosida, Phys. Rev. **106**, 893 (1957).

derive separate formulas for the normal and superconducting states. Those for the normal state follow from those for the superconducting state by writing $\epsilon_0 \equiv 0$.) The new Hamiltonian (13) will contain a great variety of terms. We assume here that the spin-other spin terms contained in it are of insufficient magnitude relative to the temperature to cause spontaneous ordering. Then the spin-spin terms contribute nothing to the partition sum in order J^2. Likewise terms of the form $(S_i^+)^2$, $(S_i^-)^2$ or any linear functions of the $\mathbf{S}_i$ that will occur in the evaluation of $(\mathcal{H}^1, \mathcal{S})$ contribute nothing. The only terms that do make themselves felt are the "self" terms out of $S_{\mathbf{p}'-\mathbf{q}'}^+ \cdot S_{\mathbf{p}-\mathbf{q}}^-$, $S_{\mathbf{p}'-\mathbf{q}'}^- \cdot S_{\mathbf{p}-\mathbf{q}}^+$, $S_{\mathbf{p}'-\mathbf{q}'}^z \cdot S_{\mathbf{p}-\mathbf{q}}^z$, that is terms involving the same spin twice. Bearing these facts in mind, we find after some tedious but straightforward evaluations of commutators that[13]

$$\begin{aligned}\mathcal{H}_{\text{new}} &= \mathcal{H}^0 - S(S+1) \\ &\times \frac{J^2}{4}\frac{N_I}{N^2}\Bigg[\sum_{\mathbf{pq}}\left(\frac{\alpha_{\mathbf{pq}}^2}{E_\mathbf{p}-E_\mathbf{q}} - \frac{\beta_{\mathbf{pq}}^2}{E_\mathbf{p}+E_\mathbf{q}}\right) \\ &\times (d_{\mathbf{q}\uparrow}^* d_{\mathbf{q}\uparrow} + d_{\mathbf{q}\downarrow}^* d_{\mathbf{q}\downarrow}) + \sum_{\mathbf{pq}} \alpha_{\mathbf{pq}}\beta_{\mathbf{pq}} \\ &\times \left(\frac{1}{E_\mathbf{p}+E_\mathbf{q}} + \frac{1}{E_\mathbf{p}-E_\mathbf{q}}\right)(d_{\mathbf{q}\uparrow}^* d_{-\mathbf{q}\downarrow}^* + d_{-\mathbf{q}\downarrow} d_{\mathbf{q}\uparrow}) \\ &+ \sum \frac{\beta_{\mathbf{pq}}^2}{E_\mathbf{p}+E_\mathbf{q}}\Bigg] \equiv \mathcal{H}^0 + \mathcal{H}_{\text{new}}^1. \qquad (15)\end{aligned}$$

The first of the correction terms in the bracket is a shift in the kinetic energy of the new fermions. It is important only insofar as a finite temperature permits excitation of such fermions. The last term in the bracket is a "zero point" shift,[14] and, as we shall see, it gives the most important contribution to the lowering of T_c. The middle term, involving d^*d^* and dd does not affect the calculation of the free energy to second order in J, since (with $\beta = 1/kT$),

$$\begin{aligned}\operatorname{Tr}\exp[-\beta(\mathcal{H}^0+\mathcal{H}_{\text{new}}^1)] &= \operatorname{Tr}\exp(-\beta\mathcal{H}^0) \\ &- \operatorname{Tr}\left[\exp(-\beta\mathcal{H}^0)\int_0^\beta \exp(x\mathcal{H}^0)\mathcal{H}_{\text{new}}^1\exp(-x\mathcal{H}^0)dx\right],\end{aligned}$$

and in a representation in which d^*d is diagonal the contribution to the second trace on the right from the middle term in $\mathcal{H}_{\text{new}}^1$ is zero. However it is clear that in a situation in which the true energy gap is very small, the middle term enters the gap condition in a vital way, and the simple expansion procedure for the free energy is not satisfactory as indicated in the introduction. One should really return to the full Hamiltonian, *not* determine ϵ_0 from the unperturbed Hamiltonian alone, but include perturbation terms in the coefficient of (d^*d^*+dd) before equating it to zero. Then the "true gap" (to second order) can be evaluated. Disregarding this problem, we omit the middle term, retaining only the diagonal portions of $\mathcal{H}_{\text{new}}^1$, including the zero-point term. We then have

$$\begin{aligned}F &= -(1/\beta)\ln\operatorname{Tr}\exp[-\beta(\mathcal{H}^0+\mathcal{H}_{\text{new}}^1)] \\ &= F^0 - \xi\delta F,\end{aligned}$$

where $\xi = N_I/N$ is the impurity concentration, F^0 the unperturbed free energy and

$$\begin{aligned}\delta F &= \frac{1}{\xi}\frac{\operatorname{Tr}\mathcal{H}_{\text{new}}^1\exp(-\beta\mathcal{H}^0)}{\operatorname{Tr}\exp(-\beta^0)} \\ &= \frac{J^2}{2N}S(S+1)\sum\left(\frac{\alpha_{\mathbf{pq}}^2}{E_\mathbf{p}-E_\mathbf{q}} - \frac{\beta_{\mathbf{pq}}^2}{E_\mathbf{p}+E_\mathbf{q}}\right)f(E_\mathbf{q}) \\ &\quad + \frac{J^2}{4N}S(S+1)\sum\frac{\beta_{\mathbf{pq}}^2}{E_\mathbf{p}+E_\mathbf{q}}. \qquad (16)\end{aligned}$$

As outlined in the introduction, in the case of a first-order transition, the temperature T at which the free energies of normal and superconducting states become equal for a given concentration ξ, so that the specimen becomes normal, is given by the equation

$$F_n^{(0)}(T) - \xi\delta F_n(T) = F_s^{(0)}(T) - \xi\delta F_s(T),$$

which may be written

$$\xi = \frac{F_n^{(0)}(T) - F_s^{(0)}(T)}{\delta F_n(T) - \delta F_s(T)},$$

or

$$\xi = \frac{(1/8\pi)H_c^2(T)\Omega}{\delta F_n(T) - \delta F_s(T)}, \qquad (17)$$

where Ω is the sample volume, and $H_c(T)$ the critical field at temperature T. As already noted, we derive δF_n as a special case from (16) by setting $\epsilon_0(\mathbf{p})$, $\epsilon_0(\mathbf{q})$ equal to zero everywhere, not just outside the interval $-\hbar\omega < \epsilon_p < \hbar\omega$.

Utilizing the expressions for $\sin\theta_\mathbf{p}$, $\sin\theta_\mathbf{q}$ from (3), and using the definitions (10), we obtain from (16)

$$\begin{aligned}\delta F_s &= S(S+1)\frac{J^2}{4}\frac{1}{N}\Bigg[8\sum_{\epsilon_\mathbf{p}>0,\epsilon_\mathbf{q}>0}\frac{E_\mathbf{q}^2+\epsilon_0(\mathbf{p})\epsilon_0(\mathbf{q})}{E_\mathbf{q}(E_\mathbf{p}^2-E_\mathbf{q}^2)}f(Eq) \\ &\quad + 2\sum_{\epsilon_\mathbf{p},\epsilon_\mathbf{q}>0}\frac{E_\mathbf{p}E_\mathbf{q}-\epsilon_0(\mathbf{p})\epsilon_0(\mathbf{q})}{(E_\mathbf{p}+E_\mathbf{q})E_\mathbf{p}E_\mathbf{q}}\Bigg], \qquad (18a)\end{aligned}$$

$$\begin{aligned}\delta F_n &= S(S+1)\frac{J^2}{4}\frac{1}{N} \\ &\times\left[8\sum_{\epsilon_\mathbf{p}>0,\epsilon_\mathbf{q}>0}\frac{\epsilon_\mathbf{q}f(\epsilon_\mathbf{q})}{\epsilon_\mathbf{p}^2-\epsilon_\mathbf{q}^2} + 2\sum_{\epsilon_\mathbf{p},\epsilon_\mathbf{q}>0}\frac{1}{\epsilon_\mathbf{p}+\epsilon_\mathbf{q}}\right]. \qquad (18b)\end{aligned}$$

---

[13] Actually, for obvious symmetry reasons, only the S^z part of the interaction need have been retained, if in the final result for $\mathcal{H}_{\text{new}}$, $(S_i^Z)^2$ is replaced by $(S_i^x)^2+(S_i^y)^2+(S_i^z)^2 = S(S+1)$.

[14] The name "zero point" is meant to imply independence of excitation of the d's. The term still depends on temperature through ϵ_0.

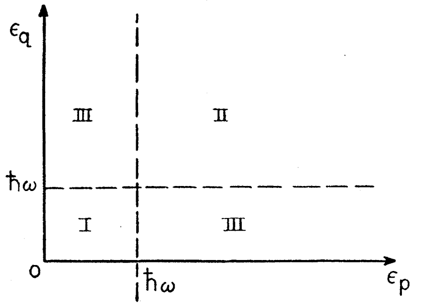

FIG. 1. Division of the ϵ_p-ϵ_q plane for evaluation of the free energy shifts.

It will turn out that the f-dependent terms make a negligible contribution to $\delta F_n - \delta F_s$. Therefore we begin with a discussion of the f-independent "zero point" terms. We divide the ϵ_p, ϵ_q plane into three regions (Fig. 1). Region I, is the square $0<\epsilon_p<\hbar\omega$; $0<\epsilon_q<\hbar\omega$. Region II is $\epsilon_p>\hbar\omega$, $\epsilon_q>\hbar\omega$. Region III consists of two parts: $(\epsilon_p>\hbar\omega, 0<\epsilon_q<\hbar\omega)$ and $(0<\epsilon_p<\hbar\omega, \epsilon_q>\hbar\omega)$. Over Region I, the number of states per unit energy range hardly varies, and is almost equal to $N(0)$, the density of states near the Fermi level. In Region I we have therefore

$$\sum_{0<\epsilon_p,\epsilon_q<\hbar\omega} \frac{1}{\epsilon_p+\epsilon_q} = [N(0)]^2 \int_0^{\hbar\omega}\int_0^{\hbar\omega} \frac{1}{\epsilon_p+\epsilon_q} d\epsilon_p d\epsilon_q$$
$$= [N(0)]^2 \hbar\omega 2 \ln 2. \tag{19}$$

On the other hand, writing $\epsilon_p = \epsilon_0 \sinh\theta_p$ etc., we have

$$\sum_{0<\epsilon_p,\epsilon_q<\hbar\omega} \frac{E_pE_q-\epsilon_0^2}{E_pE_q(E_p+E_q)}$$
$$= [N(0)]^2\epsilon_0 \int_0^{\varphi}\int_0^{\varphi} \frac{\cosh\theta_p \cosh\theta_q - 1}{\cosh\theta_p+\cosh\theta_q} d\theta_p d\theta_q,$$

where $\varphi = \sinh^{-1}(\hbar\omega/\epsilon_0)$. The integral may obviously be written

$$\left[\varphi \sinh\varphi - \int_0^{\varphi}\int_0^{\varphi} \frac{\sinh^2\theta_q}{\cosh\theta_p+\cosh\theta_q} d\theta_p d\theta_q\right]$$
$$-2\int_0^{\varphi}\int_0^{\varphi} \frac{d\theta_p d\theta_q}{\cosh\theta_p+\cosh\theta_q}. \tag{20}$$

We have

$$\int^{\varphi} \frac{d\theta_p}{\cosh\theta_p+\cosh\theta_q} d\theta_p$$
$$= \frac{1}{\sinh\theta_q} \ln\left(\cosh\frac{\theta_q+\varphi}{2} \Big/ \cosh\frac{\theta_q-\varphi}{2}\right). \tag{21}$$

For the purpose of evaluating the last integral in (20), we express the logarithm in (21) as

$$\theta_q + \ln(1+e^{-(\varphi+\theta_q)}/1+e^{-(\varphi-\theta_q)}). \tag{22}$$

Bearing in mind that φ in practice should be a large number, at least in the weak coupling approximation, we may expand the logarithm as a power series. Then we find that the integrals in the series all have the form $e^{-n\varphi}\int_0^{\varphi}(\sinh n\theta/\sinh\theta)d\theta$, and thus tend to zero as $e^{-\varphi}$. Hence the last integral in (20) is effectively

$$\int \frac{\theta_q}{\sinh\theta_q} d\theta_q = \frac{\pi^2}{4}$$

neglecting terms of order $(\epsilon_0/\hbar\omega)$. The integral in the square bracket can be evaluated without approximation, using (21) and integrating by parts. The final result is

$$\sum_{0<\epsilon_p,\epsilon_q<\hbar\omega} \frac{E_pE_q-\epsilon_0^2}{E_pE_q(E_p+E_q)}$$
$$= [N(0)]^2\epsilon_0\left[-\frac{\pi^2}{2} + \frac{\hbar\omega}{\epsilon_0} 2\ln 2 - \frac{\epsilon_0}{\hbar\omega}\ln\frac{\hbar\omega}{\epsilon_0} + O\left(\frac{\epsilon_0}{\hbar\omega}\right)\right].$$

Hence the f-independent contribution to $\delta F_n - \delta F_s$ from Region I is

$$2S(S+1)\frac{J^2}{4N}[N(0)]^2\epsilon_0\left[\frac{\pi^2}{2} + \frac{\epsilon_0}{\hbar\omega}\ln\frac{\hbar\omega}{\epsilon_0} + O\left(\frac{\epsilon_0}{\hbar\omega}\right)\right]. \tag{23}$$

In Region II, δF_n and δF_s are equal so that $\delta F_n - \delta F_s = 0$. In Region III, since we have to integrate over a large energy range with respect to one of the two variables it is necessary to make some assumption about the variation of the state density. We assume a simple parabolic energy dependence. If we pick the region $\epsilon_p>\hbar\omega$, $0<\epsilon_q<\hbar\omega$ of the two regions of type III (for the other the f-independent contribution is the same) we then have

$$N(\epsilon_p) = N(0)(1+\epsilon_p/\epsilon_f)^{\frac{1}{2}},$$

where ϵ_f is the Fermi energy.

From the two regions of type III we thus get a total f-independent contribution

$$4\left[\sum_{\mathrm{III}} \frac{1}{\epsilon_p+\epsilon_q} - \sum_{\mathrm{III}} \frac{1}{\epsilon_p+E_q}\right]$$
$$= +\sum_{\mathrm{III}} \frac{E_q-\epsilon_q}{(\epsilon_p+\epsilon_q)(\epsilon_p+E_q)}$$
$$= 4[N(0)]^2 \int_0^{\hbar\omega} d\epsilon_q \int_{\omega/\epsilon_f}^{\infty} \frac{(1+x)^{\frac{1}{2}}}{(x+\epsilon_q/\epsilon_f)(x+E_q/\epsilon_f)}$$
$$\times (E_q-\epsilon_q)dx.$$

Writing $1+x=z^2$, one can easily evaluate this integral, bearing in mind that, in $(0,\hbar\omega)$, ϵ_q is much less than ϵ_f. After integration with respect to ϵ_p, one is left with

$$4[N(0)]^2\int_0^{\hbar\omega}\ln\left[1+\frac{(E_{\mathrm{q}}-\epsilon_{\mathrm{q}})/\hbar\omega}{1+\epsilon_{\mathrm{q}}/\hbar\omega}\right]d\epsilon_{\mathrm{q}}.$$

Now $(E_{\mathrm{q}}-\epsilon_{\mathrm{q}})/\hbar\omega$ is of order $\epsilon_0/\hbar\omega$ which is much less than one. Hence the integral is

$$4[N(0)]^2\int_0^{\hbar\omega}\frac{E_{\mathrm{q}}-\epsilon_{\mathrm{q}}}{\hbar\omega+\epsilon_{\mathrm{q}}}d\epsilon_{\mathrm{q}} =4[N(0)]^2\epsilon_0^2\int_0^{\varphi}\frac{e^{-\theta}\cosh\theta d\theta}{\hbar\omega+\epsilon_0\sinh\theta}.$$

To lowest order in $\epsilon_0/\hbar\omega$ it finally becomes

$$4[N(0)]^2\epsilon_0\left[\frac{\epsilon_0}{2\hbar\omega}\ln\frac{\hbar\omega}{\epsilon_0}+O\left(\frac{\epsilon_0}{\hbar\omega}\right)\right].$$

Thus from the f-independent terms the contribution to $\delta F_n-\delta F_s$ from all regions is

$$S(S+1)\frac{2J^2}{4N}[N(0)]^2\epsilon_0\left[\frac{\pi^2}{2}+2\frac{\epsilon_0}{\hbar\omega}\ln\frac{\hbar\omega}{\epsilon_0}+0\left(\frac{\epsilon_0}{\hbar\omega}\right)\right]. \tag{24}$$

In estimating the f-dependent contribution, we first note that there is no difficulty with vanishing denominators, since

$$\sum\frac{\epsilon_{\mathrm{q}}f(\epsilon_{\mathrm{q}})}{\epsilon_{\mathrm{p}}^2-\epsilon_{\mathrm{q}}^2}=-\frac{1}{4}\left[\sum\frac{f(\epsilon_{\mathrm{p}})+f(\epsilon_{\mathrm{q}})}{\epsilon_{\mathrm{p}}+\epsilon_{\mathrm{q}}}+\sum\frac{f(\epsilon_{\mathrm{p}})-f(\epsilon_{\mathrm{q}})}{\epsilon_{\mathrm{p}}-\epsilon_{\mathrm{q}}}\right],$$

etc., and all the summands are well-behaved near $\epsilon_{\mathrm{p}}=\epsilon_{\mathrm{q}}$. Therefore the sum on the left, when converted to an integral, is equal to its principal value at any point, in particular at $\epsilon_{\mathrm{p}}=\epsilon_{\mathrm{q}}$. This is also the reason why it was not necessary to raise the question if the principal part sign should or should not precede the transformation $\mathcal{S}$.

In Region I we have

$$\begin{aligned}\sum&\left[\frac{\epsilon_{\mathrm{q}}f(\epsilon_{\mathrm{q}})}{\epsilon_{\mathrm{p}}^2-\epsilon_{\mathrm{q}}^2}-\frac{E_{\mathrm{q}}^2+E_0^2}{E_{\mathrm{q}}(E_{\mathrm{p}}^2-E_{\mathrm{q}}^2)}\right]f(E_{\mathrm{q}})\\ &=[N(0)]^2\left\{\int_0^{\hbar\omega}\left[\epsilon_{\mathrm{q}}f(\epsilon_{\mathrm{q}})-\frac{\epsilon_{\mathrm{q}}^2}{E_{\mathrm{q}}}f(E_{\mathrm{q}})\right]\right.\\ &\quad\times\left[\mathrm{P}\int_0^{\hbar\omega}\frac{d\epsilon_{\mathrm{p}}}{\epsilon_{\mathrm{p}}^2-\epsilon_{\mathrm{q}}^2}\right]d\epsilon_{\mathrm{q}}+2\int_0^{\hbar\omega}\frac{\epsilon_0^2}{E_{\mathrm{q}}}f(E_{\mathrm{q}})\\ &\quad\left.\times\left[\mathrm{P}\int_0^{\hbar\omega}\frac{d\epsilon_{\mathrm{p}}}{\epsilon_{\mathrm{p}}^2-\epsilon_{\mathrm{q}}^2}\right]d\epsilon_{\mathrm{q}}\right\}.\end{aligned} \tag{25}$$

Now

$$\mathrm{P}\int_0^{\hbar\omega}\frac{d\epsilon_{\mathrm{p}}}{\epsilon_{\mathrm{p}}^2-\epsilon_{\mathrm{q}}^2}=\frac{1}{2\epsilon_{\mathrm{q}}}\ln\frac{\hbar\omega-\epsilon_{\mathrm{q}}}{\hbar\omega+\epsilon_{\mathrm{q}}},$$

and both $f(\epsilon_{\mathrm{q}})$ and $f(E_{\mathrm{q}})$ are appreciable only for $\epsilon_{\mathrm{q}}\ll\hbar\omega$. Hence the logarithm may be expanded so that for the present purpose

$$\mathrm{P}\int_0^{\hbar\omega}\frac{d\epsilon_{\mathrm{p}}}{\epsilon_{\mathrm{p}}^2-\epsilon_{\mathrm{q}}^2}=-\frac{1}{\hbar\omega}.$$

Thus the last integral in (25) is

$$-2[N(0)]^2\frac{\epsilon_0^2}{\hbar\omega}\int\frac{f(E_{\mathrm{q}})}{E_{\mathrm{q}}}d\epsilon_{\mathrm{q}} =-2[N(0)]^2\frac{\epsilon_0^2}{\hbar\omega}\int_0^{\varphi}f(\epsilon_0\cosh\theta_{\mathrm{q}})d\theta_{\mathrm{q}}. \tag{26}$$

Bearing in mind the definition of f, we see that this integral is less than

$$\int e^{-(\epsilon_0/kT)\cosh\theta}d\theta=K_0(\epsilon_0/kT),$$

one of the modified Bessel functions. For large ϵ_0/kT this varies as $\exp[-(\epsilon_0/kT)]$, for small values it behaves as $\ln(kT/\epsilon_0)$. That is to say the contribution made by (26) is at most of order $(\epsilon_0^2/\hbar\omega)\ln(kT/\epsilon_0)$, which is an order $|\ln(kT/\epsilon_0)/\ln(\hbar\omega/\epsilon_0)|$ lower than the second term in (24). In Region III (only one of the two Regions III is now effective), the last integral in (25) does not exist at all. The first integral, extended over Regions I and III is likewise of order $(\epsilon_0^2/\hbar\omega)\ln kT/\epsilon_0$. Thus we conclude that the f-dependent terms contribute negligibly to the free energy. Our result to lowest order, from (24) and (17), becomes

$$\xi=\frac{(1/8\pi)H_c^2(T)\Omega}{(J^2/4N)[N(0)]^2\pi^2\epsilon_0(T)S(S+1)} \tag{27}$$

for the concentration required to depress the transition temperature to T.

When T is near T_c, the transition temperature of the pure sample, we may show from the B.C.S. paper that

$$\left[\frac{H_c(T)}{H(0)}\right]^2\sim\frac{2(1-\ln2)}{1.75}\left[\frac{\epsilon_0(T)}{\epsilon_0(0)}\right]^2,$$

which shows that, for T near T_c, ξ varies as $\epsilon_0(T)$. Since $\epsilon_0(T)$ varies as $[1-(T/T_c)]^{\frac{1}{2}}$ near that point we see that the T^* *versus* ξ curve has zero slope near $\xi=0$, demonstrating the point made in the introduction. On the other hand, near $T=0$, ϵ_0 is essentially constant and, from B.C.S. [Eq. (3.43)] $dH_c^2(T)/dT\rightarrow0$. Thus the $T^*-\xi$ curve should have a vertical tangent at $T=0$. Exactly at $T=0$ neither the prediction of the present theory nor that based on the law of corresponding states is necessarily reliable. For less extreme concentrations, using Herrings differential equation method gives, from (24),

$$\frac{d\epsilon_0(0)}{d\xi} = -\frac{\delta F_n(0)-\delta F_s(0)}{N(0)\epsilon_0(0)} = -\frac{J^2}{4}\nu(\epsilon_f)\pi^2 S(S+1), \quad (28)$$

where $\nu(\epsilon_f)=N(0)/N$ is the number of states per atom per unit energy range near the Fermi surface. Since $\epsilon_0 = 1.75kT_c^*$, we finally obtain

$$kT_c^* = kT_c - \frac{J^2}{4}\,\frac{\nu(\epsilon_f)\pi^2\xi S(S+1)}{1.75}. \quad (29)$$

The extrapolated curve of reference 8 gave $T_c^*=0$ at $\xi=0.01$. Taking $\nu(\epsilon_f)=0.2$ (ev)$^{-1}$, $S=\frac{7}{2}$ for gadolinium, and $kT_c \sim 4\times10^{-4}$ ev we then get

$$J=0.165 \text{ ev},$$

an entirely reasonable estimate.

4. SPIN-ORBIT COUPLING

For the rare earths other than gadolinium there may well be an important spin-orbit coupling even in the lanthanum surroundings. In general, the introduction of an $\mathbf{L}\cdot\mathbf{S}$ term in $\mathcal{H}^0$ complicates the calculation considerably. Some of the energy denominators now have added to them, others subtracted from them, energies corresponding to the interval between adjacent multiplet levels. A specially simple calculation may be made, however, in the case of very strong spin-orbit coupling. Then we may neglect the matrix elements of $\mathbf{S}$ between levels of different multiplicity, and by the rules of angular momentum algebra we may make the replacement

$$\mathbf{S} \to \mathbf{A}\frac{(\psi_A,\mathbf{A}\cdot\mathbf{S}\psi_A)}{A(A+1)} = \mathbf{A}\frac{A(A+1)+S(S+1)-L(L+1)}{2A(A+1)},$$

where $\mathbf{A}=\mathbf{L}+\mathbf{S}$ is the total angular momentum. Hence in our final formulas we make the substitution

$$S(S+1) \to [A(A+1)+S(S+1)-L(L+1)]^2/4A(A+1).$$

For the elements to the left of gadolinium, $A=L-S$ in the lowest state, and then

$$S(S+1) \to S^2/(1+1/A).$$

For the elements to the right of (and including) gadolinium $A=L+S$, and

$$S(S+1) \to S^2(1+1/A).$$

Figure 2 shows three sets of points, giving the depression of T_c as a function of atomic number, relative to the depression for gadolinium. The circles are the observations, the crosses assume zero spin-orbit coupling; the squares infinite spin-orbit coupling. For most points the squares come closer to the observations than the crosses. The most notable exception is europium, for which $A=0$. But since europium has a finite magnetic moment, in spite of the fact that $A=0$, one cannot expect agreement.

5. CHANGES IN THE FREE ENERGY DUE TO NONMAGNETIC IMPURITIES[15]

Lynton, Serin, and Zucker[1,2] have observed that very small additions of diamagnetic impurities to a superconductor lower T_c by an amount that is a universal function of the residual resistance of the sample, rather than of the impurity concentration. This result becomes plausible in the light of the present theory.

Let $v(\mathbf{r}-\mathbf{R}_i)$ be the difference in energies of an electron at $\mathbf{r}$ in the field of an impurity at lattice site $\mathbf{R}_i$, and the field of a normal atom at $\mathbf{R}_i$. We assume the electrons to be in plane wave states, and suppose that $v(\mathbf{r}-\mathbf{R}_i)$ is appreciable only over regions small compared with all electron wavelengths involved. Thus in terms of the c's the perturbing Hamiltonian is

$$\mathcal{H}^1 = \frac{w}{N}\sum_{\mathbf{pq}\sigma} U_{\mathbf{p}-\mathbf{q}} c_{\mathbf{p}\sigma}^* c_{\mathbf{q}\sigma}, \quad (30)$$

where $w=(1/\Omega_0)\int v(\mathbf{r})dv$, $U_{\mathbf{p}-\mathbf{q}}=\sum \exp[-i(\mathbf{p}-\mathbf{q})\cdot\mathbf{R}_i]$, Ω_0 is the atomic volume, and σ denotes spin orientation. In terms of the d-operators

$$\mathcal{H}^1 = (w/N)\sum[U_{\mathbf{p}-\mathbf{q}}\alpha_{\mathbf{pq}}^+(d_{\mathbf{p}\uparrow}^* d_{\mathbf{q}\uparrow} + d_{\mathbf{p}\downarrow}^* d_{\mathbf{q}\downarrow}) + U_{\mathbf{p}-\mathbf{q}}\beta_{\mathbf{pq}}^+ d_{-\mathbf{p}\downarrow} d_{\mathbf{q}\uparrow} + U_{\mathbf{p}-\mathbf{q}}^*\beta_{\mathbf{pq}}^+ d_{\mathbf{q}\uparrow}^* d_{-\mathbf{p}\downarrow}^*], \quad (31)$$

with

$$\alpha_{\mathbf{pq}}^+ = \cos\frac{\theta_\mathbf{p}+\theta_\mathbf{q}}{2}; \quad \beta_{\mathbf{pq}}^+ = \sin\frac{\theta_\mathbf{p}+\theta_\mathbf{q}}{2}.$$

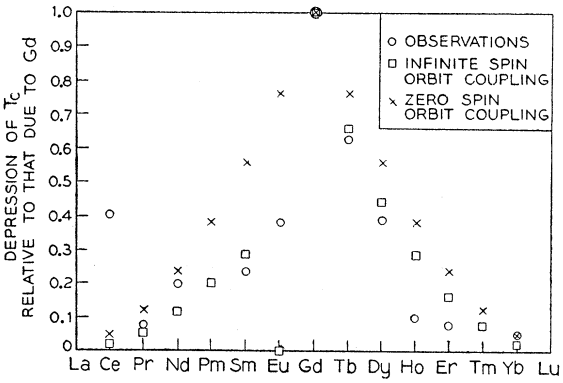

FIG. 2. The reduction of T_c due to exchange scattering of conduction electrons by rare-earth impurities. The exchange integral has been assumed constant over the whole range.

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[15] *Note added in proof.* Since this paper was submitted, a similar calculation on nonmagnetic scattering has been published [K. Nakamura, Prog. Theoret. Phys. (Kyoto) **21**, 435 (1959)]. Nakamura's results for the reduction in the free energy difference between normal and superconducting states are essentially the same as those given here. His interpretation is that it arises from a changed electron interaction, so that the impure superconductor obeys the same relation of transition temperature to energy gap as the pure superconductor. [See Sec. 7, and also H. Suhl and B. T. Matthias, Phys. Rev. Letters **2**, 5 (1959).]

The canonical transformation now has the form

$$\mathcal{S}=\frac{iw}{N}\sum_{pq}\left[\frac{U_{\mathbf{p}-\mathbf{q}}\alpha_{\mathbf{pq}}{}^{+}}{E_{\mathbf{p}}-E_{\mathbf{q}}}(d_{\mathbf{p}\downarrow}{}^{*}d_{\mathbf{q}\downarrow}+d_{\mathbf{p}\uparrow}{}^{*}d_{\mathbf{q}\uparrow})\right.$$
$$\left.-\frac{U_{\mathbf{p}-\mathbf{q}}\beta_{\mathbf{pq}}{}^{+}}{E_{\mathbf{p}}+E_{\mathbf{q}}}d_{-\mathbf{p}\downarrow}d_{\mathbf{q}\uparrow}+\frac{U_{\mathbf{p}-\mathbf{q}}{}^{*}\beta_{\mathbf{pq}}{}^{+}}{E_{\mathbf{p}}+E_{\mathbf{q}}}d_{\mathbf{q}\uparrow}{}^{*}d_{-\mathbf{p}\downarrow}{}^{*}\right].$$

In evaluating the commutator $(\mathcal{H}^1,\mathcal{S})$ required in the establishment of the new Hamiltonian there occur terms of the form

$$U_{\mathbf{p}'-\mathbf{q}'}U_{\mathbf{p}-\mathbf{q}}=\sum_{ij}e^{-i(\mathbf{p}'-\mathbf{q}')\cdot\mathbf{R}_j-i(\mathbf{p}-\mathbf{q})\cdot\mathbf{R}_i}.$$

The sum over i and j may be split up:

$$\sum=\sum_{i=j}+\sum_{i\neq j}.$$

Neglecting the effect of the very slight correlation introduced by the requirement $i\neq j$ in the second sum, we see that it will be negligible, unless $p'=q'$ and $p=q$. Such terms, however, could have been included in the kinetic energy from the beginning and would only lead to a slight shift in the zero of energy. Henceforth we assume that this has been done and that $\mathbf{p}\neq\mathbf{q}$ throughout. Then only the part $i=j$ produces a major effect; the remainder just leading to second-order scattering terms. But when $i=j$, the sum is still small, unless we also have

$$\mathbf{p}'-\mathbf{q}'+\mathbf{p}-\mathbf{q}=0,$$

in which case it equals N_I, the number of impurities in the specimen. Bearing these points in mind we finally obtain a new Hamiltonian

$$\mathcal{H}_{\text{new}}=\mathcal{H}^0-\xi\frac{w^2}{N}\left[\sum\left(\frac{\alpha_{\mathbf{pq}}{}^{+2}}{E_{\mathbf{p}}-E_{\mathbf{q}}}-\frac{\beta_{\mathbf{pq}}{}^{+2}}{E_p+E_q}\right)\right.$$
$$\times(d_{\mathbf{q}\downarrow}{}^{*}d_{\mathbf{q}\downarrow}+d_{\mathbf{q}\uparrow}{}^{*}d_{\mathbf{q}\uparrow})+\alpha_{\mathbf{pq}}{}^{+}\beta_{\mathbf{pq}}{}^{+}\left(\frac{1}{E_{\mathbf{q}}-E_{\mathbf{p}}}-\frac{1}{E_{\mathbf{q}}+E_{\mathbf{q}}}\right)$$
$$\left.\times(d_{\mathbf{q}\uparrow}{}^{*}d_{-\mathbf{q}\uparrow}{}^{*}+d_{-\mathbf{q}\downarrow}d_{\mathbf{q}\uparrow})+\sum\frac{\beta_{\mathbf{pq}}{}^{+2}}{E_{\mathbf{p}}+E_{\mathbf{q}}}\right].\tag{32}$$

The calculation proceeds just as for the spin case. we have, for the concentration ξ that causes the transition temperature to decline to T,

$$\xi=\frac{(1/8\pi)H_c{}^2(T)\Omega}{\delta F_n(T)-\delta F_s(T)},$$

and again the f-dependent terms make a negligible contribution to the shift. This leaves the "zero-point" terms which are

$$\delta F_s=w^2\sum\frac{(\beta_{\mathbf{pq}}{}^{+})^2}{E_{\mathbf{p}}+E_{\mathbf{q}}}=\frac{w^2}{2}\sum\frac{1-\cos(\theta_{\mathbf{p}}+\theta_{\mathbf{q}})}{(E_{\mathbf{p}}+E_{\mathbf{q}})}$$
$$=2w^2\sum_{\epsilon_p,\epsilon_q>0}\frac{E_{\mathbf{p}}E_{\mathbf{q}}+\epsilon_0(\mathbf{p})\epsilon_0(\mathbf{q})}{(E_{\mathbf{p}}+E_{\mathbf{q}})E_{\mathbf{p}}E_{\mathbf{q}}},\tag{33}$$

$$\delta F_n=2w^2\sum_{\epsilon_p,\epsilon_q>0}\frac{1}{\epsilon_{\mathbf{p}}+\epsilon_{\mathbf{q}}}.$$

Again the ϵ_p, ϵ_q quadrant is divided into three regions. The contribution to $\delta F_n-\delta F_s$ from Region II is again zero. That from either Region III is just the same as in the previous case, since $\epsilon_0(p)\epsilon_0(\mathbf{q})$ is zero throughout III, and it is only in the sign of that term that δF_s differs from the δF_s of the spin-dependent case. However, in Region I the result is quite different. There

$$\delta F_s\sim\sum_{\mathrm{I}}\frac{E_{\mathbf{p}}E_{\mathbf{q}}+\epsilon_0{}^2}{E_{\mathbf{p}}E_{\mathbf{q}}(E_{\mathbf{p}}+E_{\mathbf{q}})}$$
$$=[N(0)]^2\epsilon_0\int_0^{\varphi}\int_0^{\varphi}\frac{\cosh\theta_{\mathbf{p}}\cosh\theta_{\mathbf{q}}+1}{\cosh\theta_{\mathbf{p}}+\cosh\theta_{\mathbf{q}}}d\theta_{\mathbf{p}}d\theta_{\mathbf{q}}$$
$$=[N(0)]^2\left[\varphi\sinh\varphi-\int_0^{\varphi}\int_0^{\varphi}\frac{\sinh^2\theta_{\mathbf{q}}}{\cosh\theta_{\mathbf{p}}+\cosh\theta_{\mathbf{q}}}d\theta_{\mathbf{p}}d\theta_{\mathbf{q}}\right].$$

This is just the same as the integral (20), *except that the last term of (20) is missing*. But that is precisely the one which gave a contribution of order ϵ_0 to $\delta F_n-\delta F_s$. Thus for the spin-independent scattering we get just the same result (except, of course, for the coefficient) as in the spin case, but with the ϵ_0 term missing:

$$\delta F_n-\delta F_s=\frac{4w^2}{N}[N(0)]^2\frac{\epsilon_0{}^2}{\hbar\omega}\ln\frac{\hbar\omega}{\epsilon_0}\tag{34}$$

to lowest order in $\epsilon_0/\hbar\omega$. Thus we finally have, from the viewpoint appropriate to a first-order transition,

$$\xi w^2=\frac{(1/8\pi)H_c{}^2(T)\Omega}{(4/N)[N(0)]^2\epsilon_0(T)[\epsilon_0(T)/\hbar\omega]\ln[\hbar\omega/\epsilon_0(T)]}.\tag{35}$$

For T close to T_c $H_c{}^2(T)$ varies as $\epsilon_0(T)^2$, hence $dT/d\xi$ is again zero near T_c as in the previous case. Likewise, near $T=0$, $dT/d\xi=\infty$.

On the other hand, the differential equation method gives

$$-\frac{d\epsilon_0}{d\xi}=4w^2\nu(\epsilon_f)\frac{\epsilon_0}{\hbar\omega}\ln\frac{\hbar\omega}{\epsilon_0},\tag{36}$$

which integrates to yield

$$\epsilon_0=\hbar\omega\left[\frac{\epsilon_0(\text{pure})}{\hbar\omega}\right]^{\exp[4w^2\nu(\epsilon_f)\xi/\hbar\omega]}.\tag{37}$$

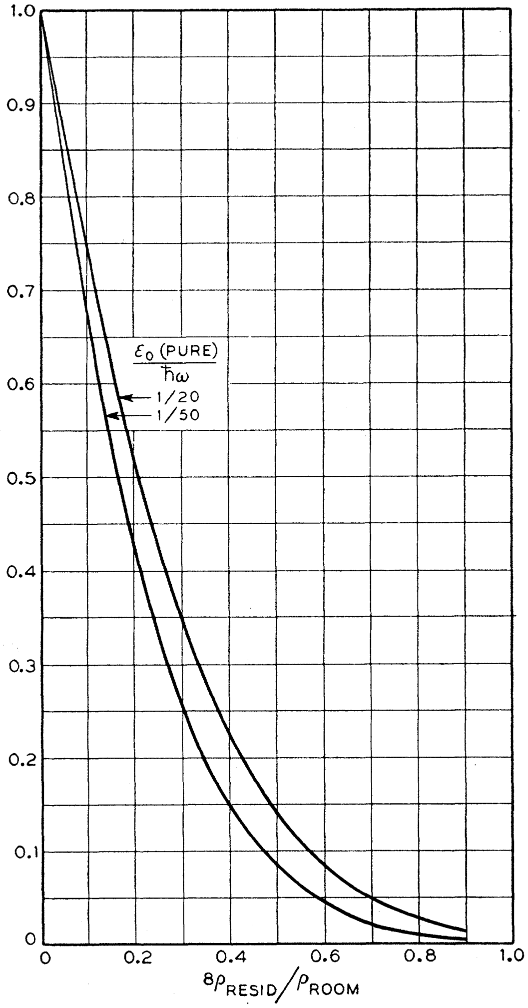

FIG. 3. Predicted course of the transition temperature *versus* residual resistance ratio of the impure metal. (The experimental curves show such universal dependence only for extremely small values of $\rho_{\text{resid}}/\rho_{\text{room}}$.)

6. RELATION TO THE RESIDUAL RESISTANCE

In the Born approximation, the residual resistivity due to the impurities also involves $w^2\xi$, in the same way as Eq. (35). All other quantities appearing in (35) and in the expression for the residual resistivity are properties of the host metal. A standard expression for this resistivity may be found in Wilson's book on metals:

$$\rho=(m^*/2e^2\hbar n_0)\nu(\epsilon_f)w^2\xi.$$

Hence we have

$$4w^2\xi\nu(\epsilon_f)/\hbar\omega=8\rho e^2 n_0/m^*\omega.$$

But $m^*\omega/e^2n_0$ is of the order of the room-temperature resistivity due to lattice scattering, which we denote by ρ_l. Thus we may rewrite (37) as

$$kT_c{}^*=\frac{\hbar\omega}{1.75}\left[\frac{\epsilon_0(\text{pure})}{\hbar\omega}\right]^{\exp(8\rho/\rho_l)}. \tag{38}$$

The relation (38) is shown in Fig. 3.[16] The curve declines much faster, initially, than any of the curves in reference 1. There might be several reasons for this. We have assumed a δ-function scattering potential. In calculating $\delta F_n-\delta F_s$ we therefore had to integrate over *all* momenta, while for a scatterer with finite range, there would be much less contribution for large values of $|\mathbf{p}-\mathbf{q}|$ in the sums (33). (Such large values actually occur in all three regions of Fig. 1.) This could lead to a substantial reduction in the exponent of Eq. (38). Further, in estimating the contribution of Region III, we assumed a state density appropriate to a parabolic band extending to infinity. In cases in which the Fermi level is close to the zone boundary, this would be a very poor approximation, the contribution from region III being negligible in that case. Thus it is quite possible that the predicted slope is too large by a factor ten. In that case theory and experiment would agree better.

7. CONCLUSIONS

We have shown that for calculating a transition temperature in the presence of perturbations, the perturbation theory of B.C.S. can safely be applied only if the transition becomes first order as the result of the perturbation. When it does not, one should revert to an earlier stage in the theory and recalculate the effective electron interaction, excitation spectrum, etc., *ab initio* in the presence of the perturbation. An easier way out is to assume that the impure superconductor behaves much like the pure superconductor, in that it obeys the same relation of transition temperature to energy gap at absolute zero. This gives good qualitative agreement with the facts, for nonmagnetic scattering, suggesting that the impurities leave the order of the transition unchanged. The more rigorous viewpoint, beginning with the full electron-phonon Hamiltonian, will be presented in a later paper. A few final remarks will indicate how such a theory would develop: As for nonmagnetic impurities, general arguments due to Anderson,[17] based on time reversal, and due to Abrahams and Weiss,[18] based on specific models, indicate that superconductors with nonmagnetic impurities should behave just like the pure substance, but with changed constants, particularly with a changed effective "V" of the B.C.S. theory. This viewpoint is consistent with our result

$$\delta T_c/\delta\xi\sim\epsilon_0\ln(\hbar\omega/\epsilon_0),$$

which is of the same form as one would deduce from the relation $T_c\sim\exp[-1/N(0)V]$ when V suffers an incremental change. For the spin-dependent case, time reversal cannot be invoked directly; however, since our calculations are all quadratic in the impurity spins, time reversal should hold on the average. Yet in that case $\delta T_c/\partial\xi\sim$constant, a result which cannot be de-

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[16] For obvious reasons, Eq. (38) is to be trusted only for small values of ρ/ρ_l.

[17] P. W. Anderson (private communication).

[18] E. Abrahams and P. R. Weiss (to be published).

duced from a changed interaction constant alone. The reason for this apparent contradiction lies in the peculiar nature of the B.C.S. pair states. One may show that if Ψ_0 is some state of the system, and the two operations $c_{\mathbf{p}\uparrow}{}^*c_{\mathbf{q}\uparrow}$, $c_{\mathbf{p}\downarrow}{}^*c_{\mathbf{q}\downarrow}$ generate two orthogonal states from Ψ_0, then the spin-dependent case to any even order in the impurity spins must give the same result as the spin-independent case. However, if Ψ_0 is a B.C.S. state, the two new states are not in general orthogonal, and this leads to coherence effects that are different in the two cases, as already pointed out in B.C.S. At the level at which one treats the full electron-phonon Hamiltonian this difference becomes particularly apparent.

8. ACKNOWLEDGMENTS

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APPENDIX I. ESTIMATE OF THE EFFECT OF A RANDOM DIPOLAR FIELD ON THE SUPERCONDUCTING TRANSITION TEMPERATURE

To obtain a rough estimate of the effect on the free energy of the random dipole field, we restrict ourselves to the absolute zero of temperature. In principle, the calculation should proceed as follows: Each dipole gives rise to a field that can be represented as a vector potential whose divergence vanishes. In vacuo, dipoles of magnetic moment μ_i placed at R_i set up a vector potential whose spatial Fourier transform may be written

$$\mathbf{A}_{\text{vac}}(\mathbf{q})=-\frac{4\pi i}{(2\pi)^{\frac{3}{2}}}\frac{\sum \boldsymbol{\mu}_i\times\mathbf{q}}{q^2}e^{i\mathbf{q}\cdot\mathbf{R}_i}. \qquad \text{(i)}$$

When the dipoles are immersed in the conductor, in either state, **A** has to be recalculated, account being taken of the current distribution set up in the medium. **A** is then deduced from Poisson's equation

$$-q^2\mathbf{A}(\mathbf{q})=-\frac{4\pi}{c}[\mathbf{j}_c(\mathbf{q})+\mathbf{j}_m(\mathbf{q})], \qquad \text{(ii)}$$

where

$$\mathbf{j}_m(\mathbf{q})=\frac{c}{4\pi}q^2\mathbf{A}_{\text{vac}}(\mathbf{q}) \qquad \text{(iii)}$$

is the driving current, and where $\mathbf{j}_c(\mathbf{q})$ is the conduction electron current due to **A**, calculated to first order in **A** by a perturbation expansion, such as that given by B.C.S. The result of this calculation has the form

$$\mathbf{j}_c(\mathbf{q})=-\frac{c}{4\pi}\kappa(\mathbf{q})\mathbf{A}(\mathbf{q}) \qquad \text{(iv)}$$

where $\kappa(q)$ is a function of q which falls off as $1/q$ when q exceeds about 10^4 cm^{-1}. The result of solving (ii) and (iv) is now

$$\mathbf{A}(\mathbf{q})=\frac{4\pi}{c}\frac{\mathbf{j}_m(\mathbf{q})}{q^2+\kappa(q)}. \qquad \text{(v)}$$

Having found **A** we may calculate the energy in the field:

$$-\frac{1}{2c}\int \mathbf{A}(\mathbf{q})\cdot\mathbf{j}^*(\mathbf{q})d\mathbf{q}, \qquad \text{(vi)}$$

where $\mathbf{j}(q)=\mathbf{j}_m+\mathbf{j}_c$. Using (v), this may be written

$$-\frac{4\pi}{2c^2}\int\frac{q^2j_m(\mathbf{q})j_m{}^*(\mathbf{q})}{[q^2+\kappa(q)]^2}d\mathbf{q}. \qquad \text{(vii)}$$

When (vii) is averaged over all R_i and all orientations of μ_i, there obviously remain only the N_I equal self-energy terms of the individual dipoles, and these diverge, since the integrand varies as q^2 for large q. However, we are interested only in the difference in the shift of the energies, and this converges.

To continue the calculation rigorously would require an exact knowledge of κ_s and κ_n, which are only known implicitly, as complicated integrals. However, we may safely restrict the integral (vii) to values of $q>10^4$cm^{-1}. Most of the energy resides within this range, in either state. For $q<10^4$ cm^{-1}, the magnetic fields in the normal state are minuscule, and in the superconducting state they become negligible since $\kappa(q)\rightarrow$ const. as $q\rightarrow 0$. In computing the difference in normal and superconducting energies, we may use (vii), neglecting κ except where it occurs in the form $\kappa_n-\kappa_s$. Thus we have, to lowest order in κ, and using the previous notation

$$\begin{aligned}-\xi(\delta F_n-\delta F_s)&=-\frac{2\pi}{c^2}\int\frac{j_m(\mathbf{q})j_m{}^*(\mathbf{q})}{q^4}[\kappa_s(q)-\kappa_n(q)]d\mathbf{q}\\&=-\frac{1}{8\pi}\int \mathbf{A}_{\text{vac}}(\mathbf{q})\mathbf{A}_{\text{vac}}{}^*(\mathbf{q})[\kappa_s(q)-\kappa_n(q)]d\mathbf{q}. \qquad \text{(viii)}\end{aligned}$$

The "paramagnetic" contribution to the two κ's are equal and therefore need not be considered. Then if we denote by $j_m{}^D$ the diamagnetic current in a potential $\mathbf{A}_{\text{vac}}$, we have

$$\xi(\delta F_n-\delta F_s)=\frac{1}{2c}\int \mathbf{A}_{\text{vac}}(\mathbf{q})[\mathbf{j}_{ms}{}^D(\mathbf{q})-\mathbf{j}_{mn}{}^D(\mathbf{q})]d\mathbf{q}. \qquad \text{(ix)}$$

The diamagnetic currents are related to **A** by formula (5.19) of B.C.S. At absolute zero, this formula and Eq.

(ix) give (if random phase terms are equated to zero)

$$\xi(\delta F_n-\delta F_s)=N\xi\frac{e^2\hbar^2}{4m^2c^2}\frac{2}{(2\pi)^3}\int\frac{d\mathbf{p}d\mathbf{q}}{q^4}[(\boldsymbol{\mu}\times\mathbf{q})\cdot\mathbf{p}]^2$$

$$\times\left\{\frac{1-[\epsilon_{p+q}\epsilon_p+\epsilon_0(p)\epsilon_0(p+q)]/E_pE_{p+q}}{E_p+E_{p+q}}\right.$$

$$\left.-\text{same expression with } \epsilon_0\equiv 0\right\}$$

$$=N\xi\frac{e^2\hbar^2}{4m^2c^2}\frac{2}{(2\pi)^3}\int\frac{d\mathbf{p}d\mathbf{q}}{|\mathbf{p}-\mathbf{q}|^4}[\boldsymbol{\mu}\cdot(\mathbf{p}\times\mathbf{q})]^2$$

$$\times\left\{\frac{1-[\epsilon_\mathbf{p}\epsilon_\mathbf{q}+\epsilon_0(\mathbf{p})\epsilon_0(\mathbf{q})]/E_\mathbf{p}E_\mathbf{q}}{E_\mathbf{p}+E_\mathbf{q}}-\cdots\right\}.$$

Here $\boldsymbol{\mu}$ is some one typical magnetic moment. Assuming the energies to depend only on the magnitude of the wave vector, we may perform the angular integrations, to obtain

$$\xi(\delta F_n-\delta F_s)$$

$$=N\xi\frac{e^2\hbar^2}{4m^2c^2}\frac{4\pi\mu^2}{(2\pi)^3}\int\left\{\left[\frac{1}{p^2q^2}+\frac{p^2+q^2}{4p^3q^3}\ln\left|\frac{\mathbf{p}-\mathbf{q}}{\mathbf{p}+\mathbf{q}}\right|\right]\right.$$

$$\times\left[\frac{1-\operatorname{sgn}\epsilon_\mathbf{p}\operatorname{sgn}\epsilon_\mathbf{q}}{\epsilon_p+\epsilon_q}-\frac{1-[\epsilon_p\epsilon_q+\epsilon_0(p)\epsilon_0(q)]/E_pE_q}{E_p+E_q}\right]$$

$$\left.\times\frac{p^3q^3d\epsilon_pd\epsilon_q}{(\hbar^2/2m^*)^2}\right\}. \quad \text{(x)}$$

Obviously the integral may be converted into one over the positive $\epsilon_\mathbf{p}$, $\epsilon_\mathbf{q}$ quadrant alone, just as in the main text. As before, the integrand vanishes in region II of Fig. 1. In region I it is well behaved, for at $\mathbf{p}=\mathbf{q}$, where the logarithm goes to infinity, the remainder of the integrand goes to zero more strongly. For an order of magnitude estimate it will therefore be permissible to ascribe some typical value which the explicitly p- and q-dependent part of the integrand takes in region I, that is to say, close to the Fermi surface, and to move it outside the integrand. This typical value is

$$k_f^2/(\hbar^2/2m^*)^2=k_f^6/\epsilon_f^2.$$

The remaining integral is then exactly the same as that or the case of spin exchange discussed in the main text. Finally, the contribution to (x) from region III is again smaller by an order $(\epsilon_0/\hbar\omega)\ln(\hbar\omega/\epsilon_0)$ than that from region I. Using, then, the value of the integral already calculated, (i.e., $\epsilon_0\pi^2$) we obtain an estimate of

$$\frac{Ne^2\hbar^2\mu^2k_f^6}{4mc^2\epsilon_f^2}\xi\epsilon_0\pi^2$$

for the reduction in F_n-F_s due to the magnetic fields. This must be compared with Eq. (24) for the reduction due to exchange. The condition that the magnetic lowering be less thus becomes

$$(e\mu/\hbar^2c)(m\epsilon_f)^{\frac{1}{2}}<\tfrac{1}{2}\pi\nu(\epsilon_f)J[S(S+1)]^{\frac{1}{2}}.$$

The left-hand side, with $\mu\sim 10$ Bohr magnetons, is of order 10^{-4}, while the right-hand side, with $J\sim 0.15$ ev and $\nu(\epsilon_f)\sim 0.2$ (ev)$^{-1}$ ranges from about 0.04 for gadolinium down to 0.002 near the edge of the rare-earth series. Hence the magnetic fields of the dipoles cannot be responsible for the observed effect.