Reentrant behavior of superconducting alloys

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Abstract
A dirty BCS superconductor with magnetic impurities is studied. The asymptotic solution of the thermodynamics of such a superconductor with spin 1/2 and 7/2 magnetic impurities is found. To this end, the system’s free energy $f(H, \beta)$ is bounded from above and below by mean-field type bounds, which are shown to coalesce almost exactly in the thermodynamic limit, provided the impurity concentration is sufficiently small. The resulting mean-field equations for the gap $\Delta$ and a parameter $\nu$, characterizing the impurity subsystem, are solved and the solution minimizing $f$ is found for various values of magnetic coupling constant $g$ and impurity concentration $x$. The phase diagrams of the system are depicted with five distinct phases: the normal phase, unperturbed superconducting phase, perturbed superconducting phase with nonzero gap in the excitation spectrum, perturbed gapless superconducting phase and impurity phase with completely suppressed superconductivity. In the perturbed superconducting phase, superconductivity coexists with magnetic order. The computed phase diagrams are in good agreement with experimental data for Ce$_{1-x}$Gd$_x$Ru$_2$ and for certain pseudoternary systems, e.g. (Er$_{1-x}$Ho$_x$)Rh$_4$B$_4$.

Furthermore, evidence of reentrant superconductivity and Jaccarino–Peter compensation is found.

The credibility of the theory is verified by testing the dependence of the superconducting transition temperature $T_c$ on $x$. Very good quantitative agreement with experimental data is obtained for several alloys: (La$_{1-x}$Ce$_x$)Al$_2$, (La$_{1-x}$Gd$_x$)Al$_2$ and (La$_{0.8-x}$Y$_{0.20}$)Ce$_x$. The theory presented improves earlier developments in this field.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is well known that doping may substantially change the properties of a superconductor. The superconducting transition temperature $T_c$ in most dirty superconductors decreases with impurity concentration $c$ [1]. However, alloys of zirconium with iron, cobalt or nickel have higher transition temperatures than pure zirconium [2]. Similar behavior was observed in titanium doped by chromium, manganese, iron and cobalt [3]. One of the properties which does not change under doping is the order of the transition in the absence of external magnetic field [4, 5].

Early attempts to explain lowered $T_c$ in the presence of magnetic impurities were founded on perturbation theory. Nakamura [6] and Suhl et al [7] explained this effect by treating the s–d interaction $V_{\text{s-d}}$ [8] as an additive term in the total Hamiltonian, which perturbs a BCS superconductor [9]. However, their theory predicts a first order phase transition to the superconducting state in zero magnetic field.

The well-known Abrikosov–Gor’kov theory [10] (AG) of dirty superconductors explains the strong decrease in $T_c$ due to magnetic impurities and also predicts ‘gapless superconductivity’, confirmed experimentally by Reif and Woolf [11]. Disagreement with this approach is observed in a number of Kondo superconductors, e.g. La$_{1-x}$Ce$_x$Al$_2$ [12], LaCe and LaGd [13] and PbCe and InCe [14].

Such compounds manifest reentrant superconductivity (RSC) which is due to competition between the Kondo effect and superconductivity. The RSC effect was predicted theoretically by Müller-Hartmann and Zittartz [15] (MHZ) and is expected to occur when the superconducting transition
temperature of the host compound $T_{c0}$ is much larger than the Kondo temperature $T_K$. In such a case the equation for $T_c(c)$ has three solutions: $T_{c1}$, $T_{c2}$ and $T_{c3}$ for certain values of impurity concentration. As the temperature $T$ is lowered the alloy becomes superconducting at $T_{c1}$. When the value of $T$ is comparable to $T_K$ the pair-breaking effect of impurities increases and superconductivity is suppressed at $T_{c2}$. The alloy re-enters the superconducting state at $T_{c3}$, where the pair-breaking passes through its maximum value. Such reentrant behavior was observed experimentally in La$_{0.79}$Ce$_0.008$Y$_{0.20}$ with $T_{c1} = 0.55$ K, $T_{c2} = 0.27$ K and $T_{c3} = 0.05$ K [16].

According to Müller-Hartmann and Zittartz theory, superconductivity is never completely suppressed for any value of impurity concentration if $T_k/T_{c0} \ll 1$. This statement disagrees with experiment, which shows that disappearance of superconductivity above a critical value of $c$ is possible. Furthermore, significant deviations from this approach were observed for (La, Ce)In$_{3−x}$Sn$_x$ [17].

The first experimental observations of reentrant superconductivity [18, 19] revealed no evidence of $T_{c2}$, corresponding to a second phase transition, introducing superconducting $T_{c3}$. For this reason, MHZ theory was reformulated (e.g. [20–23]) and also other proposals for a theory of $T_c(c)$ were given. In particular, Jarrell performed Monte Carlo simulations of the superconducting transition temperature in terms of Eliashberg–Migdal perturbation theory [24]. These calculations raised doubts about the existence of $T_{c3}$, contrary to experiments accomplished by Winzer [16], confirming the presence of a transition back to the superconducting state.

The effect of magnetic impurities on superconductivity is still under debate. Recently, Barzykin and Gor’kov [25] studied s-wave superconductivity in the Anderson lattice and demonstrated excellent agreement of the resulting $s$-wave superconductivity in the Anderson lattice of impurity concentration if $c$ is still under debate. Recently, Barzykin and Gor’kov [25] introduced superconductivity separated by domains of aligned spins. In such an FFLO state the order parameter is spatially modulated along the field direction. There are strong experimental suggestions for the occurrence of an FFLO state in some heavy-fermion compounds, e.g. in CeCoIn$_5$ [30].

The coexistence hypothesis was confirmed shortly after Matthias’ suggestion in the following superconducting alloys: Ce$_{1−x}$Gd$_x$Ru$_2$ [31] and Y$_{1−x}$Gd$_x$Os$_2$ [32], although it was not found to occur in the same volume element. The phase diagrams obtained by Wilhelm and Hillenbrand for Ce$_{1−x}$Tb$_x$Ru$_2$ [33] also contain the coexistence phase. Specific-heat measurements showed short-range ordering in this alloy, typical of spin-glass systems [34].

The coexistence of superconductivity and long-range antiferromagnetic ordering of the rare earth R magnetic moments was discovered in RMo$_5$S$_8$ (R = Gd, Tb and Er) [35], RRh$_x$B$_4$ (R = Nd, Sm and Tm) [36] and RMo$_5$S$_4$ (R = Gd, Tb, Dy and Er) [37]. A similar overlap between superconductivity and ferromagnetism was observed in ErRh$_2$B$_4$ [38] and HoMo$_5$S$_8$ [39].

The phase diagrams of superconducting alloys, containing the coexistence phase, have been computed by several theorists. Gor’kov and Rusinov extended the AG theory to include magnetic ordering. Correspondence with the phase diagrams observed experimentally is expected to occur for very strong spin–orbit scattering. Balseiro et al [40] studied a BCS superconductor perturbed by magnetic impurities interacting via a nearest neighbor Heisenberg potential. The resulting phase diagrams comply qualitatively with experiment.

Theories of dirty superconductors contribute significantly to our understanding of the superconductivity phenomenon. One can expect that further investigations of superconducting alloys will explain the microscopic mechanism of unconventional superconductivity displayed by some materials, e.g. high-temperature superconductors [41], heavy-fermion compounds [42] and iron pnictides [43].

This yet unresolved issue, as well as some shortcomings of the models presented above, motivate the present work. We investigate a BCS Hamiltonian [9]

$$H_{BCS} = H_0 + V_{BCS},$$

supplemented by a reduced s–d interaction

$$V = g^2 N^{-1} \sum_{\alpha=1}^{M} \sigma \cdot S_{\alpha},$$

where

$$H_0 = \sum_{k\sigma} \varepsilon_k n_{k\sigma},$$

with $\varepsilon_k = \varepsilon_k - \mu$, $n_{k\sigma} = a_{\sigma}^\dagger a_{\sigma}$, is the free fermion kinetic energy operator and

$$V_{BCS} = -|\Lambda|^{-1} \sum_{kk'} G_{kk'} a_{k\sigma}^\dagger a_{-k'\sigma}^\dagger a_{-k\sigma} a_{k'\sigma},$$

is the Cooper pairing potential. $|\Lambda|$ denotes the system’s volume and $G_{kk'}$ is real, symmetric, invariant under $k \rightarrow -k$ or $k' \rightarrow -k'$ and nonvanishing only in a thin band close to the Fermi surface, namely,

$$G_{kk'} = G_0 \chi(k) \chi(k'), \quad G_0 > 0,$$

where $\chi(k)$ denotes the characteristic function of the set

$$\mathcal{P} = \{k : \mu - \delta \leq \varepsilon_k \leq \mu + \delta\}, \quad \varepsilon_k = \hbar^2 k^2 / 2m.$$
In equation (2), $\sigma_\alpha$ denotes the spin operator of the magnetic ion, whereas 
$$\sigma_\alpha = \sum_k (n_{k_+} - n_{k_-})$$
describes the spin operator of each conducting fermion. $M$ is the number of magnetic impurities, $N$ the number of host atoms.

We assume the perturbation implemented by the localized distinguishable magnetic impurities to be a reduced long-range $s$–$d$ interaction, which involves only the $z$-components of the impurity and fermion spin operators (equation (2)). The reason for this simplification is that the thermodynamics of the resulting Hamiltonian $H = H_0 + V_{\text{BCS}} + V$ admits a mean-field solution which improves with decreasing impurity density.

Furthermore, this solution is thermodynamically equivalent to the one obtained for $H$ with a Heisenberg type reduced $s$–$d$ interaction
$$V_{\text{Hi}} = -\frac{g^2}{N} \sum_{k\alpha} \left[ (a_{k+}^\dagger a_{k-} - a_{k+}^\dagger a_{k-}) S_{\alpha-} - a_{k+}^\dagger a_{k-} S_{\alpha+} \right],$$
replacing $V$ (224), section 6.2.5). (Similarly, the thermodynamics of a classical superconductor can be explained in terms of a reduced BCS interaction, whereas a gauge-invariant theory of the Meissner effect requires a more general pairing potential.) The reduced form of $V_{\text{Hi}}$, obtained by rejecting the sum $\sum_{k\neq k} V_{kk}$ in the $s$–$d$ interaction $V_{s-d}$, is an approximation which resorts to the fact that spin-exchange processes, and not momentum exchange processes, are primarily responsible for the Kondo effect caused by $V_{s-d}$ [44].

In sections 2 and 3 the upper and lower bound to the system’s free energy $f(H, \beta)$ are derived by exploiting the method developed in [45–48]. These bounds are shown to be almost equal if the impurity density $M/|\Lambda|$ is sufficiently small (section 4). The mean-field equations for the gap $\Delta$ and parameter $v$, characterizing the impurity subsystem, are derived in sections 5 and 6 and solved in section 7 for various values of $g$, $\delta$, and $\Delta$. In section 8 the values of these parameters are adjusted to fit the experimental $T_c(x)$ curves for La$_{1-x}$Ce$_x$Al$_2$, La$_{1-x}$Gd$_x$Al$_2$, La$_{0.8}$Y$_{0.2}$Ce$_2$, and La$_{1.4}$Ho$_{0.6}$Rh$_2$B$_4$. Quantitative agreement is found for each alloy. Furthermore, the phase diagrams derived in section 7 are in good agreement with experimental data for Ce$_{1-x}$Gd$_x$Ru$_2$ and for certain pseudoternary systems, e.g. (Er$_{1-x}$Ho)$_x$Rh$_2$B$_4$. These phase diagrams reproduce the experimental observations of the coexistence phase, reentrant behavior, gapless superconductivity and Jaccarino–Peter compensation.

2. Lower bound to the free energy

A version of the Tindemans and Capel method [46, 47], introduced recently in order to study thermodynamics of the Fermi gas interacting with randomly distributed magnetic impurities [45], will be applied in this section to derive a lower bound to the system’s free energy.

The full Hamiltonian of the system is
$$H^{(M)} = T_0 + V_{\text{BCS}} + V.$$  (5)

Exploiting the identity
$$g^2 \sigma_\alpha S_{\alpha} = -\frac{1}{2} g^2 (\sigma_- S_{\alpha})^2 + \frac{1}{2} g^2 (\sigma_+ S_{\alpha})^2 + \frac{1}{2} g^2 S_{\alpha}^2,$$
the partition function can be written in the following form:
$$Z(M) = \text{Tr} \exp(-\beta H^{(M)})$$
$$= \text{Tr} \exp \left[ -\beta H_{\text{BCS}} + \frac{g^2}{2N} \sum_{\alpha} (\sigma_- S_{\alpha}^2 - \sigma_+ S_{\alpha}^2) \right].$$  (6)

The Gaussian integral
$$\exp(a^2) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp \left( -\frac{1}{2} v^2 + \sqrt{2} av \right) dv$$
and the commutation relations
$$\left[ V_{\text{BCS}}, \sum_k n_{k\alpha} \right] = 0,$$
satisfied for $G_{kk}$ of the form $G_{kk} = G_{0\alpha}(x)(k)(k')$, allow us to separate the electron and impurity spin operators in (6),
$$Z(M) = \left( \frac{\beta N}{2\pi} \right)^{M/2} \text{Tr} \left\{ \exp[-\beta H_{\text{BCS}}] \times \prod_{\alpha} \int_{-\infty}^{\infty} dv_{\alpha} \exp[-\frac{1}{2} \beta v_{\alpha}^2 + \beta g v_{\alpha} (\sigma_- S_{\alpha})] \right\},$$  (7)
where $H_{\text{BCS}} = H_0 + V_{\text{BCS}}$. In order to linearize quadratic terms in $\sigma_\alpha$ in the exponent of the integrand on the rhs one exploits the inequality
$$\frac{1}{N} N^{-1} g^2 \sigma_\alpha^2 = \frac{1}{N} - 2 N^{-1} (g \sigma_- N\eta)^2 + g \eta \sigma_\alpha - \frac{1}{2} N\eta^2 \geq g \eta \sigma_\alpha - \frac{1}{2} N\eta^2,$$
where $\eta$ is an arbitrary function of $v_1, \ldots, v_M$. This yields an upper bound to the partition function
$$Z(M) \leq \left( \frac{\beta N}{2\pi} \right)^{M/2} \text{Tr} \exp[-\beta H_{\text{BCS}}]$$
$$\times \prod_{\alpha} \int_{-\infty}^{\infty} dv_{\alpha} \exp[-\frac{1}{2} N^{-1} g^2 \sigma_\alpha^2 - g \eta v_{\alpha} S_{\alpha} - \frac{1}{2} N\beta(\sigma_- S_{\alpha} - \eta)^2 + \beta g(v_{\alpha} - \eta) \sigma_\alpha].$$  (9)

Following Pearce and Thompson [49], let us now add and subtract the term $\frac{1}{2} N\beta x^{-1} v^2_{\alpha}$, with $x > 1$ in the exponent of the integrand. The resulting expression is next split into two factors and one of them is replaced by its maximum with respect to $v_{\alpha}$:
$$Z(M) \leq \left( \frac{\beta N}{2\pi} \right)^{M/2} \max_{v_{\alpha}} \exp(G(v_1, \ldots, v_M, \eta))$$
$$\times \prod_{\alpha} \int_{-\infty}^{\infty} dv_{\alpha} \exp[-\frac{1}{2} N\beta v_{\alpha}^2 (1 - x^{-1})]$$
$$= \max_{v_{\alpha}} \exp(G(v_1, \ldots, v_M, \eta))(1 - x^{-1})^{-M/2},$$  (10)
where
\[ G(v_1, \ldots, v_M, \eta) = \ln \text{Tr} \exp\left[ -\beta H_{\text{BCS}} + \beta \frac{1}{2} N \sum_{\alpha=1}^{M} \left[ g(v_\alpha - \eta) \sigma_\alpha - \frac{1}{2} N x^{-1} v_\alpha^2 \right] \right] - \frac{1}{2} N^{-1} g^2 S_{\alpha \alpha} - g v_\alpha S_{\alpha \alpha} + \frac{1}{2} N \eta^2 \] \tag{11}

Inequality (10) yields the relevant lower bound to the free energy \(|\Lambda| f(H, \beta) = -\beta^{-1} \ln Z_{\text{BCS}}|
\]
\[ |\Lambda| f(H, \beta) \geq -\min_{v} \beta^{-1} G(v_1, \ldots, v_M, \eta) \]
\[ + \frac{1}{2} \beta^{-1} M \ln(1 - x^{-1}) \tag{12}\]
The function \(\eta\) will now be chosen as the solution of the equation
\[ \frac{\partial G}{\partial \eta} = 0, \tag{13}\]
which according to (11) reduces to
\[ \eta = g N^{-1}(\sigma_z)_{\bar{h}_M}, \tag{14}\]
where
\[ \bar{h}_M = H_{\text{BCS}} - g \sum_{\alpha} (v_\alpha - \eta) \sigma_\alpha, \tag{15}\]
and
\[ \langle A \rangle_H := \frac{\text{Tr}(A \exp[-\beta H])}{\text{Tr} \exp[-\beta H]}. \tag{16}\]
The solution \(\eta(v_1, \ldots, v_M)\) of equation (14) is unique. The proof can be found in [46, 47]. For this choice of \(\eta\), the condition for the minimum in (12)
\[ \frac{\partial G}{\partial v_\lambda} = 0, \quad \lambda = 1, \ldots, M, \tag{17}\]
simplifies to
\[ x^{-1} v_\lambda = -g \frac{\text{Tr} S_{\lambda \lambda} \exp\left[ -\frac{1}{2} \beta g^2 S_{\alpha \alpha}^2 - \beta g S_{\alpha \lambda} v_\lambda \right]}{\text{Tr} \exp\left[ -\frac{1}{2} \beta g^2 S_{\alpha \alpha}^2 - \beta g S_{\alpha \lambda} v_\lambda \right]} + g N^{-1}(\sigma_z)_{\bar{h}_M}, \quad \lambda = 1, \ldots, M. \tag{18}\]
The form of these equations is independent of \(\lambda\), thus
\[ v_1 = \cdots = v_M = v. \tag{19}\]

As a consequence, equation (17) simplifies to the form
\[ x^{-1} v = -g \frac{\text{Tr} S_{\lambda \lambda} \exp\left[ -\frac{1}{2} \beta g^2 S_{\alpha \alpha}^2 - \beta g S_{\alpha \lambda} v \right]}{\text{Tr} \exp\left[ -\frac{1}{2} \beta g^2 S_{\alpha \alpha}^2 - \beta g S_{\alpha \lambda} v \right]} + g N^{-1}(\sigma_z)_{\bar{h}}, \tag{20}\]
where
\[ \bar{h}(v, \eta) = H_{\text{BCS}} - g M(v - \eta) \sigma_z. \tag{21}\]

From equations (11) and (12) one obtains a suitable lower bound to the system’s free energy:
\[ |\Lambda| f(H, \beta) \geq -\min_{v} \beta^{-1} G(v) + \frac{1}{2} \beta^{-1} M \ln(1 - x^{-1}), \quad x > 1, \tag{22}\]
where \(G(v)\) denotes the function defined in (11) for \(v_1 = \cdots = v_M = v\) and \(\eta(v)\) satisfies equation (14).

3. Upper bound to the free energy by Bogolyubov’s method

An upper bound on \(f(H, \beta)\) can be expressed in terms of the Hamiltonian \(h(M)(v, \eta)\), which is related to \(H(M)\) by the following formulas
\[ H(M) = h(M)(v, \eta) + H_R'M, \tag{23}\]
where
\[ h(M)(v, \eta) = \bar{h} + h_{\text{imp}} + \frac{1}{2} MN(v^2 - \eta^2), \tag{24}\]
\[ \bar{h} = H_{\text{BCS}} + \kappa \sigma_z, \quad \kappa = -g M(v - \eta), \tag{25}\]
\[ h_{\text{imp}} = g N \sum_{\alpha} S_{\alpha \alpha} + \frac{1}{2} N^{-1} g^2 \sum_{\alpha} S_{\alpha \alpha}^2, \tag{26}\]
\[ H_R'M = -\frac{1}{2} N^{-1} \sum_{\alpha} (g(\sigma_\alpha - S_{\alpha \alpha}) - v N)^2 \tag{27}\]

Bogolyubov’s inequality
\[ F(H_1 + H_2) \leq F(H_1) + \langle H_2 \rangle_{H_1}, \tag{28}\]
with \(H_1 = h(M)(v, \eta)\), yields
\[ F(h(M)(v, \eta), \beta) \leq F(h(M)(v, \eta), \beta) \]
\[ + \frac{1}{2} N^{-1} \sum_{\alpha} (g(\sigma_\alpha - \eta N)^2)_{h(M)}. \tag{29}\]

The inequality \(\text{Tr}(\rho A^2) \leq \text{Tr}(\rho A)^2\), valid for any bounded self-adjoint operator \(A\) and density matrix \(\rho\), allows us to bound from above the second term in (28)
\[ \langle (g(\sigma_\alpha - \eta N)^2)_{h(M)} \leq g^2(\sigma_z)^2_{h(M)} - 2 g N \langle \sigma_z \rangle_{h(M)} + \eta^2 N^2. \tag{30}\]

From equation (14) one obtains
\[ \langle (g(\sigma_\alpha - \eta N)^2)_{h(M)} \leq \eta^2 N^2 - 2 \eta^2 N^2 + \eta^2 N^2 = 0, \tag{31}\]
which yields the relevant upper bound to the free energy
\[ F(H(M), \beta) \leq F(h(M)(v, \eta), \beta) = -\beta^{-1} G(v). \tag{32}\]

4. Thermodynamic equivalence of \(H(M)\) and \(h(M)\)

By passing to the limit \(|\Lambda| \to \infty\) in equations (21), (29), and subsequently \(x \to 1 + \epsilon, \epsilon > 0\) in equation (21), one finds that the upper and lower bound on \(f(H, \beta)\) coalesce almost exactly, if the impurity density is sufficiently small, namely,
\[ \lim_{|\Lambda| \to \infty} \text{d-lim} f(h(M)(v_m, \eta_m, \beta)) \approx \lim_{|\Lambda| \to \infty} \text{d-lim} f(h(M)(v_m, \eta_m, \beta)), \tag{33}\]
where \(\text{d-lim}\) denotes the limit of small \(c\) and \(v_m, \eta_m\) are the minimizing solutions of the equations
\[ \nu = g N^{-1}(\sigma_z)_{\bar{h}} - \frac{g}{\text{Tr} S_{\lambda \lambda}} \exp\left[ -\frac{1}{2} \beta g^2 S_{\alpha \alpha}^2 - \beta g S_{\alpha \lambda} v \right] \tag{34}\]
\[ \eta = g N^{-1}(\sigma_z)_{\bar{h}}. \tag{35}\]
On these grounds we shall assume that the thermodynamics of the original system, characterized by $H^{(M)}$, is equivalent, under these restrictions, to that of $\tilde{H}^{(M)}$.

The two equations (31) and (32) reduce to a single one for $v$ if $g > 0$. The general form of equations (31) and (32) is

$$v = f_1(v - \eta) + f_2(v),$$

$$\eta = f_1(v - \eta).$$

Let $g > 0$, then $f_2 > 0$. Furthermore,

$$\eta = v - f_2(v),$$

which yields the equation for $v$

$$v = f_1(f_2(v)) + f_2(v),$$

where according to equations (33) and (34)

$$f_1(v) = (MN\beta)^{-1} \frac{\partial}{\partial v} \ln \text{Tr} \exp[-\beta \tilde{h}(v, 0)],$$

$$f_2(v) = (N\beta)^{-1} \frac{\partial}{\partial v} \ln \text{Tr} \exp[-\beta h^{(1)}].$$

5. Mean-field description of $\tilde{h}$

The form of the Hamiltonian $\tilde{h}$ (24) is analogous to

$$H_{\text{BCS}}(\mathcal{H}) = H_0 + V_{\text{BCS}} + \mu B \mathcal{H} \sigma_z,$$

(39)

describing a system of electrons with attractive BCS interaction in the presence of an external magnetic field $\mathcal{H} (\mu B$ denotes the Bohr magneton). The explicit form of the system’s free energy $f(\tilde{h}(\nu, \eta), \beta)$ can therefore be derived by exploiting the Bogolyubov–Valatin transformation [50, 51] and the method developed in [48] for $H_{\text{BCS}}(\mathcal{H})$. The Bogolyubov–Valatin transformation,

$$\alpha_{k+} = u_k a_{k+} + v_k a_{k-}^\dagger, \quad \alpha_{k-} = u_k a_{k-} + v_k a_{k+}^\dagger,$$

(40)

yields

$$\sigma_z = \sum_k (\alpha_{k+}^\dagger \alpha_{k+} - \alpha_{k-}^\dagger \alpha_{k-}).$$

(41)

One expects the energies of the states $k+, -k-$ to be different, since the products $\alpha_{k+}^\dagger \alpha_{k+}, \alpha_{k-}^\dagger \alpha_{k-}$ appear with the opposite signs in equation (41). Thus, the trial equilibrium density matrix, approximating $Z^{-1} \exp[-\beta \tilde{h}]$, has the form (see [48])

$$\rho_0 = \frac{\exp[-\beta \tilde{H}_0]}{\text{Tr} \exp[-\beta \tilde{H}_0]},$$

(42)

which is characterized by the following Hamiltonian:

$$\tilde{H}_0 = \sum_k (E_k \sigma_{k+}^\dagger \alpha_{k+}^\dagger + E_k \sigma_{k-}^\dagger \alpha_{k-}^\dagger + E_0),$$

(43)

where $E_0$ denotes the ground state energy. According to (23) and (30) the system’s free energy can be decomposed into three summands

$$F = F_{\text{el}} + F_{\text{imp}} + \frac{1}{2} MN (\nu^2 - \eta^2),$$

(44)

where

$$F_{\text{imp}} = -\beta^{-1} \ln \text{Tr} \exp[-\beta \tilde{h}_{\text{imp}}]$$

is the free energy of impurities and

$$F_{\text{el}} = U_{\text{el}} - T S_{\text{el}}$$

denotes free energy of electrons, with

$$U_{\text{el}} = \text{Tr} (\tilde{h} \rho_0)$$

(47)

and

$$S_{\text{el}} = -\langle \beta \rangle^{-1} \text{Tr} (\rho_0 \ln \rho_0).$$

(48)

For $\rho_0$ defined by equation (42),

$$S_{\text{el}} = -\langle \beta \rangle^{-1} \sum_k [f_{k1} \ln f_{k1} + (1 - f_{k1}) \ln (1 - f_{k1}) + f_{k2} \ln f_{k2} + (1 - f_{k2}) \ln (1 - f_{k2})].$$

(49)

where

$$f_{k1} = \frac{\exp(-\beta E_{k1})}{1 + \exp(-\beta E_{k1})}, \quad f_{k2} = \frac{\exp(-\beta E_{k2})}{1 + \exp(-\beta E_{k2})}.$$  

The projectors on the ground and excited BCS states

$$P_{\text{el}} = |\text{BCS}\rangle \langle k| \text{BCS},$$

$$P_{k+} = \alpha_{k+}^\dagger |\text{BCS}\rangle \langle k| \text{BCS}|\alpha_{k+},$$

$$P_{k-} = \alpha_{k-}^\dagger |\text{BCS}\rangle \langle k| \text{BCS}|\alpha_{k-},$$

$$P_{k+, -k-} = \alpha_{k+}^\dagger \alpha_{k-}^\dagger |\text{BCS}\rangle \langle k| \text{BCS}|\alpha_{k-} - \alpha_{k+},$$

allow us to rewrite equation (42) in the following form:

$$\rho_0 = \prod_k [f_{k1}(1 - f_{k2}) P_{\text{el}} + f_{k1}P_{k+} + f_{k2}P_{k-} + f_{k1}f_{k2}P_{k+,-k-}].$$

(51)

Thus, one obtains

$$U_{\text{el}} = \sum_k \left[ f_{k1}(1 + f_{k2}) + f_{k2}(1 - f_{k1}) \right] + \langle \Delta \rangle^{-1} \sum_{kkk} G_{kkk} u_k v_k u_k v_k \times (1 - f_{k1} - f_{k2})(1 - f_{k1} - f_{k2}),$$

(52)

which yields

$$F_{\text{el}} = U_{\text{el}} + \beta^{-1} \sum_k [f_{k1} \ln f_{k1} + (1 - f_{k1}) \ln (1 - f_{k1}) + f_{k2} \ln f_{k2} + (1 - f_{k2}) \ln (1 - f_{k2})].$$

(53)

The parameters $u_k, v_k, E_{k1}$ and $E_{k2}$, are found by minimizing the free energy. The thermodynamic perturbation method of Bogolyubov et al [52] shows that for such a choice of these parameters, the following relation holds up to negligible terms:

$$\lim_{|\Delta| \rightarrow \infty} f(\tilde{h}, \beta) = \lim_{|\Delta| \rightarrow \infty} \min_{|\Delta|} f(\tilde{h}_0, \beta),$$

(54)

where $\tilde{h}_0 = \tilde{H}_0 + \kappa \sigma_z$ and

$$\Delta_0 = |\Delta|^{-1} \sum_k \sum_{kk} G_{kk} u_k v_k (1 - f_{k1} - f_{k2}).$$

(55)
Minimization of equation (53) with respect to \(v_p\) yields
\[
\frac{\partial F_{cl}}{\partial v_p} = 4\xi_p v_p (1 - f_{p1} - f_{p2}) - 2|\lambda|^{-1} \\
\times \sum_k G_{kk} u_k u_k (1 - f_{k1} - f_{k2}) \\
\times (1 - f_{p1} - f_{p2}) = 0.
\]
(56)

Then, from the normalization condition \(u_k^2 + v_k^2 = 1\) and the demand that the density matrix \(\rho_0\) should represent the Fermi-Dirac distribution of free fermions for \(\Delta = 0\), one obtains
\[
u_k^2 = \frac{1}{2} \left( 1 + \frac{\xi_k}{E_k} \right), \quad v_k^2 = \frac{1}{2} \left( 1 - \frac{\xi_k}{E_k} \right),
\]
(57)

The equation
\[
\frac{\partial F_{cl}}{\partial f_{k1}} = \xi_k + \kappa - 2\xi_k v_k^2 + 2|\lambda|^{-1} \sum_k G_{kk} u_k u_k v_k u_k v_k \\
\times (1 - f_{k1} - f_{k2}) + \beta^{-1} (\ln f_{k1} - \ln (1 - f_{k1})) = 0,
\]
combined with equations (50) and (55), yields
\[
E_{k1} = \xi_k (u_k^2 - v_k^2) + \kappa + 2\Delta_k u_k v_k = E_k + \kappa.
\]
(58)

Analogously, for \(E_{k2}\) one obtains
\[
E_{k2} = \xi_k (u_k^2 - v_k^2) - \kappa + 2\Delta_k u_k v_k = E_k - \kappa.
\]
(59)

Using equations (35), (50), (57) we get the equation for the gap parameter
\[
\Delta_k = \frac{\kappa}{4|\lambda|^{-1}} \sum_k G_{kk} \Delta_k E_k^{-1} f_3(\beta, E_k, \xi_k, f_2),
\]
(60)

where
\[
f_3(\beta, E_k, \xi_k, f_2) = \frac{\sinh(\beta E_k)}{\cosh(\beta E_k) + \cosh(\beta M f_2(v))}.
\]
(61)

Equation (60) resembles the gap equation in BCS theory. The convexity properties of \(f_3(\beta, E_k, \xi_k, f_2)\) differ in general from those of \(f_{bcs} = \tanh(\beta E_k)\). However, in the limit of extremely weak magnetic coupling, \(g \to 0\), \(f_3\) reduces to \(f_{bcs}\), namely
\[
f_3|_{g=0} = \frac{\sinh(\beta E_k)}{\cosh(\beta E_k) + 1} = \frac{2 \sinh(\frac{\beta}{2} E_k) \cosh(\frac{\beta}{2} E_k)}{2 \cosh^2(\frac{\beta}{2} E_k)} = \tanh(\frac{\beta}{2} E_k) = f_{bcs}.
\]
(62)

Equallities (52), (53), (57), (60) and (61) now lead to the following expression for the free energy:
\[
F_{cl} = \frac{1}{k}\sum_k \left[ E_k + \frac{\kappa}{2} \Delta_k E_k^{-1} f_3(\beta, E_k, \xi_k, f_2) \right] \\
- \beta^{-1} \ln[2 \cosh(\beta E_k) + 2 \cosh(\beta \kappa)]].
\]
(63)

The definition (37), where \(\eta = 0\), together with equation (63), yields the explicit form of the function \(f_1(v)\):
\[
f_1(v) = \frac{c g}{M \cosh(g \beta M v) + \cosh(\beta E_k)}.
\]
(64)

The free energy of the impurities and the function \(f_2\) depend on the value of their spin. In the present work we examine the critical temperature \(T_c\) of alloys containing Ce and Gd magnetic impurities. According to Matthias et al [1] the spin of the Ce ion is 1/2 and that of Gd is 7/2. For spin 1/2 impurities one obtains
\[
F_{imp}^{(\frac{1}{2})} = -\beta^{-1} \ln \text{Tr} \exp[-\beta h_{imp}^{(\frac{1}{2})}] \\
= -\beta^{-1} \sum_{a=1}^M \ln \text{Tr} \exp[-\beta h_{imp}^{(a)}] \\
= -M \beta^{-1} \ln[2 \cosh(\beta g v)] + \frac{1}{2} cg^2,
\]
(65)

and
\[
f_2^{(\frac{1}{2})}(v) = \frac{cg}{M} \tanh(\beta g v).
\]
(66)

Analogously, for spin 7/2 impurities
\[
F_{imp}^{(\frac{7}{2})} = -M \beta^{-1} \ln \left[2 \exp[-24g^2 \beta N^{-1}] \cosh(7 \beta g v) + \exp[-12g^2 \beta N^{-1}] \cos(5 \beta g v) + \exp[-4g^2 \beta N^{-1}] \cosh(3 \beta g v) + \cosh(\beta g v)]\right] + \frac{1}{2} cg^2.
\]
(67)

with
\[
f_2^{(\frac{7}{2})}(v) = \frac{cg}{MR} \left[7 \exp[-24g^2 \beta N^{-1}] \sinh(7 \beta g v) + 5 \exp[-12g^2 \beta N^{-1}] \sinh(5 \beta g v) + 3 \exp[-4g^2 \beta N^{-1}] \sinh(3 \beta g v) + \sinh(\beta g v)\right],
\]
(68)

where
\[
R = \exp[-24g^2 \beta N^{-1}] \cosh(7 \beta g v) + \exp[-12g^2 \beta N^{-1}] \cosh(5 \beta g v) + \exp[-4g^2 \beta N^{-1}] \cosh(3 \beta g v) + \cosh(\beta g v).
\]

6. The chemical potential

Passing from the summation in equation (60) over momentum \(k\) to integration over the single electron energies \(\xi\), one obtains for a sufficiently thin conduction band \(S\):
\[
\Delta = \frac{\kappa}{2} \rho \int_{-\Delta}^\Delta E f_3(\beta, E, \xi, f_2^{(s)}(v)) d\xi \quad s = 1/2, \ 7/2,
\]
(69)

where \(\rho\) denotes the density of states in \(\mathcal{P}\). This equation, together with the one for \(v\),
\[
v = f_1(f_2^{(s)}(v)) + f_2^{(s)}(v)
\]
(70)

constitutes the set of equations for \(\Delta\) and \(v\). The properties of a superconductor with magnetic impurities can be determined by solving this set of equations, which is supplemented by the following condition for the chemical potential \(\mu\):
\[
\sum_{k \sigma} \text{Tr}(\pi k \sigma \rho_0) = n,
\]
(71)

\(n\) denoting the average number of fermions in the system. According to equations (40), (50), (51) and (61), this condition takes the form
\[
\sum_{k \sigma} \left[ 1 - \frac{\xi_k}{E_k} f_3(\beta, E_k, \xi_k, f_2^{(s)}(v)) \right] = n.
\]
(72)
Equation (72) is analogous to the BCS equation for $\mu$ and the properties of $f_s$ are similar to $f_{BCS} = \tanh(\beta E_k/2)$, e.g. both are odd functions in $\xi$. The solution of equation (72) is therefore exactly the same as in BCS theory, namely, $\mu = \varepsilon_F$. The numerical calculations in subsequent sections are thus performed under the following assumptions:

$$\mu = \varepsilon_F, \quad \frac{\partial \mu}{\partial T} = 0, \quad \rho = \rho_F,$$

(73)

where $\rho_F$ denotes the density of states at the Fermi level,

$$\rho_F = \frac{mp_F}{2\pi^2\hbar^2}.$$

We have also imposed the condition

$$g MF(v) < E_k \quad \text{at} \quad T = 0 \text{K},$$

(74)

which expresses weak coupling between conduction electrons and impurities. Equation (69) then takes the limiting form

$$G_0\rho_F \arcsinh \left( \frac{\delta}{\Delta(0)} \right) = 1, \quad \text{as} \quad T \to 0,$$

(75)

whereas equation (70) is satisfied by $v(0) = \frac{2xg}{M}$ in this limit. Thus at sufficiently low temperatures $T$, close to 0 K, $\Delta(T)$ is the solution of equation (75). This solution is substituted into equation (70), which is then solved for one-fermion energies $\xi \in \mathcal{P}$ by exploiting the Newton–Raphson method. The resulting values of $v(\xi)$ are used to obtain $\Delta(T + \Delta T)$ from (69) by deploying Newton–Cotes quadrature as long as the result is self-consistent. The resulting value of $\Delta(T + \Delta T)$ is used to compute $v(\xi)$ at temperature $T + \Delta T$. This procedure is continued until $T$ reaches the specified value. To ensure numerical stability the step $\Delta T$ should be sufficiently small, e.g. $\Delta T = 10^{-3}$ K.

In the opposite case, namely, $g MF(v) > E_k$ for $T = 0 \text{K}$, one has

$$\Delta(0) = 0, \quad v(0) = \frac{2xg}{M}.$$  

In such anomalous circumstances, superconductivity is completely suppressed at $T = 0 \text{K}$ and the system is described only by the impurity parameter $v$. The intermediate case, when $g MF(v) = E_k$, has not been examined numerically.

7. Phase diagrams

The system’s state is characterized, according to equations (30) and (54), by the solution of equations (69) and (70), which minimizes $F(h^{(B)}, \beta)$. It will be denoted by $[\Delta_m, v_m]$. Passing from summation in equation (63) over $k$ to integration over the single-fermion energies $\xi$ and exploiting equation (44), one obtains the following expression for the free energy:

$$F^{(s)} = \min_{[\Delta, v]} \left\{ \rho_F[A] \int_{-\delta}^{\delta} \left[ \frac{1}{2} \Delta^2 E^{-1} f_3(\beta, E, \xi) + F^{(s)} \right. \right.$$

$$\left. - \beta^{-1} \ln(2cosh(\beta E) + 2cosh(g\beta MF^{(s)})) \right] d\xi^2$$

$$+ M^2 E^{-1}(v f_3^{(s)} - \frac{1}{2} (f_3^{(s)})^2) + F^{(s)} + E_0(\Delta = 0)$$

$$+ \rho_F \delta^2 \left. \right\} , \quad s = 1/2, \ 7/2.$$  

(76)

where $F^{(s)}$ are given by the equations (65) and (67), whereas $E_0(\Delta = 0)$ denotes the ground state energy of free fermions. The last two terms are the contribution to the free energy density from one-fermion states, lying outside $S$.

Equations (69) and (70) clearly possess the solution $\Delta = v = 0$ for all values of $\beta \geq 0$. At sufficiently large values of $\beta$ one finds also other solutions, namely $[\Delta \neq 0, v = 0]$, $[\Delta = 0, v \neq 0]$, $[\Delta \neq 0, v \neq 0]$. Accordingly, we distinguish the following phases:

- paramagnetic phase $P$ with $[\Delta_m = 0, v_m = 0]$,
- unperturbed superconducting state $SC$ with $[\Delta_m \neq 0, v_m = 0]$,
- ferromagnetic phase $F$ without bound Cooper pairs and $[\Delta_m = 0, v_m \neq 0]$, in which impurity spins tend to align opposite to those of conduction fermions (cf equations (24) and (25)),
- intermediate phase $D$ in which superconductivity coexists with ferromagnetism and $[\Delta_m \neq 0, v_m \neq 0]$.

We define the following temperatures corresponding to the respective phase transitions.

- $T_C$, second order transition $SC \to P$.
- $T_{FP}$, Curie temperature of second order transition $F \to P$.
- $T_{SCD}$, first order transition $D \to SC$.
- $T_{DF}$, first order transition $D \to F$.
- $T_{SCF}$, first order transition $SC \to F$.

The set of equations (69) and (70) has been solved numerically for different values of $g, M, \delta$ and $G_0\rho_F$. The parameters were adjusted to fit the experimental specific-heat curves for (La$_{1-x}$Ce$_x$)$_2$Al$_2$ and LaGd and the critical field curve in the case of ThGd [53]. These values are used to compute the phase diagrams of these alloys on the grounds of equation (76).

The phase diagrams of (La$_{1-x}$Ce$_x$)$_2$Al$_2$, for which the free energy is given by equation (76) with $s = 1/2$ and impurity concentration $c = x/(3 - x)$, are depicted in figure 1. The values of $M$, $g$, $\delta$ and $G_0\rho_F$ are given in table 1. These diagrams show the decline of the D and SC phases with increasing impurity concentration. The critical temperature $T_c$ is a decreasing function of impurity concentration. It follows, therefore, that the destructive effect of impurities increases with $c$ and suppresses the superconductivity if $g$ or $c$ reaches its critical value. This complies with experimental data, in which superconductivity is expunged for Ce content larger than 0.67% [12, 54, 55].
The supplementary phase NG with gapless superconductivity and $\Delta_m > 0$ is present, as a subregion of the SC, D or F phase. The appearance of NG subregion is due to the negative term $-gM_f(\nu)$ present in $E_{k1}$ (58).

For sufficiently small magnetic coupling constant $g$, the NG phase for $(\text{La}_{1-x}\text{Ce}_x)\text{Al}_2$ lies between the D and F phases. Thus, the pair-breaking mechanism, which increases with $g$, induces gapless superconductivity and then superconductivity is suppressed for sufficiently large $g$. The system undergoes a phase transition to a ferromagnetic F state (cf figure 1(a)).

The resulting phase diagrams also show the reentrant superconductivity, which is seen in figure 1(a) for $g \approx 0.72 \sqrt{eV}$. As temperature $T$ is lowered, the system undergoes the first phase transition to a superconducting state ($P \rightarrow \text{SC}$) when $T = T_c$. After further cooling superconductivity is suppressed at $T = T_{SCF}$ and the alloy displays ferromagnetic properties until $T > T_{FD}$. For $T < T_{FD}$ superconductivity reappears in the D phase, where it coexists with ferromagnetism.

It is worth noting at this point that reentrant superconductivity due to the Kondo effect was observed for the first time in $(\text{La}_{1-x}\text{Ce}_x)\text{Al}_2$ [18, 19]. These measurements showed destruction of superconductivity below the second critical temperature $T_{c2} < T_{c1}$, but the second phase transition, reintroducing superconductivity, was not confirmed. This scenario with $T_{c1} = T_c$ and $T_{c2} = T_{SCF}$ is also present in the computed phase diagrams, e.g. in figure 1(b) for $g \geq 0.65 \sqrt{eV}$.

The phase diagrams of LaGd and ThGd alloys, for which the free energy is given by equation (76) with $s = 7/2$, are depicted in figures 2 and 3. The values of the parameters exploited in these computations are collected in table 1. Figures 2 and 3 show that the perturbative effect of Gd is larger than that of Ce impurities, namely, the area of the D phase is smaller than in figure 1. Furthermore, superconductivity is already suppressed at smaller values of $g$. This complies with experimental observations by Matthias et al, who showed that indeed the depression of superconductivity of doped lanthanum increases with the spin of the rare earth ions [1].

The $T_{SCF}$ temperature increases almost linearly with the value of $g$. One also observes decrease of $T_{FD}$ with $g$ and increase of $T_{WF}$ with $g$. Furthermore, rapid disappearance of the D phase is observed for critical values of $g$.

The intermediate phase D in which superconductivity coexists with ferromagnetism of impurities is present in each phase diagram depicted in figures 1–3. The first experimental suggestion concerning the presence of a coexistence phase in superconducting alloys was made by Matthias et al [1]. This hypothesis was later confirmed in Ce$_{1-x}$Gd$_x$Ru$_2$ [31] and Y$_{1-x}$Gd$_x$O$_{32}$ [32]. However, the basic question, as to whether superconductivity and magnetic order occur in the same volume element, was still open. Wilhelm and Hillenbrand measured the phase diagrams of Ce$_{1-x}$Tb$_x$Ru$_2$, which contain the coexistence phase [33]. As temperature was lowered, one observed the following phase transitions, depending on the value of impurity concentration $c$.

1. A phase transition $P \rightarrow \text{SC}$, which occurs for sufficiently small $c$.
2. For intermediate values of $c$ the system undergoes a phase transition $P \rightarrow \text{SC}$ and then from SC to D phase.
Figure 2. Phase diagrams of LaGd for the values of $M$, $g$, $\delta$ and $G_0\rho_F$ given in table 1 and under varying Gd concentration: (a) $c = 0.10\%$ Gd, (b) $c = 0.20\%$ Gd and (c) $c = 0.30\%$ Gd.

Figure 3. Phase diagrams of ThGd for the values of $M$, $g$, $\delta$ and $G_0\rho_F$ given in table 1 and under varying Gd concentration: (a) $c = 0.10\%$ Gd, (b) $c = 0.20\%$ Gd.

(3) Two phase transitions occur for sufficiently large values of $c$: $P \rightarrow F$ and then $F \rightarrow D$.

(4) For some special value of $c$ the system undergoes a phase transition $P \rightarrow D$.

The phase diagrams depicted in figures 1–3 reveal the transitions 1–3. In particular, one phase transition $P \rightarrow SC$ (variant no. 1) is visible in every diagram depicted in figure 1 for $g \leq 0.05 \sqrt{eV}$, which states the weak coupling of Cooper pairs to impurity ions. The options 2 and 3 are clearly seen in every diagram. However, variant no. 3 is most distinct in figure 1(a) for $g \approx 0.9 \sqrt{eV}$. The computed phase diagrams do not exhibit the fourth transition. However, figure 1(a) shows that the phase transition $P \rightarrow D$ may appear for sufficiently large values of $g$, $G_0\rho_F$ and small $M$ and $c$, since in this case the D region is relatively large.

The specific-heat measurements of Ce$_{1-x}$Tb$_x$Ru$_2$ revealed a short-range magnetic order in this compound, which is typical of spin-glasses [34]. The coexistence of superconductivity with long-range ferromagnetic order was discovered a few years later, e.g. in (Er$_{1-x}$Ho$_x$)Rh$_2$B$_4$ [56–58].

The phase diagrams of these compounds show the following phase transitions:

(1) $P \rightarrow SC$ for $x \approx 0.1$,
(2) $P \rightarrow SC \rightarrow D$ for $x \approx 0.3$,
(3) $P \rightarrow SC \rightarrow F \rightarrow D$ for $x \approx 0.4$,
(4) $P \rightarrow F \rightarrow D$ for $x \approx 0.9$,
(5) $P \rightarrow F$ for $x \approx 0.95$.

The theoretical phase diagrams depicted in figures 1–3 only fail to reproduce the third scenario.
The intermediate phase, where superconductivity coexists with long-range antiferromagnetic order, was discovered in RM06Se8 (R = Gd, Tb and Er) [35], RRhB4 (R = Nd, Sm and Tm) [36] and RM06S8 (R = Gd, Tb, Dy and Er) [37]. The upper critical field, \( H_{c2} \), in most of these compounds decreases below the Néel temperature \( T_N \). Accordingly, the superconducting state is perturbed by antiferromagnetically aligned impurity spins. However, a rapid increase of \( H_{c2} \) below \( T_N \) was also observed, e.g. in SmRhB4, GdMo6S8, TbMo6S8, Sm1−xEu1−xMo6S8, Pbn−xEuMo6S8, and La1−x−yEu1−yMo6S8 [59, 60], implying enhancement of superconductivity by antiferromagnetism of impurities.

Fischer et al [61] have pointed out that this boost of superconductivity may be due to the Jaccarino–Peter effect [62], in which superconductivity is induced by applying a high magnetic field \( \mathcal{H} \). This effect can arise in a type-II superconductor, in which the impurity magnetic moments are antiferromagnetically coupled to conduction electrons. This interaction generates an exchange field \( \mathcal{H}_J \), which acts on the spins of conduction electrons equivalently to an applied magnetic field, namely, breaks the Cooper pairs. However, the negative sign of the coupling between the magnetic moments and the conduction fermions’ spins, determines the direction of \( \mathcal{H}_J \) to be opposite to that of \( \mathcal{H} \). Thus, an applied magnetic field will be compensated by an exchange field, since the net magnetic field \( \mathcal{H}_T \) is given by \( \mathcal{H}_T = \mathcal{H} - [\mathcal{H}_J] \). A given compound displays superconducting properties as long as the following relation holds:

\[
-\mathcal{H}_p \leq \mathcal{H}_T \leq \mathcal{H}_p,
\]

where

\[
\mathcal{H}_p = \sqrt{\frac{\rho \mathcal{E}}{\chi_p - \chi_{SC}}},
\]

\( \chi_p \) and \( \chi_{SC} \) denote the susceptibility of the normal and superconducting state respectively. \( \mathcal{H}_p \), defined by equation (78), is the Chandrasekhar–Clogston limiting paramagnetic field [63, 64].

The Jaccarino–Peter mechanism was observed experimentally in Eu0.75Sn0.25Mo6S7Se0.8 [65]. In the low-temperature scale and with increasing applied magnetic field four phase transitions were recognized: SC → P → SC → P. This effect can explain the reappearance of superconductivity for sufficiently large values of \( g \) in the theoretical phase diagrams (figures 1–3). For \( T \approx 0 \) K, it is firmly seen that the system undergoes the following transitions: SC → D → F → SC, which can be interpreted as SC → P → SC, since the given compound displays features characteristic of superconductors and magnetically ordered systems in a D phase and in the F phase superconductivity is suppressed.

In conclusion it is worth pointing out that the interplay between superconductivity and magnetism is believed to be a possible mechanism of high-\( T_c \) superconductivity [66], since the undoped state of cuprate superconductors is a strongly insulating antiferromagnet. The existence of such a parent correlated insulator is viewed to be an essential feature of high-temperature superconductivity.

8. Critical temperature

According to section 5, equation (69) for the solution \( \Delta \neq 0, \nu = 0 \) reduces to the BCS gap equation

\[
\Delta_{BCS} = \frac{1}{2} \frac{G_0 \rho \mathcal{F}}{\Delta_{BCS}} \int_{-\beta c}^{\beta c} \frac{\Delta_{BCS}}{E_{BCS}} \tanh \left( \frac{\beta E_{BCS}}{2} \right) d\xi,
\]

\[
E_{BCS} = \sqrt{\xi^2 + \Delta_{BCS}^2}.
\]

The transition temperature \( T_{c(BCS)} \) in BCS theory is defined as the boundary of the region beyond which there is no real, positive \( \Delta_{BCS} \) satisfying (79). Below \( T_{c(BCS)} \) the solution \( \Delta_{BCS} \neq 0 \) minimizes the free energy and the system is in superconducting phase. Therefore, \( T_{c(BCS)} \) can be obtained from equation (79) with \( \Delta_{BCS} = 0 \), which yields [9]

\[
T_{c(BCS)} = 1.148 \exp \left[ -(G_0 \rho \mathcal{F})^{-1} \right].
\]

It should be possible to estimate the change in \( T_{c(BCS)} \) under impurity doping, since the density of states enters equation (80) were observed experimentally for a number of superconductors containing magnetic impurities. This inadequacy of equation (80) is most distinct for large values of impurity concentration. BCS theory is therefore incapable of describing the superconducting alloys.

The results obtained in section 7 show that the phase transition to a superconducting state in a superconductor with magnetic impurities, depending on the value of magnetic coupling constant, can be first or second order. The next two subsections are concerned with computation of the transition temperature \( T_{c} \) on the grounds of equations (69), (70) and (76). These calculations strongly depend on the order of the transition.

8.1. Second order phase transition

The expression for transition temperature \( T_{c} \) for the second order phase transition can be computed analogously as in BCS theory. It suffices to put \( \Delta = 0 \) in equations (69) and (70). Thus, one obtains the following set of equations for \( T_{c} = 1/k\beta c \):

\[
2 = \frac{G_0 \rho \mathcal{F}}{\Delta_{BCS}} \int_{-\beta c}^{\beta c} \frac{\sinh(\beta\xi)}{\cosh(\beta\xi) + \cosh(g\beta c M f_2^{(\nu)}(v c))} d\xi,
\]

\[
\nu c = \frac{c g}{M} \frac{\sinh(g\beta c M f_2^{(\nu)}(v c))}{\cosh(g\beta c M f_2^{(\nu)}(v c)) + \cosh(\beta c |\xi|)} + f_2^{(\nu)}(v c),
\]

where \( v c = v(\beta c), s = 1/2, 7/2 \). Numerical analysis shows that in the low-temperature scale \( v c \) is almost independent of \( T \), namely,

- for spin 1/2 impurities:

\[
v c \approx 0, \quad \text{for } x \leq 0.0010, \quad v(0) = \frac{c g}{M}, \quad \text{for } x \geq 0.0019,
\]
of $\nu$ under the assumption that $T$ containing 1 impurities. The values of the parameters $g$, $G_0\rho_F$ and $M$ are given in table 2.

![Figure 4](image1.png)

**Figure 4.** The superconducting transition temperature $T_c$ under varying impurity concentration $c$ for superconducting alloy, containing 1/2 impurities. The values of the parameters $g$, $G_0\rho_F$ and $M$ are given in table 2.

![Figure 5](image2.png)

**Figure 5.** The superconducting transition temperature $T_c$ under varying impurity concentration $c$ for superconducting alloy, containing 7/2 impurities. The values of the parameters $g$, $G_0\rho_F$ and $M$ are given in table 2.

| Impurity spin | Curve no. | $M$ | $g$ (eV) | $\delta$ (eV) | $G_0\rho_F$ |
|---------------|-----------|-----|---------|------------|-----------|
| 1/2           | 1         | 1   | 0.10    | 0.01       | 0.2610    |
|               | 2         | 4   | 0.189   | 0.01       | 0.2515    |
|               | 3         | 7   | 0.19    | 0.01       | 0.2435    |
|               | 4         | 8   | 0.23    | 0.01       | 0.2250    |
| 7/2           | 1         | 5   | 0.16    | 0.01       | 0.2825    |
|               | 2         | 10  | 0.18    | 0.01       | 0.2750    |
|               | 3         | 15  | 0.20    | 0.01       | 0.2670    |

Table 2. Parameter values.

• for spin 7/2 impurities:

$$\nu_c \approx \nu(0) = \frac{cg}{M}$$

This result complies with experimental data, showing that the perturbative effect of impurities on superconductivity is an increasing function of their spin. Furthermore, the reduction of $T_c$ by adding a small amount of spin 1/2 impurities can be satisfactorily described by equation (80) by adjusting the value of $G_0\rho_F$, since for $\nu_c = 0$, equations (81) and (82) reduce to $T_{c}(\text{BCS})$. Accordingly, the set of equations (81), (82) is solved under the assumption that $\nu_c = \frac{cg}{M}$.

The solution for $T_c$ resulting from equations (81) and (82) for $s = 1/2, 7/2$ and under varying impurity concentration $c$ is depicted in figures 4 and 5. In general, the values of the parameters $M$, $g$, $\delta$ and $G_0\rho_F$, depend on the impurity concentration $c$. However, to minimize the number of adjustable parameters, the values of $M$, $g$, $\delta$ and $G_0\rho_F$ have been kept constant.

Figures 4 and 5 show how variation of $c$ affects $T_c(c)$. For certain values of $c$ (e.g. $c \in (0.0225, 0.0275)$ for curve no. 1 in figure 4) equation (81) with $\nu_c \approx \nu(0)$ possesses two solutions: $T_{c1}$, $T_{c2}$. Thus, superconductivity is suppressed below $T_{c2}$. The dependence of $T_c$ on $c$ shown in figures 4 and 5 does not indicate the existence of a third transition temperature $T_{c3}$. This, can be a consequence of the applied approximation in which $M$, $g$, $\delta$ and $G_0\rho_F$ do not depend on $c$. However, the dependence of $T_c$ on impurity concentration $c$ shown in figure 4 is typical of the (La$_{1-x}$Ce$_x$)Al$_2$ alloy [12].

The destructive influence of impurities on superconductivity is analogous to the effect of an external magnetic field $\mathcal{H}$ applied to a superconducting compound. Sarma [67] obtained a numerical solution for $T_c(\mathcal{H})$ of the system described by the Hamiltonian $H_S = H_{\text{BCS}} + \mu_b \mathcal{H} \sigma_z$. His result for $T_c(\mathcal{H})$ agrees qualitatively with the $T_{c}(c)$ graphs depicted in figures 4 and 5, since the expression for $T_c(\mathcal{H})$ obtained in [67] is of a similar form to equation (81) with $gMf^{(1)}(\nu_c)$ replacing $\mu_b \mathcal{H}$.

8.2. The first order phase transition

In the case of first order phase transition, the assumption that the gap parameter $\Delta$ vanishes at the transition temperature does not hold. According to the results obtained in section 7, one can expect that $T_c$ possesses three solutions ($T_{c1} \geq T_{c2} \geq T_{c3}$) for certain values of $g$ and $c$. These solutions can be determined numerically from the following equations:

$$T_{c1}: \quad F_F - F_{SC} = 0,$$  \hspace{1cm} (83)

$$T_{c2}: \quad F_{SC} - F_{\Phi} = 0, \quad \Phi = D, F,$$  \hspace{1cm} (84)

$$T_{c3}: \quad F_F - F_D = 0.$$  \hspace{1cm} (85)

The existence of $T_{c3}$ depends on the type of phase transition occurring at $T_{c2}$. If the system undergoes a phase transition to ferromagnetic phase at $T_{c2}$, then $T_{c3} > 0$ for certain values of $g$ (cf section 7). If $T_{c2} = T_{SCD}$, then $T_{c3} = 0$ and the system does not re-enter the superconducting phase (SC or D).

In order to obtain a reliable comparison of the transition temperature resulting from equations (83)–(85) to experimental data, we let the parameters $G_0\rho_F$, $g$ and $M$ vary with impurity concentration. The parameters are then adjusted independently for each experimental point. The best fitting of $T_c(c)$ to experiment for (La$_{1-x}$Ce$_x$)Al$_2$, (La$_{1-x}$Gd$_x$)Al$_2$ and...
Figure 6. The superconducting transition temperature versus Ce impurity concentration \( x \) for \((\text{La}_{1-x}\text{Ce}_x)\text{Al}_2\). Squares denote theoretical values of \( T_c \) obtained from equations (83) to (85). Rhombus are experimental points from [18]. The star at the point \( x = 0.0067 \) denotes the experimentally estimated turning point in \( T_c \), above which superconductivity is destroyed.

Figure 7. The superconducting transition temperature versus Gd impurity concentration \( x \) for \((\text{La}_{1-x}\text{Gd}_x)\text{Al}_2\). Squares denote theoretical values of \( T_c \) obtained from equations (83) to (85). Rhombus are experimental points from [68]. The value of critical concentration \( x_c \), where \( T_c = 0 \) is 0.59 at\% Gd.

Figure 8. The superconducting transition temperature versus Ce impurity concentration \( x \) for \((\text{La}_{0.8-x}\text{Y}_{0.20})\text{Ce}_x\). Squares denote theoretical values of \( T_c \) obtained from equations (83) to (85). Rhombus are experimental points from [16]. For \( x = 0.0085 \) there are three \( T_c \) solutions, which demonstrate reentrant superconductivity observed experimentally in \((\text{La}_{0.8-x}\text{Y}_{0.20})\text{Ce}_x\) at this value of \( x \) (inset).

The model studied here gives considerably better results for \( T_c \) than previous theories, although an analytic expression for \( T_c \) cannot be obtained for the first order phase transitions.

9. Concluding remarks

We have shown that the thermodynamics of a BCS superconductor, perturbed by a reduced s–d interaction, is solvable if the impurity density is sufficiently small. The essential properties of dilute magnetic superconducting alloys have been demonstrated: the decrease of superconducting transition temperature \( T_c \) with increasing impurity concentration, the occurrence of a coexistence phase of magnetism and superconductivity, the existence of reentrant and gapless superconductivity and the presence of Jaccarino–Peter compensation related to the magnetic field induced superconductivity. Good quantitative agreement of the resulting dependence of \( T_c \) on impurity concentration was demonstrated for several superconducting compounds: \((\text{La}_{1-x}\text{Ce}_x)\text{Al}_2\), \((\text{La}_{1-x}\text{Gd}_x)\text{Al}_2\) and \((\text{La}_{0.8-x}\text{Y}_{0.20})\text{Ce}_x\). The theory presented provides better agreement with experiment than earlier AG, MHZ theories and their various extensions and refinements given in [20–23, 69].

We have also performed a fit of specific-heat and critical field curves for \((\text{La}_{1-x}\text{Ce}_x)\text{Al}_2\), \( \text{LaCe} \), \( \text{LaGd} \), and \( \text{ThGd} \). We shall report on this study elsewhere [53].

These investigations will be extended to include the effect of a general s–d exchange interaction \( V_{s-d} \) and a BCS-type attraction between Cooper pairs \( V_{dd} \) [70–72] in order to study other properties of superconducting alloys.

References

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