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Thermodynamics of the Two-Band Superconductors in the Presence of Nonmagnetic Impurities

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The thermodynamics of the two-band model for the superconducting states of transition metals containing nonmagnetic impurities are developed using the Green's-function technique. The thermodynamic functions of the system are expressed in terms of the densities of state of the *s* and *d* electrons. Changes caused by the presence of the impurities of the various functions are obtained. It is shown that in the intraband limit $g_{sd}=0$, the specific heat of transition metals in the superconducting phase is decreased because of the presence of the nonmagnetic impurities.

I. INTRODUCTION

The observed ratios[1] between the jump in the specific heat ΔC and the electronic specific heat of the normal phase at the transition temperature, $\Delta C/\gamma\, T_c$, for the transition elements are different from those predicted by the BCS theory. Those specific-heat anomalies, along with the absence[2] of the isotope effect in some transition elements, have indicated that the superconductivity of these elements arises from a mechanism different from that proposed in the BCS theory.[3] Suhl, Matthias, and Walker (SMW)[4] proposed a two-band model for these elements. Kondo,[5] using a slightly modified model, was able to explain the absence of the isotope effect in some of the transition metals. Other authors[6] have applied the SMW model to explain the specific-heat anomalies of some of the transition metals.

The usual approach to the problem, the Bogoliubov transformations, could not easily be extended to include the presence of nonmagnetic impurities in the transition metals. The Green's-function technique,[7] however, can easily incorporate the effects of the nonmagnetic impurities. All the information needed to determine the thermodynamic and electrodynamic properties of the two-band model in the presence of impurities are contained in the Green's function.[8] In Sec. III, the Green's function for the system, developed in Sec. II, are applied in a manner similar to the analysis performed on the one-band superconductor[9] containing paramagnetic impurities.

The special case of the intraband limit $g_{sd}=0$ is treated in Sec. IV. In this limit, the Green's-functions for the system reduce to the usual one-particle propagators. It is seen that the nonmagnetic impurities cause a decrease in the specific heat of the transition element in the superconducting phase. The effects of the impurities are seen to enter into the thermodynamic properties through the modification of the densities-of-state functions.

II. GREEN'S FUNCTION

The Hamiltonian for the two-band model in the absence of impurity atoms is taken to be[8]

$$\begin{aligned}H_0=&\sum_\sigma \int d^3x\{\psi^\dagger_{s\sigma}(x)[-(\nabla^2/2m_s)-\mu]\psi_{d\sigma}(x)+\psi^\dagger_{d\sigma}(x)\;[-(\nabla^2/2m_d)-\mu]\psi_{d\sigma}(x)\}\\&-\tfrac{1}{2}g_s\sum_\sigma\int d^3x\,\psi^\dagger_{s\sigma}(x)\psi^\dagger_{s-\sigma}(x)\psi_{s-\sigma}(x)\psi_{s\sigma}(x)-\tfrac{1}{2}g_d\sum_\sigma\int d^3x\,\psi^\dagger_{d\sigma}(x)\psi^\dagger_{d-\sigma}(x)\psi_{d-\sigma}(x)\psi_{d\sigma}(x)\\&-g_{sd}\sum_\sigma\int d^3x\,\psi^\dagger_{s\sigma}(x)\psi^\dagger_{d-\sigma}(x)\psi_{d-\sigma}(x)\psi_{s\sigma}(x),\end{aligned}\tag{2.1}$$

where $\psi_{s\sigma}(x)$ and $\psi^\dagger_{s\sigma}(x)[\psi_{d\sigma}(x)$ and $\psi^\dagger_{d\sigma}(x)]$are, respectively, the destruction and creation operators for the s-band (d-band) electrons with the spins specified by σ (can be either ↑ or ↓ and with $-$↑ equal to ↓). μ is the chemical potential from which the single-particle energy is measured. The phonon-induced attractions are represented by g_s, g_s, and g_{sd}.

Transforming to the Heisenberg representation, we introduce the time-dependent Heisenberg operators $\overline{\psi}_{s\sigma}(x)$, $\overline{\psi}^\dagger_{s\sigma}(x)$, $\overline{\psi}_{d\sigma}(x)$, and $\overline{\psi}^\dagger_{d\sigma}(x)$. Naturally, these operators satisfy the commutation relation

$$-i\frac{\partial}{\partial t}\,\overline{\psi}(x)=[H_0,\,\overline{\psi}(x)]\,.\tag{2.2}$$

To treat all the operators simultaneously, we introduce Chow's four-component operators.[8] Using these operators and the commutation relations that they satisfy, the same 4×4 Green's function as found in Refs. 8 is obtained.

To treat the effects of the impurities being added to the system, we introduce the interaction Hamiltonian

$$\begin{aligned}H_I=&\sum_{i,\sigma}\int d^3x\,[V_s(x-R_i)\psi^\dagger_{s\sigma}(x)\psi_{s\sigma}(x)\\&+V_d(x-R_i)\psi^\dagger_{d\sigma}(x)\psi_{d\sigma}(x)]\\&+\sum_{i,\sigma}\int d^3x\,V_{sd}(x-R_i)\\&\times[\psi^\dagger_{s\sigma}(x)\psi_{d\sigma}(x)+\psi^\dagger_{d\sigma}(x)\psi_{s\sigma}(x)].\end{aligned}\tag{2.3}$$

The interaction terms $V_s(x-R_i)$, $V_d(x-R_i)$, and $V_{sd}(x-R_i)$ are, respectively, the potential of any impurity atom at position R_i as felt by a s, d electron, and the potential which causes an interband transition. The density of the impurity atoms is given by n_i.

The procedure for determining the new propagators in the presence of impurity scattering is exactly the same as that found in the references cited. The propagators, which are of most interest to here, are

$$G_{ss}(p,i\tilde{\omega}_n)=-\frac{[i\tilde{\omega}_n(s)+\epsilon_s][\tilde{\omega}^2_n(d)+\epsilon^2_d+\tilde{\Delta}^2_n(d)]-\tilde{\Delta}^2_n(sd)[i\tilde{\omega}_n(d)+\epsilon_d]}{\{\cdot\circ\cdot\}}\,,\tag{2.4}$$

$$G_{dd}(p, i\tilde{\omega}_n) = -\frac{[i\tilde{\omega}_n(d)+\epsilon_d][\tilde{\omega}_n^2(s)+\epsilon_s^2+\tilde{\Delta}_n^2(s)] - \tilde{\Delta}_n^2(sd)[i\tilde{\omega}_n(s)+\epsilon_s]}{\{\circ\ \circ\ \bullet\}}, \tag{2.5}$$

where the denominators are

$$[\tilde{\omega}_n^2(s)+\epsilon_s^2+\tilde{\Delta}_n^2(s)][\tilde{\omega}_n^2(d)+\epsilon_d^2+\tilde{\Delta}_n^2(d)] - \tilde{\Delta}_n^2(sd)\{\tilde{\Delta}_n^2(sd)+[i\tilde{\omega}_n(d)+\epsilon_d][i\tilde{\omega}_n(s)-\epsilon_s]$$
$$+[i\tilde{\omega}_n(d)-\epsilon_d][i\tilde{\omega}_n(s)+\epsilon_s]\}\ \tilde{\Delta}_n(s)\tilde{\Delta}_n(d)[\tilde{\Delta}_n^*(sd)]^2 - \tilde{\Delta}_n^*(s)\tilde{\Delta}_n^*(d)[\tilde{\Delta}_n(sd)]^2,$$

with

$$\tilde{\omega}_n(s) = \bar{\omega}_n + n_i\int\frac{d^3p}{(2\pi)^3}\,V_{sd}^2 G_{dd}(p, i\tilde{\omega}) + n_i\int\frac{d^3p}{(2\pi)^3}\,V_s^2 G_{ss}(p, i\tilde{\omega}), \tag{2.6}$$

$$\tilde{\omega}_n(d) = \bar{\omega}_n + n_i\int\frac{d^3p}{(2\pi)^3}\,V_{sd}^2 G_{ss}(p, i\tilde{\omega}) + n_i\int\frac{d^3p}{(2\pi)^3}\,V_d^2 G_{dd}(p, i\tilde{\omega}), \tag{2.7}$$

$$\tilde{\Delta}_n(s) = \bar{\Delta}_s + n_i\int\frac{d^3p}{(2\pi)^3}\,V_s^2 F_{ss}(p, i\tilde{\omega}) + n_i\int\frac{d^3p}{(2\pi)^3}\,V_{sd}^2 F_{dd}(p, i\tilde{\omega}), \tag{2.8}$$

$$\tilde{\Delta}_n(d) = \bar{\Delta}_d + n_i\int\frac{d^3p}{(2\pi)^3}\,V_{sd}^2 F_{ss}(p, i\tilde{\omega}) + n_i\int\frac{d^3p}{(2\pi)^3}\,V_d^2 F_{dd}(p, i\tilde{\omega}). \tag{2.9}$$

Expressions for $\tilde{\Delta}_n(sd)$, $F_{ss}(p, i\omega)$, $F_{dd}(p, i\omega)$, and the others can be found in the author's previously cited paper.

The densities of states in the s band and d band can be determined from (2.4) and (2.5) by using the relation

$$N_s(\omega) = (N_{s0}/\pi)\int_{-\infty}^{\infty} d\epsilon\,\mathrm{Im}G_{ss}(p, i\tilde{\omega}), \tag{2.10}$$

$$N_d(\omega) = (N_{d0}/\pi)\int_{-\infty}^{\infty} d\epsilon\,\mathrm{Im}G_{dd}(p, i\tilde{\omega}), \tag{2.11}$$

where Im means the imaginary part. N_{s0} and N_{d0} are, respectively, the densities of states at the Fermi surface of the s band and d band. The entropy of each band can be obtained from the density of states through

$$S_S(s) = 4k_B\int_0^{\omega_D'} d\omega\,N_s(\omega)\left(\ln(1+e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega}+1}\right), \tag{2.12}$$

$$S_S(d) = 4k_B\int_0^{\omega_D''} d\omega\,N_d(\omega)\left(\ln(1+e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega}+1}\right), \tag{2.13}$$

where the capital S subscript means the entropy is of the superconducting phase.

III. TOTAL ENERGY OF THE SUPERCONDUCTING PHASE

The total Hamiltonian for the two-band model doped with nonmagnetic impurities is

$$H_{\mathrm{Total}} = \sum_\sigma\int d^3x\left[\psi_{s\sigma}^\dagger(x)\left(-\frac{\nabla^2}{2m_s}-\mu\right)\psi_{s\sigma}(x) + \psi_{d\sigma}^\dagger(x)\left(-\frac{\nabla^2}{2m_d}-\mu\right)\psi_{d\sigma}(x)\right]$$
$$-\tfrac{1}{2}\sum_\sigma\int d^3x\,[g_0\psi_{s\sigma}^\dagger(x)\psi_{s-\sigma}^\dagger(x)\psi_{s-\sigma}(x)\psi_{s\sigma}(x) + g_d\psi_{d\sigma}^\dagger(x)\psi_{d-\sigma}^\dagger(x)\psi_{d-\sigma}(x)\psi_{d\sigma}(x)]$$
$$-\sum_\sigma\int d^3x\,g_{sd}\psi_{s\sigma}^\dagger(x)\psi_{d-\sigma}^\dagger(x)\psi_{d-\sigma}(x)\psi_{s\sigma}(x)$$
$$+\sum_{i,\sigma}\int d^3x\,[V_s(x-R_i)\psi_{s\sigma}^\dagger(x)\psi_{s\sigma}(x) + V_d(x-R_i)\psi_{d\sigma}^\dagger(x)\psi_{d\sigma}(x)] + \sum_{i,\sigma}\int d^3x\,V_{sd}(x-R_i)$$
$$\times[\psi_{s\sigma}^\dagger(x)\psi_{d\sigma}(x) + \psi_{d\sigma}^\dagger(x)\psi_{s\sigma}(x)]. \tag{3.1}$$

Transforming to the Heisenberg representation, we get the following set of equations:

$$i\frac{\partial}{\partial t}\bar{\psi}_{s\sigma}(x)=-\left(\frac{\nabla^2}{2m_s}+\mu\right)\bar{\psi}_{s\sigma}(x)-g_s\bar{\psi}^{\dagger}_{s-\sigma}(x)\bar{\psi}_{s-\sigma}(x)\bar{\psi}_{s\sigma}(x)-g_{sd}\bar{\psi}^{\dagger}_{d-\sigma}(x)\bar{\psi}_{d-\sigma}(x)\bar{\psi}_{s\sigma}(x)$$

$$+\sum_i V_s(x-R_i)\bar{\psi}_{s\sigma}(x)+\sum_i V_{sd}(x-R_i)\bar{\psi}_{d\sigma}(x),\tag{3.2}$$

$$-\frac{\partial}{\partial t'}\bar{\psi}^{\dagger}_{s\sigma}(x')=-\bar{\psi}^{\dagger}_{s\sigma}(x')\left(\frac{\nabla^2}{2m_s}+\mu\right)-g_s\bar{\psi}^{\dagger}_{s-\sigma}(x')\bar{\psi}^{\dagger}_{s-\sigma}(x')\bar{\psi}_{s\sigma}(x')-g_{sd}\bar{\psi}^{\dagger}_{s\sigma}(x')\bar{\psi}^{\dagger}_{d-\sigma}(x')\bar{\psi}_{d-\sigma}(x')$$

$$+\sum_i V_s(x-R_i)\bar{\psi}^{\dagger}_{s\sigma}(x')+\sum_i V_{sd}(x-R_i)\bar{\psi}^{\dagger}_{d\sigma}(x'),\tag{3.3}$$

$$i\frac{\partial}{\partial t}\bar{\psi}_{d\sigma}(x)=-\left(\frac{\nabla^2}{2m_d}+\mu\right)\bar{\psi}_{d\sigma}(x)-g_d\bar{\psi}^{\dagger}_{d-\sigma}(x)\bar{\psi}_{d-\sigma}(x)\bar{\psi}_{d\sigma}(x)-g_{sd}\bar{\psi}^{\dagger}_{s-\sigma}(x)\bar{\psi}_{s\sigma}(x)\,\psi_{d\sigma}(x)$$

$$+\sum_i V_d(x-R_i)\bar{\psi}_{d\sigma}(x)+\sum_i V_{sd}(x-R_i)\bar{\psi}_{s\sigma}(x),\tag{3.4}$$

$$-\frac{\partial}{\partial t'}\bar{\psi}^{\dagger}_{d\sigma}(x')=-\bar{\psi}^{\dagger}_{d\sigma}(x')\,(\frac{\nabla^2}{2m_d}+\mu)-g_d\bar{\psi}^{\dagger}_{d\sigma}(x')\bar{\psi}^{\dagger}_{d-\sigma}(x')\bar{\psi}_{d\sigma}(x')-g_{sd}\bar{\psi}^{\dagger}_{d\sigma}(x')\bar{\psi}^{\dagger}_{s-\sigma}(x')\bar{\psi}_{s-\sigma}(x')$$

$$+\sum_i V_d(x-R_i)\bar{\psi}^{\dagger}_{d\sigma}(x')+\sum_i V_{sd}(x-R_i)\bar{\psi}^{\dagger}_{s\sigma}(x')\quad.\tag{3.5}$$

If we perform the following sequence of operations: Multiply (3. 2) and (3. 4) on the right-hand side by $\bar{\psi}^{\dagger}_{s\sigma}(x')$ and $\bar{\psi}^{\dagger}_{d\sigma}(x')$, respectively; multiply (3. 3) and (3. 5) from the left-hand side by $\bar{\psi}_{s\sigma}(x)$ and $\bar{\psi}_{d\sigma}(x)$, respectively; set $x=x'$; integrate over d^3x; add together the resulting equations; finally, do a summation over the spins, we have

$$\sum_\sigma\int d^3x\left(i\frac{\partial}{\partial t}-i\frac{\partial}{\partial t'}\right)(\bar{\psi}^{\dagger}_{s\sigma}(x')\bar{\psi}_{s\sigma}(x)+\bar{\psi}^{\dagger}_{d\sigma}(x)\psi_{d\sigma}(x)]_{x=x'}=2H_{\text{Total}}-g_s\sum_\sigma\int d^3x\,\bar{\psi}^{\dagger}_{s\sigma}(x)\bar{\psi}^{\dagger}_{s-\sigma}(x)\bar{\psi}_{s-\sigma}(x)\bar{\psi}_{s\sigma}(x)$$

$$-g_d\sum_\sigma\int d^3x\,\bar{\psi}^{\dagger}_{d\sigma}(x)\bar{\psi}^{\dagger}_{d\sigma}(x)\,\psi_{d\sigma}(x)\,\psi_{d\sigma}(x)-2g_{sd}\sum_\sigma\int d^3x\,\bar{\psi}^{\dagger}_{s\sigma}(x)\bar{\psi}^{\dagger}_{d-\sigma}(x)\bar{\psi}_{d-\sigma}(x)\bar{\psi}_{s\sigma}(x)\,.\tag{3.6}$$

Taking the ensemble average, (3. 6) becomes

$$i\int d^3x\left(i\frac{\partial}{\partial t}-i\frac{\partial}{\partial t'}\right)[G^{<}_{ss}(xx')+G^{<}_{dd}(xx')]_{x=x'}$$

$$=E_S-\frac{\Delta^2}{g_s}-\frac{\Delta^2}{g_d}-2\frac{\Delta^2_{sd}}{g_{sd}},\tag{3.7}$$

where

$$G^{<}(xx')=-i\langle\bar{\psi}^{\dagger}_{\dagger}(x')\,\bar{\psi}_{\dagger}(x)\rangle,\quad t-t'<0\,,$$

$$E_S=\langle H_{\text{Total}}\rangle,$$

$$\begin{aligned}\frac{\Delta^2_s}{g_s}&=\tfrac{1}{2}g_s\sum_\sigma\int d^3x\,\langle\bar{\psi}^{\dagger}_{s\sigma}(x)\,\bar{\psi}^{\dagger}_{s-\sigma}(x)\,\bar{\psi}_{s-\sigma}(x)\,\bar{\psi}_{s\sigma}(x)\rangle,\\ \frac{\Delta^2_d}{g_d}&=\tfrac{1}{2}g_d\sum_\sigma\int d^3x\langle\bar{\psi}^{\dagger}_{d\sigma}(x)\,\bar{\psi}^{\dagger}_{d-\sigma}(x)\bar{\psi}_{d-\sigma}(x)\,\bar{\psi}_{d\sigma}(x)\rangle,\\ \frac{\Delta^2_{sd}}{g_{sd}}&=\tfrac{1}{2}g_{sd}\sum_\sigma\int d^3x\langle\bar{\psi}^{\dagger}_{s\sigma}(x)\,\bar{\psi}^{\dagger}_{d-\sigma}(x)\,\bar{\psi}_{d-\sigma}(x)\,\psi_{s\sigma}(x)\rangle\,.\end{aligned}\tag{3.8}$$

Expanding the Green's function in terms of its Fourier transform[10]

$$G^{<}(xx')=k_BT\sum_n\int\frac{d^3p}{(2\pi)^3}\,G(p,i\omega)$$

$$\times\exp[ip(x-x')+\omega_n(t-t')],\tag{3.9}$$

where

$$\omega_n=(2n+1)\pi/\beta,$$

we have

$$E_S=\frac{\Delta^2_s}{g_s}+\frac{\Delta^2_d}{g_d}+2\frac{\Delta^2_{sd}}{g_{sd}}-2i\sum_p\int_C\frac{d\omega}{2\pi}\,\omega e^{\omega 0^+}$$

$$\times\tanh\tfrac{1}{2}\beta\omega[G_{ss}(p,i\tilde{\omega})+G_{dd}(p,i\tilde{\omega})]\tag{3.10}$$

with C being the contour enclosing the imaginary ω axis in the positive sense.

For further discussion, the superscript I will denote the thermodynamic functions for the system containing the impurities and the superscript 0 will denote the system without impurities. The δ symbol is used to denote the change in any quantity caused by the presence of the impurities. An example is the change in the total energy of the superconducting phase caused by the impurity scattering

$$\delta E_S = E_S^I - E_S^0 = \frac{(\delta\Delta_s)^2}{g_s} + \frac{(\delta\Delta_d)^2}{g_d} + 2\frac{(\delta\Delta_{sd})^2}{g_{sd}} + 2\,\frac{\Delta_s^0\Delta_s^I}{g_s}$$

$$+ 2\,\frac{\Delta_d^0\Delta_d^I}{g_d} + 4\,\frac{\Delta_{sd}^0\Delta_{sd}^I}{g_s} - 2i\sum_p \int \frac{d\omega}{2n}\,\omega e^{\omega 0^+}\tanh\tfrac{1}{2}\beta\omega$$

$$\times[\delta G_{ss}(p, i\tilde{\omega}) + \delta G_{dd}(p, i\tilde{\omega})]. \tag{3.11}$$

In the next Sec. IV, it will be seen that the change in total energy caused by the presence of the impurity atoms is related to the change of the densities of states caused by the impurities. In fact, most of the changes in the thermodynamics are due to the effect of the impurities on the densities of states. If the assumption is made[9] that the impurities do not affect the densities of states for the normal phase, then the decreased or increased ratios between properties of the superconducting phase and thermal phase are governed by the effects of the impurities on the densities of states in the superconducting phase.

IV. INTRABAND LIMIT

The intraband limit is of special interest, since the propagators (2.4) and (2.5) have the simple forms

$$G_{ss}^{g_{sd}=0}(p, i\tilde{\omega}) = -\frac{i\tilde{\omega}_n(s) + \epsilon_s}{\tilde{\omega}_n^2(s) + \epsilon_s^2 + \tilde{\Delta}_n^2(s)}, \tag{4.1}$$

$$G_{dd}^{g_{sd}=0}(p, i\tilde{\omega}) = -\frac{i\tilde{\omega}_n(d) + \epsilon_d}{\tilde{\omega}_n^2(d) + \epsilon_d^2 + \tilde{\Delta}_n^2(d)}, \tag{4.2}$$

where[8]

$$\tilde{\omega}_n(s) = \bar{\omega}_n + (1/2\tau_s + 1/2\tau_{sd})\bar{\omega}_n/|\bar{\omega}_n|, \tag{4.3}$$

$$\tilde{\omega}_n(d) = \bar{\omega}_n + (1/2\tau_d + 1/2\tau_{ds})\bar{\omega}_n/|\bar{\omega}_n|, \tag{4.4}$$

with

$$\begin{aligned} 1/2\tau_s &= n_i\pi N_{s0}\int |V_s(p)|^2\,d\Omega, \\ 1/2\tau_d &= n_i\pi N_{d0}\int |V_d(p)|^2\,d\Omega, \\ 1/2\tau_{sd} &= n_i\pi N_{s0}\int |V_{sd}(p)|^2\,d\Omega, \\ 1/2\tau_{ds} &= n_i\pi N_{d0}\int |V_{sd}(p)|^2\,d\Omega. \end{aligned} \tag{4.5}$$

At this point, we shall drop the superscript $g_{sd}=0$ from the propagators (4.1) and (4.2) and let it be understood that the superscript is implied whenever a propagator is now encountered.

It can be seen that these propagators are analytic in the $i\omega$ plane, except for a cut along the real axis from $-\infty$ to $-(\epsilon^2+\tilde{\Delta}^2)^{1/2}$ and from $(\epsilon^2+\tilde{\Delta}^2)^{1/2}$ to ∞. Since the $\operatorname{Im}G(p, i\omega)$ changes signs as we cross the axis, the contour can be converted to one surrounding the real axis to get

$$\delta E_s = \frac{(\delta\Delta_s)^2}{g_s} + \frac{(\delta\Delta_d)^2}{g_d} + 2\left(\frac{\Delta_d^0\Delta_s^I}{g_s} + \frac{\Delta_d^0\Delta_d^I}{g_d}\right) + 4\sum_p\left(\int_{(\epsilon_s^2+\Delta_s^2)^{1/2}}^{\infty} + \int_{-(\epsilon_s^2+\Delta_s^2)^{1/2}}^{-\infty}\right)$$

$$\times\frac{d\omega}{\omega}\operatorname{Im}\delta G_{ss}(p, i\omega)\tanh\tfrac{1}{2}\beta\omega + 4\sum_p\left(\int_{(\epsilon_d^2+\Delta_d^2)^{1/2}}^{\infty}\int_{-(\epsilon_d^2+\Delta_d^2)^{1/2}}^{-\infty}\right)\frac{d\omega}{\omega}\,\delta G_{dd}(p, i\omega)\tanh\tfrac{1}{2}\beta\omega\,. \tag{4.6}$$

Using (2.10) and (2.11), the last equation can be converted into

$$\delta E_S = \frac{(\delta\Delta_s)^2}{g_s} + \frac{(\delta\Delta_d)^2}{g_d} + 2\left(\frac{\Delta_s^0\Delta_s^I}{g_s} + \frac{\Delta_d^0\Delta_d^I}{g_d}\right) - 2\int_0^{\omega_0^2+\Delta_s^2} d\omega\,\delta N_s(\omega)\omega\tanh\tfrac{1}{2}\beta\omega - 2\int_0^{(\omega_0^2+\Delta_d^2)^{1/2}} \times d\omega\,\delta N_d(\omega)\omega\tanh\tfrac{1}{2}\beta\omega\,. \tag{4.7}$$

The change in entropy of the system caused by the impurity atoms becomes

$$\delta S_c = \delta[S_s(s) + S_s(d)] = 4k_\beta\int_0^{(\omega_0^2+\Delta_s^2)^{1/2}} d\omega\,\delta N_s(\omega)\left(\ln(1+e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega}+1}\right)$$

$$+4k_B\int_0^{(\omega_0^2+\Delta_d^2)^{1/2}} d\omega\,\delta N_d(\omega)\left(\ln(1+e^{-\beta\omega})+\frac{\beta\omega}{e^{\beta\omega}+1}\right). \tag{4.8}$$

The change in the free energy of the system is given by

$$\delta F_s=\delta E_s-T\delta S_s=(\delta\Delta_s)^2/g_s+(\delta\Delta_d)^2/g_d+2(\Delta_s^0\Delta_s^I/g_s+\Delta_d^0\Delta_d^I/g_d)-\int_0^{(\omega_D^2+\Delta_s^2)^{1/2}} d\omega\,\delta N_s(\omega)[2\omega\tanh\tfrac{1}{2}\beta\omega$$
$$+4k_BT(\ln(1+e^{-\beta\omega})+\beta\omega(e^{\beta\omega}+1))]-\int_0^{(\omega_D^2+\Delta_d^2)^{1/2}} d\omega\,\delta N_d(\omega)[2\omega\tanh\tfrac{1}{2}\beta\omega+4k_BT(\ln(1+e^{-\beta\omega})+\beta\omega/(e^{\beta\omega}+1))]. \tag{4.9}$$

Before proceeding any further, it will be necessary to determine the changes in the densities of states. In the low-impurity-density limit, the changes are

$$\delta N_s(\omega)=-\frac{N_{s0}}{\pi}\int_{-\infty}^{\infty} d\epsilon_s\,\frac{\tilde{\omega}_n(s)-\bar{\omega}_n}{\bar{\omega}_n^2+\epsilon_s^2+\Delta_s^2}, \tag{4.10}$$

$$\delta N_d(\omega)=-\frac{N_d0}{\pi}\int_{-\infty}^{\infty} d\epsilon_d\,\frac{\tilde{\omega}_n(d)-\bar{\omega}_n}{\bar{\omega}_d^2+\epsilon_d^2+\Delta_d^2}, \tag{4.11}$$

where the approximations $[\tilde{\omega}_n^2(s)+\epsilon_s^2+\tilde{\Delta}_n^2(s)]\to[\bar{\omega}_n^2+\epsilon_s^2+\Delta_s^2]$ and $[\tilde{\omega}_n(d)+\epsilon_d^2+\tilde{\Delta}_n^2(d)]\to(\bar{\omega}_n^2+\epsilon_d^2+\Delta_d^2)$ have been made. Using (4.3) and (4.4) we get

$$\delta N_s(\omega)=-(N_{s0}/\pi)(1/2\tau_s+1/2\tau_{sd})(\bar{\omega}_n^2+\Delta_s^2)^{-1/2}, \tag{4.12}$$

$$\delta N_d(\omega)=-(N_{d0}/\pi)(1/2\tau_d+1/2\tau_{ds})(\bar{\omega}_n^2+\Delta_d^2)^{-1/2}. \tag{4.13}$$

In most of the studies done on the transition elements,[6,8,11] it was assumed that $N_{s0}\ll N_{d0}$. With this assumption, the changes in densities of states of the d-band electrons is greater than the corresponding change in density of states in s band. Thus, the change in the thermodynamic properties caused by nonmagnetic impurity scattering is due mainly to the more populated d band.[11]

Using the above conclusion in (4.8), the entropy change in the superconducting phase becomes

$$\delta S_S=\delta S_S^{(d)}$$
$$=-4k_B(N_{d0}/\pi)(1/2\tau_d+1/2\tau_{ds})\int_{\Delta_d}^{(\omega_D^2+\Delta_d^2)^{1/2}} d\omega$$
$$\times\frac{\ln(1+e^{-\beta\omega})+\beta\omega/(e^{\beta\omega}+1)}{(\bar{\omega}_1^2+\Delta_d^2)^{1/2}}. \tag{4.14}$$

For values $T\ll T_c$, where the approximation

$$\ln(1+e^{-\beta\omega})+\beta\omega/(e^{\beta\omega}+1)\to e^{-\beta\omega}(1+\beta\omega) \tag{4.15}$$

holds, the change in the specific heat caused by the impurities is

$$\delta C_S=-4(1/k_BT^2)(N_{d0}/\pi)(1/2\tau_d+1/2\tau_{ds})$$
$$\times\int_{\Delta_d}^{(\omega_D^2+\Delta_d^2)^{1/2}} d\omega\,\omega^2e^{-\beta\omega}/(\omega^2+\Delta_d^2)^{1/2}, \tag{4.16}$$

a negative quantity. In the intraband limit, the presence of nonmagnetic impurity atoms causes the specific heat of the superconducting phase to be decreased.

While it is not expected that any of the transition metals are of the intraband limit type, the general feature of an observed decline in specific-heat jump should be expected. It also must be noted that the concentration of impurities must be low for the approximations made in the analysis to be valid. A high concentration may cause the electronic structure of the host transition metal to be altered in such a way as to cause an increase in the density of states.

V. CONCLUSION

Discussion of the effects of nonmagnetic impurities on the thermodynamic properties in the general case g_s, g_d, $g_{sd}\neq 0$ is complicated by the forms of the propagators (2.4) and (2.5) when none of the electron-phonon couplings vanish. However, qualitative results are seen by looking at the densities of states since, as it has been stated, the effects of the impurities enter into the thermodynamics through the changes in the densities of states. Without actually evaluating the change caused by the impurity scattering in the general case, one can see that the decrease in the specific heats would be greater.

The decrease in specific heats due to impurity scattering has indeed been seen in niobium.[12] The purer sample in their work, the one having the higher residual resistivity ratio, is seen to have the higher specific heat. This sample, however, turns out to be somewhat dirty since samples have been obtained recently which have a ratio ten times greater than the ratio for this sample. The dependence on the density of states is pointed by the fact that the ratio $N_s/(N_s+N_d)$ for pure niobium as calculated from the band structure of niobium[13] is 0.12, which differs from the above sample's value of 0.015. This increase in the density of states as the same becomes purer is well known. We would expect the specific-heat curves of pure niobium to lie above the curve for the sample used in Shen's study.

The formulism developed here may be used to redo the work in Refs. 6, since our formulation does not depend on a quasiparticle approximation. It has been shown that strong electron-phonon coupling makes the approximation over much of the energy spectrum.[14] This consideration is important, since it has been recognized that niobium is a strong coupling superconductor.

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