BULK PROPERTIES OF UNCONVENTIONAL SUPERCONDUCTORS

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ABSTRACT
In a conventional s-wave superconductor, the order parameter is totally symmetric. Therefore the low energy excitations have a gap except for the case of a gapless superconductor with magnetic impurities. For the s-wave state, there is moreover no low-lying collective mode, since in the case of charged particles the collective density fluctuations are nothing but Plasma modes. The existence of the gap in the excitation spectrum naturally leads to the exponential temperature dependence of various physical qualities, such as the specific heat, relaxation rate of nuclear magnetic resonance, (NMR) and knight shift.

1. INTRODUCTION
In an unconventional superconductor, the order parameter can have point or line zeros. Due to the excitation spectrum across these points or lines, the excitation spectrum starts from zero energy. The density of states of the quasi-particles is defined by

$$p(w) = \sum_{k\pm} \delta(w - E_{k\pm}) \tag{1}$$

where $E_{k\pm}$ is the quasi-particles energy.

In this article, we shall restrict ourselves to the case of Unitary States, $E_{k\pm=E}$

Let us consider several typical examples. In an ordinary s-wave superconductor, the density of states is

$$\rho(w) = \begin{vmatrix} 0 (w < \Delta_o) \\ N(0)\, w \big/ \sqrt{w^2 - \Delta_o{}^2}\ (w > \Delta_o) \end{vmatrix} \tag{2}$$

where $N(0)$ is the density of states at the Fermi energy in the normal phase and Δ_o is the magnitude of the gap function. The density of states has a gap of Δ_o and it diverges at $w = \Delta_o$.

Now we turn to examples of the P-wave states in rotationally symmetric space. In ^3H_e two superfluid phases exists under different pressures. The low pressure B phase is the so-called Balian-Werthaner (BW) state of p-wave pairing and the high pressure. A phase is the so-called Anderson-Brinkman – Morel (ABM or axial) state. The gap function in the BW state.

$$\Delta_{ss}(k) = \Delta_o \begin{vmatrix} \hat{K}_x + i\hat{K}_y & \hat{K}_z \\ \hat{K}_z & \hat{K}_x + i\hat{K}_y \end{vmatrix}, \tag{3}$$

has a constant product $\Delta\Delta^+ = \Delta^2$. Thus, density of states has the same form as the ordinary s-wave state. Consequently, the equilibrium thermodynamic properties of the BW state and the s-wave state are identical. This should not be misunderstood that all their properties are identical. Non-equilibrium properties of the BW state like spin susceptibility certain differences from those of the Bardeen, Cooper, Schriffer (BCS) state.

2. THEORETICAL CONSIDERATIONS AND CALCULATIONS
The gap function becomes zero at two points in the ABM or axial state, where the gap function has the form.

$$\Delta_{ss'}(K) = \Delta_o \begin{vmatrix} \hat{K}_x + i\hat{K}_y & O \\ O & \hat{K}_x + i\hat{K}_y \end{vmatrix} \tag{4}$$

Here the density of states is given by

$$\rho(w) = N(0)\, \tfrac{1}{2} \frac{\Delta_o}{w} \left\{ \frac{w}{\Delta_o} + \tfrac{1}{2} \left[\left| \frac{w}{\Delta_o} \right|^2 - 1 \right]^X \log \frac{w + |\Delta_o|}{[w - |\Delta_o|]} \right\} \tag{5}$$

It varies as w^2 at low energies and has a logarithmic divergence at
$w - \Delta_o$. The third example of the p-wave state is the polar state not realized in ^3H_e, where the gap function is

$$\Delta_{ss'}(K) = \Delta_o \begin{vmatrix} \hat{K}_z & O \\ O & \hat{K}_z \end{vmatrix} \tag{6}$$

Obviously, the gap has line zeros on the equator. For the density of states we obtain

$$\rho(w) = \begin{cases} N(0)\dfrac{\pi}{2}\dfrac{w}{\Delta_o}(w < \Delta_o), \\ N(0)\dfrac{w}{\Delta_o}\arcsin\left[\dfrac{\Delta_o}{w}\, w > \Delta_o\right] \end{cases} \tag{7}$$

It has a form linear in w for low energies ($w < \Delta_o$) and is finite at $w = \Delta_o$.

The three states of p-wave pairing considered here are representative of examples offered in order to discuss the density of states of quasi-particles in unconventional superconductors. The important point is that the generic form of $\rho(w)$ at low energies depends solely on the topology of the gap zero.

If they are line zeros, then $\rho(w)\alpha\ W$ and if they are point zeros, then $\rho(w)\alpha\ w^2$. The difference in the energy dependence of $\rho(w)$ is reflected in the temperature dependence of various physical qualities at low temperatures. As a first example, we consider the specific heat. At low temperatures where the T dependence of the order parameter can be reflected, the specific heat is given by

$$C = \frac{2}{T}\int_0^{\infty} dE \quad P(E)E^2 \left|\frac{df(E)}{dE}\right|(T << T_c) \tag{8}$$

where f(E) is the Fermi distribution function. Therefore, it is obvious that the T dependence of the specific heat depends on the topology of the gap structure in the following way.

$$C = \begin{cases} T \quad gapless \\ T^2 \ line - zero, \\ T^3 \ po\,\text{int} - zeros \end{cases} \tag{9}$$

Another example is the NMR relaxation rate, which is given by (Moriya, 1963)

$$1/T_1 = Y_N^2 A_m^2 K_B T \sum_q 1mX^{-1}(q, w_o)/w_o, \tag{10}$$

where w_o is the nuclear resonance frequency, Υ_N the gyromagnetic ratio of the nuclear spin, Am the hyperfine coupling constant, and X^{-1} (q, w) the dynamical susceptibility transverse to the magnetic field at the nucleus. It is straightforward to extend the standard BCS result (Hebel and Shchter, 1959) to include the unconventional case,

$$\frac{T_{1N}}{T_1} = \frac{2}{N(0)}\int_0^{\infty} dE \ \ \rho(E) \ \ \rho(E)A(w_o)\left[1 - \frac{<\Delta\uparrow\uparrow(\hat{K})}{E}\right] \frac{<\Delta\downarrow\uparrow(K)>}{E + w_o}\left]\left|\frac{df}{dE}\right.\right], \tag{11}$$

where $1/T_{1N}$ is the relaxation rate in the normal state and $<\Delta\uparrow\uparrow(K)>$ denotes the average of the order parameter on the Fermi surface. This average vanishes for the unconventional superconductors, which

belong to other representation than Γ_1^4 The resonance frequency is

generally small compared with energy scales of electrons. Therefore, we may take the limit of $w_o \rightarrow 0$. If the integral converges. However, for the s-wave or the BW state, the integral diverges logarithmically if w_o is set equal to zero. For superconducting states with point or line zeros, the integral converges and the temperature dependence of $^1/T_1$ at low temperature is given as

$$1/T_1\ \alpha \begin{cases} T \quad gapless \\ T^3 \ line - zero, \\ T^5 \ po\,\text{int} - zeros \end{cases} \tag{12}$$

An important consequence of group theory is that, with spin orbit coupling, line zeros are not allowed for odd-parity superconductors Volo Vik and Gor'Kov, 1984, 1985, Blount, 1985, Ueda and Rice, 1985a, 1985b. (Anderson, 1984). Blount in particular, gave a general proof of this. Therefore at very low temperatures pure samples should obey power laws corresponding to the point zeros when they are odd-parity superconductors.

Various power – law behaviour are reported in heavy-fermion materials for many properties, including the specific heat and the NMR relaxation rate discussed here. The accumulated body of data from this type of experiment indicates clearly that there are many low-lying excitations associated with nodes of gap functions in heavy-fermion superconductors. However, in some cases, there is no consistency about the gap structures among the results for different quantities among the results for different quantities experimentally observed, if we assume exponents for pure material. One possible explanation for this kind of inconsistency is that the temperature range experimentally accessible is not yet sufficiently low to derive the genuine exponents. Another, probably more plausible, explanation is that this discrepancy can be resolved when we include the effect of impurity scatterings.

The most natural framework in which to discuss the effects of impurity scattering on superconductivity is the Abrikosov – Gor'kov theory (Abrikosov and Gor'kov, 1960). The essential properties of the impurity scattering may be seen in the simple example of s-wave scattering. It is convenient to simplify the calculation by neglecting spin-orbit coupling.

In the Abrikosov – Gor'kov theory, the gap function is given by

$$\Delta_{ss'}(K) = T\sum_{V'} V(k,k')F_{ss}(K'iw_n) \qquad (13)$$

where F is the anomalous Green's function. In this formation the gap function can be considered as the (anomalous) self energy due to the pairing potential. Impurity scattering gives additional contributors to the self-energy. First we treat this problem in the Born approximation (Gor'kov and Kalugn, 1985, Ueda and Rice, 1985b). One contribution to the self-energy is of the normal type, fig.1(a).

$$\sum{}^{(1)}(iw_n) = \eta_i U^2 \sum_k G(K', iw_n) \qquad (14)$$

where η_i is the impurity concentration and U characterizes the s-wave scattering potential [G_{ss} (K, iw_n) = G(K, iw_n) $\delta_{ss'}$]. There is also a contribution of the anomalous type fig. 1(b),

$$\sum{}_{ss}^{(1)}(iw_n) = \eta_i U^2 \sum_{k'} F_{ss}\left(K'_{ss}, iw_n\right) \qquad (15)$$

In the case of non-magnetic impurities in s-wave superconductors, Anderson's theorem manifests itself in the following fact. For the s-wave state $\sum^{(1)}$ is simply proportional to iw_n and $\sum^{(2)}$ is Proportional to Δ, and their proportionality constants are the same under the assumption of a constant density of states near the Fermi-energy. Therefore, the effect of impurity scattering can be taken as a simple renormalization of the energy scale without any influence on thermodynamic properties. In contrast, for any unconventional state $\sum^{(2)}$ is zero, since the summation of equation (15) vanishes. Therefore, simple scaling no longer works in this case. Generally, a difference between the two proportionality constants leads to despairing effects.

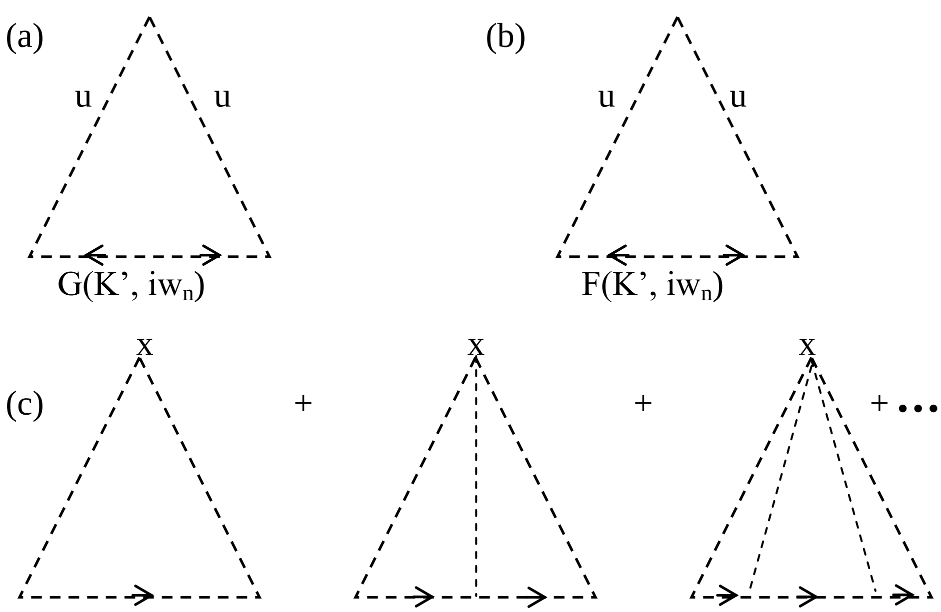

Fig.1: The two types of self-energies of impurity scattering normal and anomalous. In the Born approximation, the normal type of self-energy is expressed by the diagram (a) and the anomalous one by (b). in the T-matrix approximation, multiple scattering processes (c) are also taken into account.

With the self-energies due to impurity scattering, the Gor'kov equation, for the Green's function are modified as

$$iw_n - \varepsilon(K) - \sum{}^{(1)}(iw_n)[G(k,iw_n)]\sum{}_{ss}\Delta_{ss}(k)F_{s's}{}^{+}(K,iw_n) = 1 \qquad (16)$$

$$iw_n + \varepsilon(K) + \sum{}^{(1)}(-iw_n)F_{s's}{}^{+}(K,iw_n) - \Delta^{+}{}_{ss'}(K)G(K,iw_n) = 0 \qquad (17)$$

For the unitary states they are easy to solve

$$G(K,iw_n)=\frac{iw_n+\varepsilon(K)}{(iw_n)^2-\varepsilon(K)^2-\Delta(K)\Delta^+(K)} \quad (18)$$

$$F_{ss'}{}^{+}(K,iw_n)=\frac{+\Delta^+_{ss}(K)}{(iw_n)^2-\varepsilon(K)^2-\Delta(K)\Delta+(K)} \quad (19)$$

where $iw_n = iw_n - \sum^{(1)}(iw_n)$. By substituting equations (18) and (19) into equations (13) and (14), we obtain self consistency equations for $\Delta_{ss}(K)$ and $\sum^{(1)}(iw_n)$. We show the self-consistency equations for the BW, ABM, and Polar states as typical examples in a rotationally invariant system.

(a) BW State:

$$1=\pi N(0)VK_BT\sum_n\frac{1}{\sqrt{w_n^2+\Delta_n^2}}, \quad (20)$$

$$\overline{w}_n=w_n+\Gamma\frac{w_n}{\sqrt{\overline{w}_n^2+\Delta_n^2}} \quad (21)$$

(b) ABM state:

$$1=\tfrac{3}{2}\pi N(0)\overline{V}K_BT\sum_n\tfrac{1}{2}\Delta_o\left\{\frac{\overline{w}_n}{\Delta_o}\left|1-\left|\frac{\overline{w}_n}{\Delta_o}\right|^2\right|\frac{i}{2}\log\frac{iw_n-\Delta_o}{iw_n-\Delta_o}\right. \quad (22)$$

$$\overline{w}_n=w_n-\Gamma\frac{i}{2}\frac{\overline{w}_n}{\Delta_o}\log\frac{iw_n-\Delta_o}{iw_n+\Delta_o} \quad (23)$$

(c) Polar state:

$$1=\tfrac{3}{2}\pi N(0)\overline{V}K_BT\frac{1}{\Delta_o}\left\{\left|1+\left[\frac{\overline{w}_n}{\Delta_o}\right]^2\right]^{\frac{1}{2}}-\left[\frac{\overline{w}_n}{\Delta_o}\right]^2\right. \; Log\frac{\Delta_o+\sqrt{\overline{w}_n^2+\Delta_o^2}}{\overline{w}_n} \quad (24)$$

$$\overline{w}_n=w_n+\Gamma\tfrac{\overline{w}_n}{\Delta_o}Log\frac{\Delta_o+\sqrt{\overline{w}_n^2+\Delta_o^2}}{\overline{w}_n} \quad (25)$$

In the above expressions $\overline{V}$ is the strength of the pairing interaction defined by $V(K,K)=3V\hat{K}.\hat{K}$ (rotationally symmetric form) and $\Gamma=\pi\eta i\;N(0)u^2$ is the strength of the impurity scattering i.e. half of the scattering rate, $\Gamma=\tfrac{1}{2}T_N$. Equations (20) and (21) have the same form as for magnetic impurities in an ordinary s-wave superconductor.

The three sets of equations reduce to the same set of equations when they are linearized. The transition temperature obtained by the linearized equation decreases as a function of Γ in the same way as in ordinary gapless superconductors with magnetic impurities.

In this formalism, the density of states of quasi particles is given by

$$\rho(w)=N(0)\tfrac{1}{\Gamma}1m(iw_n)iw_n=w+i\delta \quad (26)$$

In fig. 2(a) we show the density of states for the BW state. For a weak impurity scattering, there is a gap in the density of states given by

$$w_g=\Delta_o\left[1-(\Gamma/\Delta_o)^{2/3}\right]^{3/2} \quad (27)$$

When $\Gamma/\Delta_o\geq 1,$ the system is in a gapless regime. This behaviour in the BW state is the same as for the usual paramagnetic impurity effect in an s-wave superconductor. The density of states for the ABM state is shown in fig.2(b). The density of states at low energies is given by

$$\rho(w)=\begin{cases}N(0)\left|\frac{w}{\Delta_o}\right|^2\left[1-\frac{\pi}{2}\left[\frac{\Gamma}{\Delta_o}\right]\right]^3 & (\Gamma/\Delta_o<2/\pi)\\ N(0)\frac{\Delta_o}{\Gamma}Cot\frac{\Delta_o}{\Gamma}\,(\Gamma/\Delta_o>2/\pi)\end{cases} \quad (28)$$

The most remarkable result is obtained for the polar state (fig.2c). In this case, when there are impurities, zero-energy excitations always exist and their density of states at the Fermi level is given by

$$\rho(0) = N(0)\,{}^{\Delta_o}\!/_{\Gamma}\, Sinh\left({}^{\Gamma}\!/_{\Delta_o}\right) \tag{29}$$

The main conclusion of the Born approximation is that the most serious effect would be on any polar state, i.e., a state with line zeros, since in this case the low temperature behaviour is modified by any concentration of impurities. In contrast, a state with point zero has a critical concentration before an essential modification of the power laws sets in. Although the analysis was carried through only for the simplest form of p-wave states, the results depend merely on the generic form of the density of states are therefore should be applicable with slight modification to any state with the same generic form.

In a single – site Kondo problem, resistivity becomes a constant at T = 0 after a logarithmic increase. The constant corresponds to the phase shift of π/2, the unitary limit. In many heavy-fermion systems, resistivity increases as temperature is lowered, reaches a maximum and then decreases rapidly. The value of the resistivity at the maximum, in many cases, is consistent with the value of the unitarity limit. Therefore, it would not be surprising if scatterers in heavy-fermion systems had large phase shifts, as Pethick and Pines (1986) pointed out. To treat scattering with a large phase shift, the Born approximation is not sufficient, and multiple scattering processes should be included.

Multiple scattering of electrons by magnetic impurities in ordinary superconductors was studied by Shiba (1968), using a T-matrix approximation. He found that there exists a localized excited state around a classical impurity spin, which at finite concentration forms an impurity band. For the investigation of the impurity effect in the BW state mentioned before, Buchholtz and Zwicknagl also employed the T-matrix approximation, as did Schmitt – Rink, Miyake, and Vama (1986) and Hirschfeld, Volliardt, and Wolfle (1986), independently, in studying the consequences of resonant impurity scattering in heavy-fermion systems.

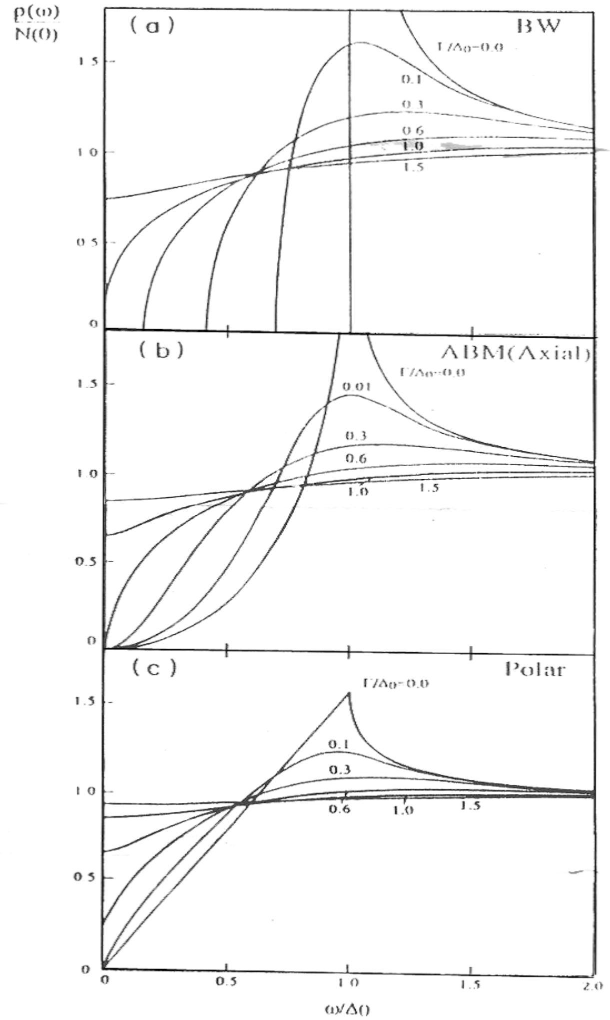

FIG. 2. Density of states of quasiparticles obtained by the born approximation: (a) for the BW state; (b) for the ABM state; (c) for the polar state (Ueda and Rice, 1985b).

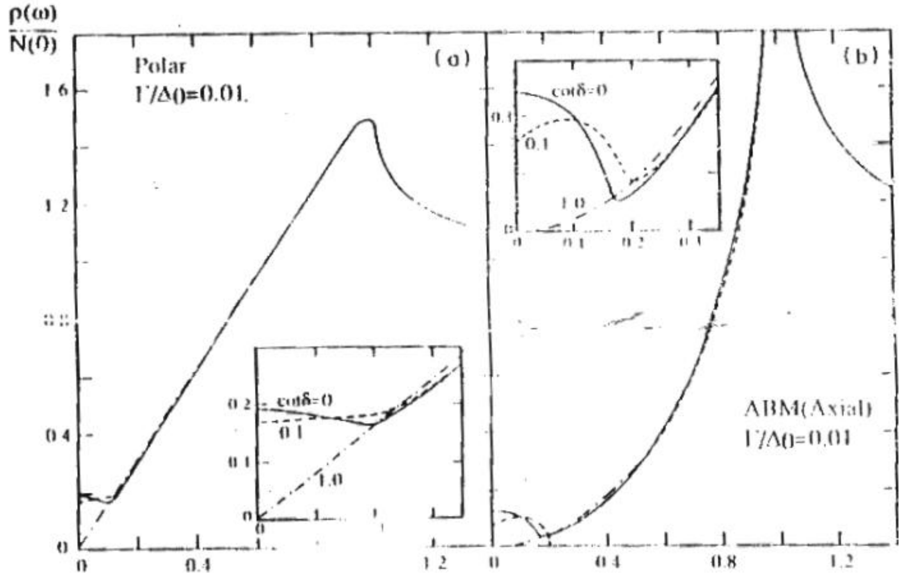

FIG. 3. The density of states of the polar and the ABM states obtained by the T-Matrix approximation for a pair-breaking parameter of $\Gamma / \Delta_0 = 0.01$ and different values of the phase shift. The insert illustrate the resonance peaks in the low-energy, gapless region. (Hirschfeld et al., 1986).

In the T-matrix approximation, the self-energy due to impurity scattering is given by fig.1(c).

$$\Sigma^{(1)}(iw_n) = \eta i U^2 \sum_k G(K, iw_n) \bigg/ \left\{1 - U \sum_k G(K, iw_n)\right\} \tag{30}$$

A self consistent theory is obtained by using the odd part of the self-energy, $[\sum^{(1)}(iw_n) - \sum^{(1)}(-iw_n)]/2$, in equations (16) and (17). The even part of the self-energy $[\sum^{(1)}(iw_n) + \sum^{(1)}(-iw_n)]/2$, is just a shift of the chemical potential and can be neglected. In this theory, impurity scattering is characterized by two parameters. One is the phase shift defined by

$$\tan \delta = -\pi u N(0), \tag{31}$$

and the second is the scattering rate $\Gamma = ½ T_N \operatorname{Sin}^2 \delta$ in the unitarity limit $\delta = \pi/2$

Schmitt – Rink et al and Hirshfeld et al, assumed that in a Kondo lattice, each magnetic ion leads to a phase shift of conduction electrons $\delta = \pi/2$. However, the net effect is zero because of the periodicity; the resistivity of a periodic system is zero at zero temperature. Therefore, a non-magnetic ion in a such a lattice would appear to offer a phase shift π/2 with respect to the background. With this assumption, the impurity scattering is characterized again by a single parameter Γ. Figure 3 shows the calculated density of quasi particle states for a polar state for various scattering potentials, setting as the pair breaking parameter $\Gamma/\Delta_o = 0.01$. At low energies, there is a resonance peak and at higher energies, the density of states is almost identical to its value without statement impurities ($\cot \delta \rightarrow \infty$). The same statement can be made for the ABM (axial) state. In both cases the width of the resonance peak increases as Γ/Δ_o gets larger.

3. RESULTS AND DISCUSSION

The power law behaviour discussed here are a manifestation of the anisotropy of the gap function of unconventional superconducting states. However, these powers give information only about the generic form of the gap function.

From the density of quasi particle states, we can immediately see the effect of resonant impurity scatterings on specific heat. At very low temperature ($T/Tc < 0.1$), it shows a small T – linear specific heat due to the appearance of the resonance while at elevated temperature, it follows closely the power law expected without impurities (Hirshfeld et al, 1986, 1988, Miyake, 1986, Ott et al, 1987). Similarly, the NMR relaxation rate shows a Korringa-like behaviour at very low temperatures and follows a power law for the pure case at higher temperatures (Hirschfeld et al, 1988).

The situation is very different for transport properties in heavy-fermion superconductors. For these quantities, the Born approximation is inadequate not only quantitatively but also qualitatively. As an example, we consider thermal conductivity K. In a simple kinematic theory, it is given by $K = 1/3\ V_F^2\ Tc$. In the Born approximation, it can be shown that the product of the relaxation time $\tau(w)$ and the density of states $\rho(w)$ is almost energy independent (Coffey et al, 1985, Pethick and Pines, 1986). In this result, the modification of $\rho(w)$ discussed in this article, is neglected, which gives only a minor change when the impurity concentration is small. Therefore, the thermal conductivity in the Born approximation is almost linear in T and the coefficient remains the same order as its normal state value, which contradicts the experimentally observed T^2 behaviours. Pethick and Pines proposed that the discrepancy may be resolved when the resonant nature of the impurity scattering in the unitarity limit is taken into account.

Calculations of the thermal conductivity using the T-matrix approximation were carried out independently by Schmitt – Rink, Miyake and Varma (1986) and Hirschfeld, Volhardt, and Wolfle (1986). Their results may be summarized as follows. At very low temperatures, K/T goes to a finite value due to the appearance of the low energy resonance. At higher temperatures, in a wide temperature range, K follows a T^2 law for the case of line zeros and a T^3 law for the point zeros. This result means that the product of $\tau(w)$ and $\rho(w)$ shows almost the same behaviour as τ_N $\rho(w)$ where ρ_N is the scattering rate in the normal state. This fact cannot be understood by the Born approximation, as we discussed before. It should also be mentioned that Vortex corrections to the thermal resistivity are discussed by Hirschfeld, Wolfle and Einzel (1988).

The T-Matrix approximation is also applied to the study of ultrasonic alternation in heavy-fermions (Hirschfeld et al, 1986; Schmitt-Rink et al, 1986). The temperature dependence of the sound attenuation depends on its polarization and propagation direction. Miyake (1986) and Schmitt-Rink et al (1986) have concluded that the assumption of a state with line zeros, together with a scattering in the impurities limit, leads to results consistent with the experimental observations in UPt_3, $CeCu_2Si_2$ and UBe_{13}.

An anomalous temperature dependence of the London penetration depth in UBe_{13} was reported by Gross et al (1986); $\lambda(T) - \lambda(O)$ follow T^2 law. The authors analyzed the temperature dependence by the Born approximation and concluded that the behaviour is consistent with an energy gap with point nodes. Recently, Choi and Muzikar (1988, 1989b) developed a theory of the superfluid density tensor which determines the penetration depth. They treated the impurity scattering by the T-matrix approximation and pointed out the possibility that impurity scattering enhances the anisotropy of the density tensor.

4. CONCLUSION

In conclusion, impurities modify the power laws, especially at low temperatures. The consequences of resonant scattering in unconventional superconductors for specific heat, thermal conductivity, ultrasonic attenuation, NMR relaxation rate, and electromagnetic absorption have been examined by several authors as we have seen in this article. In particular, Miyake (1987) and Schmitt-Rink et al (1986) have pointed out that the experimentally observed power laws are some consistent with line zeros than with point zeros. However, to draw a definite conclusion about the gap structure, we need further experiments that are directly related to the symmetry of the order parameter.

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