

Layered superconductors with anisotropic energy gap: specific heat and infrared absorption

SUDHANSHU S JHA

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

MS received 7 November 1989

Abstract. New oxide superconductors with layered structure are expected to have anisotropic energy gap in the generalized BCS pairing theory. The gap parameter $2\Delta(\vec{k})$ can be quite different for \vec{k} perpendicular to the plane of the layers as compared to \vec{k} parallel to layer planes. Because of short coherence lengths ξ , quite small compared to the normal state carrier meanfree path l , the effect of these anisotropies do not average out, as in many of the conventional superconductors. For a proper comparison of experimental results with the correct predictions of the pairing theory, a formulation is developed to obtain important physical quantities like specific heat and infrared absorption in the superconducting state of such anisotropic systems. This includes a brief account of the pairing theory generalized to layered crystals with arbitrary number of layers per unit cell, not necessarily equidistant. In an explicit model for the anisotropy of the gap parameter in \mathbf{k} -space, with a simple form for the nonspherical Fermi-surface, it is shown that the low-temperature specific heat can have even a linear or a power-law temperature-dependence in the superconducting state. Even if the gap parameter does not vanish anywhere, its smeared-out exponential temperature-dependence may be difficult to be distinguished experimentally from a power-law behaviour. Similarly, it is shown that in the case of appreciable anisotropy, infrared absorption can take place much below the in-plane gap parameter $2\Delta_{\parallel}(\vec{k}_{\parallel})$, where \vec{k}_{\parallel} is the wavevector in the plane of the layers.

Keywords. Layered superconductors; anisotropic energy gap; specific heat; infrared absorption.

PACS Nos 74-20, 74-30, 74-70

1. Introduction

The behaviour of many of the important physical parameters in the superconducting state of the recently discovered high- T_c metallic oxides is known to differ considerably from the predictions of the simple one-parameter, isotropic, weak-coupling BCS model. This need not be very surprising, since these materials have layered structures with large anisotropies in the normal state properties of the relatively low density (\sim a few times 10^{21} cm^{-3}) carriers, and they have very short anisotropic coherence lengths (3Å to 20Å) in the superconducting state. The mobility of the carriers in the conducting Cu-O layers, which are approximately parallel to the a - b plane of the crystalline unit cell, is much higher than their value in the perpendicular direction (C -axis). Moreover, significant deviations are expected (Jha 1989) because of (i) possible strong-coupling effects in the generalized BCS pairing arising from a net dynamic attractive interaction between the carriers, due to the exchange of lattice phonons and/or electronic excitations in the system, (ii) the possibility of interacting carriers in more than one narrow band or layer, and (iii) possible corrections to the usual

mean-field results of the theory. Nevertheless, due to the unusual normal and superconducting properties of these metallic oxides, very serious and fascinating attempts have been made to find an alternative to the generalized BCS pairing theory (Anderson 1987; Anderson *et al* 1987), in the form of the resonating-valence-bond (RVB) approach involving very large repulsive intra-atomic carrier-carrier interaction energy U as compared to the band width W of the single-particle electronic states. There are various other bosonic models involving some kind of pairing of fermions followed by Bose-condensation of these pairs, e.g., of possible bound bi-polarons in these materials.

As of now, it is fair to say that starting from a collection of charged fermions, the generalized BCS pairing idea, involving off-diagonal long range order in the two-particle density matrix, seems to be an ideal approach in which the superconducting transition can be demonstrated theoretically without any doubt. In view of this, it is of great interest to examine whether various experimental results on single-crystals of these new high- T_c materials can still be understood, at least in principle, within the framework of an appropriate generalization of the BCS pairing theory. In this connection, as two typical examples, we will consider the behaviour of the electronic specific heat and the infrared absorption in the superconducting state of such materials. Experimentally, it has been found that in many of these materials the electronic specific heat (Phillips *et al* 1987; Ishikawa *et al* 1987; Batlogg *et al* 1987) at low temperatures seems to vary linearly with temperature T , instead of the usual exponential expected in the simple BCS model with a finite gap parameter $\Delta(T)$. Similarly, there seems to be some residual (Schlesinger *et al* 1987; Beyerman *et al* 1987; Sulewski *et al* 1987) absorption of infrared frequencies below the identifiable energy-gap “ 2Δ ”, even in the case of experiments done on single crystals, so that the absorption edge is not as sharp as in many of the conventional superconductors (Ginsberg and Hebel 1969). Also, the values of the energy-gap measured in such experiments seem to be somewhat different than their corresponding values obtained in tunnelling experiments. However, even in tunnelling data it is difficult to find real sharp characteristics.

As indicated earlier, the layered structure of the crystal and large anisotropies in various properties can have significant consequences for the nature of superconductivity in these materials. Even when one works within the framework of the mean-field theory of the generalized BCS approach, one can obtain anisotropic gap functions $\Delta(\mathbf{k})$ which may even vanish, depending upon the symmetry of the layers and the crystal, in certain directions or regions of the \mathbf{k} -space, e.g., for \mathbf{k} perpendicular to the conducting layers in the high- T_c oxides. In such a case, a power-law behaviour for the electronic specific heat, etc., can result. Note that the conventional argument about the absence of nodes in Δ for the familiar s -wave pairing is no longer valid, because for layered crystals with highly non-spherical Fermi surfaces, a fixed orbital- l is not the correct label to describe pairing. As an approximation, we can still assume isotropy in the 2-dimensional plane of the layers, but not in the direction perpendicular to the planes. We can no longer talk of a s -wave pairing or a d -wave pairing, etc., a concept applicable to the three-dimensional isotropic case. If the gap parameter is small or vanishing in the direction perpendicular to the a - b plane of \hat{k} , it is possible to get finite infrared absorption below the larger energy-gap $2\Delta(\hat{k}_\parallel)$ in the a - b plane, depending on the direction of propagation and polarization of the incident radiation.

In what follows, we first describe briefly the recent formulation of the BCS pairing theory in layered crystals, in §2. For allowed pairing within the same conducting

layer j in any unit cell or within the same band b only, the contributions of quasi-particles in different layers or bands to thermodynamic functions are additive. In view of this, we also examine in §2, the temperature-dependence of specific heat in the superconducting state with anisotropic $\Delta(\mathbf{k})$, consistent with the approximate symmetry for the motion of carriers close to the anisotropic Fermi surface. In an explicit simple model for $\Delta_j(\mathbf{k})$, for \mathbf{k} close to the Fermi surface, where it is assumed to depend only on the direction of $\hat{\mathbf{k}}$, the specific heat is calculated analytically to show how the power-law behaviour can be obtained in such a case. The effect of the energy-gap anisotropy on thermodynamic and other properties has been considered extensively in the past for the conventional superconductors (Sheplev 1969). However, in most of these studies the anisotropic part of the gap function is assumed to be small compared to the main isotropic part. This is not necessarily the case in the new superconductors. Moreover, when the coherence length ξ is small compared to the mean free path l due to impurities etc., the effect of anisotropy in many of the physical measurements, e.g., in electromagnetic absorption, does not average out (Anderson 1959), as in most of the conventional superconductors. In §3, we present the calculation of the linear response function for electromagnetic waves in a superconductor with anisotropic energy-gap and nonspherical Fermi surface, valid for the case under discussion in which $\xi \ll l$. By an explicit calculation, we show how the imaginary part of the dielectric function $\epsilon''_{\mu\nu}(\mathbf{q}, \omega)$, i.e. the real part of the conductivity tensor $\sigma'_{\mu\nu}(\mathbf{q}, \omega)$ can have strength below the larger gap corresponding to \mathbf{k} in the a - b plane. We conclude our discussion in §4.

2. Anisotropic energy-gap and specific heat in layered crystals

Starting with the single-particle electronic-band picture and with Cooper pairing restricted to carriers in the same conducting band only, it is wellknown that the quasi-particle excitations in the superconducting state can be described by the approximate diagonalized Hamiltonian

$$H - \mu N = \langle C \rangle_{\mu} + \sum_{b\mathbf{k}} E_{b\mathbf{k}} (\gamma_{b\mathbf{k}0}^{\dagger} \gamma_{b\mathbf{k}0} + \gamma_{b\mathbf{k}1}^{\dagger} \gamma_{b\mathbf{k}1}) \quad (1)$$

where γ 's satisfy the usual Fermion anti-commutation relations and where the quasi-particle energies are given by

$$E_{b\mathbf{k}} = [(\epsilon_{b\mathbf{k}} - \mu)^2 + \Delta_b^2(\mathbf{k})]^{1/2} \equiv [\xi_{b\mathbf{k}}^2 + \Delta_b^2(\mathbf{k})]^{1/2} \quad (2)$$

in terms of the BCS energy-gap parameters $\Delta_b(\mathbf{k}, T)$ and the Bloch energy $\xi_{b\mathbf{k}}$ of the carriers measured from the chemical potential (Fermi energy) μ . In (1), the fixed- μ thermal average

$$\langle C \rangle_{\mu} = \sum_{b\mathbf{k}} [\xi_{b\mathbf{k}} - E_{b\mathbf{k}} + (\Delta_b^2(\mathbf{k})/2E_{b\mathbf{k}}) \{1 - 2f(E_{b\mathbf{k}})\}] \quad (3)$$

with

$$f(E) \equiv [1 + \exp \beta E]^{-1}, \quad \beta = 1/k_B T. \quad (4)$$

The coupled BCS equations for the energy-gap functions $\Delta_b(\mathbf{k})$ in the multi-band case were already considered by Suhl *et al* (1959) in terms of the effective interaction parameters V_{bb} . Explicitly, the determination (Jha 1988) of the effective interaction

functions $V_{bb'}(\mathbf{q}=\mathbf{k}'-\mathbf{k}, \omega)$ and the corresponding T_c involves the knowledge of an appropriate inverse dielectric matrix $\varepsilon^{-1}(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}', \omega)$ in the reciprocal \mathbf{G} -space of the crystal. Note that, in general, $\Delta_b(\mathbf{k})$ is an anisotropic function of \mathbf{k} .

For any 3-dimensional layered crystal, the above multi-band formulation is enough to obtain T_c , $\Delta_b(\mathbf{k}, T)$ and other physical properties of the superconducting material. However, we (Jha 1987) have argued that in highly-layered crystals in which the electronic motion is mostly confined to the plane of the layers, with much larger effective mass in the direction perpendicular to the layers, it is more appropriate to consider effective Cooper pairing of carriers in the same localized layers j only. In other words, to avoid consideration of large matrices in the reciprocal lattice space- \mathbf{G} and various local-field corrections in the multi-band theory, the order parameters or the energy-gap parameters are now described by $\Delta_j(\mathbf{k})=\Delta_j(\mathbf{k}_\parallel, k_z)$ where \mathbf{k}_\parallel is the wave vector in the plane of the layers and $k_z = \theta/L$, $0 \leq \theta \leq 2\pi$ is the wavevector in the z -direction, perpendicular to the layer plane, for each of the layers j in the unit cell of length L in the z -direction. Superconductivity in a layered crystal with electronic motion localized in equally-spaced alternate metallic and insulating molecular layers was already investigated by Bulaevskii and Kukharenko (1971). However, we have generalized the formulation to an arbitrary number of layers in any unit cell, which are not necessarily equidistant (Jha 1988). In such an approach, the gap functions Δ_j are determined by the solution of coupled equations

$$\Delta_j(\mathbf{k}_\parallel, k_z) = - \sum_{\mathbf{k}'_\parallel} \sum_{k'_z} \sum_j V_{jj'}^{\text{sup}}(\mathbf{q}_\parallel = \mathbf{k}_\parallel - \mathbf{k}'_\parallel, q_z = k_z - k'_z, \xi_j, \xi_{j'}) \times \Delta_{j'}(\mathbf{k}'_\parallel, k'_z) \tanh(\beta E_{j\mathbf{k}})/2E_{j\mathbf{k}} \quad (5)$$

where

$$E_{j\mathbf{k}}^2 = \xi_j^2(\mathbf{k}) + \Delta_j^2(\mathbf{k}) \equiv \xi_j^2(\mathbf{k}_\parallel, k_z) + \Delta_j^2(\mathbf{k}_\parallel, k_z) \quad (6)$$

in terms of the single-particle energies $\xi_j(\mathbf{k})$ of carriers localized in layers j , and where

$$V_{jj'}^{\text{sup}}(\mathbf{q}_\parallel, q_z, \xi, \xi') = V_{jj'}^{(0)}(\mathbf{q}_\parallel, q_z) + \frac{2}{\pi} \int_0^\infty d\omega' \frac{\text{Im} V_{jj'}(\mathbf{q}_\parallel, q_z, \omega')}{\omega' + |\xi| + |\xi'|} \quad (7)$$

In the above equation, $V_{jj'}^{(0)}(\mathbf{q}_\parallel, q_z)$ is the Fourier transform of the bare Coulomb interaction between two carriers in layers j and j' in any unit cell, and $V_{jj'}(\mathbf{q}_\parallel, q_z, \omega)$ is the corresponding effective dynamic interaction in the presence of other electrons and ions. If the z -coordinate of the n th layer is given by

$$z_n = z(N, j) = NL + R_j, \quad R_0 = 0 \quad (8)$$

where N denotes the unit cell label and j denotes the label for the layer within the unit cell, and where $R_{jj'} = R_j - R_{j'}$ denotes the distance of the j th layer from the j' th layer in the cell, for any function $g(\mathbf{q}_\parallel, z_n - z_{n'})$ we can write

$$g(\mathbf{q}_\parallel, z_n - z_{n'}) \equiv g_{jj'}(\mathbf{q}_\parallel, N - N') = \frac{L}{2\pi} \int_0^{2\pi/L} dq_z g_{jj'}(\mathbf{q}_\parallel, q_z) \exp(i(N - N')Lq_z) \quad (9)$$

For m layers in any unit cell, a simplified diagrammatic perturbation theory can then be used to find the $m \times m$ dynamic interaction matrix V in terms of $V_{jj'}^{(0)}$ and

2-dimensional electronic layer-polarization functions

$$\Pi_{jj'}(\mathbf{q}_r, \omega) = \delta_{jj'} \pi_j(\mathbf{q}_r, \omega) = \delta_{jj'} \pi_{j+m}(\mathbf{q}_r, \omega). \quad (10)$$

Explicitly, using the matrix notation, one finds

$$V(\mathbf{q}_r, q_z, \omega) = \varepsilon^{-1}(\mathbf{q}_r, q_z, \omega) V^{(0)}(\mathbf{q}_r, q_z) \quad (11)$$

$$\varepsilon(\mathbf{q}_r, q_z, \omega) = I + V^{(0)}(\mathbf{q}_r, q_z) \Pi(\mathbf{q}_r, \omega) \quad (12)$$

where I is the $m \times m$ unit matrix, and

$$V_{jj'}^{(0)}(\mathbf{q}_r, q_z) = \begin{cases} \frac{2\pi e^2}{q_t} [P(q_t, q_z) \exp(-q_t R_{jj'}) + N(q_t, q_z) \exp(q_t R_{jj'})]; & j > j' \\ \frac{2\pi e^2}{q_t} [P(q_t - q_z) \exp(q_t R_{jj'}) + N(q_t - q_z) \exp(-q_t R_{jj'})]; & j < j' \end{cases} \quad (13)$$

$$P(q_t, q_z) = \exp(iq_z L) [\exp(iq_z L) - \exp(-q_t L)]^{-1} \quad (14)$$

$$N(q_t, q_z) = \exp(-q_t L) [\exp(-iq_z L) - \exp(-q_t L)]^{-1}. \quad (15)$$

Note that $\varepsilon^{-1}(\mathbf{q}_r, q_z, \omega)$ is a $m \times m$ non-diagonal matrix so that even the effective interaction between two carriers in the same layer j depends not only on the polarization function of the same layer but also of other layers in the unit cell. These polarization functions $\pi_j(\mathbf{q}_r, \omega)$ contain contributions from all possible electronic and ionic excitations in the system.

From the above discussions, it is quite clear that for layered crystals, the energy-gap parameters are expected to be highly anisotropic in \mathbf{k} -space. Whether one uses the multi-band picture or the multi-layer picture, the total contributions to thermodynamic functions are of course additive corresponding to quasi-particles labelled by the band indices b or the layer indices j in (1). For a given form for such a gap function $\Delta(\mathbf{k})$, one has the usual result for the thermodynamic potential

$$\Omega = -\frac{1}{\beta} \ln Z = \frac{2}{\beta} \sum_{\mathbf{k}} \ln [(1 - f(E_{\mathbf{k}})) + \langle C \rangle_{\mu}] \quad (16)$$

where the partition function

$$Z = \exp(-\beta\Omega) = \text{Trace} \exp(-\beta(H - \mu N)), \quad \Omega = E - TS - \mu N. \quad (17)$$

The entropy per unit volume V is then given by

$$S = -\frac{1}{V} \left[\left(\frac{\partial \Omega}{\partial T} \right)_{\nu, \mu} \right] = -2k_B \int \frac{d^3k}{(2\pi)^3} [\ln(1 - f(E_{\mathbf{k}})) - \beta E_{\mathbf{k}} f(E_{\mathbf{k}})] \quad (18)$$

from which the specific heat per unit volume can be obtained by the relation

$$C = T \frac{\partial S}{\partial T} = -\beta \frac{\partial S}{\partial \beta}. \quad (19)$$

If one chooses suitable co-ordinates u and v on the surface of constant single-particle energy $\xi_{\mathbf{k}} = \xi$, so that k_x, k_y , and k_z can be rewritten as functions of u, v and ξ , the integral over d^3k in (18) transforms to

$$\int \frac{d^3k}{(2\pi)^3} \rightarrow \frac{1}{8\pi^3} \int du \int dv \int d\xi J(u, v, \xi) \equiv \int du \int dv \int d\xi g(u, v, \xi) \quad (20)$$

where $J(u, v, \xi)$ is the Jacobian determinant

$$J(u, v, \xi) = 8\pi^3 g(u, v, \xi) = \left(\frac{\partial \mathbf{k}}{\partial u} \times \frac{\partial \mathbf{k}}{\partial v} \right) \cdot \frac{\partial \mathbf{k}}{\partial \xi} = \frac{d^2 \sigma_\xi}{|\nabla_{\mathbf{k}} \xi|} \quad (21)$$

in terms of the element of the surface area $d^2 \sigma_\xi$ on the surface $\xi_{\mathbf{k}} = \xi$. In terms of these new variables, $\Delta(\mathbf{k}) \rightarrow \Delta(u, v, \xi)$, $E_{\mathbf{k}} \rightarrow E(u, v, \xi)$, and the entropy can then be calculated in the form

$$S = H(1) + \int_1^\infty d\lambda H(\lambda) \quad (22)$$

$$H(\lambda) = 2k_B \int du \int dv \int_{-\mu}^\infty d\xi g(u, v, \xi) \beta E [1 + \exp(\lambda \beta E)]^{-1} \quad (23)$$

$$E = [\xi^2 + \Delta^2(u, v, \xi)]^{1/2}. \quad (24)$$

As it is often the case, if the contributions to S are dominated by the region in ξ near the Fermi surface, i.e. $\xi \simeq 0$, the above general calculation can be simplified considerably. In such a case, one can replace g and Δ in (23) and (24) by their values at the Fermi surface:

$$g(u, v, \xi) \rightarrow g(u, v, 0) \equiv g_F(u, v) \quad (25)$$

$$\Delta(u, v, \xi) \rightarrow \Delta(u, v, 0) \equiv \Delta_F(u, v). \quad (26)$$

This leads to the expression

$$S = 2k_B \int du \int dv g_F(u, v) G(u, v) \quad (27)$$

where

$$\begin{aligned} G(u, v) &= 2\beta \int_{\Delta_F}^\infty dE f(E) [E^2 + \xi^2]/\xi \\ &= 2\beta \Delta_F^2 \int_0^\infty dy \frac{\cosh 2y}{[1 + \exp(\beta \Delta_F \cosh y)]} \\ &= 2\beta \Delta_F^2 \sum_{n=1}^\infty (-1)^{n-1} K_2(n\beta \Delta_F) \end{aligned} \quad (28)$$

in terms of the modified Bessel function K_2 . Note that by definition, the single-spin density of states N_F at the Fermi surface ($\xi = 0$) is simply given by

$$\int du \int dv g_F(u, v) = N_F. \quad (29)$$

For the single-particle carrier energy of the form

$$\xi_{\mathbf{k}} = \frac{\hbar^2 k_x^2}{2m_{xx}} + \frac{\hbar^2 k_y^2}{2m_{yy}} + \frac{\hbar^2 k_z^2}{2m_{zz}} - \mu \quad (30)$$

it is possible to choose spherical polar coordinates $\theta = v$, $\phi = u$ on the constant energy surface, so that

$$g_F(u, v) du dv = \frac{N_F}{4\pi} \sin \theta d\theta d\phi \quad (31)$$

$$N_F = \frac{1}{4\pi^2} \left[\frac{2}{\hbar^2} (m_{xx} m_{yy} m_{zz})^{1/3} \right]^{3/2} \mu^{1/2} \quad (32)$$

and

$$S = \frac{N_F k_B}{\pi} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \Delta_F^2(\theta, \phi) \sum_{n=1}^{\infty} (-1)^n K_2(n\beta \Delta_F(\theta, \phi)). \quad (33)$$

If one assumes isotropy in the a - b plane, one can take $m_{xx} = m_{yy}$ in (30) and (32). Further, because of the symmetry in the problem, if $\Delta_F(\theta, \phi) = \bar{\Delta}_F(|\cos \theta|)$, i.e. the gap parameter is independent of ϕ and depends only on the magnitude of $\cos \theta$, with $\theta = 0$ along the perpendicular z -axis, the above expression simplifies to

$$S = 2N_F k_B \beta \sum_{n=1}^{\infty} (-1)^{n-1} D_n(\beta) \quad (34)$$

$$D_n(\beta) = 2 \int_0^1 dx \bar{\Delta}_F^2(x) K_2(n\beta \bar{\Delta}_F(x)). \quad (35)$$

Note that when $\bar{\Delta}_F(x) = 0$, the above expression leads to the usual linear temperature dependence of the entropy in the normal state, as $T \rightarrow 0$,

$$S_{\text{normal}} = \frac{2\pi^2}{3} k_B^2 N_F T \quad (36)$$

since

$$\text{Lt}_{y \rightarrow 0} K_2(ny) = \frac{2}{n^2 y^2}, \quad \sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{n^2} = \frac{\pi^2}{12}. \quad (37)$$

Similarly, for an isotropic gap $\bar{\Delta}_F(x) = \Delta$ in the superconducting state,

$$S \rightarrow 4N_F k_B \beta \Delta^2 \sum_{n=1}^{\infty} (-1)^{n-1} K_2(n\beta \Delta) \quad (38)$$

which varies as $\beta^{1/2} \exp(-\beta \Delta)$ as $T \rightarrow 0$, since

$$\text{Lt}_{y \rightarrow \infty} K_2(ny) \rightarrow \left(\frac{\pi}{2ny} \right)^{1/2} \exp(-ny). \quad (39)$$

To illustrate the temperature-dependence of the entropy in the more general case of an anisotropic gap, let us assume that $\bar{\Delta}_F(|\cos \theta|)$ has the form

$$\bar{\Delta}_F(|\cos \theta|) = \begin{cases} \Delta(1 - p|\cos \theta|), & |\cos \theta| \leq \frac{1}{p}, \quad p \geq 0 \\ 0, & |\cos \theta| > \frac{1}{p} \end{cases} \quad (40)$$

where p is a positive number. Note that for the anisotropy parameter $p < 1$, $\bar{\Delta}_F$ does not vanish anywhere, whereas for $p = 1$, it vanishes only at points with $\theta = 0$ and π , i.e. in directions perpendicular to the layers. For $p > 1$, the above model describes regions of vanishing $\bar{\Delta}_F$, close to $\theta = 0$ and π . The isotropic case corresponds to $p = 0$. In this anisotropic model, (35) and (40) lead to the result, for $0 \leq p < 1$,

$$D_n = \frac{3\pi}{n^3 \beta^3 p \Delta_t} [n\beta\Delta_t \{K_2(n\beta\Delta_t)L_1(n\beta\Delta_t) + L_2(n\beta\Delta_t)K_1(n\beta\Delta_t)\} \\ - n\beta\Delta_t(1-p) \{K_2(n\beta\Delta_t(1-p))L_1(n\beta\Delta_t(1-p)) \\ + L_2(n\beta\Delta_t(1-p))K_1(n\beta\Delta_t(1-p))\}] \quad (41)$$

and for $p \geq 1$

$$D_n = \frac{3\pi}{n^3 \beta p \Delta_t} [n\beta\Delta_t \{K_2(n\beta\Delta_t)L_1(n\beta\Delta_t) + L_2(n\beta\Delta_t)K_1(n\beta\Delta_t)\}] \\ + \frac{4}{n^2 \beta^2} \left(1 - \frac{1}{p}\right) \quad (42)$$

where $L_n(z)$ is the modified Struve function (Abramowitz and Stegun 1968). In the limiting cases, one has

$$z \rightarrow 0: K_1(z) \rightarrow \frac{1}{z}, \quad K_2(z) \rightarrow \frac{2}{z^2}, \quad L_1(z) \rightarrow \frac{2z^2}{3\pi}, \quad L_2(z) \rightarrow \frac{2z^3}{15\pi} \\ z \rightarrow \infty: K_1(z) \rightarrow \left(\frac{\pi}{2z}\right)^{1/2} \exp(-z) \left(1 + \frac{3}{8z} + \dots\right), \quad K_2(z) \rightarrow \left(\frac{\pi}{2z}\right)^{1/2} \\ \times \exp(-z) \left(1 + \frac{15}{8z} + \dots\right) \quad (43)$$

$$\text{Lt}_{z \rightarrow \infty} L_1(z) \rightarrow \text{Lt}_{z \rightarrow \infty} I_{-1}(z) - \frac{2}{\pi} + 0 \left(\frac{1}{z^2}\right) \rightarrow \left(\frac{1}{2\pi z}\right)^{1/2} e^z \left(1 - \frac{3}{8z} + \dots\right) - \frac{2}{\pi} + \dots \\ \text{Lt}_{z \rightarrow \infty} L_2(z) \rightarrow \text{Lt}_{z \rightarrow \infty} I_{-2}(z) - \frac{2z}{3\pi} + 0 \left(\frac{1}{z}\right) \rightarrow \left(\frac{1}{2\pi z}\right)^{1/2} e^z \left(1 - \frac{15}{8z} + \dots\right) \\ - \frac{2z}{3\pi} + \dots \quad (44)$$

$$\text{Lt}_{z \rightarrow 0} [K_2(z)L_1(z) + L_2(z)K_1(z)] \rightarrow \frac{4}{3\pi} \quad (45)$$

$$\text{Lt}_{z \rightarrow \infty} [K_2(z)L_1(z) + L_2(z)K_1(z)] \rightarrow \frac{1}{z}. \quad (46)$$

Thus as $T \rightarrow 0$, i.e. $\beta \rightarrow \infty$, one has

$$S = 2N_F k_B \beta \sum_{n=1}^{\infty} (-1)^{n-1} D_n(\beta \rightarrow \infty) \quad (47)$$

which can be calculated from (41) and (42) by using the limiting values of the functions and expressing $L_n(z)$ in terms of $I_{-n}(z)$ and a power series in z . It can be shown that for $p < 1$, i.e. when Δ_F is nonvanishing everywhere, the entropy and specific heat still have temperature-dependences resembling the $\exp(-\beta\Delta_i)$, but for p closer to 1, this can be nearer to a power law behaviour, in practice. In fact, for $p \geq 1$, one finds

$$S = 2N_F k_B \beta \sum_{n=1}^{\infty} (-1)^{n-1} \left[\frac{3\pi}{n^3 \beta^3 p \Delta_i} + \frac{4}{n^2 \beta^2} \left(1 - \frac{1}{p} \right) \right], \quad \beta \rightarrow \infty, \quad p \geq 1 \quad (48)$$

Thus at low temperatures, this leads to the specific heat in the superconducting state which is of the form

$$C_s = \frac{12\pi N_F k_B^3 T^2}{\Delta_i} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{n^3} = \frac{12\pi N_F k_B^3 T^2}{\Delta_i} (0.90154), \quad \text{for } p=1 \quad (49)$$

and

$$C_s = \frac{2\pi^2 N_F k_B^2 T}{3} \left(1 - \frac{1}{p} \right) + O(T^2), \quad \text{for } p > 1. \quad (50)$$

In other words, depending upon the value of the anisotropy parameter p , at low temperatures one can get either a linear temperature-dependence for the specific heat or a higher power law or a smeared out exponential (which may be difficult to be distinguished from a power law behaviour).

Before we conclude this section, it should be emphasized here that the possibility of the spin-singlet or the spin-triplet energy gap vanishing on points or lines of the Fermi surface of a crystalline material, and the consequent T^2 or T^3 power-law behaviour of the low-temperature specific heat have been discussed extensively in recent years, particularly in connection with superconductivity in heavy fermion systems. This has, however, not been appreciated fully in the layered-crystal high- T_c literature, and very often one continues to talk in terms of s -wave or p -wave pairing with a spherical Fermi surface. Our aim here was to examine the expression for the electronic specific heat C_s , with a general form of the BCS gap as a function of \mathbf{k} , and to introduce an explicit anisotropic model for $\Delta(\hat{\mathbf{k}})$ on an ellipsoidal Fermi surface to study the resulting analytic form of C_s as a function of temperature T and the anisotropy parameter p . In light of this analysis, we will discuss some of the available experimental results in high- T_c materials in §4.

3. High frequency electromagnetic response and infrared absorption

For a superconductor with an isotropic gap, an expression for the linear conductivity $\sigma(\mathbf{q}, \omega)$ was first derived by Mattis and Bardeen (1958), and later obtained in more detail by Abrikosov and Gorkov (1959). This calculation has already been described at various other places, including the book by Rickayzen (1965) which has a good discussion of the calculation in the presence of scattering from random impurities in its Appendix IV. In fact, a more general expression for the electromagnetic response function in a superconducting crystal has been derived by Nam (1967), which includes magnetic as well as nonmagnetic impurity scattering. In superconductors, non-magnetic impurity scattering not only leads to the usual relaxation effects in the

system in the presence of an external e.m. field, but also a change in the superconducting wave function itself if the coherence length ξ is of the order of the mean free path l or larger. In the actual calculation with random impurities and weak scattering, these effects are taken into account by finding the modified quasi-particle propagators as well as the vertex corrections for the interaction of the quasi-particles with the external e.m. wave. Recently, for the case of a spherical Fermi-surface and explicit p -wave ($l=1$) pairings, Klemm *et al* (1988) have obtained the electromagnetic response in the presence of impurity scattering. However, because of the complexity in actual calculations, they have restricted to the case of $\mathbf{q} \rightarrow 0$, where \mathbf{q} is the wavevector of the e.m. wave in the material. This limits its applicability to the case in which $q\xi \ll 1$, and $ql \ll 1$. Also, it cannot be used directly to the case of a nonspherical Fermi surface with gap anisotropies relevant to high- T_c layered materials. In any case, for the situation under consideration here in which $\xi \ll l$, one may be able to avoid this rather tedious calculation by assuming the sample to behave as almost a pure material as far as the superconducting pair wavefunction is concerned. However, as in the normal case, the relaxation effects arising from various elastic and inelastic scattering mechanisms must be included, at least approximately, otherwise the induced current density even in a singly-connected bulk superconductor will not decay to zero in the absence of any dissipation, after the external e.m. field is switched off. In a general density matrix theory of relaxation in any system with Hamiltonian H_0 , in the presence of interaction H_R which is responsible for various relaxation mechanisms, and H_A which describes the interaction of the charged system with an external radiation field, one obtains the usual reduced density matrix equation

$$(\partial\rho/\partial t) - (i\hbar)^{-1}[H_0 + H_A, \rho] = -\Gamma(\rho),$$

where the relaxation term $\Gamma(\rho)$, linear in ρ , is given by integrals over times t' and t'' of the double commutator involving $H_R(t')$, $H_R(t'')$ and ρ , traced over the states of relaxation agents. Here, a small second-order energy-shift term for the system, arising from the interaction H_R , has been neglected. After a sufficiently long time, if the decay of the system to the equilibrium state can be described approximately by a single relaxation time τ_c , one can then often replace $\Gamma(\rho)$ by $(\rho - \rho_0)/\tau_c$. Note that in a normal metal, τ_c^n is usually a very slowly varying function of energy and temperature. However, in the superconducting case τ_c^s is not the same as τ_c^n , as it is evident from an approximate expression for the collision integral in the kinetic equation for a superconductor, introduced by Khalatnikov and Abrikosov (1959) (see §7 of that paper). It is the meanfree path l which remains almost the same in both cases, but

$$\tau_c^s = \tau_c^n [(\xi_{\mathbf{k}} + \Delta_{\mathbf{k}} \partial\Delta/\partial\xi_{\mathbf{k}})/E_{\mathbf{k}}] = \tau_c^n (v_s/v_n),$$

where v_s and v_n are the velocities of the quasi-particles in the superconducting state and the normal state, respectively. This may also be deduced from the expression (4.12) of Nam's paper for the electromagnetic response function in terms of the imaginary part $\Gamma(\omega)$ of the quasi-particle self-energy arising from various scattering mechanisms and the corresponding pole of the Green function $G(\omega, \mathbf{k})$, at $\omega \simeq E_{\mathbf{k}} - i(\xi_{\mathbf{k}}/E_{\mathbf{k}})\Gamma$, in the limit in which the effect of weak scattering on the real part of the quasi-particle energy is neglected. Thus, following Rickayzen (1965), as long as the scattering is weak, the relaxation effects may be included in our approach by replacing $\Gamma(\rho)$ by $\delta\rho\Omega_c$, where Ω_c is a phenomenological frequency-dependent

parameter appropriate to $\langle 1/\tau_c^s \rangle$ for the range of energy (of the order of ω) and momenta (of the order of q) involved in the transition process. This procedure, though crude, is expected to give at least a qualitative indication of relaxation effects, in the weak scattering limit.

In the presence of an external transverse electro-magnetic field described by the vector potential $\mathbf{A}(\mathbf{r}, t)$, one has to consider the Hamiltonian

$$H_T = \langle C \rangle_\mu + \sum_{\mathbf{k}} E_{\mathbf{k}} (\gamma_{\mathbf{k}0}^+ \gamma_{\mathbf{k}0} + \gamma_{\mathbf{k}1}^+ \gamma_{\mathbf{k}1}) + H_A \quad (51)$$

$$H_A \simeq \frac{e}{c} \sum_{\mathbf{k}, \mathbf{q}, \sigma} C_{\mathbf{k}+\mathbf{q}\sigma}^+ C_{\mathbf{k}\sigma} \mathbf{V}_{\mathbf{k}} \cdot \mathbf{A}(\mathbf{q}, t) \quad (52)$$

where for actual intraband transitions among the Bloch states $|\mathbf{k}\rangle$ and $|\mathbf{k} + \mathbf{q}\rangle$

$$\mathbf{V}_{\mathbf{k}}(\mathbf{q}) = \langle \mathbf{k} + \mathbf{q} | \exp(-i\mathbf{q} \cdot \mathbf{r}) \frac{\mathbf{p}}{m} | \mathbf{k} \rangle \quad (53)$$

which can be approximated by the carrier velocity

$$\mathbf{V}_{\mathbf{k}} \simeq \mathbf{V}_{\mathbf{k}}(0) = \frac{1}{\hbar} \frac{\partial \xi_{\mathbf{k}}}{\partial \mathbf{k}} \quad (54)$$

and where C 's can be transformed into quasi-particle operators γ 's by using the Bogoliubov transformation

$$C_{\mathbf{k}\uparrow} = u_{\mathbf{k}} \gamma_{\mathbf{k}0} + v_{\mathbf{k}} \gamma_{\mathbf{k}1}^+; \quad C_{-\mathbf{k}\downarrow} = -v_{\mathbf{k}} \gamma_{\mathbf{k}0}^+ + u_{\mathbf{k}} \gamma_{\mathbf{k}1} \quad (55)$$

$$u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \quad v_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \quad E_{\mathbf{k}} = + [\xi_{\mathbf{k}}^2 + \Delta^2(\mathbf{k})]^{1/2}. \quad (56)$$

To obtain the linear response function, one has to calculate the expectation value of the current density

$$\begin{aligned} \mathbf{j}_0(\mathbf{q}) + \mathbf{j}_A(\mathbf{q}, t) &= \frac{-e}{mV} \sum_{\mathbf{k}\sigma} C_{\mathbf{k}\sigma} C_{\mathbf{k}+\mathbf{q}\sigma} \mathbf{V}_{\mathbf{k}} \\ &\quad - \frac{e^2}{mcV} \sum_{\mathbf{k}\sigma} C_{\mathbf{k}+\mathbf{k}'\sigma}^+ C_{\mathbf{k}\sigma} \mathbf{A}(\mathbf{k}' + \mathbf{q}, t) \end{aligned} \quad (57)$$

up to terms linear in A . Here, V is the volume of the system. Using the density matrix approach with a phenomenological damping term, it is straightforward to find the required expression in the form

$$\begin{aligned} j_{\mu}(\mathbf{q}, \omega) &= \frac{i\omega}{c} \sum_{\nu} \sigma_{\mu\nu}(\mathbf{q}, \omega) A_{\nu}(\mathbf{q}, \omega) \\ &= \frac{\omega^2}{c} \sum_{\nu} \frac{[\varepsilon_{\mu\nu}(\mathbf{q}, \omega) - \delta_{\mu\nu}]}{4\pi} A_{\nu}(\mathbf{q}, \omega) \end{aligned} \quad (58)$$

where the linear conductivity $\sigma(\mathbf{q}, \omega)$ is given by

$$\sigma_{\mu\nu}(\mathbf{q}, \omega) = \frac{ine^2}{m\omega} \delta_{\mu\nu} - \frac{ie^2}{\omega} \int \frac{d^3k}{(2\pi)^3} V_{\mathbf{k}\mu} V_{\mathbf{k}\nu} R_T(\mathbf{k}, \mathbf{k} - \mathbf{q}, \omega) \quad (59)$$

with

$$\begin{aligned}
 R_T(\mathbf{k}, \mathbf{k}-\mathbf{q}, \omega, \Omega_c) = & \frac{(EE_1 - \xi\xi_1 - \Delta\Delta_1)}{2EE_1} [1 - f(E) - f(E_1)] \\
 & \times (E_1 + E + \hbar\omega + i\hbar\Omega_c)^{-1} + (E_1 + E - \hbar\omega - i\hbar\Omega_c)^{-1}] \\
 & + \frac{(EE_1 + \xi\xi_1 + \Delta\Delta_1)}{2EE_1} [f(E) - f(E_1)] \\
 & [(E_1 - E + \hbar\omega + i\hbar\Omega_c)^{-1} + (E_1 - E - \hbar\omega - i\hbar\Omega_c)^{-1}] \quad (60)
 \end{aligned}$$

and where we have introduced the short hand notations

$$\xi \equiv \xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu, \quad \Delta \equiv \Delta(\mathbf{k}), \quad E \equiv E_{\mathbf{k}} = + [\xi_{\mathbf{k}}^2 + \Delta^2(\mathbf{k})]^{1/2} \quad (61)$$

$$\begin{aligned}
 \xi_1 \equiv \xi_{\mathbf{k}-\mathbf{q}} = \varepsilon_{\mathbf{k}-\mathbf{q}} - \mu, \quad \Delta_1 \equiv \Delta(\mathbf{k}-\mathbf{q}), \quad E_1 \equiv E_{\mathbf{k}-\mathbf{q}} \\
 = + [\xi_{\mathbf{k}-\mathbf{q}}^2 + \Delta^2(\mathbf{k}-\mathbf{q})]^{1/2} \quad (62)
 \end{aligned}$$

$$f(E) = [\exp(\beta E_{\mathbf{k}}) + 1]^{-1}, \quad f(E_1) = [\exp(\beta E_{\mathbf{k}-\mathbf{q}}) + 1]^{-1} \quad (63)$$

As described in §2, we can again replace the integrations over d^3k to integrations over u, v and ξ introduced in (20). However, to be more definite, let us assume that the form of $\xi_{\mathbf{k}}$ and the corresponding Fermi surface are still determined by (30), with $m_{xx} \simeq m_{yy}$. In such a case, one can again introduce spherical polar coordinates $\theta = v, \phi = u$ on the constant energy surface $\xi_{\mathbf{k}} = \xi$, so that the velocity components $(1/\hbar)\partial\xi_{\mathbf{k}}/\partial k_i$ of the carriers are given by

$$\begin{aligned}
 V_{kx} &= \frac{\hbar k_x}{m_{xx}} = \left(\frac{2}{m_{xx}}\right)^{1/2} \sin\theta \cos\phi (\xi + \mu)^{1/2} \\
 V_{ky} &= \frac{\hbar k_y}{m_{yy}} = \left(\frac{2}{m_{yy}}\right)^{1/2} \sin\theta \sin\phi (\xi + \mu)^{1/2} \\
 V_{kz} &= \frac{\hbar k_z}{m_{zz}} = \left(\frac{2}{m_{zz}}\right)^{1/2} \cos\theta (\xi + \mu)^{1/2}
 \end{aligned} \quad (64)$$

In terms of the carrier density

$$n = 2 \int_{-\mu}^0 d\xi \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \frac{N_F}{4\pi} \left(1 + \frac{\xi}{\mu}\right)^{3/2} = 2 \int_{-\mu}^\infty d\xi \int du \int dv g(u, v, \xi) \quad (65)$$

the conductivity tensor $\sigma_{\mu\nu}(\mathbf{q}, \omega)$ has the form

$$\begin{aligned}
 \sigma_{xx}(\mathbf{q}, \omega) &= \frac{ine^2}{m_{xx}\omega} - \frac{ine^2}{m_{xx}\omega} D_{xx}(\mathbf{q}, \omega) \\
 \sigma_{yy}(\mathbf{q}, \omega) &= \frac{ine^2}{m_{yy}\omega} - \frac{ine^2}{m_{yy}\omega} D_{yy}(\mathbf{q}, \omega) \\
 \sigma_{zz}(\mathbf{q}, \omega) &= \frac{ine^2}{m_{zz}\omega} - \frac{ine^2}{m_{zz}\omega} D_{zz}(\mathbf{q}, \omega)
 \end{aligned} \quad (66)$$

where, due to interband terms, m is changed to $m_{\mu\nu}$ in the first term, and, where

$$\begin{aligned} \omega^{-1}D_{\nu\nu}(\mathbf{q}, \omega) &= \frac{3}{8\pi} \int_{-\mu}^{\infty} d\xi \int_0^{\pi} d\theta \sin \theta \int_0^{2\pi} d\phi b_{\nu} b_{\nu} \left(1 + \frac{\xi}{\mu}\right)^{3/2} \\ &R_T(\xi, \theta, \phi, q, \omega, \Omega_c) (\omega + i\Omega_c)^{-1} \end{aligned} \quad (67)$$

with the electromagnetic absorption due to the second term determined by

$$\text{Re}[\sigma_{\mu\mu}(\mathbf{q}, \omega) - \sigma_{\mu\mu}^{(d)}(q, \omega)] = \frac{ne^2}{m_{\mu\mu}\omega} \text{Im} D_{\mu\mu}(\mathbf{q}, \omega) \quad (68)$$

In (67),

$$b_x = \sin \theta \cos \phi, \quad b_y = \sin \theta \sin \phi, \quad b_z = \cos \theta. \quad (69)$$

If the direction of the propagation of the incident wave is assumed to be in the Z -direction, i.e. along the C -axis, so that the wave is polarized in the x - y plane, one has to determine D_{XX} and D_{YY} only. These will be equal if the gap-parameter Δ is assumed to be independent of ϕ , and to depend only on $\cos \theta$. In such a case, one finds

$$\begin{aligned} \omega^{-1}D_{XX}(q\hat{Z}, \omega) &= \frac{3}{8} \int_{-\mu}^{\infty} d\xi \int_{-1}^{+1} dx (1-x^2) \left(1 + \frac{\xi}{\mu}\right)^{3/2} R_T(\xi, x, q, \omega, \Omega_c) (\omega + i\Omega_c)^{-1} \end{aligned} \quad (70)$$

where

$$x = \cos \theta \quad (71)$$

and where R_T has the same expression as given by (60) but with

$$\xi_1 \simeq \xi - \hbar Qx, \quad Q = V_{FZ}q \quad (72)$$

$$E = +[\xi^2 + \Delta^2(x)]^{1/2}, \quad E_1 = [\xi_1^2 + \Delta_1^2(x)]^{1/2} \quad (73)$$

for transitions close to the Fermi surface. Note that for $T=0$, $f(E)=f(E_1)=0$, so that the second term in (60) for R_T does not contribute. In this case, the expression for D_{XX} reduces to

$$\begin{aligned} \omega^{-1}D_{XX}(q\hat{Z}, \omega) &= \frac{3}{8} \int_{-\mu}^{\infty} d\xi \int_{-1}^{+1} dx (1-x^2) \left(1 + \frac{\xi}{\mu}\right)^{3/2} \\ &\times \frac{1}{2} (EE_1 - \xi\xi_1 - \Delta\Delta_1) / EE_1 [(E + E_1 + \hbar\omega + i\hbar\Omega_c)^{-1} \\ &+ (E + E_1 - \hbar\omega - i\hbar\Omega_c)^{-1}] (\omega + i\Omega_c)^{-1}. \end{aligned} \quad (74)$$

In the clean limit in which the mean free path is very large, the electromagnetic absorption can be obtained from the imaginary part of D_{XX} given by (74), in the limit $\Omega_c \rightarrow 0^+$. As a simplification, if we also assume that approximately $\Delta_1 \simeq \Delta$, we then obtain

$$\text{Re} \sigma_{XX}(q\hat{Z}, \omega) \simeq \frac{3\pi ne^2}{8m_{XX}\omega} \int_{-1}^{+1} dx (1-x^2) F_z(x) \quad (75)$$

where

$$F_z(x) = \frac{[E_{m1}E_{m2} + \xi_{m1}\xi_{m2} - \Delta^2(x)]}{|\xi_{m1}E_{m2} - \xi_{m2}E_{m1}|} \theta(\omega^2 - Q^2x^2 - 4\Delta^2(x)/\hbar^2) \quad (76)$$

where the step function

$$\begin{aligned} \theta(y) &= 1, \quad y \geq 0 \\ &= 0, \quad y < 0 \end{aligned} \tag{77}$$

and where

$$\xi_{m1} = \xi_0 + \frac{\hbar Q}{2} x, \quad \xi_{m2} = -\xi_0 + \frac{\hbar Q}{2} x \tag{78}$$

$$\xi_0 = \frac{\hbar \omega}{2} [\omega^2 - 4\Delta^2/\hbar^2 - Q^2 x^2]^{1/2} [\omega^2 - Q^2 x^2]^{-1/2} \tag{79}$$

$$E_{m1} = |[\xi_{m1}^2 + \Delta^2(x)]^{1/2}|, \quad E_{m2} = |[\xi_{m2}^2 + \Delta^2(x)]^{1/2}|. \tag{80}$$

For the case of the normal state with $\Delta(x)=0$ everywhere,

$$\begin{aligned} F_z(x) \rightarrow F_n(x) &= 2Qx\delta(\omega - Qx) \\ &= \frac{2\omega}{Q} \delta(x - \omega/Q) \end{aligned} \tag{81}$$

so that

$$\begin{aligned} \text{Re } \sigma_{xx}^n(q\hat{z}, \omega) &= \frac{3\pi n e^2}{4m_{xx} Q} \left(1 - \frac{\omega^2}{Q^2}\right) \theta(Q - \omega) \\ &= \frac{3\pi n e^2}{4m_{xx} q V_{FZ}} \left(1 - \frac{\omega^2}{q^2 V_{FZ}^2}\right) \theta(q V_{FZ} - \omega) \end{aligned} \tag{82}$$

in this approximation. In fact, if one includes collisions, in the normal state

$$\sigma_{xx}^n(q\hat{z}, \omega) \simeq \frac{3ne^2}{8m_{xx}} \int_{-1}^{+1} dx(1-x^2) \left[\frac{2}{(Qx - \omega - i\Omega_c^n)} \right] \tag{83}$$

In the superconducting state, infrared absorption is possible, even at $T = 0$ K, if

$$\omega > [Q^2 x^2 + 4\Delta^2(x)/\hbar^2]^{1/2}, \quad x = \cos \theta \tag{84}$$

when the incident wave is propagating in the direction of the C -axis, as evident from the expression (76). Here, Q is equal to $V_{FZ}q$ in terms of the carrier Fermi velocity V_{FZ} in the direction of the incident e.m. wave. The minimum value of ω for which absorption can take place is determined by the minimum value of the function

$$f(x) = Q^2 x^2 + 4\Delta^2(x)/\hbar^2 \tag{85}$$

If as an illustrative model, we again take the form (40) for $\Delta(x)$, i.e.

$$\Delta(x) = \begin{cases} \Delta(1 - p|x|), & x \leq \frac{1}{p}, \quad p \geq 0 \\ 0, & x > \frac{1}{p} \end{cases} \tag{86}$$

the minimum value of $f(x)$ is obtained for

$$|x|_{\min} = \begin{cases} \frac{1}{p} \frac{p^2 g_i^2}{Q^2 + p^2 g_i^2}, & \text{for } p > p^2 g_i^2 (Q^2 + p^2 g_i^2)^{-1} \\ 1, & \text{for } p \leq p^2 g_i^2 (Q^2 + p^2 g_i^2)^{-1} \end{cases} \quad (87)$$

where

$$g_i^2 \equiv 4\Delta_i^2/\hbar^2. \quad (88)$$

In other words, the minimum value of $f^{1/2}(x)$ is given by

$$f_{\min}^{1/2} = \begin{cases} \frac{g_i}{[1 + p^2 g_i^2 / Q^2]^{1/2}}, & p > p^2 g_i^2 (Q^2 + p^2 g_i^2)^{-1} \\ [Q^2 + g_i^2 (1 - p)^2]^{1/2}, & p < p^2 g_i^2 (Q^2 + p^2 g_i^2)^{-1}. \end{cases} \quad (89)$$

Thus, in such a model, infrared absorption can take place for

$$\hbar\omega \geq \frac{2\Delta_i}{[1 + 4p^2 \Delta_i^2 / \hbar^2 q^2 V_{FZ}^2]^{1/2}} \quad \text{for } p > [1 + \hbar^2 q^2 V_{FZ}^2 / 4p^2 \Delta_i^2]^{-1} \quad (90)$$

or

$$\hbar\omega \geq 2\Delta_i (1 - p) \left[1 + \frac{\hbar^2 q^2 V_{FZ}^2}{4(1 - p)^2 \Delta_i^2} \right]^{1/2} \quad \text{for } p < [1 + \hbar^2 q^2 V_{FZ}^2 / 4p^2 \Delta_i^2]^{-1}. \quad (91)$$

This implies that depending upon the value of the anisotropy parameter p and the ratio $\hbar Q/\Delta_i = \hbar q V_{FZ}/\Delta_i$, the absorption can take place much below the in-plane gap $2\Delta_i$, provided that $2p\Delta_i/(\hbar q V_{FZ})$ is appreciable. In the isotropic case ($p=0$), there is, of course, no absorption below $2\Delta_i$. At finite temperatures, one can get similar results with additional smearing of the structure below $2\Delta_i$, when $2p\Delta_i/(\hbar q V_{FZ})$ is appreciable. More detailed calculations for finite temperatures can be performed numerically, using (59) to (63), which also include weak collision effects in an approximate way. However, the general conclusion regarding the structure below $2\Delta_i$ will be similar. But, for any actual analysis of the experimental data, one may have to take that into account explicitly.

It is clear that (59)–(63) can also be used to calculate infrared absorption when the incident wave is not necessarily along the Z -direction. For example, at $T = 0$ K and $\Omega_c \rightarrow 0$, if the incident wave is propagating along the X -direction (in the plane of the layers) and the wave is polarized either in the Y -direction or the Z -direction, one will get non-vanishing $\sigma_{YY}(q\hat{x}, \omega)$ and $\sigma_{ZZ}(q\hat{x}, \omega)$. The threshold frequency is then determined by the relation

$$\omega \geq \left[V_{FX}^2 q^2 \sin^2 \theta \cos^2 \phi + \frac{4\Delta^2 (\cos \theta)}{\hbar^2} \right]^{1/2} \quad (92)$$

instead of the expression (84). More generally, Δ can, of course, also depend on ϕ .

4. Conclusions and discussion of some experimental results

In this paper, we have considered the problem of calculating thermodynamic quantities like specific heat and nonequilibrium properties like infrared absorption in the

superconducting state of a material with nonspherical Fermi surface and anisotropic energy gap. It has been argued that such an analysis is necessary for layered oxide-superconductors with anisotropic energy gap and very short coherence lengths, if one is interested in any meaningful comparison of experimental results with the predictions of the generalized BCS pairing theory. It is no longer possible to talk in terms of the 3-dimensional isotropic model for the motion of the carriers. Although, as an approximation, isotropy in the plane of the layers may still be used, it has to be necessarily distinguished from the motion of the carriers perpendicular to the layers. The pairing can no longer be described in terms of pure *s*-wave or *p*-wave, etc., since the 3-dimensional orbital *l* is not a good label any more. The gap parameter in general can be highly anisotropic in the **k**-space. For example, $\Delta(\mathbf{k})$ with \hat{k} in the plane of the layers may be much larger than $\Delta(\mathbf{k})$ with \hat{k} perpendicular to the layers. Of course, our consideration of the problem is still within the framework of the mean-field theory for the superconducting transition. The corrections to such an approximation are expected to be small if $(k_F\xi)^2$ is still larger than 10 to 100.

The calculation described in the preceding sections for heat capacity in the superconducting state is based on the fact that at finite temperatures the excited states of the system can be described by excitations of quasi-particles with energies $E_{b\mathbf{k}} = [\xi_{b\mathbf{k}}^2 + \Delta_b^2(\mathbf{k})]^{1/2}$, in the multi-band theory or by $E_{j\mathbf{k}} = [\xi_{j\mathbf{k}}^2 + \Delta_j^2(\mathbf{k})]^{1/2}$ in the multi-layer formulation of the generalized BCS pairing theory. In the multi-layer formulation, the effective electron-electron interaction is obtained explicitly in terms of the 2-dimensional layer-polarization functions $\pi_j(\mathbf{q}_\parallel, \omega)$, and pairing is assumed within the same conducting layer only. Of course, the quantity

$$4\pi\chi_j(\mathbf{q}_\parallel, \omega) = \frac{2\pi e^2}{q_\parallel(q_\parallel L/2)} \pi_j(q_\parallel, \omega) \quad (93)$$

is an approximate projection of the three dimensional-band susceptibility function $4\pi\chi(\mathbf{q}, \omega)$ corresponding to the layer *j*. In an explicit model for $\Delta(\mathbf{k})$ in the form, $\Delta(\mathbf{k}) = \Delta_0(1 - p|\cos\theta|)$, for $|\cos\theta| \leq 1/p$, $p \geq 0$, and $\Delta(\mathbf{k}) = 0$, for $|\cos\theta| > 1/p$, where $\cos\theta$ is the angle between the *z*-direction (*C*-axis) and the unit vector \hat{k} , with the assumption of an ellipsoidal Fermi surface ($m_{zz} \neq m_{xx} \simeq m_{yy}$), the temperature-dependence of the specific heat has been calculated analytically. It is shown that as $T \rightarrow 0$ K, one can get a linear *T*-dependence for $p > 1$, a T^2 -dependence for $p = 1$, and a smeared-out exponential dependence for $p < 1$. For an appreciable value for the gap anisotropy, it would be difficult to distinguish the smeared-out exponential from a power law.

Soon after the discovery of high- T_c superconductivity in oxide materials, it was reported extensively that the low temperature electronic specific heat in their superconducting state shows an unusual linear temperature variation as $T \rightarrow 0$ K. This was taken to be an indication of the failure of the BCS pairing theory for such materials, and the possibility of RVB type of superconductivity in which uncharged "spinons" obeying Fermi statistics were supposed to give the usual linear term in C_s and the charged "holons" obeying Bose statistics were supposed to give superconductivity. The coefficient γ^* in $C_s = \gamma^*T$ was found to be of the order of 1–3 mJ/K² mol in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and of the order of 8 to 10 mJ/K² mol in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123 compound). However, more recent experiments by Eckert *et al* (1988) show that in the 123 compound, the most likely cause for the linear term is due to the presence

of the impurity phase BaCuO_2 which happens to have a large normal state γ . New experiments on most of these compounds and on various Bi and Tl-based superconductors (Chakraborty *et al* 1989; Urbach *et al* 1989; Caspary *et al* 1989) seem to indicate that with a few exceptions which need further studies, most likely value of γ^* is close to zero in all these materials, with an upper limit ranging from $0.2 \text{ mJ/K}^2 \text{ mol}$ to $1 \text{ mJ/K}^2 \text{ mol}$. The difficulty in obtaining good specific heat data to settle this important question whether $\gamma^*=0$ or not, of course, arises due to their extreme sensitivity to material imperfections on the scale of small coherence lengths in these materials. Even if $\gamma^*=0$, the presence of a small T^2 or T^3 term in the intrinsic low temperature electronic specific heat cannot be ruled out experimentally. But, it is quite fair to say that one does not have to abandon the generalized BCS pairing approach to explain such a power-law behaviour. In our explicit model for gap anisotropy discussed earlier, a value of the anisotropic parameter p close to 1 will be sufficient to give such a result. Note that for $\gamma^* \simeq 1 \text{ mJ/K}^2 \text{ mol}$ and the normal state $\gamma \simeq 10 \text{ mJ/K}^2 \text{ mol}$ (as in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$), one needs a value of $p \simeq 1.1$ to fit the data. Although, the available experimental data published in the literature are not of such a quality which can be used to find the value of p or the form of a more general structure of the gap by detailed curve-fitting, because of their dependence on sample preparations, etc., the present indication seems to be that $p < 1$ in most materials. Any deviation from the experimental temperature-dependence of the intrinsic specific heat arises from the smearing of the exponential due to gap anisotropy and from possible impurity contributions remaining after the subtraction of the phonon contribution (T^3 -term).

The calculation for infrared absorption in the superconducting state has been described in this paper only in the limit when the coherence length is small compared to the normal state mean free path, so that the change in the superconducting wave function and vertex corrections to the absorption process due to the impurity scattering, etc., can be ignored. Also, we have ignored the inter-layer or inter-band processes, by finding the electromagnetic response of quasi particles corresponding to a single-layer label j or single-band label b . Of course, this does not imply that interlayer or inter-band interactions are not included in calculating the unperturbed quasi-particle energies and the gap-parameters. Using the model for $\Delta(\hat{k})$ and the Fermi surface similar to that used for the calculation of specific heat, an explicit expression for infrared absorption is obtained in the limit $T \rightarrow 0 \text{ K}$ and the collision frequency $\Omega_c \rightarrow 0$. It is shown that appreciable absorption can take place below the in-plane gap parameter $2\Delta_i$, if the value of the anisotropy parameter p and the ratio $2\Delta_i/\hbar V_{Fq}$ are appreciable. Here, V_{Fq} is the Fermi-velocity of the carriers in the direction of the propagation vector q of the incident infrared wave.

The infrared study of reflectivity in superconducting and normal states of high- T_c materials has been made by many groups. Although, the most extensive experimental work exists on $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the form of single crystal as well as polycrystalline material and oriented thin films, one is not able to agree on any unique value for the energy gap even in 123 compound. Sometimes, one finds two gaps (Wieck *et al* 1989) in polycrystalline samples, in the vicinity of 200 cm^{-1} and 580 cm^{-1} , which are attributed to $2\Delta(\hat{k})$ with \hat{k} along the c -axis and in the a - b plane, respectively. For single-crystals, the a - b plane gap was found to be at about 500 cm^{-1} by Schlesinger *et al* (1987). However, they have found it difficult to obtain a realistic value of the gap parameter along the c -axis in the case of single crystals. In any case, from the

single-crystal reflectivity data, it seems evident that there is always some absorption below the a - b plane gap. Usually, the energy gap is identified approximately by using the Mattis-Bardeen expression for electromagnetic response for an isotropic superconductor, in the dirty limit. This implies large scattering rates, not very consistent with normal state conductivity. We feel that the actual shape of the absorption curve below the in-plane gap arises due to the anisotropy of the energy gap. In our model for the anisotropy, this implies the case in which $2\Delta_i p / \hbar V_{Fq} q$ is appreciable. If two energy gaps in the 123 compound as measured by Wieck *et al* (1989) indeed correspond to the c -axis and a - b plane gaps, it would imply a value of $p \approx 0.65$ in our anisotropy model. However, there may be other valid reasons for the experimental data obtained by Wieck *et al* (1989). At this stage, since there does not seem to be any consensus regarding the exact form of the reflectivity data on single crystals, even with \mathbf{q} perpendicular to the a - b plane, any numerical analysis of the data to obtain the anisotropy parameter p or the general form of $\Delta(\hat{k})$, even in the case of the 123 compound, seems premature.

In conclusion, we have shown that for any realistic analysis of experimental data obtained for finding the nature of various thermodynamic and nonequilibrium properties in single crystals of layered superconductors, it is necessary to include anisotropy of the gap parameter and the nonspherical nature of the Fermi surface while comparing with the predictions of the generalized BCS theory. In an actual comparison, numerical integrations involving more exact treatment of collisions when $ql \lesssim 1$, and the relaxation of the approximation involving dominant contributions coming from close to the Fermi-surface only may also be necessary, while dealing with high- T_c materials with low carrier densities.

Acknowledgements

I am grateful to Dr R T Collins and Dr Z Schlesinger for many helpful discussions regarding the nature of infrared absorption in the new high- T_c materials, while I was visiting IBM Thomas J Watson Research Center in 1988 summer. I shall also like to thank Drs P Bhattacharyya, S K Malik and E V Sampathkumaran of our Institute for many useful discussions.

References

- Abramowitz M and Stegun I A 1968 *Handbook of Mathematical Functions* (Washington DC: NMS) p. 495
 Abrikosov A A and Gorkov L P 1959 *Sov. Phys. JETP* **8** 1090
 Anderson P W 1959 *J. Phys. Chem. Solids* **11** 26
 Anderson P W 1987 *Science* **235** 1196
 Anderson P W, Baskaran G, Zou G and Hsu T 1987 *Phys. Rev. Lett.* **57** 2790
 Batlogg B, Ramirez A P, Cava R J, Van Dover R B, Reitmann E A 1987 *Phys. Rev.* **B35** 5340
 Beyerman W P, Alavi B and Gruner G 1987 *Phys. Rev.* **B35** 8826
 Bulaevskii L N and Kukharensko A Yu 1971 *Sov. Phys. JETP* **33** 821
 Caspary R, Höhr A, Spille H, Steglich F, Schmidt H, Ahrens R, Roth G, Rietschel H, Yan Y F and Zhao Z X 1989 *Europhys. Lett.* **8** 639
 Chakraborty A, Epstein A J, Cox D L, McCarron E M and Farneth W E 1989 *Phys. Rev.* **B39** 12267
 Eckert D, Junod A, Graf T and Muller J 1988 *Physica C* **153-155** 1038

- Ginsberg D M and Hebel L C 1969 *Superconductivity* (ed.) R D Parks (New York: Marcel Dekkar) Vol. 1 p. 193
- Ishikawa M, Takabatake T and Nakazawa Y 1987 *Physica* **B148** 332
- Jha S S 1987 *Pramāṇa – J. Phys.* **29** L615
- Jha S S 1988 *Rev. Solid State Sci.* (Singapore: World Scientific) **2** 307
- Jha S S 1989 in *Studies of high temperature superconductors* (ed.) A V Narlikar (New York: Nova) Vol. 1 p. 41
- Khalatnikov I M and Abrikosov A A 1959 *Adv. Phys.* **8** 45
- Klemm R A, Scharnberg K, Walker D and Rieck C T 1988 *Z. Phys.* **B72** 139
- Mattis D C and Bardeen J 1958 *Phys. Rev.* **111** 412
- Nam S B 1967 *Phys. Rev.* **156** 470
- Phillips N E, Fisher R A, Lacy S E, Morcenatc, Olsen J A, Ham W K, Stacy A M, Gordon J E, Tan M L 1987 *Physica* **B148** 332
- Rickayzen 1965 *Theory of superconductivity* (New York: John Wiley)
- Schlesinger Z, Collins R T, Kaiser D L and Holtzberg F 1987 *Phys. Rev. Lett.* **59** 1958
- Sheplev A G 1969 *Sov. Phys. Vspkhi* **11** 690, and other references in the review article
- Suhl H, Matthias B T and Walker L R 1959 *Phys. Rev. Lett.* **3** 552
- Sulewski P E, Noh T W, Mc Whirter J T, Sievers A J, Russek S E, Buhomann R A, Jec C S, Crow J E, Salomon R E and Myer G 1987 *Phys. Rev.* **B36** 2357
- Urbach J S, Mitzi D B, Kapitulnik A, Wei J Y, Morris D E 1989 *Phys. Rev.* **B39** 12391
- Wieck A D, Batke E, Merk U, Walker D and Gold A 1989 *Solid State Commun.* **69** 553