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J. Phys.: Condens. Matter **2** (1990) 939–951. Printed in the UK

Properties of granular high-T_c superconductors in an effective medium theory

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Received 4 August 1989

Abstract. We consider the transport, electromagnetic and thermodynamic properties of a granular high-T_c superconductor by constructing a model of weakly coupled (Josephson junctions) superconducting and normal grains. We start by using an effective medium theory (EMT), for the conductivity and susceptibility, *which is supplemented by London electrodynamics for the superconducting grains*, in the limit of weak magnetic field and zero transport current. Next we assume a Gaussian distribution of junction resistances R, with mean R_0 and variance $\tilde{\sigma}$, which determines the Josephson coupling energy between grains. The criterion that this energy must be greater than kT for superconducting clusters enables us to determine the superconducting fraction c_S as a function of temperature. With this we complete the determination of the conductivity and susceptibility of our model. We also discuss the specific heat, neglecting fluctuations, which is directly proportional to c_S, in our approximation. Throughout this paper, we adopt the Ginzburg–Landau (GL) expressions for the energy gap Δ (order parameter), which is valid near T_c, and for the specific heat C_H, but we allow for possible deviations of numerical coefficients in these expressions from the Bardeen, Cooper and Schrieffer (BCS) microscopic theory, by introducing phenomenological parameters. We find, in accord with experiments, differences between the temperatures of zero resistivity, of resistivity drop, and for maximum Meissner effect.

1. Introduction

The new oxide high-T_c superconductors $YBa_2Cu_3O_{7-\delta}$ and the related Bi and Tl compounds are polycrystalline due to their chemical natures and to the sintering preparation process [1]. Only recently has there been successful preparation of single crystals, where important measurements of superconducting characteristics have been made [2–5]. Even so, such crystals are often marred by defects, twinning, impurities etc. Whilst recently good single crystals have been made where observed Abrikosov flux lattices are uniform over micrometre scales [6], it is very unlikely that commercial applications of high-T_c superconductors will use other than polycrystalline materials in the forseeable future. This, together with the vast quantity of experimental data that has been gathered over the last two years on polycrystalline materials, urgently calls for the development of an adequate description of the measured properties of the granular material.

In this paper we initiate this task for the important regime near T_c, where the resistivity, susceptibility and specific heat profiles are subjects of many experimental

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investigations [7–10]. We assume that the normal state properties, far above T_c, are adequately described by effective medium theories, as considered by several workers [11–13]. For the present work we shall only consider the case of low applied current and small external magnetic field in order to avoid complications from flux flow, energy gap and phase dependences on fields etc. Our aim is to first establish the basic principles that can qualitatively account for the various measurement profiles near T_c in the zero-field, zero-current limit. We begin in section 2 by reviewing the effective medium theory (EMT), dating back to Garnett, Clausius, Mossotti and Bruggeman [14]. *We will show the necessary modifications when this theory is supplemented by London electrodynamics* [15]. In particular we shall show the consequence of the difference in boundary conditions associated with the electric current $\boldsymbol{J}$ and the magnetic induction $\boldsymbol{B}$ for a superconductor. As we shall see, this leads to a different behaviour for the resistivity compared with the susceptibility since the London penetration length λ plays an important role for the latter. We will also argue that this behaviour will persist even when the EMT is improved by incorporating percolation theory, either via a phenomenological approach [16], or by more sophisticated methods [14].

The EMT theory as constructed here predicts the dependence of the resistivity on the superconducting fraction c_s alone while, as mentioned, the magnetic susceptibility depends both on c_s and also on the temperature T (via λ). Although such a theory would be adequate for *fixed* composites, our model material in fact has a fraction c_s which varies with T due to the weak-link Josephson coupling between grains. In section 3 we shall include this temperature dependence by assuming the criterion that for superconducting clusters the Josephson coupling between grains must exceed kT. We shall argue that once this criterion is met, we can assume perfect phase coherence between grains, i.e. we shall neglect phase dependences. This is valid only because we operate in the regime of weak fields and applied currents as mentioned earlier. The specific heat C_H profile, which we assume to be proportional to c_s, is also plotted. This is added to an artificial linear background for ease of reference with experiments. Throughout this work we shall use the Ginzburg–Landau (GL) [17] expressions for the gap and specific heat jump ΔC. However, we shall include possible departures of the relevant numerical coefficients from the Bardeen, Cooper and Schrieffer (BCS) [18] microscopic theory with the use of phenomenological parameters, until a clearer picture for the mechanism of high-T_c superconductivity emerges [19]. Our results and discussions are presented in section 4 and we shall conclude with several comments on how the present model may be improved, particularly in the situation where there are finite magnetic field and transport current.

2. Effective medium theory

The effective medium theory has a long history, being developed by Maxwell, Garnett and Bruggemann [14] for their study of the electromagnetic properties of heterogeneous media. We shall not review this theory here, as an excellent article has been written by Landauer [14] and the theory further developed by Stroud [20] for transport coefficients in applied fields, e.g. the magnetoresistance. Hence we shall only outline the basic principles and carry out the calculations for the quantities we are interested in for our specific model. We remind the reader that our basic formulation can be carried over to other situations in view of the classic analogies between different quantities in electromagnetism, e.g. the electrostatic displacement $\boldsymbol{D}$, permittivity ϵ, electric field

$\boldsymbol{E}$ (which are static quantities) and the electric current $\boldsymbol{J}$, electrical conductivity σ and electric field $\boldsymbol{E}$ (which are steady-state quantities). Similar analogies apply to magnetic quantities [21]. Care however must be exercised in applying the results of EMT for a superconductor. *Not only are there essential modifications due to London electrodynamics* [15] but, as we shall see, the boundary conditions for $\boldsymbol{J}$ and $\boldsymbol{B}$ now differ in this case. We first remark here that several results in the next two subsections are pedagogical. They can be found in standard textbooks [15, 21–23], but are included here for the convenience of the reader. Experienced readers can go straight to (14) in section 2.1 and (23) in section 2.2.

2.1. *Magnetic permeability and susceptibility*

We shall start by considering the magnetic permeability of a two-component system with one superconducting medium with fraction c_s while the other medium is normal with fraction c_n ($c_s + c_n = 1$). Consider a normal spherical granular inclusion immersed in an effective medium of permeability μ_m. The equations of Maxwell [22], namely

$$\operatorname{div} \boldsymbol{B} = 0 \tag{1a}$$

$$\operatorname{curl} \boldsymbol{H} = 0 \tag{1b}$$

together with the boundary conditions for the continuity of the $\boldsymbol{B}$ and $\boldsymbol{H}$ fields normal and parallel to the boundary surface‡

$$\boldsymbol{B}_\perp \text{ continuous} \tag{2a}$$

$$\boldsymbol{H}_\parallel \text{ continuous} \tag{2b}$$

lead to the following solutions (see figure 1) for the fields $\boldsymbol{H}$ outside and inside the grain:

outside $$\boldsymbol{H} = (H_0 + 2C_m r^{-3}) \cos\theta\, \boldsymbol{a}_r + (-H_0 + C_m r^{-3}) \sin\theta\, \boldsymbol{a}_\theta \tag{3a}$$

and

inside $$\boldsymbol{H} = -A_g \cos\theta\, \boldsymbol{a}_r + A_g \sin\theta\, \boldsymbol{a}_\theta \tag{3b}$$

(see figure 1). The coefficients C_m and A_g which are determined from the boundary conditions (equations (2a) and (2b)) are given by

$$C_m = \left(\frac{\mu_g - \mu_m}{\mu_g + 2\mu_m}\right) a^3 H_0 \tag{4a}$$

$$A_g = -\left(\frac{3\mu_m H_0}{\mu_g + 2\mu_m}\right) \tag{4b}$$

in terms of the permeabilities μ_g and μ_m of the granular inclusion and the medium respectively. H_0 is the external field which is in the direction of the polar axis z. The total flux Φ_g threading the inclusion is therefore given by

$$\Phi_g = \left(\frac{3\pi a^2 \mu_m \mu_g}{\mu_g + 2\mu_m}\right) H_0. \tag{5}$$

‡ As discussed in most textbooks [23], equation (2a) follows from equation (1a) by integrating over the boundary. Equation (2b) follows similarly from equation (1b) and the absence of a surface current j_{surface}.

The above formulae are standard textbook results [21] which can be straightforwardly modified for ellipsoidal inclusions [21]:

$$\Phi_{g\ \mathrm{ellipsoid}} = \frac{\pi b^3 H_0}{\mu_m + (\mu_g - \mu_m)P} \tag{6a}$$

where b is the semi-minor axis of the ellipsoid and the depolarising factor P is given in terms of the eccentricity ε as:

$$P = \frac{1-\varepsilon^2}{\varepsilon^3}\left[\frac{1}{2}\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right) - \varepsilon\right]. \tag{6b}$$

The limiting cases are $P \to 1/3$ for spheres and $P \to 0$ for thin rods. Depolarising factors for spheroids and ellipsoids have been tabulated by, among others, Stoner [24] and Osborn [25].

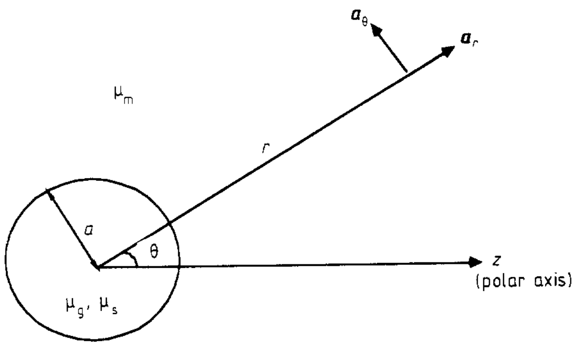

Figure 1. Spherical granular inclusion of radius a and permeability μ_g (normal) or μ_s (superconducting), in an effective medium of permeability μ_m. Various geometrical quantities are defined for use in the text.

Consider now the case when we have a superconducting inclusion with permeability μ_s. We expect that when the temperature $T \ll T_c$, the critical temperature, when there is complete flux expulsion, μ_s and therefore the total flux Φ_s will be zero. The situation changes near T_c, however, as the penetration length λ diverges. In this case we should consider inside the grain the solution of the London equation [15]:

$$\mathrm{curl\ curl}\ \boldsymbol{B} = -(1/\lambda^2)\boldsymbol{B} \tag{7}$$

where λ is the London penetration length†, which diverges at temperature T as

$$\lambda = \lambda_0[1-(T/T_c)^4]^{-1/2}. \tag{8}$$

For $YBa_2Cu_3O_{7-\delta}$, λ_0 is nearly 1400 Å, with T_c about 91.6 K [26]. In fact, outside our superconducting sphere, the solution to equation (7) is similar to that of equation (3a),

† As a matter for future consideration, it may instead be more appropriate for a granular superconductor to take $\lambda = \lambda_J$ (the Josephson penetration length); see [30] later.

but we must now allow for a different integration constant S_m to be determined by the boundary conditions equation (2):

outside $$\boldsymbol{H} = (H_0 + 2S_m r^{-3}) \cos\theta\, \boldsymbol{a}_r + (-H_0 + S_m r^{-3}) \sin\theta\, \boldsymbol{a}_\theta. \tag{9a}$$

Inside our superconducting sphere the solution to equation (7) has been written down by London [15], namely:

inside $$\boldsymbol{B} = u(r) \cos\theta\, \boldsymbol{a}_r + v(r) \sin\theta\, \boldsymbol{a}_\theta \tag{9b}$$

where the functions $u(r)$ and $v(r)$ are given by:

$$u(r) = C_0 \left(\frac{\lambda}{r}\right)^3 \left[\sinh\left(\frac{r}{\lambda}\right) - \left(\frac{r}{\lambda}\right) \cosh\left(\frac{r}{\lambda}\right)\right] \tag{9c}$$

and

$$v(r) = \frac{C_0}{2} \left(\frac{\lambda}{r}\right)^3 \left[\left(1 + \frac{r^2}{\lambda^2}\right) \sinh\left(\frac{r}{\lambda}\right) - \left(\frac{r}{\lambda}\right) \cosh\left(\frac{r}{\lambda}\right)\right]. \tag{9d}$$

Applying the boundary conditions equations (2) to these solutions we easily obtain the following expressions for our integration constants S_m and C_0:

$$C_0 = -3\mu_m H_0 \left(\frac{a}{\lambda}\right) \left[\sinh\left(\frac{a}{\lambda}\right)\right]^{-1} \tag{9e}$$

$$S_m = -\left(\frac{a^3 H_0}{2}\right) \left[1 + 3\left(\frac{\lambda}{a}\right)^2 - 3\left(\frac{\lambda}{a}\right) \coth\left(\frac{a}{\lambda}\right)\right]. \tag{9f}$$

In contrast with equation (5) the total flux threading a superconducting spherical inclusion is thus

$$\Phi_s = 3\pi \mu_m H_0 (a\lambda) G_L(a/\lambda) \tag{10a}$$

where $G_L(x)$ is the well known Langevin function of magnetism given by

$$G_L(x) = \coth(x) - 1/x. \tag{10b}$$

We note that equation (10*a*) tends to zero in the limit of complete flux expulsion $\lambda/a \to 0$, and to equation (11) below in the limit of $\lambda/a \to \infty$ ($T = T_c$), as it must. In the absence of the spherical inclusions the total flux should of course be

$$\Phi_m = \pi a^2 \mu_m H_0. \tag{11}$$

We can now define the flux deviations $\Delta\Phi_g$ and $\Delta\Phi_s$ as

$$\Delta\Phi_g = \Phi_g - \Phi_m \tag{12a}$$

$$\Delta\Phi_s = \Phi_s - \Phi_m. \tag{12b}$$

The principle of zero *average* flux deviations constitutes the effective medium approximation [14]. Thus averaging over grain fractions:

$$(1 - c_s)\Delta\Phi_g + c_s \Delta\Phi_s = 0. \tag{13}$$

We can now apply this result to our model, thus:

$$c_{\mathrm{g}}\left(\frac{\mu_{\mathrm{m}}-\mu_{\mathrm{g}}}{2\mu_{\mathrm{m}}+\mu_{\mathrm{g}}}\right)+c_{\mathrm{v}}\left(\frac{\mu_{\mathrm{m}}-\mu_{0}}{2\mu_{\mathrm{m}}+\mu_{0}}\right)+\frac{c_{\mathrm{s}}}{2}Z_{\mathrm{L}}\left(\frac{a}{\lambda}\right)=0. \tag{14a}$$

Here c_{g} is the fraction of normal grains, c_{s} is the superconducting fraction and now we also include c_{v}, the fraction of voids which we assume to have the permeability of free space μ_0. The experienced reader will recognise this as the standard EMT result, apart from the last term. This term corresponds to the magnetic dipole polarisability of a spherical superconductor. Equation (14) is a quadratic equation for the determination of the effective permeability μ_{m} of the granular composite superconductor in which $Z_{\mathrm{L}}(x)$ is the function

$$Z_{\mathrm{L}}(x)=1-(3/x)\,G_{\mathrm{L}}(x). \tag{14b}$$

However we shall make the simplifying assumption that $\mu_0=\mu_{\mathrm{g}}$ for the rest of this paper, otherwise a separate experimental measurement of μ_{g} for single crystals in the normal phase will also be necessary. We shall leave this as a refinement for the future. With this assumption equation (14a) yields the relative permeability of the granular superconductor as

$$\mu_{\mathrm{s}}=\frac{\mu_{\mathrm{m}}}{\mu_{\mathrm{g}}}=\frac{1-c_{\mathrm{s}}(1+\frac{1}{2}Z_{\mathrm{L}}(a/\lambda))}{1-c_{\mathrm{s}}(1-Z_{\mathrm{L}}(a/\lambda))}. \tag{15}$$

We note the following limiting cases: (i) $\lambda/a\to\infty$ (i.e. $T\to T_{\mathrm{c}}$), $Z_{\mathrm{L}}\to 0$ and (ii) $\lambda/a\to 0$ (i.e. $T\to 0$), $Z_{\mathrm{L}}\to 1$; where the critical (i.e. percolating) fraction $c^{*}_{\mu_{\mathrm{s}}}$ varies from 1 to 2/3 respectively. In section 4 we shall be plotting the relative susceptibility χ_{s} which is sometimes measured

$$4\pi\chi_{\mathrm{s}}=\mu_{\mathrm{s}}-1 \tag{16}$$

where the complete Meissner effect [15] corresponds with $\mu_{\mathrm{s}}=0$ or $\chi_{\mathrm{s}}=-1/4\pi$ as usual [21].

2.2. Resistivity

In view of the analogies mentioned in section 2, the case of electrical transport can be directly transcribed from the last section, for a normal conducting spherical inclusion. We merely replace the magnetic induction $\boldsymbol{B}$ by the steady-state current $\boldsymbol{J}$, the permeability μ_{m} by the electrical conductivity σ_{m} and magnetic field $\boldsymbol{H}$ by the electric field $\boldsymbol{E}$. We also note that the analogous boundary conditions are equivalent to equation (2) in this case, namely:

$$\boldsymbol{J}_{\perp}\ \text{continuous} \qquad \boldsymbol{E}_{\parallel}\ \text{continuous}. \tag{17}$$

We can therefore immediately write down the total current flux threading our normal grain from equation (5) as

$$I_{\mathrm{g}}=\left(\frac{3\pi a^2\sigma_{\mathrm{m}}\sigma_{\mathrm{g}}}{2\sigma_{\mathrm{m}}+\sigma_{\mathrm{g}}}\right)E_0\,. \tag{18}$$

From this ΔI_g follows, analogously to equation (12). One then expects that for a superconducting inclusion, I_s follows from equation (18) by setting $\sigma_g = \sigma_s = \infty$, or equivalently, the resistivity $\rho_s = 1/\sigma_s = 0$. This result is rigorous, in fact, at least at the level of London electrodynamics [15], as opposed to the Ginzburg and Landau [17] theory, where there are effects due to the short coherence lengths. This expression of I_s can be proved easily in the following way. Inside the spherical superconductor the analogous London [15] equation (7) for current density $\boldsymbol{J}$ is

$$\operatorname{curl}\operatorname{curl}\boldsymbol{J} = -(1/\lambda^2)\boldsymbol{J} \tag{19}$$

and therefore the exact solution equations (9*a*–*d*) can be transcribed. We write them here for completeness; they are:

$$\text{outside} \qquad \boldsymbol{E} = (E_0 + 2X_m r^{-3})\cos\theta\,\boldsymbol{a}_r + (-E_0 + X_m r^{-3})\sin\theta\,\boldsymbol{a}_\theta \tag{20a}$$

$$\text{inside} \qquad \boldsymbol{J} = u(r)\cos\theta\,\boldsymbol{a}_r + v(r)\sin\theta\,\boldsymbol{a}_\theta \tag{20b}$$

where the functions $u(r)$ and $v(r)$ have the same form as equations (9*c*–*d*):

$$u(r) = A_0\left(\frac{\lambda}{r}\right)^3\left[\sinh\left(\frac{r}{\lambda}\right) - \left(\frac{r}{\lambda}\right)\cosh\left(\frac{r}{\lambda}\right)\right] \tag{20c}$$

and

$$v(r) = \frac{A_0}{2}\left(\frac{\lambda}{r}\right)^3\left[\left(1 + \frac{r^2}{\lambda^2}\right)\sinh\left(\frac{r}{\lambda}\right) - \left(\frac{r}{\lambda}\right)\cosh\left(\frac{r}{\lambda}\right)\right] \tag{20d}$$

We have deliberately defined different integration constants X_m and A_0 as the boundary conditions do in fact differ from equation (2) or equation (17). They must now be [15]

$$\boldsymbol{J}_\perp \text{ continuous} \qquad \boldsymbol{E}_\parallel = 0. \tag{21}$$

As a result we find that new integration constants are necessary, and equations (9*e*–*f*) cannot therefore be transcribed. Using the new boundary conditions equation (21) we obtain the new constants as

$$X_m = E_0 a^3 \tag{22a}$$

$$A_0 = \left(\frac{3\sigma_m E_0 a^3}{2}\right)\left[\sinh\left(\frac{a}{\lambda}\right) - \left(\frac{a}{\lambda}\right)\cosh\left(\frac{a}{\lambda}\right)\right]^{-1}. \tag{22b}$$

Equations (20*b*–*d*), (22*a*–*b*), together with a simple integration, show that the total current I_s is independent of the London penetration length λ and is identical to equation (18) by setting the resistivity ρ_s to zero, quite unlike equation (10*a*) for the magnetic flux:

$$I_s = 3\pi a^2 \sigma_m E_0 \qquad \text{QED.} \tag{23}$$

The experienced reader will again recognise equation (22*a*) as the induced electric dipole moment of a perfect conductor (i.e. dipole polarisability of unity).

Following equation (13) we easily derive the resistivity ρ_s, a result similar to that given by Davidson and Tinkham [16]:

$$\rho_s/\rho_n = 1 - 3c_s \tag{24a}$$

except that here we have ρ_n which is the normal state resistivity (above T_c) given in terms of the grain resistivity ρ_g by

$$\rho_n = \frac{2\rho_g}{3(1-c_v)-1} \tag{24b}$$

where c_v is, as usual, the fraction of voids, or porosity factor. It follows from equation (24*a*) that the critical fraction for resistivity $c^*_{\rho_s} = 1/3$ *independent* of temperature T, a behaviour significantly different from equation (15).

To conclude this section we note that this difference in behaviour of the resistivity (equations (24)) compared with the permeability (equation (15)) follows directly from the difference in boundary conditions equation (21) compared with equations (2) and (17). As such this difference is no artefact of the EMT but will occur in any higher order approximations, for e.g. Lord Rayleigh's [27] regular lattice sum, or with numerical calculations [28]. Our results so far are derived using London electrodynamics alone, and the direction in which this can be improved will be discussed in section 4. Our remaining task is to develop a model for weak links that would give c_s as a function of $T - T_c$.

3. Weak-links and the superconducting fraction c_s

To obtain c_s, we envisage that grains are coupled by the Josephson energy [29] E given by

$$E = \left(\frac{\pi\hbar}{4e^2R}\right)\Delta \tanh\left(\frac{\Delta}{2kT}\right) \tag{25}$$

where R is the junction resistance, and Δ the energy gap function [18] at the temperature T, the other physical constants having their usual meaning. Here we have neglected the Josephson cosine factor [30] which involves superconductor phases, by considering the zero-field, zero-current limit. As is well known, the tunnelling current between grains is proportional to the sine of their phase differences [30]. We further neglect any capacitative or inductive effects† [31]. From equation (25) we easily obtain the criterion for superconductivity, or phase coherence between two grains: the coupling energy E must be greater than kT. This demands that

$$R < R_m \tag{26a}$$

where R_m in ohms is given by

$$R_m = 1613.3\delta^2(1 - T/T_c). \tag{26b}$$

† This depends, among other things, on the intrinsic grain permittivity ϵ_g and permeability μ_g which we have neglected; see section 2.1.

Here we have adopted the GL expression for the gap function:

$$\frac{\Delta}{kT_c} = \delta \left(1 - \frac{T}{T_c}\right)^{1/2} \tag{27}$$

where, according to the BCS theory [18] δ is about 3.06, but we shall leave it as a phenomenological parameter [19]. In equation (25) R depends on the distribution of junction resistances. This distribution $p(R)$ of junction resistances will depend on the morphology of the grains, the level of contamination or segregation or composition change close to the contact, and on other factors. There is an upper value of R, characterised by 1613.3 δ^2 Ω, (see equation (26*b*)) which we need to bear in mind. For the distribution $p(R)$ we shall use as a model a truncated Gaussian distribution, defined over the infinite half interval. We expect the detailed shape of the distribution to be unimportant, but rather that the mean and spread will be critical. Thus the distribution of resistances $p(R)$ is taken to be

$$p(R) = \frac{N_s}{\tilde{\sigma}\sqrt{2\pi}} \exp\left(-\frac{(R - R_0)^2}{2\tilde{\sigma}^2}\right) \tag{28}$$

where the normalisation constant N_s can be easily written down in terms of error functions [32]. From these expressions we can obtain c_s

$$c_s = \int_0^{R_m} \mathrm{d}R\, p(R). \tag{29}$$

Having obtained the fraction c_s we can now substitute it in the formulae f our EMT (see section 2) to predict the magnetic and electrical properties. Before giving the results, we shall also discuss the behaviour of the specific heat, albeit only qualitatively see section 3.1

3.1. Specific heat

Several controversies exist concerning the nature of the specific heat singularity(-ies) near T_c for single crystals [33]. They still remain to be resolved by experiments and theory, even at the phenomenological level [33]. As such our discussions here can only be qualitative, as the results will depend very much on the experimental resolution and sample characteristics. We include them, however, in order to obtain a flavour of what is predicted from our present theory. We first note that the tiny grain specific heat is generally well rounded [34], for grain radius $a \ll \xi$, the coherence length, and it does not show the famous BCS jump [18] which is given by

$$\Delta C = \nu C_n(T_c) \tag{30}$$

with ν =1.43, where $C_n(T_c)$ is the (normal) electronic specific heat at T_c. As in section 3, equation (27), for the energy gap Δ, we leave ν as a phenomenological parameter [19, 33] that may be varied. For our case where $a \gg \xi$, however, we expect that individual grains, when superconducting, will contribute the macroscopic GL specific heat which is given by

$$C_{GL} = \Delta C(T/T_c) \tag{31}$$

for zero current and magnetic fields, and sufficiently far from T_c that fluctuations in the order parameter are neglected. Therefore in this approximation, the specific heat C_H is related directly to the fraction c_s via

$$\frac{C_H}{C_n(T_c)} = (\nu c_s + \alpha)\left(\frac{T}{T_c}\right) \tag{32}$$

where we have added a linear background slope α to mimic the lattice and other contributions, for comparison with experiments.

We expect this to be a good qualitative feature of the specific heat for granular superconductors down to resolutions of between 0.5 and 1.0 K for grain sizes $a \gg \xi$. This resolution is limited by the fluctuation region, as given by the Ginzburg [35] and Brout [36] criterion. Unfortunately there exists the as yet unresolved question of the specific heat double transition [10, 33] and possible twin plane contributions [37], with a width of over 3 K. This complicates comparisons between our model and experiments, as there exists evidence that specific heat features due to the possible double transition are not being averaged out even for polycrystalline samples [10, 33, 38]. As such our results for the specific heat presented here are only qualitative at this stage, subject to refinement, until the above controversies are resolved.

4. Results and discussions

In figure 2(*a*) we have plotted the normalised resistivity, equation (24*a*), the relative susceptibility, equation (16), and the superconducting fraction c_s, equation (29), for the parameters $\delta = 3.06$ (BCS), $\sigma = 100\ \Omega$, $R_0 = 500\ \Omega$, $c_v = 0.2$ (20% porosity). The general features of these results agree very well with several experiments [8–10]. We have also plotted the specific heat, using $\nu = 1.43$ (BCS), in figure 2(*b*) for the same set of parameters. In figure 3 we have plotted the same results for a different set of parameters. We observe that the temperatures T_{c0}, T_{c1} and T_{c2}, as defined in our figures, are higher for figure 3. The shapes of the curves are, however, similar in both. This feature is not surprising since they are characteristics of EMT. We expect that although precise values for T_{c0}, T_{c1} and T_{c2}, as well as the power laws near these temperatures, are unlikely to be accurate within EMT [28], the general trend, like their ordering relative to the bulk T_c, will persist even for more sophisticated theories than EMT (see section 2.2). These figures are the main results of this paper.

Let us conclude this section by discussing the various improvements to our present theory. We will discuss them in what we view as their order of significance. Firstly an improvement over EMT is important for more quantitative predictions, in view of its performance being poorer (more so in three dimensions than in two) than percolation theory [28]. Davidson and Tinkham [16] have discussed a phenomenological formula that fits experiments. We will not discuss their approach here, except to mention that it constitutes an *ad hoc* adjustment of the critical threshold c_s^*, based on a one-term Padé approximant. It relies, however, on an unproved assumption for the universality of c_s^*. Incorporating this into our equation (24*a*) is straightforward. This is not so obvious for our equation (15), which requires further investigation. In any case such an approach will only be fruitful if it is supplemented with numerical calculations or cumulant expansion studies [28, 39]. The next improvement concerns the separate way in which London electrodynamics, section 2, is merged with the weak-link model,

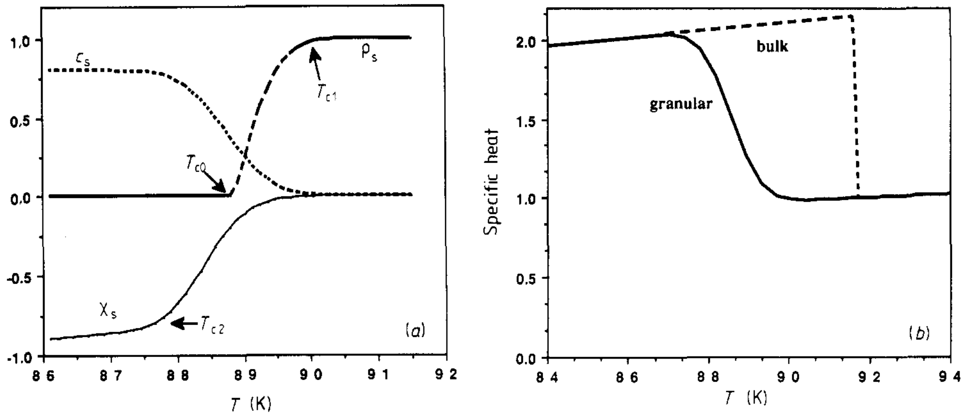

Figure 2. (*a*) Plot of resistivity ρ_s, susceptibility χ_s and superconducting fraction c_s against temperature T for a model sample with the following parameters (see text): $R_0 = 500\ \Omega$, $\tilde{\sigma} = 100\ \Omega$, $\delta = 3.06$, $T_c = 91.6$ K and 20% porosity. T_{c0} is the temperature where zero resistivity occurs, T_{c1} is where resistivity drop occurs and T_{c2} is the temperature of maximum Meissner effect. (*b*) Plot of the specific heat C_H against temperature for the same model sample as in (*a*). The parameter $\nu = 1.43$, taken from the BCS theory (see text), affects only the magnitude of the jump, which is also added to an arbitrary linear background for ease of comparison with experiments.

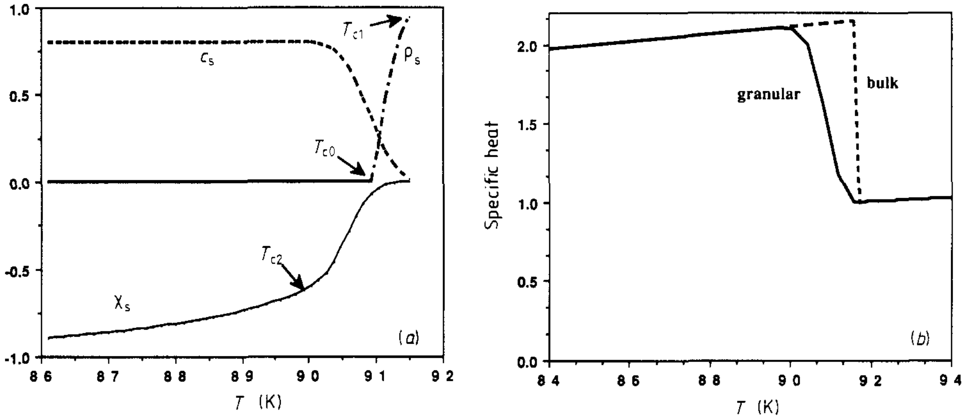

Figure 3. (*a*) Similar plot to figure 2(*a*) but for a different model sample with the following changes in parameters: $R_0 = 1000\ \Omega$, $\tilde{\sigma} = 500\ \Omega$, $\delta = 9.0$; the others remaining as before. Notice the much sharper resistivity drop but still a slow saturation of the susceptibility to maximum Meissner effect. (*b*) Similar plot to figure 2(*b*) for the model sample of figure 3(*a*). Notice the steeper roll over for this curve that is beginning to look like a jump.

section 3. They appear as separate entities in our present theory. An approach to unify both sections must involve a GL free energy functional [40] which has weak-link terms. To develop a new unified EMT based on a variational principle appears to be possible. Certainly such a theory will be able to clarify the role of the short coherence lengths and to deal with finite currents and magnetic fields. Finally, anisotropy of the various superconducting parameters as well as of transport coefficients must also be considered. In this respect, one could consider ellipsoidal inclusions or plates with tensor conductivities and susceptibilities. This last improvement is quite straightforward for the present theory, which we leave as an exercise for the reader.

5. Conclusions

In conclusion we have developed an effective medium theory (EMT) for the magnetic susceptibility and electrical conductivity appropriate for granular high-T_c superconductors. We also predict the rounding of the specific heat jump by directly relating it to the superconducting fraction c_s which has been obtained via a simple criterion that the weak-link coupling energy E be greater than kT. Our central theme is to supplement conventional EMT [14] with London electrodynamics for superconducting grains. We find that new features follow directly from the solution of London's equation for a sphere [15] and the difference in boundary conditions between the magnetic fields and electric fields for the superconductor. Since these new features are quite independent of EMT, they will also exist for higher order approximations beyond EMT or in numerical calculations [28]. The simplicity of our approach and its agreement with published data on $YBa_2Cu_3O_{7-\delta}$ makes this an attractive theory which can further be improved in several ways as outlined in section 4. There we proposed several extensions of the present theory, while maintaining its attractive features. Needless to say the development of theoretical models such as ours is a necessary tool for the processing and commercial application of high-T_c superconductors. In addition such a tool is also valuable for the interpretation of experiments that probe the mechanism of high-T_c superconductivity. Finally we note that a natural extension of our EMT to finite frequencies also predicts other interesting properties like the microwave absorption spectra in the cm region, where the magnetic susceptibility is known to play a crucial role [41]. Details of this will be published elsewhere.

Acknowledgments

This work was undertaken as part of the Underlying Research Programme of AEA Technology. One of us (TC) would like to thank P Sen for earlier discussions which led to this work.

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