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Mott insulator–high T_c bipolaronic superconductor transition in cuprates

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All 'undoped' cuprates are antiferromagnetic Mott insulators. We argue that with doping they remain insulators including the 'overdoped' samples. Hence, there is no clear dividing line between non-metallic cuprates and high-temperature superconductors. Based on the generic Hamiltonian including the electron–phonon interaction and the direct Coulomb repulsion the ground state of doped cuprates is shown to be a charged $2e$ Bose liquid of small bipolarons. A theory of the normal state transport of copper oxides is developed. The temperature dependence of the resistivity and of the Hall effect agrees remarkably well with the experimental data in $La_{2-x}Sr_xCuO_4$ for the entire temperature regime including unusual 'logarithmic' low-temperature region. The violation of Kohler's rule in magnetoresistivity is explained. The resistive and thermodynamic superconducting transitions in a magnetic field are quantitatively described.

Keywords: bipolarons; insulator–superconductor transition; cuprates; Mott insulators

1. Introduction

Are the high-T_c materials metals? The answer to this question depends on how one defines a metal (Mott 1996, personal communication). To give a definite answer one has to extrapolate the conductivity to zero temperature. Metals show the finite low-temperature conductivity while this conductivity is zero in non-metals. With this definition, of course, any superconductor must be a metal, because the conductivity at $T = 0$ is infinite. Fortunately, one can destroy the superconducting state by an external magnetic field to measure a 'true' normal state conductivity up to a very low temperature. The experiment has recently been done by applying a pulsed 61 T magnetic field (Ando *et al.* 1995; Boebinger *et al.* 1996). The underdoped and optimally doped high-T_c cuprates studied so far appear to be doped three-dimensional insulators with the divergent resistivity at low temperatures. This observation as well as many others support a large body of opinions which believes that high-temperature superconductivity, first discovered in cuprates by Bednorz & Müller (1986), is linked to small polarons and bipolarons (see, for example, Müller 1995; Salje *et al.* 1995) proposed by us as a possible explanation of high-T_c phenomenon (Alexandrov 1987). The bipolaronic 'scenario' for high-T_c cuprates is based on the fact that 'undoped' cuprates have normally one hole per unit cell in the copper–oxygen plane. If the electron–electron interaction and a lattice distortion due to the electron–phonon coupling were weak, these compounds would be Fermi liquids. In fact, they are Mott insulators and remain to be insulators if doped which leads to the polaronic and bipolaronic carriers.

The concept of polarons was introduced into physics by Landau (1933), who pointed out that an electron in the conduction band of a non-metallic ionic crystal could be trapped by 'digging its own potential hole'. Mott (1973) discussed a degenerate gas of small polarons while Alexandrov & Ranninger (1981) introduced the idea of small mobile bipolarons into the theory of superconductivity. Carriers are polarons in many doped semiconductors which may be envisaged as mobile clusters of the lattice deformation (*dielectric* polarons) and (or) of magnetic moments oriented in the opposite direction to that of the carrier (*spin* polarons). The Fermi-liquid behaviour is destroyed by the strong electron–phonon and electron-spin fluctuation interactions due to the polaron collapse of the band resulting in the non-adiabatic heavy carriers. The ground state of such carriers appears to be a bipolaronic charged Bose liquid if the coupling with phonons (the BCS coupling constant) $\lambda \geqslant 0.5$ (Alexandrov & Mott 1995). The strong electron–electron correlations play important role in the polaron formation decreasing the bare bandwidth and therefore increasing λ. This conclusion is perfectly confirmed by the numerical calculations within the Peierls–Hubbard and Holsten t–J models (Bishop & Salkola 1995; Fehske *et al.* 1995). We believe that (bi)polarons are a key element for the understanding of the unusual normal and superconducting state properties of cuprates and doped fullerenes (Alexandrov & Mott 1994). In this paper I discuss the normal state transport and the superconducting transition of cuprates considering them as doped insulators with the bipolaronic carriers partly localized by disorder.

2. Normal state bipolaron kinetics of high-T_c cuprates

(*a*) *Temperature dependence of the Hall effect and resistivity*

The absolute value and the temperature dependence of the in-plane and c-axis resistivity as well as of the Hall effect are recognized as the key to our understanding of the high-T_c phenomenon (Anderson 1995; Alexandrov & Mott 1994). They do not agree with any Fermi-liquid description. To meet this challenge some authors alleged the spin-charge separation abandoning the Fermi-liquid and Boltzmann approach.

However, there is no need to abandon the Boltzmann kinetics to explain the linear in-plane resistivity and the temperature dependent Hall effect above T_c in cuprates if the bipolaron theory is applied. A fraction of bipolarons is localized by disorder, so that the number of *delocalized* carriers is proportional to T while the boson–boson inelastic scattering rate is proportional to T^2. This allows us to explain that both the in-plane resistivity and the Hall density are proportional to T (Alexandrov *et al.* 1994). Recently we have extended the theory towards low temperatures (Alexandrov 1997) where the transport relaxation time of bipolarons is determined by the elastic boson-impurity scattering and single polarons are frozen out. The temperature dependence of the resistivity appears to be in a remarkable agreement with the experimental dependence measured in $La_{2-x}Sr_xCuO_4$ by suppressing T_c down to a mK scale with a pulsed magnetic field.

The low-energy state of cuprates is a mixture of the intersite in-plane singlet pairs (small bipolarons) and thermally excited polarons. Above T_c, which is the condensation temperature of the charged Bose-gas, these carriers are non-degenerate. Intersite singlets tunnel along the planes with an effective mass m_{ab}^{**} of the order of a single-polaron mass (Alexandrov 1996). Their c-axis tunnelling involves the simultaneous hopping of two holes. Therefore the singlet c-axis mass is strongly

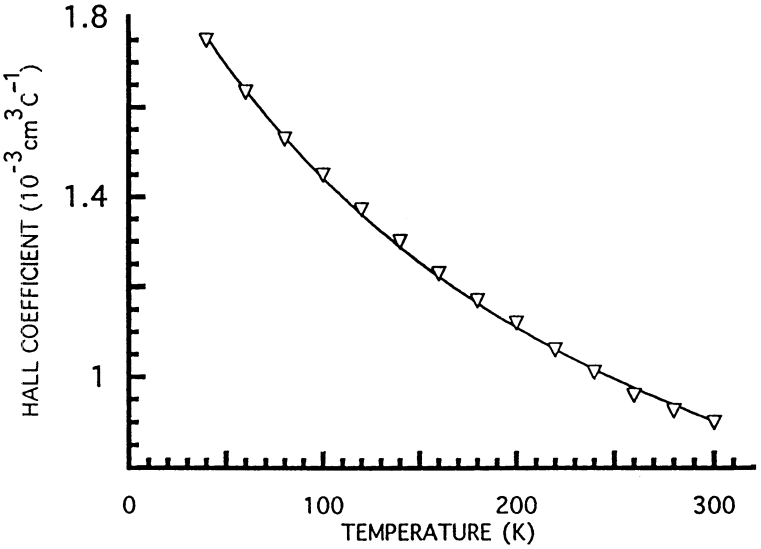

Figure 1. The Hall effect in $La_{2-x}Sr_xCuO_4$ (triangles (Hwang *et al.* 1994)) described by the theory (solid line) for $x = 0.15$.

enhanced, $m_c^{**} \gg m_{ab}^{**}$, which leads to a large transport anisotropy at low temperatures when polarons are frozen out. However, at temperatures below the c-axis bipolaron bandwidth we expect a three-dimensional anisotropic energy spectrum and a three-dimensional scattering of bipolarons dominated by the lattice defects and impurities. The number of extended bosons $n_b(T)$ above the mobility edge is determined in the 'single-well–single-particle' approximation as (Alexandrov *et al.* 1994)

$$n_b(T) = \tfrac{1}{2}x - n_L(T), \tag{2.1}$$

where $\frac{1}{2}x$ is the total number of pairs, and $n_L(T) \simeq n_L - N_L(0)T$ is the number of bosons localized by the random potential with $N_L(0)$ the density of localized states near the mobility edge. The Hall coefficient R_H measures the inverse carrier density, so that

$$\frac{R_H}{R_{H0}} = \frac{1}{1 + T/T_L}, \tag{2.2}$$

where $T_L = (x - 2n_L)/2N_L(0)$. This simple expression fits well to the Hall coefficient temperature dependence of $La_{2-x}Sr_xCuO_4$ at optimum doping ($x = 0.15$) as shown in figure 1 with $T_L = 234$ K and the constant $R_{H0} = 2 \times 10^{-3}$ cm^3 C^{-1}. If the total number of carriers $\frac{1}{2}x$ is above the total number of the potential wells n_L, which is assumed here, the carrier density is practically temperature independent at low temperatures. Hereafter, $\hbar = k_B = 1$.

The normal state of the bipolaronic superconductor is reminiscent to that of a non-degenerate semiconductor. The characteristic kinetic energy of carriers appears to be of the order of the temperature rather than of the Fermi energy of usual metals. The most effective scattering at low temperatures is then caused by the attractive shallow potential wells which for slow particles is described by the familiar Wigner resonance cross-section (see, for example, Landau & Lifshitz 1991)

$$\sigma(E) = \frac{2\pi}{m}\frac{1}{E + |\epsilon|}. \tag{2.3}$$

Here

$$\epsilon = -\tfrac{1}{16}\pi^2 U_{\min}\left(\frac{U}{U_{\min}} - 1\right)^2, \tag{2.4}$$

is the energy of a shallow virtual ($U < U_{\min}$) or real ($U > U_{\min}$) localized level, U the well depth and $U_{\min} = \pi^2/8ma^2$ with the well size a. The transport relaxation rate is the sum of the scattering cross-sections from different potential wells within the unit volume multiplied by the velocity $v = \sqrt{2E/m}$. There is a wide distribution of potential wells with respect to both U and a in real cuprates. Therefore, one has to integrate the Wigner cross-section, equation (2.5), over U and over a. By doing the integration over U we take into account only shallow wells with $U < U_{\min}$ because the deeper wells are occupied by localized carriers and cannot yield a resonant scattering. The result for the inverse mean free path is

$$l^{-1}(E) = \frac{n_{\rm L}}{A}\int_{a_{\min}}^{\infty}\langle\sigma(E)\rangle\,{\rm d}a \simeq \frac{\pi^2 N_{\rm L}(0)}{mA\sqrt{2mE}}\ln\frac{E_0}{E}, \tag{2.5}$$

for $E \ll E_0$. Here A is the width of the size distribution of the random potential, $N_{\rm L}(0) \simeq n_{\rm L}/\gamma$, $E_0 = \pi^4/128ma_{\min}^2$ and $a_{\min}$ is the minimum size. We expect a very large value of A of order of a few tens of Å due to the twin boundaries and impurity clusters in real cuprates which are not screened. On the other hand, single impurities are screened. A simple estimate of the screening radius yields a value of $a_{\min}$ of the order of the interatomic spacing (approximately 1.9 Å), which corresponds to a quite large $E_0 = 1500\,{\rm K}$ if $m = 10m_{\rm e}$. As a result, in a wide temperature range we arrive at the logarithmic transport relaxation rate as

$$\frac{1}{\tau} \equiv vl^{-1}(E) = \frac{1}{\tau_0}\ln\frac{E_0}{E}, \tag{2.6}$$

where $\tau_0 = m^2A/\pi^2N_{\rm L}(0)$ is a constant. Because the Wigner formula is somewhat more general than the assumption made in its derivation we expect that the obtained logarithmic dependence is not changed if the random potential is modified and the energy spectrum is highly anisotropic under the condition that we take $m = m_{ab}^{**}$.

The low-temperature resistivity is now derived by the use of Boltzmann theory as

$$\rho(T) = \rho_0\ln\frac{E_0}{T}, \tag{2.7}$$

where $\rho_0^{-1} = 2(x - 2n_{\rm L})e^2\tau_0/m$. At high temperatures the inelastic scattering of extended bosons by localized bosons becomes important so that

$$1/\tau = \alpha T^2, \tag{2.8}$$

with the constant, α, proportional to the density of states at the mobility edge, $N_{\rm L}(0)$ squared. Combining both elastic, equation (2.6), and inelastic, equation (2.8), scattering, and taking into account the temperature dependence of the extended boson density $n_{\rm b}(T)$, equation (2.1), we arrive at

$$\frac{\rho(T)}{\rho_0} = \frac{\ln(E_0/T) + (T/T_B)^2}{1 + T/T_{\rm L}}, \tag{2.9}$$

with the constant $T_{\rm B} = 1/\sqrt{\alpha\tau_0}$. The solid line in figures 2 and 3 is a fit to the experimental data with $\rho_0 = 7.2\times10^{-5}\,\Omega\,{\rm cm}$, $E_0 = 1900\,{\rm K}$ and $T_{\rm B} = 62\,{\rm K}$ which appears to be remarkably good. The value of E_0 agrees well with the estimate above.

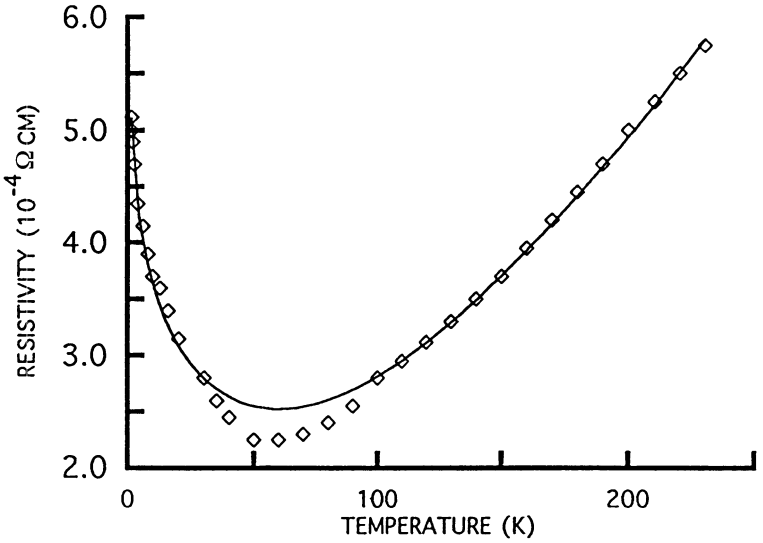

Figure 2. The 'ab' resistivity of $La_{2-x}Sr_xCuO_4$ with $x = 0.13$ (diamonds (Ando *et al.* 1995)) described by the theory in a wide temperature range (solid line).

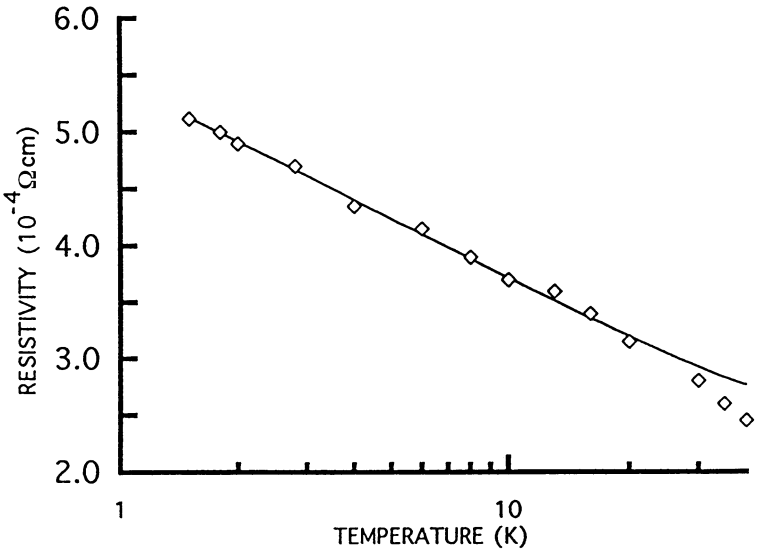

Figure 3. The same as in figure 2 at low temperatures.

Because the bipolaron energy spectrum is three dimensional at low temperatures, there is no temperature dependence of the anisotropy ρ_c/ρ_{ab} at low T as observed.

The crucial point of our theory is that polarons dominate in the c-axis transport at intermediate and high temperatures because they are much lighter in the c-direction than bipolarons. Along the planes they propagate with about the same effective mass as singlets. Therefore their contribution to the ab transport is small at any temperature due to their low density compared with the bipolaron one. As a result we have a mixture of the *non-degenerate* quasi-two-dimensional spinless bosons and the thermally excited fermions, which are capable of propagating along the c-axis. Only polarons contribute to the spin susceptibility and to the c-axis transport if the

temperature is not very low which leads to a simple fundamental relation explaining the anisotropy, the magnetic susceptibility and a so-called normal state 'pseudo-gap' (Alexandrov *et al.* 1996*a*).

(*b*) *Violation of Kohler's rule*

The bipolaron theory provides the most natural microscopic explanation of the anomalous magnetoresistance (MR) observed by Harris *et al.* (1995).

Because within our approach, high-T_c cuprates are doped semiconductors with the non-degenerate carriers above T_c the weak-field MR is described by the classical formula (Anselm 1962), $\Delta\rho/\rho = KH^2/\rho^2$, with the slope

$$K = \beta R_H^2, \tag{2.10}$$

and

$$\beta \equiv \frac{\Delta\rho}{\rho\Theta_H^2} = \frac{\langle\tau_{tr}^3\rangle\langle\tau_{tr}\rangle}{\eta\langle\tau_{tr}^2\rangle^2} - 1. \tag{2.11}$$

Here $\langle\cdots\rangle$ means an average with the Boltzmann distribution function, for instance $\langle\tau_{tr}\rangle = \int dE\, N(E)E\tau_{tr}(E)\exp(-E/T)$, $N(E)$ the density of states and $\eta = 4m_x^{**}m_y^{**}/(m_x^{**}+m_y^{**})^2$ describes the in-plane anisotropy of the bipolaron energy spectrum as derived by Alexandrov (1996). For a low amount of disorder we expect $\eta = 0.64$ due to a difference in $pp\pi$ and $pp\sigma$ 'oxygen–oxygen' hopping integrals, while in strongly disordered cuprates η might be significantly smaller. By the use of the ratio of the chemical and Hall carrier densities we found $\eta \leqslant 0.1$ in the overdoped $La_{2-x}Sr_xCuO_4$. The inelastic scattering rate of delocalized carriers by localized ones is proportional to the square of the phase volume available for the scattering, so that $\tau_{tr} \sim (T+E)^{-2}$ if the density of states $N(E)$ near the mobility edge is about constant as discussed above. As a result, one obtains $\beta = [9\, eEi(-1)/20\eta(1+2\, eEi(-1))] - 1$, where $eEi(-1) \simeq -0.596$. This yields the temperature independent constant $\beta \simeq 1.2$ with $\eta = 0.64$ and $\beta \simeq 13.0$ with $\eta = 0.1$ which is fairly close to the observed values, $\beta \simeq 1.5$–1.7 in $YBa_2Cu_3O_{7-\delta}$ and $\beta \simeq 13.6$ in $La_{2-x}Sr_xCuO_4$. By taking into account the Anderson localization the Hall 'constant' is given by $R_H \sim 1/T$ well above T_c as shown above. Then equation (2.10) provides a parameter-free fit to the experimental data, figure 4, explaining the violation of Kohler's rule.

3. Thermodynamic versus resistive transition in a magnetic field

The bipolaron theory (Alexandrov 1993) has successfully predicted the divergent resistive $H_{c2}(T)$ on cooling (see, for example, Alexandrov *et al.* 1996*b*; and references therein). Further evidence for the charged 2e Bose-liquid was provided by the quantitative mapping of the specific heat of several high-T_c cuprates in zero magnetic field to the λ curve of He^4 (Alexandrov & Ranninger 1992). By applying the bipolaron theory one can explain a startling behaviour of the thermodynamic phase transition in a magnetic field contrasting with the resistive transition (Alexandrov *et al.* 1997).

In a BCS superconductor there is a well-defined step in the specific heat at the transition temperature, this transition temperature tracks the sharp resistive transition in all magnetic fields. For most HTSCs in zero magnetic field, there is also a well-defined λ-type peak in the specific heat at the resistive transition temperature. However, as shown in the comprehensive experimental study by several groups (for a review see Marcenat *et al.* 1995) the effect of magnetic field on the specific heat

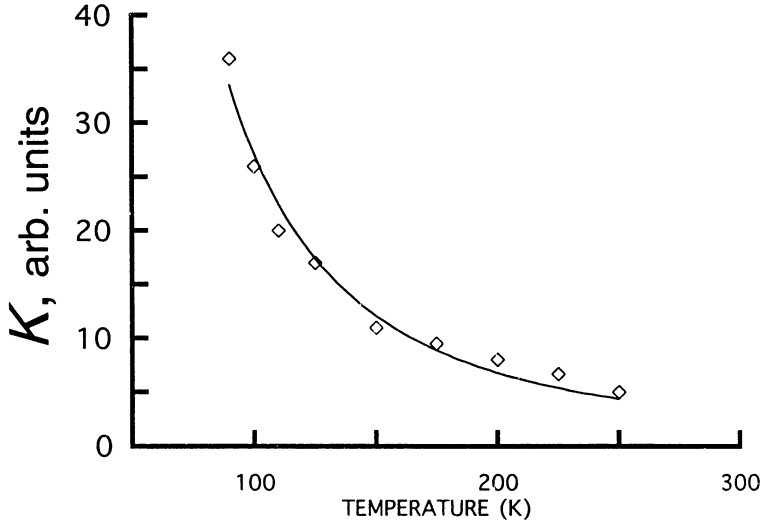

Figure 4. The temperature dependence of the slope, K, violating Kohler's rule as measured experimentally by Harris *et al.* (1995) (points) and described by the bipolaron kinetics (line).

anomaly is to reduce the peak height but leaving its position largely unchanged. The peak in specific heat is usually associated with critical fluctuations. This viewpoint is reinforced when the behaviour is compared with that of liquid helium-4. On the other hand the resistive transition shows practically parallel shift towards lower temperatures in the Lorentz-force free geometry (Alexandrov *et al.* 1996*b*). Consequently in high-T_c cuprates, the resistive behaviour does not correspond to that of the specific heat, except for zero magnetic field. Moreover, applying the canonical fluctuation theory based on the Ginsburg–Landau (GL) free energy one arrives at a quite meaningless value of the zero-temperature coherence length, which appears to be of the same order as the wavelength of holes or even less, hence invalidating the main assumption of the GL and BCS theory.

We argue that the superfluid transition temperature in cuprates is given by the resistive measurements and that the specific-heat anomaly owes its origin to a kink in the chemical potential. In the following we show that a weakly interacting charged Bose gas (CBG) in a magnetic field has precisely the property which reproduces both the specific heat and the resistive transition of cuprates. The value of the chemical potential is governed by the total density sum rule

$$n_b = \int d\epsilon\, \rho(\epsilon) f(\epsilon), \tag{3.1}$$

where $\rho(\epsilon)$ is the density of states and $f(\epsilon)$ is the Bose–Einstein distribution function,

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/T] - 1}. \tag{3.2}$$

The specific heat can be calculated from the derivative of the energy,

$$C(T, H) = \frac{d}{dT} \int d\epsilon \frac{\rho(\epsilon)\epsilon}{\exp[(\epsilon - \mu)/T] - 1}. \tag{3.3}$$

The result is

$$C(T, H) = \frac{\langle \epsilon^2 \rangle}{T^2} - \frac{\langle \epsilon \rangle^2}{T^2 \langle 1 \rangle}, \tag{3.4}$$

where

$$\langle \epsilon^x \rangle = -T \int \mathrm{d}\epsilon \rho(\epsilon) \frac{\partial f(\epsilon)}{\partial \epsilon} \epsilon^x, \tag{3.5}$$

We note that the specific heat calculated from equation (3.4) is invariant to a shift in the energy, $\epsilon \to \epsilon + \epsilon_0$ as it should be.

For a system of ideal bosons the density of states (DOS) is given by

$$\rho(\epsilon) = \frac{m^{3/2}\sqrt{\epsilon}}{\sqrt{2}\pi^2}, \tag{3.6}$$

where $m = ((m_{ab}^{**})^2 m_c^{**})^{1/3}$. With magnetic field perpendicular to the planes the bosons are quantized into Landau levels with the associated DOS,

$$\rho(\epsilon, H) = \frac{m^{3/2}\omega_H}{2\sqrt{2}\pi^2} \sum_{n=0}^{\infty} [\epsilon - \omega_H(n + \tfrac{1}{2})]^{-1/2}, \tag{3.7}$$

where $\omega_H = 2eH/m_{ab}^{**}$ is the cyclotron frequency.

The difference between the effect of the magnetic field on resistivity and on the specific heat becomes transparent if we calculate the specific heat in the presence of magnetic field. For an ideal CBG the Landau energy levels are essentially one dimensional. Thus there is no Bose–Einstein condensation in a magnetic field, and the resistive transition is immediately suppressed such that $T_c(H) = 0$ for all H. We deliberately retain the features of the non-interacting charged Bose gas which prevents Bose–Einstein condensation to investigate the behaviour of the specific heat in the absence of a condensate. This is to test our premise that the specific heat in a finite magnetic field is unrelated to the condensate formation.

The numerical calculations of the chemical potential μ, equation (3.1) and the specific heat, equation (3.4) with the exact DOS, equation (3.7) for several relative values of the magnetic field are presented in figures 5 and 6. The characteristic temperature at which the chemical potential changes its slope remains about $T_{c0} = 3.31 n_b^{2/3}/m$ as long as $\omega_H \ll T_{c0}$. Therefore, the position of the specific-heat anomaly remains largely unaffected by the moderate magnetic field, figure 6. The suppression of the maximum value of $C(T, H)$ goes as the *square root* of the magnetic field, thus even a moderate magnetic field can produce a sizable change in the value of the specific heat at $T = T_{c0}$ without any appreciable change in the peak position. On a quantitative level one can compare the theoretical change in the specific heat $C(T, H) - C(T, H_1)$ with the experimental one thus eliminating all field-independent contributions, e.g. the lattice specific heat. A parameter-free fit to the experimental data for mercury-1223 is shown in figure 7 with $H_1 = 7$ T and the in-plane bipolaron mass $m_{ab}^{**} = 17.1 m_e$. The effective mass and the number of bosons n_b affect only the absolute values of $C(T, H) - C(T, H_1)$ and $C(T, H)$ with a little effect on the anomaly shape. One could hardly expect that our simple model would be able to describe quantitatively the critical fluctuation effects which are responsible for the shape of the specific heat near the λ point. Nevertheless, the result is that the theoretical shape agrees well with the experimental evidence, figure 7. Hence the weakly interacting CBG appears to be a fair approximation for the ground state of high-T_c cuprates.

On the other hand the theory of the Bose–Einstein condensation of CBG yields a significant change of the condensation temperature in a magnetic field if $T_c\tau \gg 1$, where τ is the scattering time for zero energy excitations. Without any broadening of the Landau levels T_c drops to zero at any magnetic field as mentioned above. If the

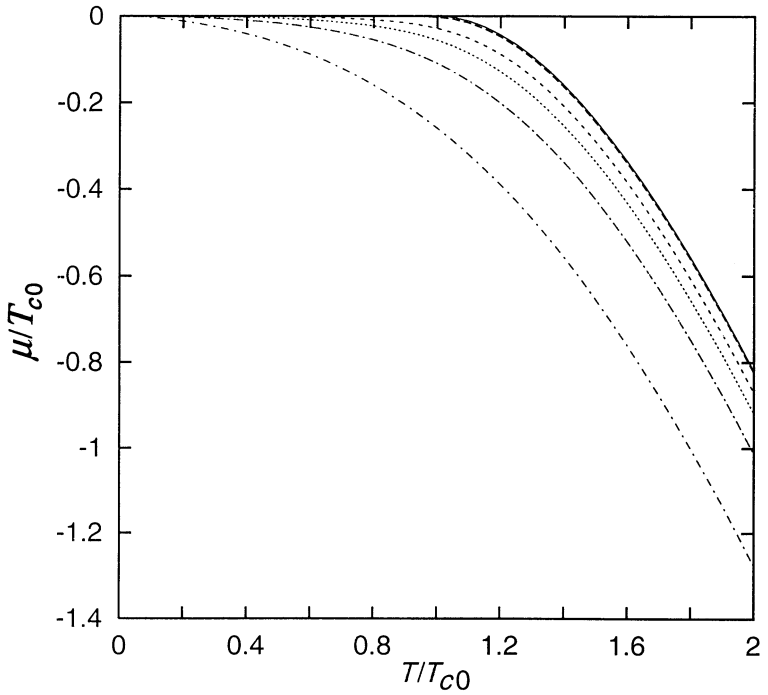

Figure 5. Chemical potential of CBG as a function of temperature and magnetic field, $\omega_{\mathrm{H}}/T_{\mathrm{c0}} = 0, 0.001, 0.1, 0.2, 0.4, 1.0$ (from top to bottom).

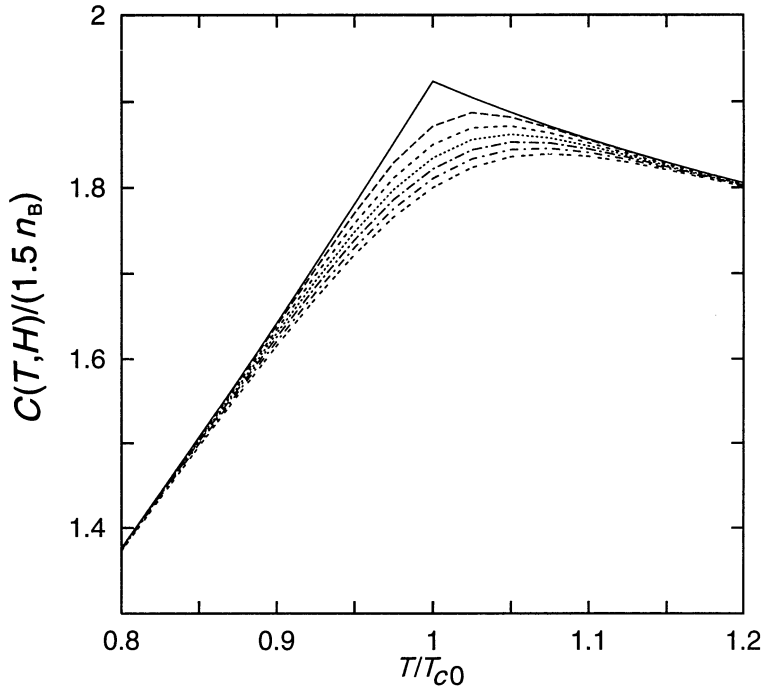

Figure 6. Specific heat anomaly of the charged Bose gas for $\omega_{\mathrm{H}}/T_{\mathrm{c0}} = 0, 0.004, 0.008, 0.012, 0.016, 0.020, 0.024$.

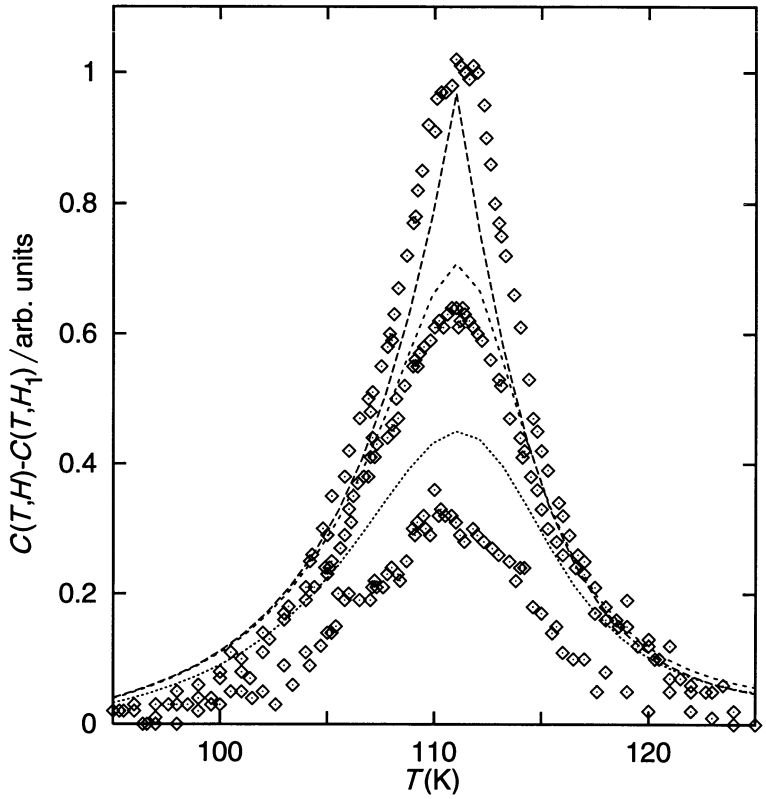

Figure 7. Change in the specific heat of CBG with an applied magnetic field (different lines correspond to $H = 0, 0.52$ T and 2 T, respectively) compared with the experiment (Marcenat *et al.* 1995) for Hg-1223.

collision broadening of the Landau levels is taken into account the resistive critical field is determined as (Alexandrov 1993)

$$H_{c2}(T) = H_d(t^{-1} - t^{1/2})^{3/2}, \tag{3.8}$$

where $H_d \sim 1/(T_c\tau)^{1/2}$ is a constant and $t = T/T_{c0}$. This equation fits well several independent resistivity measurements.

4. Conclusion

In conclusion, the bipolaron kinetics allows us to describe the anomalous power laws of the normal state properties of cuprates including the logarithmic low-temperature resistivity and the weak-field MR being at peace with the Boltzmann theory in contrast with the 'two different memory times' model hypothesized by several authors. The specific heat of a charged Bose gas shows a quantitative fit to the experimental shape explaining a contrasting behaviour of the thermodynamic and resistive transitions of cuprates in a magnetic field. A similarity between the specific heat of cuprates and that of He^4 supports our conclusion that high-T_c superconductors belong to the same 'universality' class of superfluids as He^4, which cannot be described by the BCS theory. As in the case of the metal–non-metal transitions in liquid metals (Hensel & Edwards 1996) there is no clear dividing line between non-

metallic underdoped cuprates and high-temperature superconductors. Cuprates are doped Mott insulators with bipolaronic carriers irrespective to the level of doping.

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Discussion

P. P. Edwards (*School of Chemistry, University of Birmingham, UK*). (i) First of all, let me say that Professor Alexandrov's model is highly appealing to the experimentalist working in the area of high T_c, in that he attempts to visualize (and localize) the real space origins of possible bipolaron formation; and its subsequent condensation to form the superconducting state. As he himself has always recounted, the origins of the Bose condensation of (real-space) electron pairs dates back to the ideas of M. R. Schafroth, S. T. Butler and J. M. Blatt and, indeed, earlier to R. A. Ogg in 1946 in an ingenious idea linking phase separation and high-temperature superconductivity of quenched metal–ammonia solutions. Over fifty years on, it is indeed gratifying to see that the high-temperature superconductivity cuprates, are possible candidates for such a mechanism.

(ii) Could I ask him to predict the upper limit to T_c, the superconducting transition temperature, in cuprates?

A. S. Alexandrov. (i) I highly appreciate the comment. Indeed, in many of our publications, we underlined that our microscopic theory is reminiscent of the phenomenological details by Schafroth (1955) and Butler & Blatt (1955). However, different from their phenomenology the bipolaron theory explains the mechanism of the charged boson formation representing an extension of the BCS theory to the strong-coupling limit. As a result, the well-known shortcomings of the Ogg–Schafroth model like a huge value of T_c about 10 000 K are not shared by the bipolaron theory of superconductivity. The enhanced bipolaron mass of the order of $10m_e$ and the reduced density of carriers in doped semiconductors about 10^{21} cm^{-3} push T_c into the experimental range of 100 K.

(ii) Within our theory the maximum T_c is reached in the crossover region of the electron–phonon coupling where the BCS coupling constant is about unity.

The basic phenomenon that allows the high-T_c value in this region is that of the polaron narrowing of the band. As a result, T_c is limited by the condition of the small polaron formation, which restricts the bare bandwidth. The maximum T_c appears to be about $\frac{1}{3}\omega$, where ω is the optical phonon frequency. It is experimentally well documented now that in all high-T_c cuprates the Fröhlich electron–phonon interaction is the most important with the frequency of relevant phonons about 500 K or even higher.

T. V. Ramakrishnan (*Indian Institute of Science, Bangalore, India*). There is considerable direct experimental evidence (e.g. from ARPES) for an electronic Fermi surface, i.e. for zero energy electronic excitations with a measured dispersion relation. This is not compatible with simple bipolaron theories in which electrons/holes exist only as parts of bound pairs, even above the superconducting transition temperature, T_c.

A. S. Alexandrov. The results of ARPES show the non-Fermi-liquid spectral shape of the quasi-particle spectral density. Therefore the usual interpretation of this result as being evidence for a large Fermi surface is doubtful. Moreover quite recent studies of under-doped Bi cuprates with ARPES have revealed a gap in the normal state.

Therefore I strongly believe that ARPES results are not as convincing as many people think. Definitely a large Fermi surface is completely incompatible with the semiconducting doping dependence of resistivity and with the boomerang behaviour of the London penetration depth.

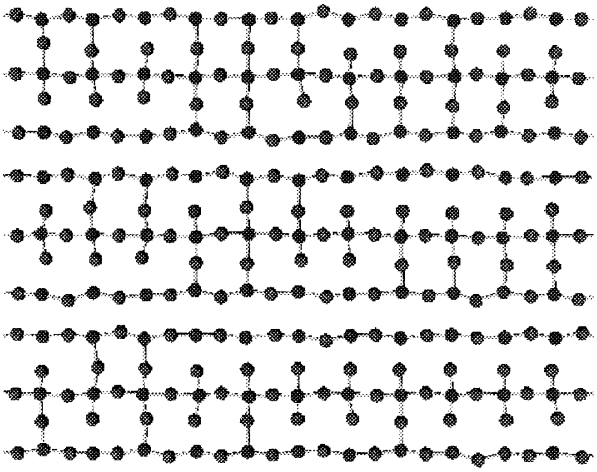

Figure 8. Cu and O atoms in the $(0, 0.5, 0)$-plane of $YBa_2Cu_3O_{6.95}$.

R. McGreevy (*Studsvik Neutron Research Laboratory, Sweden*). There now exists entirely independent evidence that strongly supports the Mott–Alexandrov bipolaron picture of high-temperature superconductivity. Figure 8 shows Cu and O atoms in the $(0, 0.5, 0)$-plane of a structural model of $YBa_2Cu_3O_{6.95}$ (the complete model contains 576 unit cells). This model is derived directly from experimental diffraction data, with no prior assumptions concerning lattice distortions, etc., and it is entirely consistent with the standard crystallographic picture of the structure. However, the model contains local correlations between the instantaneous positions of Cu(2) atoms (in the superconducting planes) and O(4) (apical oxygen). Instantaneously about half of the Cu(2)–O(4) bonds are 'short' and the other half are 'long' (in the picture long bonds are not drawn). From standard bond valence calculations each short bond corresponds to a charge transfer of $0.17|e|$ to the superconducting planes, so about 13 short bonds would be required to form a bipolaron. This gives as estimate for the superconducting coherence length in the plane of 10 Å. Another simple calculation, using the effective mass estimated from infrared data, predicts a T_c of 120 K. Both values are close to experimental values. Further work on the effect of Co doping and change of oxygen composition also produce results entirely consistent with the bipolaron picture—for example, the 'boomerang' effect in the behaviour of T_c with under/overdoping can easily be explained.

A. S. Alexandrov. This is clear evidence for a local lattice deformation and for an important role of apical oxygen. The pair-distribution analysis of neutron scattering by Egami *et al.*, the oxygen isotope effect on the effective mass of carriers observed recently by Müller, Zhao and co-workers as well as computer modelling studies by Catlow *et al.* provide the same piece of evidence.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES