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REVIEW ARTICLE

Polaron models of high-temperature superconductors

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Abstract. The work of Alexandrov and Ranninger has shown that the extrapolation of the BCS theory to strong electron–phonon interaction necessarily involves the formation of small polarons. The resulting theory can be directly applied to the cubic bismuth oxides, in which the bosons are Bi^{3+}, existing both above and below T_c. In the copper oxide materials, the role of the spins in Cu^{2+} is discussed. A model is proposed in which both spin and dielectric polarons play a role. The model is applied to electrical properties above T_c, for under- and over-doped specimens, and various other phenomena.

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1. Introduction

As long ago as 1946 it was suggested that superconductors might exist in which preformed bosons formed a degenerate Bose gas, and in which the critical temperature was that at which the gas became non-degenerate (Ogg 1946, who suggested that this might occur for solid metal–ammonia solutions). The former possibility was also discussed in detail by Shafroth (1955) and later by Alexandrov and Ranninger (1981), and since the discovery of the copper oxide superconductors by Bednorz and Müller in 1986, in many publications by

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these authors, and also by de Jongh (1989) and others. These authors identify the bosons as 'small' bipolarons, the binding energy being the result of interaction with phonons. The present author in a number of papers (Mott 1989, 1990a, b, c, d, 1991a, b, c, 1992a, b, 1993) has made a similar assumption, but has emphasized also the possible role of spin polarons. This article attempts to review the present state of this model. Although Ginsburg (1992) has recently stated that there is no clear evidence for the Shafroth model, the present author considers the evidence to be extremely strong, not only for the copper oxide materials but also for the cubic bismuth oxygen compounds ($T_c \simeq 30$ K). The role of spin polarons is more doubtful (and is unlikely to play a role in cubic bismuth oxide materials which are not magnetic) and will be reviewed in section 4 of this paper.

One eminent theorist has written 'it will be very surprising if the successful BCS theory, which describes all "old" superconductors, He^3 and even in atomic nuclei, turns out to be wrong for a very restricted class of materials like oxides'. And, rightly impressed by the success of BCS, many groups have sought an explanation through the extrapolation of BCS, a weak interaction theory, to the case of strong electron–phonon interaction. But it does not seem to be realized widely that, if this is done correctly, a Bose gas of small dielectric polarons is inevitably predicted (Alexandrov 1988, 1992c). The BCS formula for the critical temperature T_c is

$$k_B T_c = \hbar\omega \exp(-1/\lambda)$$

where ω is the frequency of a relevant phonon and

$$\lambda = N(E)V$$

V being the phonon-mediated binding energy of a Cooper pair. As V is increased, a strong interaction regime sets in when $\lambda \simeq 1$, with small correlation length as described for instance by Nozières and Schmidt-Rink (1985). But as first pointed out by Alexandrov and Ranninger (1981) the condition that $\lambda \simeq 1$ is also the criterion for small-polaron formation. In an ionic medium an electron forms a small polaron when the displacement of the ions round it is sufficiently great for self-trapping to occur, as pointed out by Landau in 1933. But if V is great enough for self-trapping it will be great enough for strong interaction in the BCS theory, and *vice versa*.

This is easily seen. In polaron theory the electron is bound with energy W_D, and the hopping energy for $T > \frac{1}{2}\Theta_D$ is $W_H \simeq \frac{1}{2}W_D$. Below the Debye temperatures the polaron is a pseudoparticle with effective mass (Mott and Davis 1979 p 89)

$$m = M_0 \exp(W_H/\tfrac{1}{2}\hbar\omega) \qquad M_0 = \hbar/2R^2\omega$$

where R is the hopping distance.

So if the wave function of another electron overlaps onto this potential well, V_0 should be identical with W_D. So the condition for a small polaron, $W_D > \hbar\omega$, is equivalent to $V_0 > \hbar\omega$. $N(E)$ is unlikely to be smaller than $1/\hbar\omega$, so small polarons will normally be formed *before* the BCS interaction has become strong.

Once the polarons are formed the Fröhlich Hamiltonian for pairing by electron–phonon interaction is no longer valid and the limitation arising from the Migdal (1958) theory no longer appears. For a recent detailed discussion, see Alexandrov and Krebs (1992).

The value of W_H is of interest. It has been stated in the literature that the above formula should give so high a value of m ($\sim 10^6 m_e$) that the polaron should be immobile due to the smallest disorder. This is not correct. For W_H we should write

$$W_H = (e^2/a)(1/\kappa_\alpha - 1/\kappa).$$

κ is very large for these materials. As shown by Salje (1988), following his work in polarons in niobium tungsten oxides, a is of the dimension of a copper oxide group, perhaps 10 Å. Also, $\hbar\omega$ for the oxygen vibration is ~ 0.1 eV. So values of m of the order of $5\text{–}10m_e$ are readily explicable, and found by Salje in other oxides and by co-workers in W–Nb oxides (see for instance Rüscher *et al* 1988).

As the parameters are changed we can ask whether the transition to polarons is discontinuous or not. In non-polar lattices we believe that it is. Figure 1 shows the energy E of an electron as a function of q, the displacement in a potential well Θ, varied. The elastic energy Aq^2 is represented by (i), and the energy of the electron as in the potential well by (ii). Curve (iii) shows the sum. At the minimum E may have a negative or positive value, and a stable polaron (E negative) is formed discontinuously for a finite value of q. This is not the case for 1D, or for a polar lattice, where curve (ii) should pass through the origin (see Mott and Davis 1979, Gerlach and Löwen 1991).

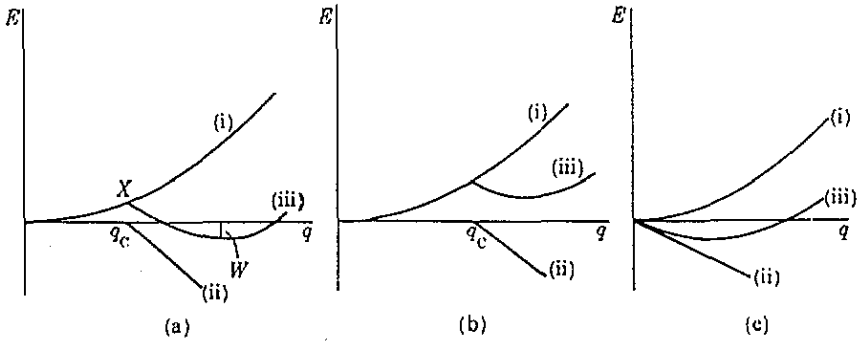

Figure 1. Energy of a polaron in terms of the ionic displacement q: (*a*) stable polaron form; (*b*) no stable polaron; (*c*) one or two dimensions.

We consider, then, possibly discontinuously, at any rate within a short range of the parameters, that an electron gas at zero temperature forms a gas of polarons as the interaction increases. Moreover the polarons attract each other at small distances (figure 2) and form bipolarons. Certainly the stability of a bipolaron should be greater in 2D than in 3D.

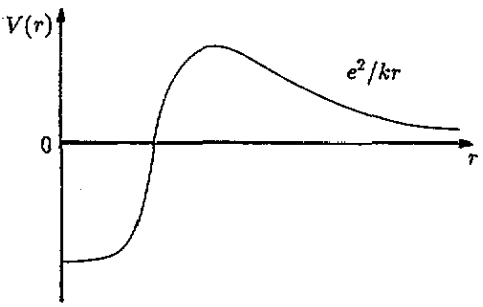

Figure 2. Energy $V(r)$ of two polarons at distance r.

If interaction between them is neglected a boson gas in 3D becomes non-degenerate at a temperature T_c given by

$$kT_c = 3.3\hbar^2 n^{2/3}/m \tag{1}$$

where m is the mean boson mass $m = (m_1 m_2 m_3)^{1/3}$ (Prelovsek *et al* 1987) and n the density of bosons. In many cases, particularly for low doping, we suppose that all the carriers form bosons, again in contrast with the Cooper pairs of BCS. Equation (1) is easily derived, since for a Bose gas (below T_c)

$$n = \int N(E)/\{\exp(E/kT) - 1\}\,\mathrm{d}E \tag{2}$$

where n is the number of bosons *not* in the $k = 0$ state. At T_c they all are, so if n is the total number of bosons T_c is given by (2) and if $N(E) = (1/4\pi^2)(2m/\hbar^2)^{3/2}E^{1/2}$, equation (1) follows.

In 2D $N(E)$ is constant at small E and the integral (2) diverges, but treatments including interaction give

$$k_B T_c \simeq \frac{n\hbar^2}{m \ln L}$$

where L depends on the interaction (Fisher and Hohenberg 1988).

It will be seen that if kT_c given by (1) (or a formula modified on account of interaction) is less than the binding energy of the bipolaron, then the behaviour of the high-temperature superconductor should be similar to that of superfluid He. In asking what value of T_c could in principle be reached by such a mechanism, one clearly wants m to be as small as possible; but small m means as small W_H, and probably a small dissociation energy for the bosons.

For (1) to be valid the dissociation energy must be greater than the right-hand side of (1)†. The optimum occurs when $kT_c \simeq \hbar\omega$—considerably higher than yet achieved.

Both for helium, and for the superconductors (n in the latter case being deduced from the chemical formula and m^* from the London magnetic penetration depth Λ, given by

$$m^* = 4\pi n \Lambda^2 q^2/c^2) \tag{3}$$

equation (1) with $q = 2e$ gives a fair estimate of the observed T_c, as the following values show.

Table 1.

	T_c (calc)	T_c (obs)	m^*/m_e
Helium 4	3	2.2	1
Cubic Bi O	40	30	240

For the copper oxide superconductors the value of n is of some doubt since it should refer to the number of bosons above a mobility edge; but the work of Uemura *et al* (1991a, b) shows a proportionality between the penetration depth, determined from muon lifetimes, and T_c; both should depend on n/m^*.

It is perhaps surprising that interaction makes so little difference. The clue comes from the Bogolubov (1947) formula for the excitations of a Bose gas:

$$\hbar\omega_k = \hbar(k^2 N V_k/m + k^4/4m^2)^{1/2}$$

† A similar argument is given by Bucher *et al* (1990), whose model is similar to ours.

where V_k is the Fourier transform of the interaction between a pair of bosons. If the interaction between charges is coulombic, the first term in the bracket becomes

$$4\pi\hbar^2 q^2 n/\epsilon_0 m$$

the term due to plasmon formation.

Here ϵ_0 is the dielectric constant, and n according to Micnas *et al* (1990) and Alexandrov and Ranninger (1981) is the density of bosons in the condensate, and will vanish at and above T_c. This has been queried by Emin (1992), but this term, though existing above T_c, cannot in our view be coupled with $k^2/2m$ and also is small compared with $k^2/2m$ at T_c. This then appears to be the reason why (1) gives satisfactory values for T_c. The first term is thought to vanish at and above T_c, so the free particle term is dominant in determining T_c.

Alexandrov and Ranninger (1992) have pointed out the similarity between the specific heat anomaly at T_c in the superconductors, as shown later in figure 13, and liquid helium. A difference between them is that there is nothing in the superconductors corresponding to the roton contribution in helium. This point has not been discussed in the literature.

A roton is now thought to be an interstitial helium atom moving through the material (Wilks and Betts 1987, Wyatt 1984). It must be remembered that in the superconductors the bosons are formed on a lattice, while in helium they are free, and it may be that the roton-like energy is therefore much higher in the superconductors.

Extensive investigation of the *electronic* specific heat by Loram *et al* (1990 and references therein) have shown that in the peak x is some 20% of the value $Nk\ln 2$ expected for a non-degenerate boson gas. According to de Jongh (1989) this can be explained for a 2D system, the remaining entropy occurring above T_c, although this explanation has been queried (Salje 1990, Marnis *et al* 1991).

The entropy should be then $nk_B \ln 2$ for the cubic bismuth components, but the measurements subtracting the phonon terms have not been made.

Another property of helium is the demonstration from neutron diffraction confirmed by calculation that, as a result of interaction, only a fraction f ($\simeq 0.1$) of the atoms are in the state $k = 0$, the rest being described by wave functions similar to those in a normal liquid in which overlap is minimized. f decreases under pressure. The present author (1993) has suggested that the free energy due to repulsive interaction will be of the form

$$Rf^2 + (1 - f)B.$$

R is the direct repulsive energy; B is of the order of $\hbar^2/ma^2$ because the states not in the condensate are localized. Minimizing we find $f = B/2R$. f will drop with increasing R, which increases with increasing concentration, but will not vanish. A possible application to overdoped superconductors is given in section 6, but we do not think that an analogous property of the superconductivity, if it exists, affects T_c.

2. The cubic bismuth oxide compounds

Of these materials, with $T_c \simeq 30$ K, $BaBi_xPb_{1-x}O_3$ is typical. In all of them the bismuth concentration is such that Bi^{3+} can be envisaged as existing in a sea of Bi^{5+}. It has been suggested by many authors that the Bi^{3+}, stabilized by polaron formulation, moves as a boson in the superconducting phase and persists as a boson above T_c, Bi^{4+} being

chemically unstable. The effective mass of the boson can be deduced from the measured London penetration given by (3) with $\Lambda \simeq 10000$ Å, $n = 6 \times 10^{21}$ cm^{-3}; one finds $m^* = 240m_e$. Equation (1) then gives $T_c = 40$ K, not far from the observed value.

Above T_c the resistivity must be determined by boson–boson collisions, which would give $\rho \propto T^{-2}$ for a non-degenerate gas with Coulomb interactions, dropping with increasing T as observed.

Alexandrov (1992b) and Uemura *et al* (1991a, b) have presented evidence that M_xC_{60} also belong to this class of superconductors.

3. The copper oxide superconductors

These show by far the highest values of T_c (up to 125 K) and have attracted most of the experimental and theoretical work. $La_{2-x}Sr_xCuO_4$ is typical. The phase diagram is shown in figure 3. For $x = 0$ the material is an antiferromagnetic (AF) insulator, with charge transfer coupling between the moments in Cu $3d^9$ ions. The Mott–Hubbard band gap is ~ 2 eV. Doping with Sr leads to a rapid drop in the Néel temperature, followed by a 'spin glass' region of composition in which variable range hopping is observed. There is then the transition to metallic behaviour with superconduction. The present author (Mott 1992a) has suggested that the doping gives rise to an insulator-to-metal transition of normal Anderson type, and that as soon as free carriers (polarons) are formed they combine to form bosons. The differences from the case of Si:B for instance are that the material has high static dielectric constant allowing polaron formation, and that here one starts with an AF insulator. The present author concluded that the carriers must be spin polarons. He now thinks that this is probably so, but the medium outside the range of the spin polarons must be polarized in the dielectric sense, and the arguments for polaron formation in the strong interaction case outlined in section 1 remain valid. We discuss the spin polaron hypothesis in section 4.

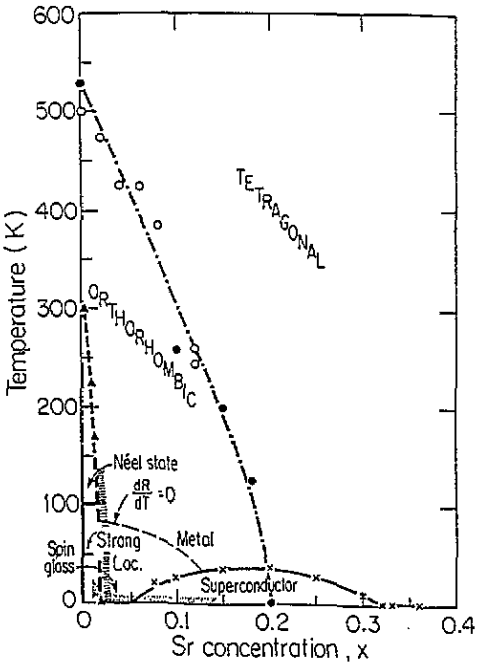

Figure 3. Phase diagram of $La_{2-x}Sr_xCuO_4$.

For all the copper oxide superconductors, with increasing doping T_c rises to a maximum and then drops, eventually to zero. The properties of overdoped materials are discussed in section 6; we think that, due to overcrowding† they contain a mixture of bosons and fermions.

All these materials, apart from a recent announcement of a ceramic with a cubic structure (Volkov *et al* 1992), are quasi-2D. For most one can estimate the number of carriers (including any that may be Anderson localized) from the chemical composition. $YBCO_{7-\delta}$ is an exception, owing to the presence of chains as well as planes, which act as reservoirs of carriers which do not normally take part in the superconductivity; also, some of the carriers in them may be Anderson localized.

The carriers are thought to be holes in the oxygen 2p band, hybridized with Cu 3d. According to evidence cited by de Jongh (1989) the ratio at E_F of Cu to O squared wave functions is 20% to 80%.

Tallon (1992) points out that n at the concentration for which T_c is a maximum is about the same for all these materials, so that T_c in equation (1) depends only on m, and that it is small when the proportion of 3d wave function compared with oxygen 2p is small.

We now discuss some evidence for our model which does not depend on whether spin polarons are formed or not.

Dewing and Salje (1992) have measured the infra-red conductivity $\sigma(\omega)$ for YBCO, and find a broad peak in the absorption, shown in figure 4. This is interpreted as the excitation of the boson to an unstable state leading to dissociation. Although the width and position of the band are independent of T, its intensity drops with increasing T. These authors assume that in equilibrium a triplet state for the bipolaron exists and at high enough temperatures its intensity will saturate to three times that of the singlet. It is then assumed that the spin on the triplet bipolarons are responsible for the broadening of the NMR line of Cu and O, which does not obey the Korringa relation (figure 5). As will be seen, this rises exponentially and then becomes constant, the parameters agreeing with those obtained by Dewing and Salje (see also Mott 1993a).

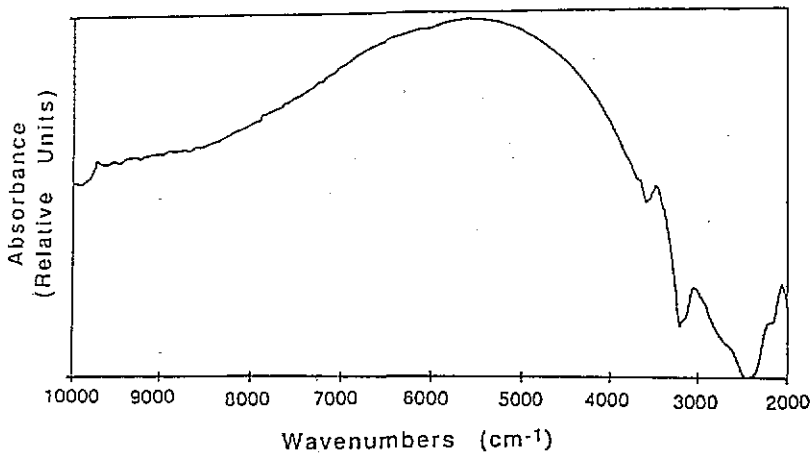

Figure 4. Peak in $\sigma(\omega)$ for YBCO.

† See Salje (1990) and previous papers which show the effect of overcrowding in tungsten oxides leading to a limitation in the formation of bipolarons.

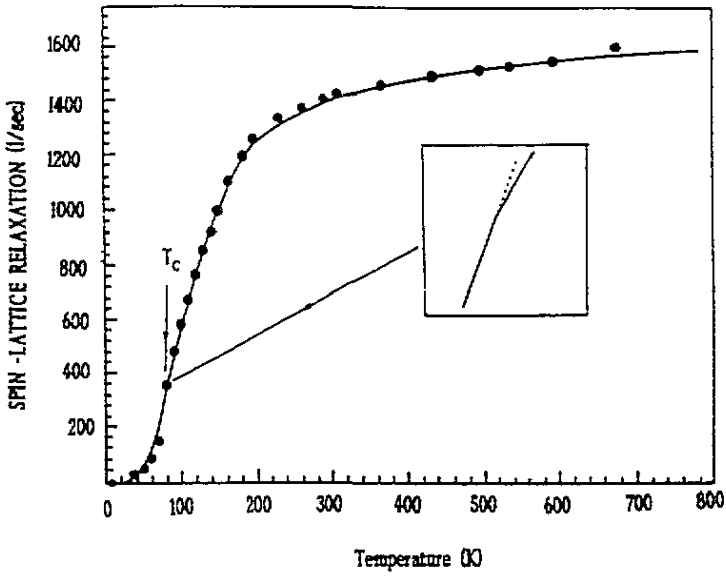

Figure 5. $1/T_1$ as a function of T for copper NMR in $YBa_2Cu_4O_8$ (experimental data from Machi *et al* 1991); theoretical curve after Alexandrov (1992d).

If these considerations are correct, above about 200 K the carriers should be triplet polarons. Bucher *et al* (1993) find a change in the slope of the ρ–T curve at this temperature. Mott (1993b) suggests that this is the cause. These considerations do not necessarily apply to strongly doped specimens, where on account of overcrowding fermions may be present.

4. Spin polarons

The concept of a spin polaron was introduced by de Gennes (1961), as a pseudoparticle formed in magnetic semiconductors. In a material such as Gd_3S_4, which is antiferromagnetic, an electron in the conduction band is thought to orient a group of Gd 4f moments in a direction antiparallel to itself, forming a pseudoparticle with heavy effective mass as shown in figure 6, the mass depending exponentially on the number of spins. In the material $Gd_{3-x}V_xS_4$, where V is a vacancy, there are x electrons per formula unit, but the material is not a metal because these heavy particles are Anderson localized by the field of the vacancies. A strong magnetic field which at low T saturates the spins, so that polarons cannot form, allows metallic conduction at low T (von Molnar *et al* 1983).

Nagaev (1983) in his book on magnetic semiconductors calls these pseudoparticles ferrons and considers that their formation in magnetic semiconductors is normal. It is natural, therefore, to suppose that the carriers in doped La_2CuO_4 and the other copper oxide materials are of this kind.

Kamimura and co-workers (1989) were the first to construct a theory in which the carriers in $La_{2-x}Sr_xCuO_4$ are spin polarons, and Wood and Cooke (1992) also carried out calculations on their properties. In both these investigations T_c was thought to be the temperature at which a bipolaron dissociates, and so they differ fundamentally from the model presented here. The present author's earlier papers proposed that the properties of the carrier were wholly those of spin polarons, the bonding energy being of the order of

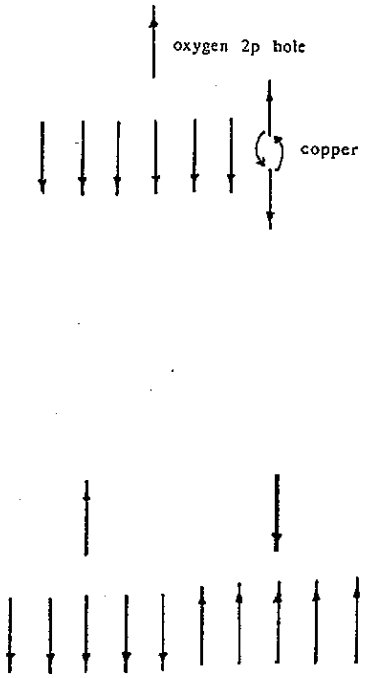

Figure 6. Spins in a spin polaron (schematic).

$Jn^{1/2}$, as illustrated in the lower part of figure 6, J being the magnetic interaction between the spins and n the number of spins in the polaron. He now considers it probable that spin polarons do form, but the surrounding medium is polarized by the charge, so both the spins and the polarity contribute to the cohesive energy. The fact that an isotope effect is normally found shows that the phonons must play some part (section 7).

The present author has made use of an interesting property of spin polarons first predicted by Vigren (1973). This is that the diffusive coefficient of a spin polaron (or, we maintain a spin bipolaron) is independent of the temperature. The argument is as follows. The spin polaron will move a small distance a_0 ($a_0 < a$) each time a spin at its periphery moves (in figure 6) from an up to a down position. At the periphery the activation energy for such a process will be zero, and we expect it to take place with frequency $\omega_N = kT_N/\hbar$, where T_N is a Néel frequency, giving a diffusion coefficient

$$D \simeq \omega_N a_0^2 \tag{4}$$

independent of T.

The motion of a spin polaron (or bipolaron) above T_c will thus be diffusive, like that of a dielectric polaron for $T > \frac{1}{2}\Theta_D$. If this is the mechanism, we expect no residual resistance. We return to this possibility in section 5.

The strongest evidence against the existence of spin polarons is the work with polarized neutrons carried out at Grenoble by Bruckel *et al* (1987, 1989), which in the superconducting range of composition shows no moments. Mott (1993) has suggested, following a suggestion by Professor Capellmann, that the antiferromagnetic arrangement of the spins goes through a kind of 'Mott transition' to the form of a metallic disc, this being assumed to have lower energy. It is also assumed that such a polaron would have the property of the diffusive motion proposed by Vigren. The more recent work of Rossat-Mignod *et al* (1992) suggests an antiferromagnetic correlation between the spins.

5. Electrical properties above T_c

In BCS superconductors, above T_c the electrical behaviour is normal, except that the electron–electron scattering, giving rise to the Landau–Baber T^2 term in the resistivity, is exceptionally large. In the copper oxide superconductors this is not so. The resistivity is approximately of the form

$$\rho = \rho_0 + AT \tag{5}$$

and for a single crystal ρ_0 can be small or vanish.

Our interpretation is based on the model of mixed spin and dielectric polaron, and the former is expected to be more important near the maximum of T_c because the overcrowding effect will first cut down the outer part of the polarons, which is dielectric. Actually both lead to $d\rho/dT$ = constant. For spin polarons we have already seen that D is independent of T, and so for a non-degenerate gas, of spin polarons or bipolarons, by Einstein's relation

$$\sigma = Nq^2D/kT \tag{6}$$

which yields (5). If the dielectric forces predominate, and the resistivity is wholly due to collisions with phonons (that is, particle–particle collisions are neglected, which for a non-degenerate gas gives us a term in $T^{3/2}$), Alexandrov (1992d) shows that, in 2D, $d\rho/dT$ is constant. The argument is that for heavy 2d particles the number of states with energies in a range dE is independent of E and the number of phonons proportional to T down to very low T. But the two models differ in one important respect. If the diffusive kind of motion predicted by Vigren obtains, we should not expect a residual resistance caused by impurities. A large value of ρ_0 indicates, in our view, scattering by disorder and thus a behaviour of the carriers as normal heavy particles. It could also occur if fermions (whether or not polarons) are present.

On the experimental side, for the superconductor LSCO the linear ρ–T curve is observed only for a composition near the maximum of T_c (Takagi *et al* 1992).

As regards the thermopower, S, if the spin component predominates in determining mobility, the Heikes formula for polarons should be valid:

$$S = (k_B/q)\ln[(1-z)/z] \tag{7}$$

where z is the ratio of carriers to sites. If as in $La_{2-x}Sr_xCuO_4$ conduction is in an impurity band, then the number of bosons should be half the number of sites, so that $z = \frac{1}{2}$ and $S = 0$. Results on YBCO obtained by Howson and co-workers (1989) and by Ouseph and Bryan (1990) (figure 7) and by Obertelli *et al* (1992) (figure 8) show that small, temperature-independent values of either sign can be obtained. As the temperature is raised sites in the valence band should become available, so z decreases and the behaviour should become more n like. This explains behaviour as shown in figure 9.

5.1. Hall effect

In YBCO the Hall constant above T_c is found to be proportional to $1/T$ (Penney *et al* 1988†). The present author (Mott 1990c) has given a model based on the assumption that the carriers are spin bipolarons, and that their concentration does not depend on T.

† See also Forro *et al* (1990) who found similar behaviour for $Bi_2Sr_2CaCu_2O_5$.

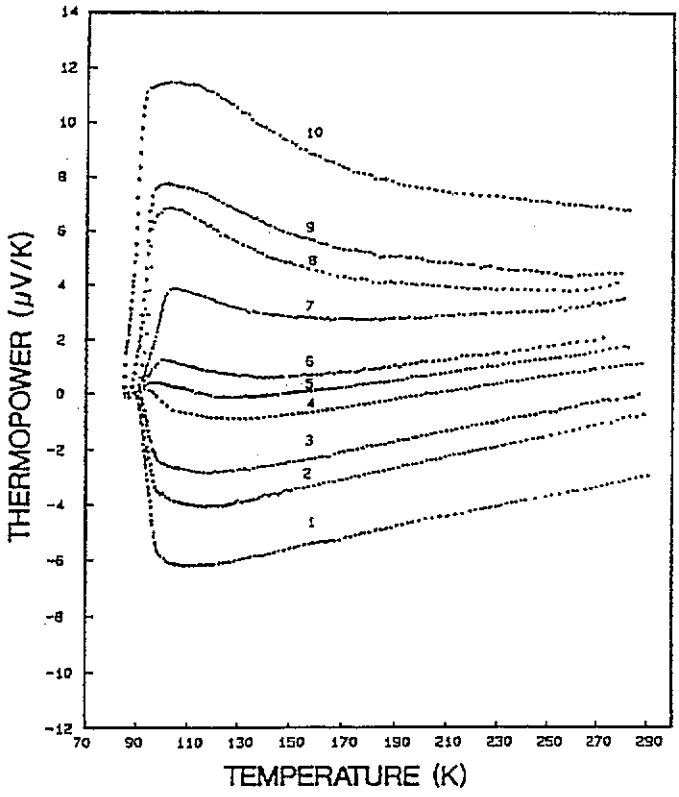

Figure 7. Thermopower of YBCO (Ouseph and Bryan 1990): curve 1, oxygen content; curve 10, 6.18.

The result is

$$R_H = (T_0/T)/nqc \qquad q = 2e$$

where $kT_0 = Ma^2\omega_N^2$. M is the mass of a bipolaron, and a is the distance diffused by the bipolaron each time an additional electron is incorporated in the cluster. ω_N is $k_B T_N/\hbar$. a is unknown.

If part of the current is carried by spin polarons, a similar behaviour is expected but with a different constant. If however the polarons are of dielectric type and the temperature is below Θ_D, the normal formula is expected. Only at higher temperatures, in the regime where the carrier moves by thermally activated hopping, is a Hall coefficient experimentally dependent on T expected (Friedman and Holstein 1963).

A review of experiment and theories on the Hall effect is given by Iye (1992); normally the slope of the $R - 1/T$ curve decreases when YBCO is alloyed with Zn, suggesting that the carriers are partly electrons (see section 8).

6. Overdoped specimens

As shown in figure 3, overdoping for all copper oxide superconductors reduces T_c and eventually reduces it to zero, the material then behaving as a normal metal. This we believe

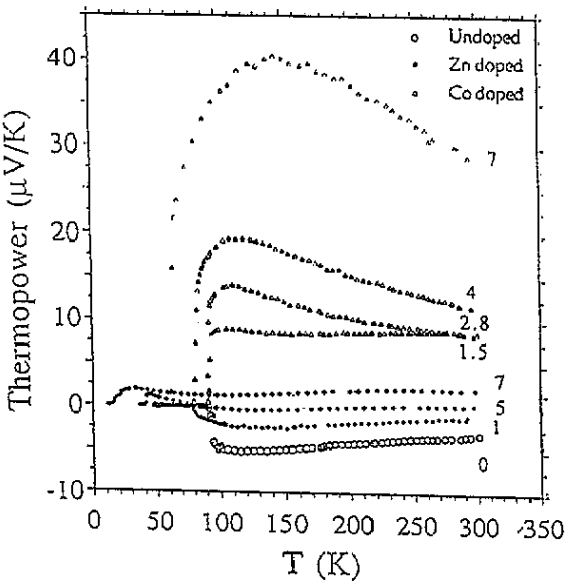

Figure 8. Thermopower of YBa_2 $(M_xCu_{1-x})O_7$ where M = Cu or Zn (Obertelli *et al* 1992).

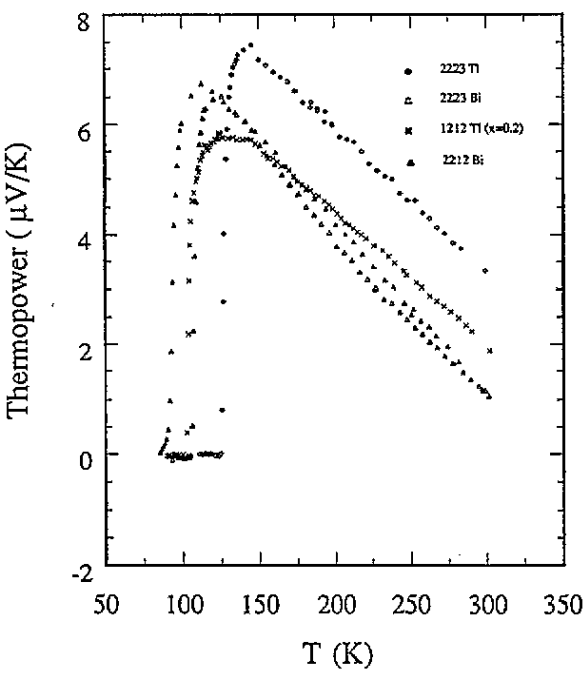

Figure 9. Thermopower of materials shown (Obertelli *et al* 1992).

to be related to overcrowding; there is not space in the lattice for all the carriers to form bosons, so a mixture of fermions and bosons is present. If the (lighter) fermions carry the current above T_c, and form a degenerate gas, we should expect Landau–Baber scattering above T_c, giving $\rho \propto T^2$ and $S \propto T$. Figure 10 shows that for some overdoped specimens, the latter appears to be the case.

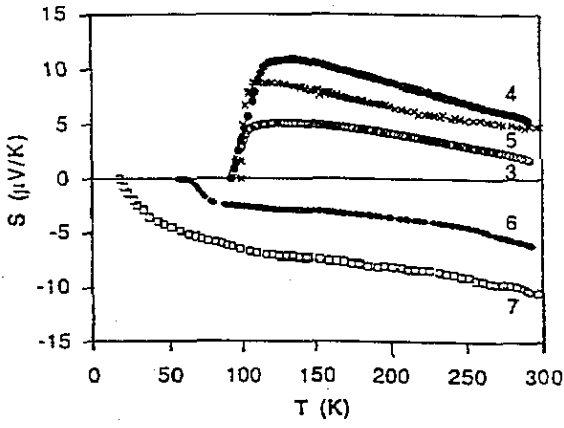

Figure 10. Thermopower showing metallic behaviour of an overdoped specimens of $Tl_{0.5-x}Pb_{0.5+x}Sr_2Ca_{1-3}\ Y_yCu_2O_7$. (6) and (7) are overdoped. (Subramanian *et al* 1992.)

But overcrowding alone cannot be the cause of the drop in T_c. The present author has suggested (Mott 1993a) that in the superconductors, as in helium, only a fraction f of the bosons are in the $k = 0$ state, and that as the doping increases these states become Anderson localized, giving no superconductivity. If so, the non-superconducting material still contains a non-superconducting boson gas, and should show the peak in $\sigma(\omega)$ observed by Dewing and Salje (figure 4). Other effects expected are a metallic form of the thermopower (cf. figure 10).

7. Isotope effect

If the effective mass of a boson is mainly due to a spin polaron's formation, we expect no isotope effect. A small value is expected in the overcrowded regime, if it is assumed that the dielectric polaron regime is absent.

If dielectric polarons are responsible for the effective mass, then from equation (1), if $m = m_0 \exp(W/\frac{1}{2}\hbar\omega)$ we find

$$\delta T_c/T_c = \tfrac{1}{2}(\delta M/M^0)W/\hbar\omega \tag{8}$$

with $W/\hbar\omega = \ln(3.3\hbar^2 n^{2/3}/m_0 k T_c)$ where M and δM are the oxygen mass and its isotope change, correspondingly. Thus a large isotope effect should be associated with low T_c, while for high T_c a small or even a negative value is possible. For a qualitative discussion of these ideas, see Alexandrov (1992a) who considers the transition from Fermi liquid of small polarons to charged Bose liquid of small bipolarons. Figure 11 from this paper, reproduced here, plots the ratio of α $(= -\mathrm{d}\ln T_c/\mathrm{d}\ln M)$ against T_c, the full line being the theoretical value. The BCS value is $\frac{1}{2}$.

8. Disorder

On the theoretical side, Mott (1991b) has pointed out that, given disorder of the kind (diagonal) introduced by Anderson (1968), Coulomb repulsion may have the result that one (or some finite number) may be the maximum number of bosons that can be accommodated in one state. States may then be occupied up to a maximum E'_{F-}, behaving like a Fermi

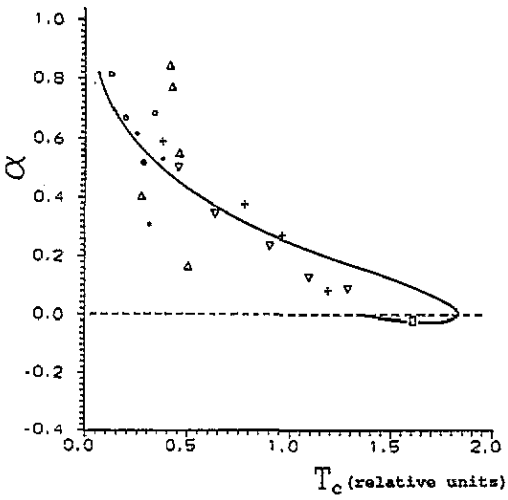

Figure 11. α *(the isotope effect,* $M\delta T_c/T_c\delta M$*) for* known high-T_c superconductors (Alexandrov 1992a).

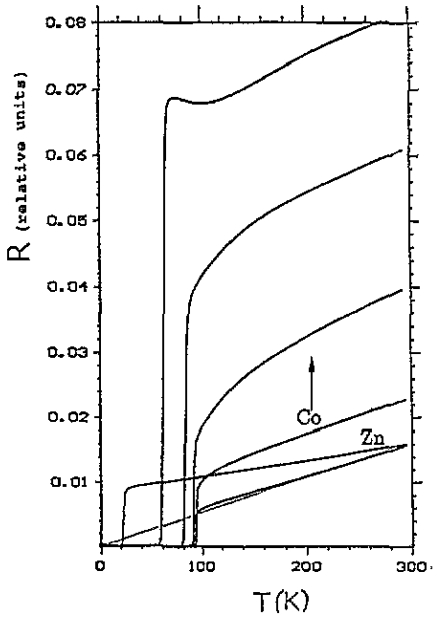

Figure 12. Effects of Co and Zn on the resistivity of YBCO.

energy, and also a kind of mobility edge E_B above which states are delocalized. Thus a kind of Anderson transition may be expected, with variable range hopping if E'_{F-} lies below E_B.

Another suggestion is that in strong disorder, if the energy fluctuations are greater than the binding energy of the boson, the distinction between bosons and fermions breaks down, and equations appropriate to fermions may describe the transport and other properties.

We reiterate here that, if spin polarons determine the motion of the boson above T_c, and Vigren's proposals are correct, one would not normally expect a residual resistance due to disorder, so that ρ_0 should be zero in equation (5). As in LSCO and $YBCO_{7-\delta}$ except for $\delta = 0$ the carriers move in an impurity band, some disorder must be present, and the absence of ρ_0 seems to us evidence for the spin polaron mechanism. On the other hand, the addition of Co and Zn to YBCO have marked consequence. Zn is thought to substitute for Cu in the copper oxide planes, Co between the planes. Co as shown in figure 12 has a large effect both on ρ and S. We think it should produce long-range fluctuations of potential, so that above T_c the number of mobile carriers will increase with T, and the observed behaviour may be related to this, because at $T = 0$ very few carriers will be mobile.

Zinc on the other hand produces Anderson localization in the planes. According to Mott (1992b), when an Anderson transition takes place, $C_V \simeq N(E)k^2T$ as for fermions. That this is so is shown in figure 13, from Mott (1992b) taken from the work of Loram *et al* (1990).

Another example of the effect of disorder comes from the study of thin films. Some results for $Nd_{2-x}Ce_xCuO_4$ are shown in figure 14. The surfaces of the films must introduce strong disorder. The fact that ρ appears independent of T suggests that the carriers are dielectric rather than spin bipolarons, so that a large residual resistance is expected.

The sheet resistivity at the transition when $T_c \to 0$ is $h^2/(2e)^2$ (see also Haviland *et al* 1989, Pang 1989). The analysis by Tanda *et al* (1991) of the results shown in figure 14

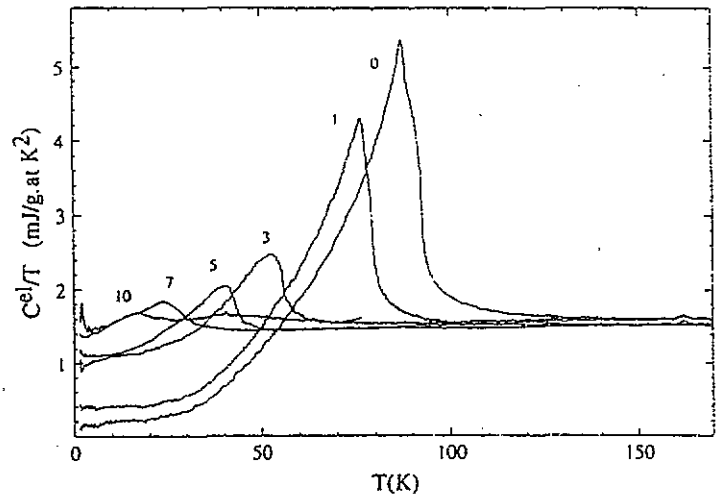

Figure 13. Specific heat of $YB_2(Cu_{1-x}Zn_x)_3O_7$.

show that the first insulating state obeys the formula for variable-range hopping in 2D:

$$\sigma = \sigma_0 \exp(-T_c/T)^{1/3}.$$

The argument given earlier suggests that with strong disorder bosons behave like fermions, so this is not unexpected.

However curve B obeys the logarithmic formula

$$\rho \simeq A - B \ln T$$

which derives from weakly localized fermions in the metallic regime

$$\sigma = \sigma_B[1 - (2/\pi k_F l) \ln(L/e)] \qquad L = \text{constant}/T^{1/2}.$$

We suggest, then, that the random field is strong enough to destroy the boson, but not to localize the fermion.

9. Angle-resolved photoemission

Experimental work on angle-resolved photoemission shows a form of the Fermi surface. Figure 15 shows the results of Olson *et al* (1990) and Liu *et al* (1992). The results are similar to those obtained from calculations. The energy breadth of the apparent Fermi level is linear, that is to say,

$$\tau^{-1} = \beta(E - E_F)^{\alpha} \tag{9}$$

with $\alpha = 1$, in contrast to the value $\alpha = 2$ in the Landau theory of Fermi liquids. The present author (Mott 1991b, 1992a) has maintained that these results are compatible with the model proposed here.

Electrons are ejected from states below E_F across a band gap into a conduction band, as shown in figure 16. States below E_F are not polaronic, so the Fermi surface obtained should correspond with calculations. The bosons are formed from holes, in the area shown

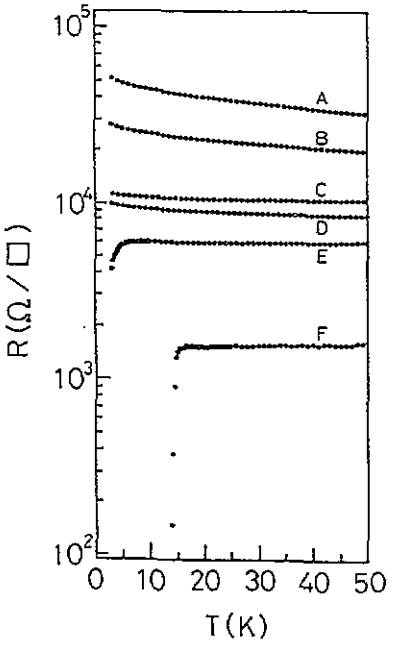

Figure 14. Resistivity of thin films of $Nd_{2-x}Ce_xCuO_4$.

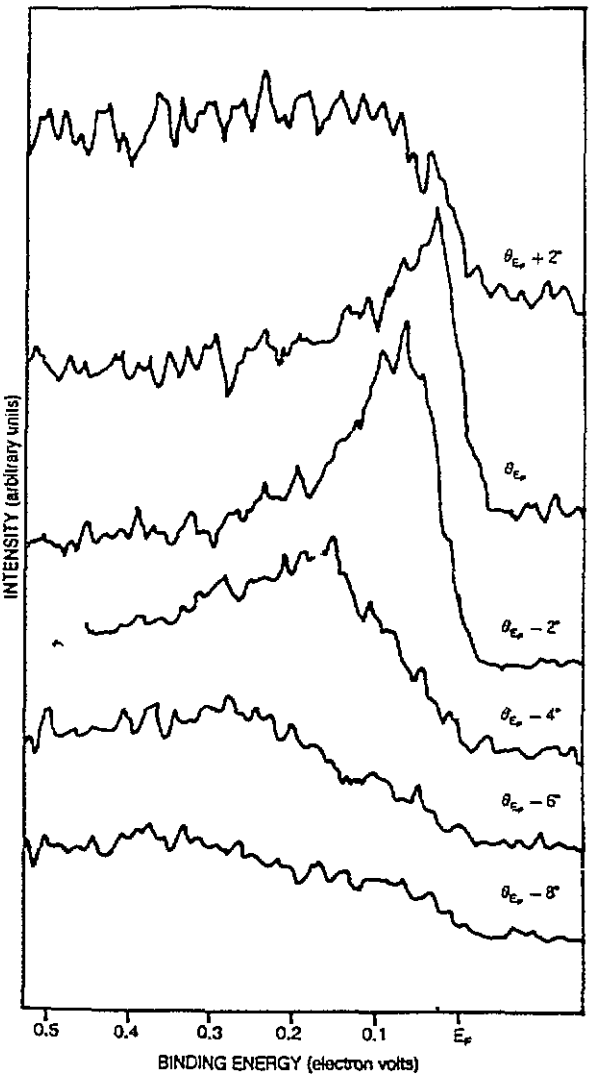

Figure 15. Intensity of angle-resolved photoemission in $Ba_2Sr_2CaCu_2O_8$.

shaded. So there are no fermion states in this area of the diagram. Thus excitation above E_F, to states that should obey (9) with $\alpha = 2$ on account of Auger transitions, cannot occur. Empty states just below E_F have a lifetime determined by interaction with the bosons, and for these we expect $\alpha = 1$. For a true Fermi surface, the number of electrons with which an excited electron can interact is proportional to $|E - E_F|$, as is the number of states into which it can jump, giving $\alpha = 2$; while if the interaction is with bosons, the first factor is absent.

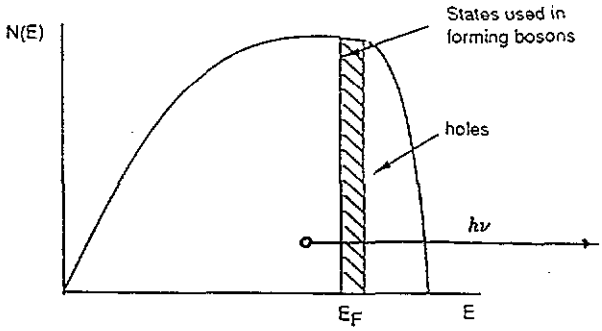

Figure 16. Density of states, showing mechanism for angle-resolved photoemission.

10. Thermal conductivity

Mott (1992a) suggested that measurements of the thermal conductivity K above T_c could be used to show that the carriers were bosons, because the Wiederman–Franz equation

$$K/\sigma T = 3(k/q)^2 \tag{10}$$

should determine whether q is e or $2e$. Hagen *et al* (1989) have found that for a single crystal of $YBCO_7$ K_{ab}- is about twice that calculated from the conductivity using (10) with $q = e$. On the other hand they find K_{ab} is changed for a smaller δ in the insulating AF state. They assume that the phonon contribution is drastically changed. The present author (Mott 1993) considers it more likely that the explanation is that $q = 2e$, so that the electronic contribution is small.

Fisher (1988) in a review remarked that doping La_2CuO_2 makes little difference to K_{ab}, indicating again that $q = 2e$ and the electronic contribution is small.

Thermal conduction, and the rise in K below T_c, is discussed by Alexandrov and Mott (1993).

11. Critical magnetic fields

We shall conclude our discussion in an attempt to fit the experimentally observed temperature dependence of the penetration depth $\lambda_H(T)$ and the upper critical field $H_{c2}(T)$ within the framework of a charged Bose liquid.

As far as $\lambda_H(T)$ is concerned, it is now generally accepted (Annett *et al* 1991) that in a wide temperature region it behaves as

$$\lambda_H^2 \simeq 1 - (T/T_c)^2 \tag{11}$$

and differs significantly from $1-(T/T_c)^4$, which is the canonical empirical law for classical BCS-like superconductors: the quadratic temperature dependence of λ_H^2. Equation (11) on the contrary is what one would expect for a weakly interacting Bose liquid (Alexandrov and Traven 1988).

As far as $H_{c2}(T)$ is concerned, an upward curvature near T_c has been observed in practically all high-temperature superconducturs. Reversible DC magnetization measurements on single crystals (Welp *et al* 1989) proved that this curvature is a truly thermodynamic property. Magnetization measurement data on single untwinned crystals

(Welp *et al* 1989) indicate that this upward curvature depends on the quality of the sample, but is always present. The prediction for a 'dirty' charged Bose liquid with boson impurity scattering yields

$$H_{c2}(T) = H_d[(1 - t^{3/2})^{3/2}/t^{3/2}] \tag{12}$$

and in the clean limit (Alexandrov *et al* 1987)

$$H_{c2}(T) = H_{c1}(1 - t^{3/2})^{3/2}/t \tag{13}$$

where $t = T/T_c$ and H_d and H_{c1} are temperature independent. Both expressions (12) and (13) predict the upward curvature near T_c:

$$H_{c2}(T) \simeq (1 - t)^{3/2}. \tag{14}$$

Expression (14) differs from any mean-field BCS-like expression (see, for example, Ginsberg 1992), which gives the well known behaviour linear in T in the vicinity of T_c.

Applying small magnetic fields, the transition quickly broadens and $H_{c2}(T)$ rises abruptly upon lowering the temperature. This in general restricts the experimental verification of the upward curvature of H_{c2} over a sizeable temperature interval. One exception to this is the electron doped compound $Nd_{1.85}Ce_{0.15}Cu_{4-\delta}$ where the upward curvature was seen in a wide temperature interval ranging from 5 K to $T_c = 20$ K (Seamon *et al* 1989), which can be fitted very well with equation (14).

12. The tunnelling gap

In our model this is equal to the binding energy of the boson (Alexandrov and Ray 1991). Unlike BCS, this is not related to T_c. Experimental work shows that the gap is practically independent of T, and some work shows that it exists above T_c; for a summary of the evidence, see Mott (1992b).

13. Negative Hubbard U and chalcogenide glasses

The small-bipolaron model outlined here is a specific case of the negative U theories, for which there is an extensive literature (see for instance Wilson 1991). The concept of a negative U was first introduced in discussions of chalcogenide glasses (Mott *et al* 1975, Kastner *et al* 1977), following a suggestion by Anderson (1975). In this connection, it is interesting that Savransky (1986) has recorded that under pressure both crystalline and glassy AS_2Te_3, both containing negative U centres, can become superconducting.

14. Low T_c in $Bi_{2.2}Sr_{1.8}CuO_{6-\delta}$

This material, investigated by Fiory *et al* (1990) has a very low value of T_c (~ 9 K), but the resistivity ρ above T_c is proportional to T up to $\frac{1}{2} \times 600$ K. According to observations made in Cambridge (Mackenzie 1991), small changes in composition cause T_c to disappear, but the linear increase of ρ to persist.

We suggest, following Varma *et al* (1989) that the phonon scattering mechanism is unlikely, and the carriers are spin polarons. The composition suggests a strongly overdoped n-type material. We think we have, following section 6, a material in which the fraction of $k = 0$ states is low, and most of them localized so that small changes in composition make them all localized. The material will then no longer be a superconductor but the carriers are still bipolarons, giving the linear T dependence of ρ above T_c. These assumptions seem to account for the observed facts.

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