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REVIEW ARTICLE

The high-T_c superconductors: a conservative view

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Abstract. This brief review deals only with the basic properties of the new oxide superconductors, in single-crystal form. It assumes a minimum knowledge of this new field.

The layered structure leads to a quasi-two-dimensional situation, not yet completely characterised or understood. Using the classical BCS weak coupling scheme, such a quasi-two-dimensional situation is optimal and can explain, for suitable dopings of the layers, the high T_cs observed.

The usual objections to such a scheme are discussed, as well as some of the difficulties met by other schemes. The classical BCS scheme is indeed acceptable only if full account is taken of competitive antiferromagnetic fluctuations. There is then a continuous transition to other possible schemes of more strongly correlated Fermi liquids.

1. Introduction

Condensed matter research was deeply stirred when critical superconductive temperatures T_c between 30 and 40 K were observed in perovskite copper oxides: $La_{2-x}Ba_xCuO_4$ (Bednorz and Müller 1986, Bednorz *et al* 1987), then $La_{2-x}Sr_xCuO_4$ (Takagi *et al* 1987, Tarascon *et al* 1987). This discovery was rapidly followed by that of $YBa_2Cu_3O_7$ with $T_c \simeq 90$ K (Chu *et al* 1987, Cava *et al* 1987), then by those of similar Bi, Tl and Pb oxides with T_c up to 125 K (Michel *et al* 1987, Maeda *et al* 1988, Hazen *et al* 1988; Parkin *et al* 1987, 1988, Cava *et al* 1988b, Subranian *et al* 1988). But the Nobel prize went to the initial discovery at $T_c \simeq 30$ K; and one can rightly ask, in retrospect, why?

The main reason is surely that many people had become convinced over the years that the $T_c \leqslant 25$ K observed in the V_3Si family of compounds were very near to the maximum one could hope for, at least in a 'classical' BCS coupling scheme.

Indeed, within the usual approximations of this scheme, i.e. close to an isotropic 3d dimensional situation, with delocalised carriers weakly coupled through phonons, T_c is necessarily related to the Debye temperature T_D by (Bardeen *et al* 1957) (BCS)

$$T_c \simeq T_D \exp(-1/\lambda) \tag{1}$$

where the exponential is very small for a weak relative coupling

$$\lambda = Vn(E_F) \simeq V/E_F \tag{2}$$

(in which V is the phonon-mediated electron–electron coupling, $n(E_F)$ the electronic

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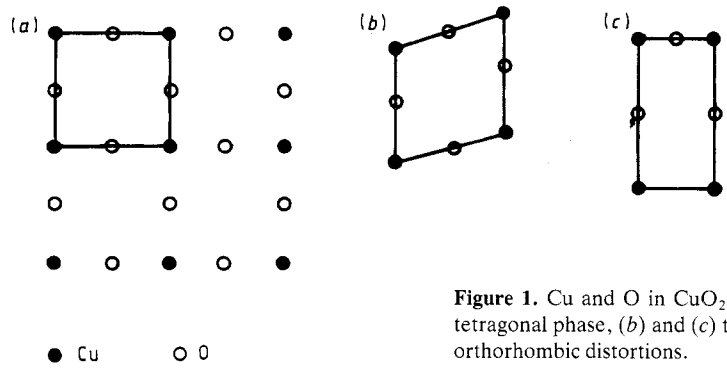

Figure 1. Cu and O in CuO_2 planes: (*a*) tetragonal phase, (*b*) and (*c*) two types of orthorhombic distortions.

density of states, E_F the Fermi energy). Indeed with $T_D \leq 300$ K and $\lambda \ll 1$, T_c up to 25 K should be very exceptional.

McMillan's improved treatment (McMillan 1968) of not-so-small couplings λ does not really help, especially if one takes also into account a competitive direct electron–electron repulsion term μ. Then λ is replaced by

$$\lambda_{\text{eff}} = (\lambda - \mu^*)/(1 + \lambda) \tag{3}$$

where μ is replaced by a smaller μ^*

$$\mu^* = \mu/[1 + \mu \ln(E_F/k_B T_D)]$$

due to a difference in effective frequencies in λ and μ (Morel and Anderson 1962). With such corrections, λ_{eff} is still positive but never large enough to explain the high T_cs observed. Further terms in the development in λ and μ^* of Eliashberg's equation do not change this conclusion, as they decrease T_c from McMillan's formula (Combescot 1989).

It is then natural to examine the basic assumption in the classical BCS model: *three dimensions*; *weak coupling*; *phonon mediated coupling*. We shall look at these points in succession, keeping to essentials. In such a brief report, we shall assume the basic facts of the field to be already known, and will not touch at all on the effects of defects or on more applied aspects. Finally in a still very controversial field a clearly personal view will be kept which has been already aired elsewhere (Friedel 1987a, 1988a, b).

A brief general outlook of the field can be found in *MRS Bulletin* (1989), and more detailed studies are appearing in the 1989 issues of *Studies in High Temperature Superconductors* (1989). Other recent reviews on structure and theoretical models include Cyrot (1989), Azhkenazi (1989) and Weber (1988a), together with the Conferences of Interlaken (1988) and Les Houches (1988).

2. Quasi-two-dimensionality

2.1. Structural anisotropy

The new superconductors considered here are all layer oxides, where each unit cell contains one or several parallel CuO_2 conducting planes (Muller Buschbaum 1977, Michel and Raveau 1984).

Each CuO_2 plane is built with one Cu atom bound with four O atoms. In many cases, the Cu lattice is square, with one O at the centre of each Cu–Cu bond (figure 1(*a*)). A

piling up of such planes gives rise to a tetragonal lattice. There are two observed orthorhombic distortions. They correspond to the copper square distorted into a lozenge (figure 1(*b*)) or a rectangle (figure 1(*c*)).

In all cases, one or two O atoms sit above and below the Cu atoms of the CuO_2 plane, along a direction essentially normal to the plane. These O atoms are further away from the Cu than those in the CuO_2 planes and do not seem to play a large role in the covalent bonding of the CuO_2 responsible for their metallic conductivity. The orthorhombic distortion pictured figure 1(*b*) is observed in $La_{2-x}Cr_xCuO_{4-y}$ for $x + 2y < 0.15$: due to Madelung Coulomb terms (Barisic and Batistic 1988, 1989b, Noguera 1989), each CuO_6 hexahedron is slightly rotated without much distortion; the O atoms pictured figure 1(*b*) are then alternately slightly above and below the Cu planes, due to the alternating signs of neighbouring rotations.

Finally the CuO_2 planes are piled parallel to each other, with supplementary atomic planes in between. In $La_{2-x}Cr_xCuO_4$, the CuO_2 planes are equidistant (Michel *et al* 1987, Pouget *et al* 1988). In $YBa_2CuO_{7-\delta}$, the CuO_2 planes go by pairs, with a plane of Y in the middle of each pair; looser bonding between pairs is through Ba and O atoms and through intermediary Cu planes which contain more or less continuous and parallel CuO chains, depending on the value of δ: for small δ, where the chains are well developed, the orthorhombic distortion pictured in figure 1(*c*) is observed (Beno *et al* 1987). Y can be replaced by many rare earths in this compound, without changing structure or properties, except for the magnetism (Tagaki *et al* 1987, Engler *et al* 1987). The same regrouping in families of n parallel CuO_2 planes is observed in Bi, Tl and Pb compounds, with $n = 1, 2, 3, 4$. Each CuO_2 plane is then essentially square; but an incommensurate modulation is observed in the Bi planes (Raveau *et al* 1988, Hervieu *et al* 1988, Martin *et al* 1988b, Bordet *et al* 1988, Parkin *et al* 1988, Torrance *et al* 1988, Maeda *et al* 1988, Hazen *et al* 1988, Hewat *et al* 1988, Albouy *et al* 1988).

It is worth pointing out at this stage that, in the antiferromagnetic phases observed in $La_{2-x}Sr_xCuO_4$ (Shirane *et al* 1987), the moments are essentially localised on the Cu atoms, so that, in each CuO_2 plane, each Cu is surrounded with Cu of opposite moments. Then a magnetic coupling between CuO_2 planes can only exist due to the orthorhombic distortion. No such difficulty occurs for the interplanar magnetic coupling of other oxides (Wu *et al* 1987, Petitgrand and Collin 1988, Yang *et al* 1989).

In the orthorhombic phase, each CuO_2 plane carries a small magnetic moment normal to the plane. These moments, which are normally arranged antiferromagnetically, can be aligned ferromagnetically under a small field (Hammann *et al* 1987, Johnston *et al* 1988).

2.2. *Anisotropy of transport properties at low temperatures*

In all these compounds, transport properties show that the carriers are much more mobile parallel to the CuO_2 planes than in the normal direction. Thus the resistivities $\rho_\parallel$, $\rho_\perp$ and the plasmon frequencies $\omega_\parallel$, $\omega_\perp$ in the metallic state as well as the penetration depths $\lambda_\parallel$, $\lambda_\perp$ in the superconductive state show a large anisotropy (Tozu *et al* 1987, Bassat *et al* 1987, Umezawa *et al* 1988, Vinnikov *et al* 1988, Ong *et al* 1988, Beille *et al* 1988, Iye *et al* 1988, Forro *et al* 1989, Martin *et al* 1988a):

$$\rho_\perp/\rho_\parallel \simeq \omega_\parallel/\omega_\perp \simeq (\lambda_\parallel/\lambda_\perp)^2 \simeq \alpha. \tag{4}$$

In good single crystals, the values of α as measured by these three types of data are similar and do not vary much with temperature. Indeed, with increasing purity, $\rho_\perp$

goes from a semiconductive or localised to a metallic behaviour, more like that of $\rho_{\parallel}$. Depending on the compound considered,

$$25 < \alpha < 100 \tag{5}$$

the lower limit being valid for $YBa_2Cu_3O_7$.

Such marked anisotropies are similar to those met in chain-like organic superconductors, although not quite as strong (Jérome and Schulz 1982). They are characteristic of *quasi-low-dimensionality*, where it is useful to think of the subunits (here CuO_2 planes) as independent, with strong intra-unit couplings, and then to introduce inter-unit couplings as perturbations (Friedel 1985, 1987b).

The fact that the compounds considered possess both high-T_c and quasi-two-dimensional (quasi-2D) structures leads to some characteristic low-temperature superconductive properties which we shall analyse in this section in terms of free carriers with anisotropic effective masses following a Ginzburg–Landau theory (Lawrence and Doniach 1975). A mean-field analysis of the situation in terms of Josephson junction couplings between CuO_2 planes would lead to similar results with a reinterpretation of masses (Barisic 1967, Barisic and de Gennes 1968, Bulaewski 1973).

A better Ginzburg–Landau analysis would take into account the specific band structure as discussed in § 3. The corresponding Josephson junction approach has not yet been developed, especially beyond the mean field approximation.

First, because of their high T_cs, and hence large superconductive gaps Δ, the oxides considered have necessarily short coherence lengths ξ, because for a free carrier model

$$\xi \simeq 2hv_F/\pi\Delta \tag{6}$$

(where v_F is the Fermi velocity). Their penetration depths λ, inversely proportional to the plasmon frequencies, will be large because the number of carriers per unit volume n will be small, being at most one per Cu atom, and their effective mass m large

$$\lambda \simeq (mc^2/4\pi ne^2)^{1/2} \tag{7}$$

One necessarily deals with *type II superconductors*, with $\lambda \gg \xi$ and a large range of applied fields $H_{c1} < H < H_{c2}$ for inhomogeneous penetration along vortex lines (Kittel 1966).

But, because of the very strong anisotropy in transport properties, one expects and indeed observes a strong anisotropy of λ and ξ, and thus of H_{c1} and H_{c2}. More precisely, all measurements fit with

$$\lambda_\perp/\lambda_\parallel \simeq \xi_\parallel/\xi_\perp \simeq 5\text{–}10 \tag{8}$$

(Umezawa *et al* 1989, Worthington *et al* 1987, Noel *et al* 1987, Krusin Elbaum *et al* 1989a, b, Klee *et al* 1988, Dolas *et al* 1989 cf Deutscher 1989). The order of magnitude is indeed the square root of the ratio α of the effective masses perpendicular and parallel to the CuO_2 planes, equations (4) and (5).

Typical values of λ and ξ are respectively in the 1000 and 10 Å ranges. $\xi_\parallel$ is about 20–30 Å, less than the mean free path along the CuO_2 planes in most cases: the *clean limit* applies; $\xi_\perp$ is equal to a very few Ångströms, thus usually less than the distance between CuO_2 planes: an *unusually strong anisotropy* prevails normal to the CuO_2 planes.

These estimates are less accurate for ξ than for λ, because of some uncertainty in the measurement of H_{c2} (Tinkham 1988, Deutscher 1989); they are also based on a Landau free-anisotropic-carriers model which can only be approximate. They seem, however, to fit with known properties of vortex lines.

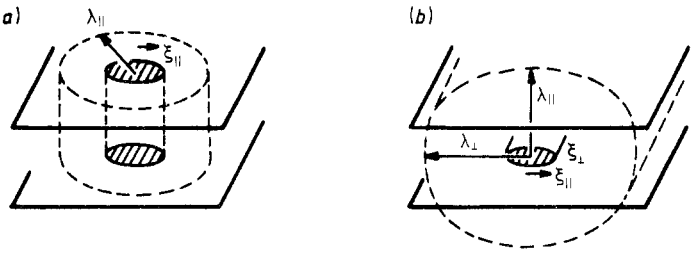

Figure 2. Structure of vortex lines: (*a*) normal to CuO_2 planes; (*b*) parallel to CuO_2 planes.

Such anisotropies reflect on the configuration of vortex lines (Friedel 1988a). Thus, for vortices normal to the CuO_2 planes, one expects a cylindrical geometry defined by $\xi_\parallel$ and $\lambda_\parallel$ (figure 2(*a*)). For vortices parallel to the CuO_2 planes, the core is elongated parallel to these planes, with a size $\xi_\parallel$ much larger than the thickness $\xi_\perp$ normal to the planes; the long range penetration with current normal to the planes, $\lambda_\perp$, is on the other hand, much larger than that ($\lambda_\parallel$) parallel to the planes (figure 2(*b*)).

Because $\xi_\perp$ is of atomic dimensions, the parallel configuration of figure 2(*b*) should have a *Peierls friction* (Friedel 1987b, 1988a). The vortex line should have a lower energy if its core is between CuO_2 planes than if it is on such planes; in compounds where families of $n > 1$ planes are separated by larger distances, these vortices should be most stable when lying between such families. A solid friction energy should thus be spent to move these vortices in a direction normal to the CuO_2 planes at 0 K; a thermally activated creep should also occur at finite temperatures, involving the creation and propagation of kinks (Friedel 1964). When rotating the vortices away from such a parallel position under an applied field, this friction should give rise to a sudden motion at a critical angle of applied field (Villard and Feinberg 1989); this may have been observed (Fruchter *et al* 1989). No such Peierls friction is observed for the glide of vortices parallel to the CuO_2 planes, indicating that $\xi_\parallel$ is indeed definitely larger than the lattice parameter along those planes.

Besides this somewhat minimal effect, the line tension of a vortex should show a large and continuously varying *anisotropy* when it is rotated from being parallel to being perpendicular to CuO_2 planes.

For *low* fields, H, vortices are essentially isolated, their enthalpy per unit length reads very approximately (Kittel 1966)

$$\begin{aligned} g_\perp &\simeq \tfrac{1}{8}[\xi_\parallel^2 H_c^2 - \lambda_\parallel^2 H^2] \\ g_\parallel &= \tfrac{1}{8}[\xi_\parallel \xi_\perp H_c^2 - \lambda_\parallel \lambda_\perp H^2] \end{aligned} \tag{9}$$

where $\frac{1}{8}H_c^2$ is the condensation energy density. Thus

$$g_\perp - g_\parallel \simeq \xi_\parallel(\xi_\parallel - \xi_\perp)H_c^2 + \lambda_\parallel(\lambda_\perp - \lambda_\parallel)H^2 > 0. \tag{10}$$

The difference in enthalpy favours the parallel direction, irrespective of whether H is smaller or larger than H_{c1}. For *high* fields near H_{c2}, the anisotropy of H_{c2} shows on the contrary that the normal direction is preferred.

Some consequences follow from this anisotropy.

First, under a rotating (small) field H, a maximum torque should be applied to the vortices of a single crystal to take them away from the parallel position. This indeed seems to have been observed (Miyajima *et al* 1988).

Second, in powders of freely rotating grains, the application of a field somewhat larger than H_{c1} should introduce vortices in the grains. The anisotropy of the g could produce a torque tending to align the grains with their CuO_2 planes parallel to the applied field. This has been observed by neutron scattering (Farnoux *et al* 1987) and used to produce a texture in a powder before sintering.

Third, in a polycrystal at low fields one could expect the vortices to follow preferentially directions parallel to CuO_2 planes in each grain. The resulting strongly zigzagging shape should lead to a strong hysteresis under an applied field gradient, which should move the line by successive local jumps from one zigzagging form to another. The situation is usually made more complex by the fact that grain boundaries are zones of weaker superconductivity, perhaps owing to local chemical composition. Vortices should then be attracted by grain boundaries, spread along them and follow them preferentially under weak fields, leading also to large hysteresis. A full discussion is, however, beyond the limits of this review.

Finally, the large anisotropy should easily destabilise the lattice of vortices produced in single crystal slices parallel to CuO_2 planes when a moderate field is applied normal to the slice. Thus the bending of the vortices under thermal fluctuations should destroy the long-range order of the lattice for thick enough slices (Nelson 1988, Nelson and Seung 1989). This seems to be observed at high temperatures (Gammel *et al* 1987, 1988) and might explain easy vortex creep under small fields in that temperature range (van Dover *et al* 1989).

2.3. 2D *thermal fluctuations near* T_c?

Besides the weak thermal fluctuations of pre-existing vortices just mentioned, one must discuss the possibility of strong thermal fluctuations which can be described in terms of the creation of new vortices. We wish to stress here that these fluctuations are probably not as important as previously stated by the author (Friedel 1988c). Indeed a mean-field analysis is probably sufficient for computing T_c.

This will be first discussed in terms of a simple magnetic analogue.

2.3.1. Classical XY magnetism. We consider a model of magnetic atoms with classical moments S rotating freely in a XY direction, with exchange interactions between nearest neighbours. With the same topology as in the oxides considered here, each atom has a strong coupling $J_\parallel$ with four neighbours in its plane, and a weaker coupling $J_\perp$ with two atoms on neighbouring planes (figure 3(a)). An extension considers families of n planes with couplings $J'_\perp$ between planes of the same family intermediate in size between $J_\parallel$ and the coupling $J_\perp$ between different families (figure 3(b)). Because of the alternate topology of these models, the ferro- and antiferromagnetic cases are equivalent. For ease of notation, we shall consider the ferromagnetic case, with

$$J_\parallel > J'_\perp > J_\perp > 0. \tag{11}$$

When $J_\perp$ (and $J'_\perp$) *vanish*, the independent planes have a Kosterlitz–Thouless temperature T_{KT} (Berezenski 1972, Berezenski and Blank 1973, Kosterlitz and Thouless 1973), related to $J_\parallel$, under which a certain magnetic rigidity corresponds to an infinite magnetic susceptibility at $k = 0$ (Banawar and Jasnow 1978). Finally T_{KT} can be computed as the temperature at which pairs of thermally excited vortices of opposite signs piercing each plane are numerous enough to interact and 'melt' (figure 4(a)). Writing

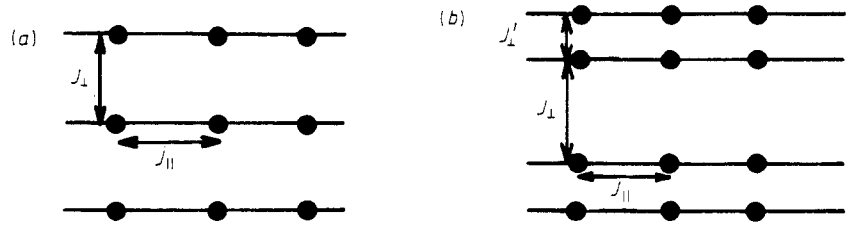

Figure 3. Magnetic interactions between Cu atoms: (*a*) $n = 1$; (*b*) $n > 1$.

that the average distance l between pairs of vortices becomes comparable with their size d

$$l \simeq d \tag{12}$$

gives (Kosterlitz 1974)

$$k_B T_{KT} \simeq 2J_\parallel |S|^2 \tag{13}$$

when the size of a pair, treated as isolated, is related to its energy V by (Kléman 1983)

$$V \simeq 2\pi J_\parallel S^2 \ln(d/a) \tag{14}$$

and the distance l is related to the lattice constant a by

$$c \simeq a^2/l^2 \simeq (\pi d/2a) \exp(-V/k_B T). \tag{15}$$

Account has been taken here that the core of vortices has a size a and that, for a size d, each pair has an entropy of rotation related to $\pi d/2a$ different positions. Criterion (12) occurs for practically the same temperature (13) for all sizes d. Better treatments including the renormalisation of V with c only changes the numerical factor in (13) from 2 to 1.8 (Villain 1974, 1975). This is to be compared with the mean field temperature $T_\parallel$, where the numerical factor is 4 (Kittel 1966).

When $J_\perp \neq 0$, and $n = 1$ (figure 3(*a*)) the usual argument is that, because of the infinite susceptibility, for $J_\perp = 0$, three dimensional order sets in for all temperatures below T_{KT}, and that the magnetic critical temperature T_M increases from T_{KT} with $J_\perp$ (Hikami and Tsuneto 1980, Deutsch and Doniach 1984). This can be seen as an increase in energy with $J_\perp$ of the interplanar parts of the vortex loops that bind together the Kosterlitz–Thouless vortices (figure 4(*a*)). And consideration of correlation between pairs of vortices on different planes, which can be viewed as vortex loops piercing several planes (figure 4(*b*)) does not alter this prediction (Pokrovsky and Uimin 1973). Writing that the thermal energy equals the interplanar coupling over an area of size the coherence length $x(T)$

$$k_B T_m \simeq J_\perp S^2 x^2(T_m)/a^2$$

with (above T_{KT})

$$x(T) \simeq a \exp[(\pi/2)(T/T_{KT} - 1)]^{1/2}$$

this gives

$$k_B T_m \simeq k_B T_{KT}[1 + \pi^2/\ln^2(S_\parallel/J_\perp)] \tag{16}$$

which is of the order of the mean field value for $J_\perp \simeq 10^{-3} J_\parallel$.

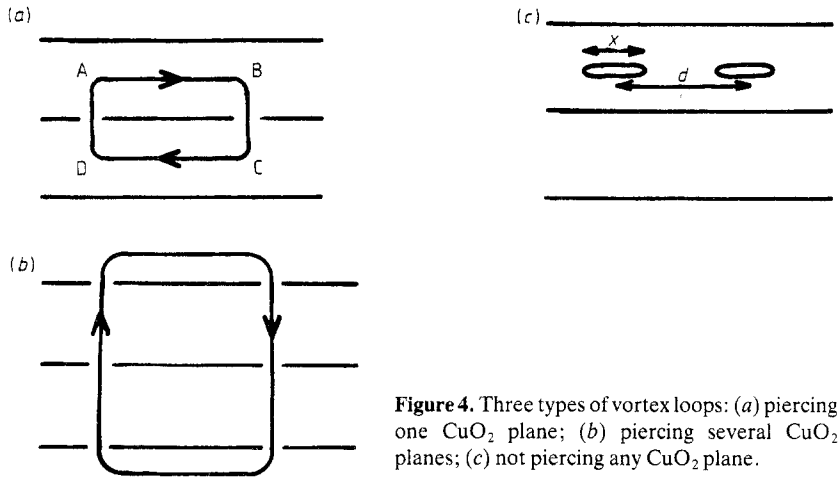

Figure 4. Three types of vortex loops: (*a*) piercing one CuO_2 plane; (*b*) piercing several CuO_2 planes; (*c*) not piercing any CuO_2 plane.

However, another type of vortex loop is possible (figure 4(*c*)): its core lies between two CuO_2 planes, analogous to the superconducting vortex sketched in figure 2(*b*). A classical analysis then gives a loop energy U which goes to zero with $J_\perp$ (Peierls 1940, Feinberg and Friedel 1988)

$$U \simeq (\pi^2 d/a)\sqrt{J_\parallel J_\perp}\, S^2 \ln(ed/2\xi_\parallel). \tag{17}$$

Here

$$\xi_\parallel \simeq a\sqrt{J_\parallel/J_\perp} \tag{18}$$

is the width of the core. A criterion of melting is less easy to give here, because of a difficulty in computing the entropy of position. By analogy with 1D solitons (Currie *et al* 1980), we can probably assume the area per independent vortex loop of size d to be $d\xi_\parallel$. Equation (15) is then replaced by

$$c \simeq d\xi_\parallel/l^2 \simeq \exp(-U/k_B T) \tag{19}$$

and the corresponding melting temperature of these vortices, with

$$l \simeq d + \xi_\parallel \tag{20}$$

is then

$$k_B T_c \simeq (\pi^2 d/a)\sqrt{J_\parallel J_\perp}\, S^2 \ln(ed/2\xi)/\ln[(d+\xi_\parallel)^2/d\xi_\parallel)].$$

The minimum value of T_c is obtained for vortices of minimum size

$$d \simeq \xi_\parallel \tag{21}$$

in which case

$$k_B T_c \simeq 2J_\parallel S^2. \tag{22}$$

T_c is a *finite* temperature, equal to T_{KT} for $J_\perp = 0$, and thus below T_m (equation (16)) for likely values of $J_\perp$. The melting of the interplane vortex loops thus destroys the 3D ordering below T_M and probably fixes the real magnetic critical temperature.

If now $n \neq 1$ (figure 3(*b*)), extensions of equation (16) show easily that the melting of Kosterlitz–Thouless vortex loops leads to T_m larger than mean field values, and thus

not physical, whether one considers simple loops (figure 4(*a*)) or multiple ones (figure 4(*b*)) across each family of planes. Melting of interplanar vortex loops along the weak regions between families leads to an equation such as (22), where $J_\parallel$ is replaced by $nJ_\parallel$: for such loops, each family of n planes acts as an effective plane through which the angle of the magnetic moment does not vary much if $J'_\perp$ is larger than the thermal energy. As a consequence, the 2D interplanar fluctuations probably still dominate for $n \simeq 2$, but would not be expected to play any specific role for $n \gg 2$.

We shall defer to a later stage the possible application of this discussion to the antiferromagnetic phases observed in some of the oxides of this review.

2.3.2. Quasi-2D superconductors. One could expect a similar discussion to hold in this case, because of the analogies in topology and number of degrees of freedom in the order parameters. We want to stress that 2D fluctuations should play an even more restricted role here.

First, for isolated CuO_2 planes the energy of a Kosterlitz–Thouless vortex pair reads, for T well below $T_\parallel$,

$$U \simeq (\Phi_0^2 b/8\pi^2\lambda_\parallel^2)\ln(d/\xi_\parallel) + (2\pi\xi_\parallel^2/a^2)k_B T_\parallel \tag{23}$$

where b is the thickness of the plane, a the lattice parameter, $T_\parallel$ measures the mean-field 2D superconductive coupling and

$$\Phi_0 = 2\pi hc/2e \tag{24}$$

is the flux quantum. In the first term, d must be replaced by $\lambda_\parallel$ when $d > \lambda_\parallel$. Melting of such pairs ($l \simeq d$) occurs for a condition such as (15), where a is replaced by $\xi_\parallel$, for the same reasons concerning the entropy of position as in equation (19). If we neglected the core term, melting of microscopic loops ($d < \lambda_\parallel$) which could be produced in finite time by thermal fluctuations would occur for a temperature of order $\Phi_0^2 b/8\pi^2\lambda_\parallel^2$. This very large temperature has no relation to the superconductive coupling involved and is indeed much bigger than $T_\parallel$ except in the immediate neighbourhood of $T_\parallel$, where $\lambda_\parallel$ tends to infinity. Inclusion of the core term reinforces the conclusion that the Kosterlitz–Thouless mechanism only operates at T_c lower than $T_\parallel$ by at most a few degrees.

If now we consider oxides with one CuO_2 plane per family ($n = 1$), the energy of an interplanar vortex loop of size d can be written similarly

$$U \simeq (\pi d/a)[(\Phi_0^2 a/8\pi^2\lambda_\parallel\lambda_\perp)\ln(d/\xi_\parallel) + (\xi_\parallel\xi_\perp/a^2)k_B T_\perp] \tag{25}$$

where d is again replaced by $\lambda_\parallel$ when $d > \lambda_\parallel$ and $k_B T_\perp$ is the mean-field superconductive coupling between CuO_2 planes. If again we neglect the core term, equations (19), (20), (21) lead to a melting temperature of these loops of order $\pi\Phi_0^2\xi_\parallel/8\pi^2\lambda_\parallel\lambda_\perp$. Relation (8) with $\xi_\perp \simeq b$ shows that this is again a very large temperature compared with $T_\parallel$. For $n > 1$, the same conclusions apply *a fortiori*.

In conclusion, both the critical temperature for uncoupling of superconducting planes T_{c1} and the Kosterlitz–Thouless temperature T_{c2} for individual planes must be very close to $T_\parallel$ and made possible only by the divergences of λ and ξ near $T_\parallel$. One predicts more precisely

$$T_{c1} < T_{c2} < T_\parallel$$

with temperature differences of only a few degrees.

Experimentally, and in agreement with these predictions, the very limited thermal range of superconductive fluctuations has been stressed by Deutscher (1989) (cf also

Yeh and Tsuei 1989). In $Bi_2Sr_2CaCu_2O_x$ single crystals, a Kosterlitz–Thouless temperature T_{c2} for individual planes has been deduced from resistivity measurements, 3 K below $T_{\parallel}$; this analysis demands $T_{c1} < T_{c2}$ (Artemenko *et al* 1989).

3. The nature of microscopic coupling

The failure of the classical BCS equation (1) has encouraged many people to look for other mechanisms of superconductivity. The response has been such that one often wonders why no room-temperature superconductor has been definitely observed yet!

Three experimental properties, which seem now to be well established, will help us to select a few possible ones out of the mass of proposals at hand.

First, tunnelling experiments have shown early that the superconductive charge quantum was $2e$ (Estève *et al* 1987): superconductivity involves *electronic carriers* making *Cooper pairs*.

If we take into account new coupling schemes, either strong couplings or electron–electron couplings, we can then consider three families of coupling schemes besides the classical weak phonon-mediated one:

(i) strong phonon-mediated couplings;
(ii) weak electron couplings;
(iii) strong electron couplings.

The argument for introducing weak-electron–electron couplings is that the cut off energy $k_B T_D$ is replaced by an electronic energy in equation (1), which can be much larger. Equation (1) breaks down in strong-coupling situations, where T_c is usually expressed in terms of a power of the coupling, in a way which is model dependent.

Second, the NMR studies show fairly clearly the existence of a Knight shift which disappears below the critical temperature and in the non-conductive phases (Alloul *et al* 1988, Wzietek *et al* 1989, Takigawa *et al* 1989, Kheiman 1989). This indicates that the carriers which condense in Cooper pairs are *fermions*. It rules out superfluidity by condensation of bosons, as is predicted in most strong coupling schemes, and especially phonon- or 'polaron'-mediated ones (Micnas *et al* 1989). As a result, we will *not* consider such schemes, despite the fact that they inspired Müller in his search among perovskites (Chakraverty 1979, Alexandrov and Ranninger 1981, de Pasquale *et al* 1989). Values of $\xi_{\parallel}$ definitely larger than the lattice parameter also exclude really strong coupling schemes for fermions (Garoche and Noguera 1987).

Finally, there seems to be a general agreement that the superconductive phases do not show any anomalously large specific heat varying linearly or as a higher power in T well below T_c (Fisher *et al* 1989, Eckert *et al* 1988, Kuentzler *et al* 1988, Kumegai *et al* 1988): the anomalies reported earlier seem due to $BaCuO_2$ inclusions with very large specific heats or, in $La_{2-x}Sr_xCuO_4$, to magnetic couplings in the 'spin-glass' phase observed at intermediary dopings x. As a result, there is no evidence of there being a fermion gas below T_c which would not take part in superconductivity; furthermore, *isotropic* (s) *coupling* and not anisotropic (d?) coupling prevails in superconductivity: this excludes many electron–electron coupling schemes.

These three experimental results are coherent with the *classical, weak phonon* BCS *coupling*. But, besides the difficulty with equation (1), a number of experimental results have been interpreted as evidence for *strong electron–electron couplings*. It is therefore not surprising that strong electron coupling schemes dominate the scene at present.

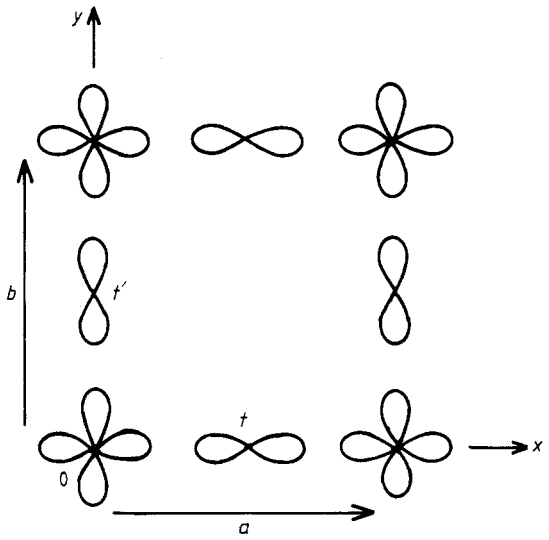

Figure 5. Cu 3d and O 2p orbitals and corresponding transfer integrals t, t' in a CuO_2 plane.

In this short review, we want to question this one-sided point of view. We want to show that the experimental evidences against a classical BCS scheme must be qualified, and that objections can also be raised against some aspects of strong electron coupling schemes. Our general conclusion will be that a phonon-mediated BCS scheme probably holds, but between electrons that have usually sizeable and detrimental antiferromagnetic interactions.

3.1. Objections to weak couplings

Weak coupling schemes start from the band structure of delocalised electrons. In the oxides considered, this has specific properties which must first be recalled. Experimental objections to the BCS scheme will then be reviewed.

3.1.1. Approximate band structure. The band structure has been computed in some details for representative cases of all the oxide families (Mattheiss 1987, Massida *et al* 1987, Yu *et al* 1987b, Gupta and Gupta 1987, 1988, Herman *et al* 1988, Mattheiss and Hamman 1988, Freeman *et al* 1988, Hybertsen and Mattheiss 1989). The results are similar near the Fermi level and can be fitted to a simplified model which treat the CuO_2 planes independently or in weak interaction (Weber 1987). In a tight-binding limit, the Fermi level falls near the middle of the antibonding CuO_2 band which couples the $3d_{x^2-y^2}$ orbitals of Cu and the $2p_\sigma$ orbitals of O (figure 5). The band-structure of an isolated CuO_2 plane is then given by

$$(E_k - E_d)(E_k - E_p) = 2t^2(1 - \cos(k_x a)) + 2t'^2(1 - \cos(k_y b)) \tag{26}$$

where t and t' are the 3d–2p transfer integrals in the x and y directions, equal in the cases pictured in figure 1(a) and 1(b) and slightly different in the case of figure 1(c). The surfaces of constant energy are given in figures 6(a) and 6(b) in the corresponding cases,

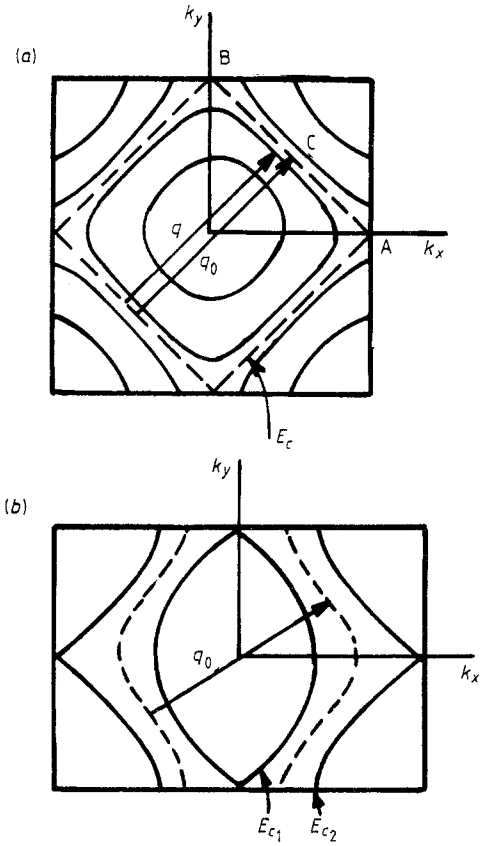

Figure 6. Band structure of antibonding CuO band: (*a*) for structures of figures 1(*a*) and 1(*b*); (*b*) for structure of figure 1(*c*).

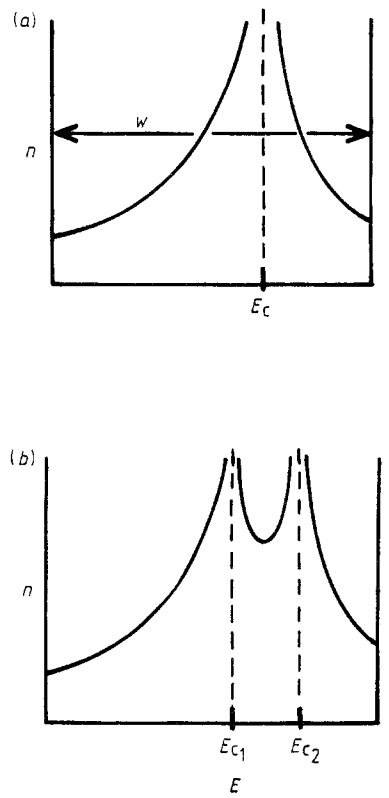

Figure 7. Density of states $n(E)$ and van Hove anomalies: (*a*) for figure 6(*a*); (*b*) for figure 6(*b*).

near the energy for a half filled band; this would correspond to the punctuated curve and is given by

$$t^2 \cos k_x a + t'^2 \cos k_y b = 0. \tag{27}$$

The corresponding densities of states $n(E)$ are pictured in figures 7(*a*) and 7(*b*). The infinite (logarithmic) van Hove anomalies (van Hove 1953) correspond to energies E_c when the surface of constant energy just touches the Brillouin zone boundary. The total band width of the upper (antibonding) band is

$$w = \tfrac{1}{2}\{[(E_d - E_p)^2 + 8(t^2 + t'^2)]^{1/2} - (E_d - E_p)\}. \tag{28}$$

A full account of the three dimensional structure leads to the following differences near the Fermi energy:

(i) Small supplementary pockets of electrons or holes (due e.g. to CuO chains in $YBa_2Cu_3O_{7-\delta}$ or BiO planes in Bi oxides, cf Peter *et al*, 1988 for instance).

(ii) A small dispersion of E_k in the third dimension, which can be described in terms of a small interplanar transfer integral $t_\perp$ which rounds off the centre of the van Hove anomaly and therefore changes somewhat the form of the Fermi surface (Park *et al* 1988). In cases of families of n CuO_2 planes ($n \neq 1$), one has to introduce a slightly larger

transfer integral $t'_\perp$ between planes of the same family. This lifts the degeneracy of the van Hove anomalies of the various planes of a family without changing their form (Friedel 1988c, Labbe 1989a).

Comparison with more exact band-structure computations lead, in all these compounds, to the following orders of magnitude:

$$\begin{aligned} &E_d - E_p \simeq 1\,\text{eV} \\ &t \simeq 2\,\text{eV} \\ &|t' - t| \simeq 10^{-2}\,\text{eV (orthorhombic } YBa_2Cu_3O_{7-\delta}) \\ &t_\perp \simeq 10^{-2}\,\text{eV} \\ &t'_\perp \simeq 10^{-1}\,\text{eV} \end{aligned} \tag{29}$$

and thus

$$w \simeq 5\,\text{eV}. \tag{30}$$

Thus $E_d - E_p$ is small compared with w. One is then near the limit

$$E_d - E_p = 0 \tag{31}$$

where the bonding and antibonding bands are contiguous in energy. Equation (26) then reads

$$E_k \simeq E_d + [2t^2(1 - \cos k_x a) + 2t'^2(1 - \cos k_y b)]^{1/2} \tag{32}$$

and

$$w = 2\sqrt{2}t. \tag{33}$$

It is easy to check that half of the electronic density of the band is on the Cu, half on the oxygens. The same is true for the (full) bonding band: *the holes of the antibonding CuO band are equally shared between the Cu in the two O of each cell.*

The other limit has often been considered:

$$E_d - E_p \gg t \simeq t'. \tag{34}$$

This would lead to an effective tight binding picture between Cu atoms of

$$E'_k \simeq 2(t_\parallel + t'_\parallel) - 2t_\parallel \cos k_x a - 2t'_\parallel \cos k_y b \tag{35}$$

with

$$t_\parallel \simeq t^2/(E_d - E_p) \tag{36}$$

and

$$w \simeq 8t_\parallel. \tag{37}$$

It is similarly easy to check that the holes of the CuO band system would then be concentrated mostly on the Cu sites in the CuO antibonding band.

This second approximation is not very different from the first if we fix $t_\parallel$ so as to give the right width, equations (33), (37), thus if $t_\parallel \simeq t/2\sqrt{2}$. It is then easy to check that the two densities of states have van Hove anomalies in the ratio

$$n'(E')/n(E) \simeq \sqrt{2} \tag{38}$$

at energies E_c, E'_c, which in both cases are near the middle of the band.

For order of magnitude estimates, we can therefore safely replace the cumbersome 'exact' equations (26) or (32) by the simpler expression (35), if $t_\parallel$ is fixed by (37). This is what will be mostly done in this paper.

3.1.2. High values of T_c. The difficulty raised by equation (1) can be met if one takes into account the quasi-2D character of the oxides. This was pointed out by Hirsch and Scalapino (1986) *before* superconductivity was discovered in these oxides. In the 1960s Labbé had made a similar remark for quasi-1D compounds (Labbé *et al* 1967, Labbé 1968; Barisic 1972). The argument was revived in more detail by Labbé and Bok (1987).

Indeed if the Fermi level E_F is near enough to the (infinite) van Hove anomaly of figure 7, the BCS integral

$$\frac{2}{V} = \int_{E_F - k_B T_D}^{E_F + k_B T_D} \tanh\left(\frac{E - E_F}{2k_B T_\parallel}\right) n(E) \frac{dE}{E - E_F} \tag{39}$$

averages out this infinite anomaly to give for $T_\parallel$ a value much bigger than equation (1), obtained with $n(E)$ constant.

The maximum value of $T_\parallel$ occurs when the Fermi level sits on the van Hove anomaly, thus here for a nearly half filled conduction band. For large values of T_D, (39) then gives, from (35),

$$k_B T_\parallel \simeq 2t_\parallel \exp(-\sqrt{\pi t_\parallel / V}). \tag{40}$$

This is *much* larger than equation (1), both because λ is replaced by $\sqrt{\lambda}$ in the exponential and because $k_B T_D$ is replaced by an electronic energy $t_\parallel$ in front of the exponential: the cutoff in (39) is provided by the fast fall of the wings of the van Hove anomaly, and not by T_D.

With $t_\parallel \simeq 1$ eV, (40) then leads easily to large values of $T_\parallel$, of the order of those observed for *small* values of λ, of order 0.1, even if one takes into account the correction (38) and a splitting of the density of states by orthorhombic distortions or by interference between planes in families of n planes. With such corrections

$$\lambda \simeq V/4t_\parallel \simeq 0.1 \qquad \text{gives} \qquad T_\parallel \simeq 100 \text{ K}. \tag{41}$$

This is indeed a *weak coupling limit*, such as could be obtained by standard electron–phonon couplings.

This maximum value is rather *insensitive* to various possible perturbations (Friedel 1987a, 1988b).

Because of the Lorentzian character of the BCS integral (39) with the main contribution in the wings, $T_\parallel$ is not much decreased by a *broadening* of the van Hove anomaly or a *shift* of the Fermi level, as long as these are not very large compared with the superconductive gap $\Delta_\parallel$, with

$$2\Delta_\parallel = 3.5\, T_\parallel. \tag{42}$$

This is the case for intraplane scattering in reasonably stoichiometric compounds, for the doping by 10–20% holes per Cu atom; it is also the case for the effect of inter-family transfer integrals $t_\perp$ (cf also Schneider *et al* 1989a, b). The actual deviations of the Fermi surface from the simple ones computed for independent planes should also be negligible if, as seems to be the case, the corresponding broadening of the van Hove anomaly is not too large. This is contrary to the views expressed by Park *et al* (1988) and Pickett (1989).

As discussed above, *thermal fluctuations* should not depress the 3D critical temperature from the mean-field value (39). This is to be contrasted with the quasi-1D case, where the maximum mean-field critical temperature in one dimension is even higher (Labbé *et al* 1967)

$$T_{\parallel} \simeq V^2/8t_{\parallel} \tag{43}$$

but the thermal fluctuations strongly depress T_c (Efetov and Larkin 1974, Uzelac and Barisic 1975)

$$T_c \simeq \sqrt{T_{\parallel} T_{\perp}}. \tag{44}$$

With, for instance, a very rough relation between $T_{\perp}$ and $t_{\perp}$ inspired by a Josephson coupling mechanism (Friedel 1987a)

$$k_B T_{\perp} \simeq t_{\perp}^2/k_B T_{\parallel} \tag{45a}$$

one easily sees that over a large range of ratios

$$\alpha = t_{\parallel}/t_{\perp} \tag{45b}$$

the quasi-2D situation is by far the *best compromise* between high mean-field $T_{\parallel}$ and low fluctuations.

3.1.3. Weak isotope effect. The observation of what was thought a null isotope effect was taken as a proof of electron–electron couplings. Later measurements showed that the effect was small, but not zero, especially in $La_{2-x}Sr_xCuO_4$.

This could be explained in many ways. But it should be pointed out that it is precisely the result predicted in the model just discussed. Equation (40) is independent of T_D, and hence independent of isotopic mass. Small corrections occur, however, for finite values of T_D, leading to an isotope parameter α much smaller than unity (Labbé 1989b). A similar effect was pointed out by Labbé for the quasi-1D topology (Labbé *et al* 1967, Labbé 1968).

More precisely, in $La_{2-x}Sr_xCuO_4$ α was measured near the maximum of T_c at $x \simeq 0.13$ (Kang *et al* 1987, Torrance *et al* 1988). The Fermi level is then fairly far from E_c, reached for $x \simeq 0$; and one expects sizeable values of α, consistent with the values near 0.2 observed (Faltens *et al* 1987). In $YBa_2Cu_3O_7$, where the central van Hove anomaly is split both by the orthorhombic distortion and by the interference between the $n = 2$ CuO_2 planes, one expects the Fermi level to be nearer to one of the lower energy van Hove anomalies, because some electrons of the $Cu^{2+}(O^{2-})_2$ planes, with a half-filled conduction band, are probably attracted to the Cu^{3+} O^{2-} chains. This could probably explain lower values of α, nearer to 0.05 (Zur Loye 1987).

If this interpretation is correct, α should increase when the Fermi level shifts away from the van Hove anomaly, thus when x increases in $La_{2-x}Sr_xCuO_4$.

3.1.4. Magnetism—Phase diagrams. The existence of antiferromagnetism in at least three of the oxide families is a direct proof of sizeable electron–electron interactions. This was taken by many as an indication that electron–electron interactions dominate in the superconductivity of these materials.

However, in all known phase diagrams showing of these oxides where antiferromagnetism and superconductivity both occur, the magnetic and superconductive

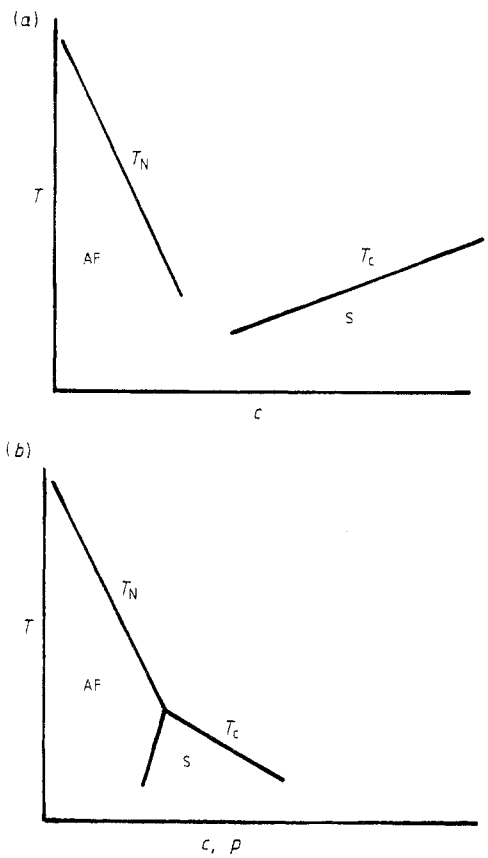

Figure 8. Phase diagrams for antiferromagnetism (T_N) and superconductivity (T_c): (*a*) oxide; (*b*) organic superconductors.

phases tend to be mutually exclusive (figure 8(*a*)): T_c decreases systematically with concentration when approaching T_N, even if some range of overlap possibly occurs in these compounds (Imbert *et al* 1988, Imbert and Jéhanno 1988, Petitgrand *et al* 1989). This is quite different from the case of organic superconductors (Jérome and Schulz 1982), where the maximum of T_c is observed next door to an antiferromagnetic phase (figure 8(*b*)). Indeed, in this second case, a careful analysis of the fluctuating regime above T_c shows that superconductivity arises most probably by electron–electron couplings through antiferromagnetic fluctuations (Jérome *et al* 1969, Bourbonnais 1989). Oxides behave much more like many transition-metal alloys, where BCS superconductivity is through electron–phonon interactions λ, and the decrease of T_c can be attributed, at least in part, to an increase of the corrective electron–electron interactions μ^* (equation (3)).

A similar explanation might be valid here. However, very strong antiferromagnetic fluctuations are observed along the CuO_2 planes in this intermediate regime (Endoh 1988, Birgeneau *et al* 1989). It is then tempting to relate the decrease of T_c simply to the development of a corresponding *pseudogap* near the Fermi level, due to the scattering of the conduction electrons on the antiferromagnetic fluctuations (Friedel 1988a): as the magnetic fluctuations survive well above T_c, such a pseudogap is expected to be larger than the superconductive one; it could therefore depress the electronic density near the Fermi level, and thus T_c, in the same way as charge density waves depress T_c in transition-metal dichalcogenides (Friedel 1975).

3.1.5. Magnetism—Electron localisation or delocalisation. The detailed analysis of the antiferromagnetic properties has been fitted in terms of *strong localisation* of electrons on Cu atoms of the CuO_2 planes; this has confirmed in the mind of many a belief in strong electron–electron couplings. The model used assumes magnetic electrons with quantum spin $\frac{1}{2}$, interacting strongly by exchange $J_\parallel$ between neighbours in the planes (Chakravarty *et al* 1988, 1989). It shows many characteristics similar to the antiferromagnetism of La_2CuO_4 and $YBa_2Cu_3O_6$ in the fluctuating range above T_N (also Tyc *et al* 1989). In such compounds, one expects indeed one electron per Cu atom in the CuO_2 planes; quantum fluctuations would reduce the local moment to about 0.6 μ_B, as observed; reasonable values of T_N can be obtained with a modest interplanar exchange coupling $J_\perp$, because, for such a Heisenberg model (Regnault and Rossat Mignot 1989)

$$k_B T_N \simeq 2J_\parallel S^2/\ln(J_\parallel J_\perp). \tag{46}$$

Finally the steep drop in T_N with doping x, both in $La_{2-x}Sr_xO_4$ (Endoh *et al* 1988) and in $YBa_2Cu_3O_{6+x}$, has been attributed to local ferromagnetic couplings induced by the holes in the CuO_2 planes due to doping and localised either on the Cu (Kitaoka *et al* 1988a, b) or on O atoms (Aharony *et al* 1988, 1989, Dzyaloshinskii 1989). The multiplication of these distortions could lead to a spin glass phase, as seems to be observed in $La_{2-x}Sr_xCuO_4$ for $x_1 < x < x_2$ (figure 9, cf Kumegai *et al* 1987, Kitaoka *et al* 1988a, b, Imbert *et al* 1988, Imbert and Jéhanno 1988).

However, most of these experimental facts could be equally well explained, starting from the opposite extreme of *weakly-coupled, delocalised electrons*. Thus, for single CuO_2 planes with one electron per Cu, the Fermi surface shows a very special property of *perfect nesting* by vectors (figure 6)

$$\boldsymbol{q}_0 = (\pm\pi/a, \pm\pi/b). \tag{47}$$

Equation (27) shows that this is equally true in the orthorhombic and tetragonal phases pictured in figure 1 (Friedel 1987a). Such nestings can be produced by local electron–electron repulsions for spin modulations corresponding to vectors $\boldsymbol{q}_0$ which, together, produce the antiferromagnetic arrangement observed on Cu atoms. The mean-field condition for the appearance of such spin-density waves (SDW) reads, in terms of the magnetic susceptibility χ:

$$\frac{4}{U_{dd}} = \sum_{\boldsymbol{q}_0} \chi(\boldsymbol{q}_0) = -\sum_{k,\boldsymbol{q}_0} \frac{f(E_k) - f(E_{k+\boldsymbol{q}_0})}{E_k - E_{k+\boldsymbol{q}_0}} \tag{48}$$

if U_{dd} is the electron–electron repulsion on Cu atoms and

$$f = \exp[(E_k - E_F)/k_B T_N - 1]^{-1}. \tag{49}$$

The factor 4 comes from the fact that only half the holes are on Cu atoms. The study of the stability of the SDW for $T < T_N$ requires a BCS-type treatment of the gap g. (Hirsch 1985, Dzyaloshinskii 1987b, Schulz 1989a). The variation of stability with amplitude or wavelength gives the atomic moment and the strength of the spin waves, while treatments beyond the simple mean-field approximation would lead to 2D fluctuations, both below and above T_N.

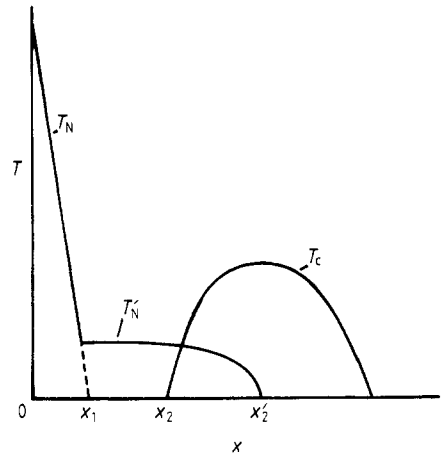

Figure 9. Magnetic and superconductive phase diagram for $La_{2-x}Sr_xCuO_4$ (schematic).

The fairly large values of T_N observed for La_2CuO_4 where nesting is optimum can be explained by modest values of U_{dd}, definitely less than half the bandwidth and of order

$$U_{dd} \simeq 2\,\text{eV} \tag{50}$$

(Hasegawa and Fukuyama 1987). Such low values of U_{dd} are met in transition metals (Friedel 1980, 1982). Due to fluctuations, T_N should be somewhat smaller than the mean-field value (48), (49). On the other hand, it should not be appreciably depressed by the rounding-off of the van Hove anomaly due to intraplanar scattering ($\rho_\parallel$) or interplanar couplings ($t_\perp$), while this perturbation can kill a possible spontaneous Jahn–Teller distortion from the configurations in figure 1 (Friedel 1988d). Moments of about 0.5 μ_B per Cu atom, as observed, are easily explained in this scheme. Because of the perfect nesting condition, even values of U_{dd} definitely less than the band width w lead to rather 'strong' antiferromagnetism, where the local moment is near to or equal to its maximum possible value (Schulz 1987); but, as stressed before, the strong Cu 3d–O 2p covalency delocalises half the electron holes on the O $2p_\sigma$ orbitals which, by symmetry, cannot become spin polarised. One then expects a local moment μ per Cu atom near to an upper limit equal to half a Bohr magneton. As in transition metals, these moments are expected to be frozen at low temperatures, with quantum fluctuations reduced to spin waves of fairly weak amplitudes. In this scheme, the magnetic gap is easily computed to be

$$g \simeq 4(U_{dd}/4)\mu/\mu_B \simeq \tfrac{1}{2}U_{dd}.$$

With (50), this fits in order of magnitude with the gap observed (van der Marel *et al* (1988), cf also Nücker *et al* (1989) for $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$). In this model, spin waves are expected to have a large intraplanar exchange $J_\parallel$, as has been observed (Shirane *et al* 1987, Rossat Mignault *et al* 1989). $T_N(\boldsymbol{q}_0)$ should decrease fast with doping in $La_{2-x}Sr_xCuO_4$, where it should disappear for $x \simeq 2$–10^2 for the values of w and U_{dd} given by (30) and (50) (Friedel, 1987a, cf figure 9. Finally the fact that the superconductive temperature T_c is lower than T_N for undoped La_2CuO_4, but decreases less rapidly than T_N with doping x in $La_{2-x}Sr_xCuO_4$, so that it becomes sizeable over an

intermediate range of doping x (figure 9) follows directly from the comparison of their mean-field equations for T_N and T_c, which read approximately

$$\frac{8}{U_{dd}} \simeq \int \frac{n(E)}{E - E_0} \tanh\left(\frac{E - E_F}{2k_B T_N}\right) dE \tag{51}$$

$$\frac{2}{V} \simeq \int \frac{n(E)}{E - E_F} \tanh\left(\frac{E - E_F}{2k_B T_c}\right) dE. \tag{52}$$

When E_F is near the logarithmic anomaly of $n(E)$ at mid band energy E_0, integration by parts shows that T_N starts from a larger value than T_c (if (41) and (50) apply), but decreases much faster than T_c when E_F deviates from E_0 because of doping: when E_F differs from E_0, the logarithmic anomaly is squared for T_c but no longer for T_N (Friedel 1987a, Labbé 1989b).

One objection to such a scheme has been that more complete band computations, using the 'local-density approximation' LDA to treat electron–electron interactions, do not lead to stable magnetic phases (Stocks *et al* 1988, Temmerman *et al* 1989). This seems, however, to be a weakness of the LDA, and is no serious objection to strongly delocalised electron schemes (Hybertsen and Schlüter 1989).

The validity of the simple approach, with two parameters U, V related to on-site electron–electron and to phonon-mediated interactions, respectively, can be tested by more elaborate 'geology' studies which take into account more explicitly the possible interferences of electron states near different saddle points such as A and C in figure 6(*a*). These weak interaction studies are straight extensions of an approach developed for (quasi)-1D conductors (cf Jérome and Schulz 1982). They use at least 4 parameters G_i related to interactions of Cooper pairs on one or two saddle points (respectively G_2 and G_3) and to intra- and inter-saddle points scatterings (respectively G_1 and G_4). These G_i could be expressed in terms of U, V and longer-range Coulomb and exchange interactions, with the same type of complication as that involved in replacing μ by μ^* in equation (3) if V is, as assumed here, a phonon-mediated coupling. One then finds that, depending on the relative values of these G_i, six instabilities are possible (Schulz 1989a) or a mixture of them (Dzyaloshinskii and Yakovenko 1988, 1989): singlet superconductivity with s or d symmetry; charge-density wave or charge-flux phase; spin-density wave or spin-flux phase. The flux phases and d superconductivity are due to antisymmetric coupling of the saddle points. Similar flux phases were first considered for two-band excitonic instabilities (Halperin and Rice 1968). However, as long as the on site parameters U and V of equations (51), (52) are dominant as expected here, these new phases have less stability than the classical s superconductivity, spin density waves (SDW) and charge density waves (CDW).

In a similar way, a fifth coupling constant G_5 can be considered, due to Umklapp processes acting on the three quarter full bonding and antibonding Cu 3d–O 2p band system. This could lead to a Mott gap at the Fermi level, proportional to the gap Δ between the bonding and antibonding bands. According to (26), Δ is proportional to $E_d - E_p$. However, for the numerical values (29) reported above, Δ is small and the Mott gap negligible in comparison with the Slater gap due to the SDW instability (Barisic and Batistic 1989a). This is not necessarily the case for other CuO_2 base compounds where $E_d - E_p$ can be much larger, owing to different Madelung terms due to the surrounding ions. The corresponding larger gap Δ can lead to insulators with a sizeable Mott gap (Torrance and Metzger 1989).

In $YBa_2Cu_3O_{6+x}$, a similar discussion could apply, with some added complications. First the electron transfer from CuO_2 planes to CuO chains, which is zero for $x = 0$, increases with x but remains modest and also probably keeps to very small values up to $x \simeq 0.2$ (Torrance *et al* 1989). Second, in this $n = 2$ family, the transfer integral $t'_\perp$ between the two CuO_2 planes of a family should lift the degeneracy of the densities of states in the two planes by an energy $2t'_\perp$ (Friedel 1988c). With $t'_\perp \simeq 0.1$ eV (cf (29)), this is much less than the magnetic gap of order U_{dd}, which should essentially ignore this effect; $t'_\perp$ only plays a role in the fairly strong magnetic coupling between the two CuO_2 planes of a family (Alloul *et al* 1988). The vanishing of T_N with increasing doping x would be explained as in $La_{2-x}Sr_xCuO_4$; a further splitting of the van Hove anomalies by the orthorhombic distortion due to CuO chains would multiply the number of van Hove anomalies at energies E_c somewhat different from the mid-band energy E_0. It would then be likely that the Fermi level should be, for $YBa_2Cu_3O_7$, near one of the two van Hove anomalies of lower energy E_c, a situation which, as equations (51) and (52) show, would reinforce T_c much more than T_N (cf Lederer *et al* 1987, Friedel 1987a).

One does not know enough about the Bi, Tl and Pb oxides to propose any firm delocalised electron scheme. It seems, however, that some electron transfer occurs between the CuO_2 planes and other planes (e.g. BiO), so that the CuO_2 planes are never in the half-filled band situation favourable for antiferromagnetism (so far except in the $Ba_2Sr_{3-x}Y_xCu_2O_{8+y}$ family). The situation is then comparable to that in $YBa_2Cu_3O_7$, except for the lack of orthorhombic distortion due to CuO chains. Again the transfer integrals $t'_\perp$ split the van Hove anomaly in n anomalies of equal amplitude; T_c should be maximum when the Fermi level sits on one such anomaly, according to equation (39). More quantitatively, the amplitude of each anomaly *per Cu atom* is inversely proportional to their number n (to be compared to $2 \times 2 = 4$ in $YBa_2Cu_3O_7$). One can therefore predict *maximum* values of T_c in the ratio $1/n$ for $n \geqslant 3$ in the Bi, Tl, Pb families, to be compared with $\frac{1}{4}$ for $YBa_2Cu_3O_{6+x}$. For $n = 1$ or 2, the situation is analogous to $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+x}$, and one expects rather lower values of T_c, to be replaced by antiferromagnetism if one approaches optimal conditions for T_c, near mid-band filling ($x = 0$).

In conclusion, the BCS scheme can explain the optimal value of T_c at $n = 3$ observed in the Bi, Tl and Pb oxides if one takes into account a general decrease of T_c with n, compensated for $n = 1$ and 2 by a competition with antiferromagnetism and for $YBa_2Cu_3O_7$ a lowering of T_c due to the orthorhombic distortion. Other explanations of the variations of T_c with n have been put forward. Besides variations of 2D fluctuations with n (Friedel 1988c) which has been shown in § 2 not to occur, these explanations rely on Josephson coupling schemes which lead to unphysical values of T_c, larger than the mean-field value (39) (Birman and Liu 1988, Wheatley *et al* 1988) or mistakenly take in (39) the density-of-states per unit cell and not per Cu atom (Kasowski *et al* 1988, Bok 1988, Weber 1988a, b, Schneider and Baeriswyl 1989).

3.1.6. Magnetism—Direct proofs of delocalisation? It would obviously be of interest to distinguish experimentally between these two extreme descriptions of magnetism, or to ascertain that an intermediate one is valid. The question is not quite straightforward, as the following discussion shows.

(i) *Positron annihilation.* Experiments on antiferromagnetic La_2CuO_4 have been interpreted in terms of pockets of electrons at the centre of the Brillouin zone and hole pockets at the corners with, in between, zones of variable electronic density (Tanigawa

et al 1987). This is at least roughly what one expects when antiferromagnetism develops by nesting for a half-filled band (Berko and Plaskett 1958, Friedel and Peter 1988, Gyorffy *et al* 1988): each SDW of wavevector $\boldsymbol{q}_0$ mixes two non-magnetic Bloch functions of vectors $\boldsymbol{k}$ and $\boldsymbol{q}_0 - \boldsymbol{k}$ to produce a magnetic state of vector $\boldsymbol{k}$. For magnetic states $\boldsymbol{k}$ occupying the square defined by the first magnetic Brillouin zone, one then expects a progressive occupation f of non-magnetic Bloch states, between pockets of electrons ($f = 1$) and holes ($f = 0$) from the centre to the corners of the crystal Brillouin zone. This is indeed observed; the width of the intermediate range is compatible with an energy gap g somewhat smaller but comparable with the total bandwidth w. As, for SDW, $g \simeq U_{dd}\,\mu/\mu_B$ and $\mu \simeq \frac{1}{2}\,\mu_B$, values (30) and (50) are again reasonable.

However, this reasoning neglects the k-dependence of the atomic form factors in the non-magnetic Bloch functions. Recent computations explain the experimental results in that way (Wachs *et al* 1988).

(ii) *Incommensurate spin-density waves versus spin glass in $La_{2-x}Sr_xCuO_4$.* Recent neutron experiments suggest that, in the intermediate range of dopings $x_1 < x < 2_2$ (figure 9), a random spin glass is replaced by somewhat short range spin-density waves with an incommensurate wavevector of modulus q, with

$$|q - q_0| \simeq \alpha x q_0 \tag{53}$$

and α of order unity (Birgeneau *et al* 1989, Birgeneau 1988, Yoshiwara *et al* 1989).

This is precisely what could be expected in a delocalised electron picture, where the Fermi surface diameter decreases with a vector $\boldsymbol{q}$ pictured in figure 6(a) which follows an equation such as (53). A simple nesting by $\boldsymbol{q}$ might indeed be expected to become more stable than the commensurate one $\boldsymbol{q}_0$ for a sufficiently large doping x (Friedel 1988a).

Schulz (1989b, c) has actually pointed out that a different nesting condition, by vectors

$$\boldsymbol{q}' \simeq \boldsymbol{q}_0 - (2\delta/\pi a, 0) \text{ or } \boldsymbol{q}_0 - (0, 2\delta/\pi b)$$

leads to a more stable SDW than

$$\boldsymbol{q} = \boldsymbol{q}_0 - (\delta/\pi a, \delta/\pi b).$$

For weak U_{dd}, such incommensurate modulation is actually more stable than the commensurate one even in the limit $x \to 0$, at least at low temperatures. Below a critical value of x, the supplementary holes introduced by doping are captured in equidistant walls of discommensurations, parallel to the Cu chains. This explains non-conductive properties of these compounds. A transition to a low-temperature conductive phase is expected for larger values of x, but before the limit of x where the SDW disappears. The gap of these SDW is then weak enough to disappear in the neighbourhood of the van Hove anomalies such as A and B in figure 6(a), while remaining finite in intermediate regions such as C. It is then understandable that, in this intermediate range of doping, incommensurate SDW could coexist with a fairly strong superconductivity, and that, as suggested in a more general way above, T_c increases while T'_N decreases (figure 9).

It must be stressed, however, that incommensurate spin modulations with vector $\boldsymbol{q}$ can also be obtained starting from delocalised but highly correlated electrons, as described below (Poilblanc and Rice 1989, Machida 1989, Zaanen and Gunnarson 1989, Gabay 1989). The reason is again a spatial localisation of excess holes due to doping along walls of discommensuration, more than the Luttinger theorem (1961) by which the Fermi surface for delocalised electrons is independent of their correlations.

In conclusion, the mere observation of incommensurate spin modulations with a wavevector following (53) cannot be taken as evidence of the nesting of delocalised electrons. Indeed, a more detailed study is required to decide whether the vector of the modulation is $\boldsymbol{q}$ as pictured in figure 6(*a*) and predicted in strong correlation models, or whether it is $\boldsymbol{q}'$ as described in Schulz' analysis for weak correlations. Indeed a switching from one direction to the other of the corresponding domain walls at low doping is expected for $U \simeq \frac{1}{2}w$ (Schulz 1989c). It would also be of interest to check whether commensurate fluctuations at $\boldsymbol{q}_0$ dominate at high temperatures, as predicted in that model for not-too-large dopings.

(iii) *Form factor of magnetic moments.* The neutron form factor of Cu atoms corresponds to $3d_{x^2-y^2}$ orbitals (Gillon *et al* 1989). This fits equally well with a localised or delocalised picture of the valence electrons, although it excludes other more complex schemes with several active d orbitals per Cu atom. However, under an applied magnetic field, some oxygen atoms become spin-polarised: this shows that holes can be present on O 2p orbitals and coupled with the Cu magnetic orbitals. Some degree of CuO covalency must be considered, as discussed later.

(iv) *Magnetic anisotropy.* All the magnetic compounds show by neutron scattering some degree of *XY* anisotropy at low temperatures of order 20 K (Birgeneau *et al* 1989, Petitgrand and Collin 1988, Rossat Mignault *et al* 1989).

Such anisotropy must be extremely small for localised spin $\frac{1}{2}$ (Stevens 1963). Indeed, to second order in spin-orbit coupling S, the anisotropy is proportional to

$$\langle S_z^2 \rangle - \tfrac{1}{2}[\langle S_x^2 \rangle + \langle S_y^2 \rangle]$$

and therefore vanishes because of the equalities of $\langle S_x^2 \rangle$, $\langle S_y^2 \rangle$ and $\langle S_z^2 \rangle$. A low-energy inelastic line in the neutron diffusion spectra has indeed been attributed to the energy necessary to bring the spins out of the *XY* plane (Birgeneau *et al* 1989, Rossat Mignot *et al* 1989, Aharony *et al* 1989, Vettier *et al* 1989); this should be of the order of the geometrical mean between the energy of anisotropy and the exchange term $J_{\parallel}$. This observed energy, of order 10 K, corresponds to an energy of anisotropy of 10^{-4} eV per Cu atom; it could be due to an anisotropic exchange term and would justify the use of a Heisenberg (isotropic) model above 20 K.

Now if, on the contrary, the magnetic properties are due to weak interactions of otherwise delocalised electrons, i.e. for $U_{dd} \ll w$, quantum fluctuations leading to non-zero $\langle S_x^2 \rangle$ and $\langle S_y^2 \rangle$ can be neglected at low temperatures. As a result, the site anisotropy in λ^2 is now only due to the $\langle S_z^2 \rangle$ term (Brooks 1940, Fletcher 1952, Bennett and Cooper 1971, Bruno 1989). It reads (Friedel 1988a)

$$E_z - E_{xz} = (75/4\pi^2)[4/(E_0 - E_2) - 1/(E_0 - E_3)]\lambda^2 \tag{54}$$

where E_0, E_2 and E_3 are the average energies of the $x^2 - y^2$, xy and xz, zx orbitals. With $E_0 - E_2 \leqslant E_0 - E_3 < 20$ eV, and $\lambda \simeq 0.07$ eV, this energy is necessarily positive, in agreement with an in-plane *XY* anisotropy. With the large $J_{\parallel}$ exchange term observed, such a value of anisotropy should preserve an *XY* model up to T_N and beyond, in the fluctuation regime, at least as long as the coherence length is definitely larger than the interatomic distance. Indeed, the discussion above has shown that magnetic fluctuations over a fairly large temperature range above T_N are compatible with an *XY* model, and cannot be taken as a proof of Heisenberg coupling.

The measurement of the *XY* magnetic anisotropy and its variation with temperature is therefore a very direct measurement of the more-or-less localised character of the valence electrons, or of the ratio U_{dd}/w responsible for the magnetic gap. It would be of

great interest to check this point by neutron scattering above 20 K under a magnetic field applied normal to the CuO_2 planes. However, two experimental results point towards a strong *XY* anisotropy and thus a strongly delocalised picture.

The small ferromagnetism due in La_2CuO_4 to a small rotation of the spins with the CuO_6 hexahedra away from a perfect flat planar *XY* anisotropy, as described in § 2, remains to high temperatures (Kastner *et al* 1988): this would be incomprehensible in a Heisenberg model.

Fe^{3+} replacing Cu^{2+} in $La_{2-x}Sr_xCuO_4$ has an isotropic spin $\frac{5}{2}$, and therefore tests the magnetic anisotropy of the surrounding medium. Mössbauer measurements show a complete *XY* anisotropy up to T_N in the phase diagram of figure 9, and also in the 'spin glass' regime (T_N') at sufficiently low Fe concentrations for their interactions to be negligible (Imbert and Jéhanno 1988, Imbert *et al* 1988).

We conclude from this long discussion that a fair amount of *delocalisation*, with U_{dd} at most of order w or less, is necessary to explain the magnetic properties of these oxides.

3.1.7. Hall effect. The first measurements on $La_{2-x}Sr_xCuO_4$ (Ong *et al* 1987) were interpreted as giving a purely hole conduction, with a number of carriers per Cu atom equal to x. This was seen as a very strong argument in favour of a localisation of one d electron per Cu in La_2CuO_4, leading to a Mott insulator; for $x \neq 0$, hole carriers could be due to the transfer of electrons of the CuO_2 planes to the Sr atoms which, replacing La atoms, would each act as Sr^- dopant. This point of view was reinforced by the observation of positive hole conduction along CuO_2 planes in $YBa_2Cu_3O_7$ (Iye *et al* 1988), where, as we have already stressed, one can assume a small transfer of electrons from CuO_2 planes to CuO chains.

Such results are clearly incompatible with the simple band picture such as in figures 6 and 7 which should apply directly to $La_{2-x}Sr_xCuO_4$: the Fermi surface, being below the van Hove anomaly, does not touch any Brillouin zone boundary and electron conduction should occur in the CuO_2 planes. The objection is less telling for $YBa_2Cu_3O_7$ or the Bi, Tl or Pb families: in these cases the exact position of the Fermi level is not known with respect to the multiple van Hove anomalies, and it is quite likely that some at least of the large Fermi surfaces are hole-like. This is for instance what is computed for $YBa_2Cu_3O_7$ (Yu *et al* 1987a, b), in agreement with an interpretation of the positron annihilation data (Peter *et al* 1988).

For $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$, we have seen that extensive antiferromagnetic fluctuations along the CuO_2 planes are observed in the metallic range. As already stressed for T_c, even in a delocalised electron approach, one should take into account their scattering by these antiferromagnetic fluctuations. The corresponding theory would follow what has been done in a quasi-1D topology (Jérome and Schulz 1982). Roughly speaking, one could expect an *antiferromagnetic pseudo-gap* at or near the Fermi level. This would reduce the number of free carriers; it would change their sign when, as seems to be the case here, the fluctuations are with vector q_0, thus the middle of the pseudogap is above the Fermi level. The magnetic fluctuations, being commensurate, would not provide any supplementary current.

In agreement with such a point of view, one would expect the number of holes to vary somewhat with the amplitude of the pseudogap, thus with the amplitude and coherence length of the magnetic fluctuations. Indeed the number of holes deduced from the Hall effect increases by a factor 2 or 3 from T_c to $2T_c$ in $La_{2-x}Sr_xCu_4$ (Takagi *et al* 1989) and in $YBa_2Cu_3O_6$ (Forro *et al* 1988). Even near T_c, the concentration of carriers in $La_{2-x}Sr_xCuO_4$ is already larger than x by a very large factor. Also the Hall effect

changes sign as expected rather suddenly for $x > 0.13$, when T_c no longer increases with x and the magnetic fluctuations are weak and very short range. It is indeed remarkable that no great change of T_c or of $\rho_\parallel$ occurs at that critical concentration.

Finally, the large positive slope $d\rho_\parallel/dT$ of the in-plane resistivity with temperature can be related to the thermal variation of the coherence length of the antiferromagnetic fluctuations (Papoular 1988).

In conclusion, it is clear that antiferromagnetism dominates at least in some ranges the conductive properties of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$. But Hall-effect measurements are not in general compatible with total localisation of one electron per Cu in the CuO_2 plane. In addition, transport theories are not advanced enough to give the magnitude of electron–electron correlations needed to explain the observations.

3.1.8. Electronic excitations. A careful study of electronic excitations on Cu (x-rays, photoemission, Auger effects) shows satellite lines which can be attributed to the excitation of two holes in the conduction band (Thiry *et al* 1987, Bianconi *et al* 1987).

An analysis based on a localised picture of these electrons (Sawatzki 1977) leads to a fairly large value of the Coulomb interaction (Nakazawa *et al* 1988)

$$U_{dd} \simeq 5\text{–}10\,\text{eV}. \tag{55}$$

This is of the same order or somewhat larger than the computed bandwidth (30). It has been taken as a confirmation of a localised picture for these electrons, and even of extreme localisation ($U_{dd} \gg w$).

This evidence is perhaps not as clear-cut as it seems. A similar discussion occurred in the context of the d band of transition metals, where the observation of a Fermi surface with strong d character is a direct proof of the delocalisation of d electrons. Indeed, starting with delocalised electrons and treating U_{dd} as a perturbation with respect to the band width w, one predicts a satellite line at the maximum of the imaginary part of (Treglia *et al* 1980)

$$\frac{1}{\pi}\sum_k \frac{1}{E - \Sigma_k + i\varepsilon} \tag{56}$$

where the self-energy Σ_k is computed to second order in U_{dd}. This is shifted from the Fermi level by an energy that depends both on U_{dd} and w. Indeed, experimental results are coherent in that way with $U_{dd} < w$ and both given by (30), (50) (Bianconi *et al* 1987).

3.1.9. NMR. The large relaxation rates T_1^{-1} observed on Cu atoms in $YBa_2Cu_3O_{7-\delta}$ are not consistent with the classical Korringa relation for delocalised electrons; they have been fitted with a model of localised magnetic electrons in a fluctuating regime (Horvatic *et al* 1989).

These results seem a good proof for magnetic fluctuations on the Cu atoms, which are indeed observed by neutron scattering. These in turn denote some electron–electron interactions but do *not* tell whether they are strong or weak.

Other NMR data on the contrary indicate at least some degree of delocalisation. The main results concern the observation of a Knight shift which disappears under T_c and seems to indicate the fermionic character of the carriers responsible for superconductivity. The positive sign of these shifts can be understood in terms of a covalent bonding between the Cu 3d and O 2p states (Wzietek *et al* 1989), possibly reinforced for Cu by an admixture of Cu 4s states (Mila and Rice 1989). The strong variation of the Knight shift with δ and T for Y in $YBa_2Cu_3O_{7-\delta}$ (Alloul *et al* 1989) might be due

principally to the shift with respect to the Fermi level and broadening of an antiferromagnetic pseudo-gap with decreasing δ. The plasma frequency, which averages out this effect on a sizeable energy, might be less sensitive to δ (Bontemps *et al* (1989), but cf Uemura *et al* (1988, 1989a, b)). Finally a peak in T_1^{-1} just below T_c (Bleier *et al* 1988, Takigawa *et al* 1989, Smith and Schwarz 1989) can be attributed to the peak of the BCS distribution of states below the superconductive gap. A similar peak seems to be observed in photoemission (Schneider *et al* 1989a, b, Imer *et al* 1989).

The Korringa relation between T_1^{-1} and Knight shift observed on Y in $YBa_2Cu_3O_{7-\delta}$ is also a convincing indication of a Fermi gas (Alloul *et al* 1989).

It must be pointed out that the gaps deduced from the low temperature variations of the relaxation rates T_1^{-1} do not always seem to follow the BCS relation (42) (Cooper *et al* 1988, 1989). Rather systematically in $YBa_2Cu_3O_{7-\delta}$, the numerical factor is nearer to 8 for the Cu in CuO_2 planes (Seidel *et al* 1988); one can however wonder whether this is not an artefact due to electronic excitations to the edge of a magnetic pseudo gap or to a secondary van Hove anomaly.

3.2. Objections to some strong electron correlation schemes

In the light of what we know of the Cu–O covalency, objections or comments can be made to a number of schemes involving strong electron correlations.

3.2.1. Cu–O covalency. The fairly large width computed for the conduction band in the Cu_2O planes comes from the large covalent character of these ionocovalent bonds (Friedel 1988a). In the perturbation language of equation (36), this comes from the progressive stabilisation of the 3d orbitals through the 3d series, which makes $E_d - E_p$ minimum for Cu. This difference is indeed small enough to make the bonding and antibonding CuO bands quasi-continuous in energy, thus broadening the bands further. This total band width seems clearly seen in x-ray spectra. As a result, one cannot transfer without discussion results and concepts from transition metal oxides, where the ionic character is more marked.

A direct experimental proof of this Cu–O covalency is deduced from the excitations of the s shells of O towards 2p levels: they show that the 2p shells are not full, but contain pre-existing holes (Tranmada *et al* 1987, Shen *et al* 1987, Nücker *et al* 1988, 1989). The symmetry of these holes is indeed compatible with the covalency described in figure 5 (Himpsel *et al* 1989). Their general intensity increases roughly in proportion to x in $La_{2-x}Sr_xCuO_4$ (Nücker *et al* 1987, Kuiper *et al* 1989b, c). But they seem to exist even in the undoped compound La_2CuO_4, $YBa_2Cu_3O_6$, although their presence is somewhat shifted and blurred by the magnetic gap (Petroff *et al* 1987). A similar covalency effect seems observed in insulating NiO (Kuiper *et al* 1989a).

This evidence works against 'ionic' models but, as we shall see, is no conclusive proof of covalent heavy fermion models.

3.2.2. Ionic models. A number of models start from an ionic description of the CuO_2 planes, with one electron per $3d_{x^2-y^2}$ copper orbital. They mostly assume these electrons to be localised by their Coulomb repulsions U_{dd} in the stoichiometric compounds La_2CuO_4, $YBa_2Cu_3O_6$. Weaker exchange interactions are assumed, of an antiferromagnetic nature between spins on neighbouring sites. This is indeed possible if U_{dd} is much larger than the band width $w = 8t_\parallel$ for non-interacting electrons, but small enough for the kinetic exchange term $J = t_\parallel^2/U_{dd}$ to be larger than the very weak

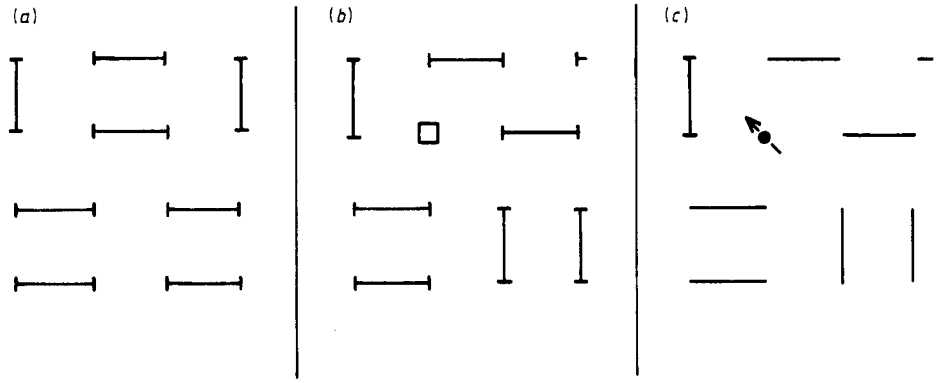

Figure 10. $|\psi_\alpha\rangle$ state for RVB: (*a*) perfect; (*b*) plus holon; (*c*) plus Fermion.

(ferromagnetic) Heisenberg terms. Besides the neglect of the Cu–O covalency, which will be discussed later, these models present other difficulties. They are usually called *tJ* models.

Some initial models tried to apply variational models inspired by that of *Gutzwiller* (1965) to describe the motion of holes introduced on Cu atoms by doping, say in $La_{2-x}Sr_xCuO_4$ (Polyakov and Wiegmann 1987, Dzyaloshinskii 1987a, Dzyaloshinskii *et al* 1988, Cyrot *et al* 1988, 1989, cf Cyrot 1989). Besides the difficulties of statistics, such models neglect the possibility, in an antiferromagnetic environment, for these positive holes to create *magnetic polarons*: because they are more mobile in a ferromagnetic than antiferromagnetic environment, such holes are expected to delocalise over a certain magnetic range (Héritier 1988). For some range of the ratio of the exchange coupling $t_\parallel^2/U_{dd}$ to the transfer integral $t_\parallel$, such magnetic polarons are just large enough to accept two holes, despite their long range repulsions, and no more (Pokrovsky 1987). This could provide a (ferromagnetic) coupling between holes. But, besides the poor mobility of such polarons and the absence of any sign of entities with large magnetic moments, the model fails because, in the limit $U_{dd} \gg t_\parallel$, the magnetic polarons are always too large to accept only two holes (Lederer 1989); the situation is not improved if one considers a regime of magnetic fluctuations, because $t_\parallel$ is much larger than k_BT.

In the *resonant valence-bond* (RVB) *model* (Anderson 1987, 1988, Baskaran *et al* 1987, Anderson *et al* 1987), the antiferromagnetic state is assumed, under some conditions, to be less stable than a state based on a collection of singlet pairs of electrons on neighbouring sites. There are many possible spatial configurations, such as $|\varphi_\alpha\rangle$ pictured in figure 10(*a*). The RVB state must be a coherent combination of such states, at least if, as assumed here, the production of singlet states does not disturb the length of the interatomic bonds

$$|\varphi_{RVB}\rangle = \Sigma_\alpha \alpha |\varphi_\alpha\rangle. \tag{57}$$

The idea of such a RVB state originates from Landau's prewar description of antiferromagnetism. The mathematical difficulty of its treatment comes from the choice of the parameters α. However detailed exact computations on finite size models (Kohmoto and Shapir 1988, Hirsch and Liu 1988, Liu *et al* 1988, Poilblanc 1989a, b, Hasegawa and Poilblanc 1989) have essentially justified the validity of some simpler variational schemes. And it seems established now that, for a Mott insulator, the RVB state is less

stable than the antiferromagnetic one, in agreement with experiment on La_2CuO_4 and $YBa_2Cu_3O_6$.

The real question in this context comes from the holes created on Cu atoms by doping. A number of configurations can be considered. The creation of a hole on one site can shift the surrounding singlet pairs without breaking them: one produces a 'holon', i.e. a charged boson pictured in figure 10(b). If such a hole is filled with an unpaired electron, one would have a neutral fermion (Pomeranchuk 1941) (figure 10(*c*)). Couples of holon plus fermion or two holons can be considered. The initial proposal was that holons created by doping stabilised the RVB phase by a mechanism analogous to the magnetic polaron, because they were assumed to be more mobile in the RVB than in the antiferromagnetic phase. It is not clear at present that this is true (Gabay *et al* 1988, Doniach *et al* 1988, Inui *et al* 1988, Gros 1988, Lederer *et al* 1988, Lederer and Takahashi 1988a, b, Inoue *et al* 1989). It might be that couples of holon plus fermion (Héritier 1987) or pairs of holons (Kohmoto and Friedel 1988) are more mobile than independent holons. And the initial proposals of a boson condensation of the holons leading to superfluidity, coupled with the possible existence of a fermion gas below T_c do not seem to fit experimental data, as explained at the beginning of this chapter.

The two sites exchange at the basis of the RVB state can be extended to circular exchange rings on more than two sides, a mechanism known to exist for instance for nuclear diffusion in crystalline ^3He. The simplest periodic state involving such exchange rings on square planes is the $\frac{1}{2}$ flux state of Affleck and Marston (1988). It is the equivalent for strong correlations of the flux phases mentioned above in the weak coupling limit. The concept can be extended to supercell commensurate flux phases (Kalmeyer and Laughlin 1987, Wiegman 1988); it has been proposed that, for dopings different from half filled bands, the corresponding states could have superconductive properties (Anderson *et al* 1989). Such states also appear in the quantum Hall analysis for carriers on a lattice (Hofstadter 1976). As in that case, when studied in the Gutzwiller approximation, an energy cusp with filling (meta) stabilises an order of commensurability related to doping (Lederer *et al* 1989, Poilblanc 1989c). It is difficult to understand how the physical properties of such a state could vary smoothly with doping; and there is of course no proof of it being a specially stable solution.

Anyway, such purely ionic models seem contradicted by the *covalent* character of the Cu–O bonds. In this context, it has been argued that strong enough repulsions U_{dd} can localise electrons even in the presence of a covalent character of CuO_2 planes (Zang and Rice 1988). It is true that, with one electron per Cu, an antiferromagnetic arrangement can be described in terms of localised wavefunctions each centred on a copper atom but with a fringe of the surrounding O 2p orbitals, with opposite spins on neighbouring copper sites (Mila 1989). Such orthogonal sets of functions are indeed essentially the Wannier functions of the occupied half of the conduction band, separated by the magnetic gap from the unoccupied half as soon as $U_{dd} \neq 0$ (Kohn 1959). In addition, a doping localised hole can be obtained by suppressing the electron localised on one such Wannier function. But by the well known equivalence in Hartree–Fock between descriptions of full bands using Bloch and Wannier functions, this is no 'proof' of Mott localisation. It is just *magnetic* localisation, obtained even for small values of U_{dd}. The real question is more whether localisation subsists in the presence of deviations from simple antiferromagnetism. In such cases, and especially in RVB, the 'effective' Cu orbitals with their fringe of O 2p orbitals are no longer orthogonal. In fact the Cu 3d and O 2p orbitals act then as independent variables. Complete localisation would require all the Coulomb interactions involved, i.e. at least U_{dd}, U_{pp} and U_{dp} (with obvious notations)

to be larger than the total width of the bonding and antibonding CuO bands (Hirsch 1987). This is unlikely, especially for the intersite interaction U_{dp}. Some measure of delocalisation must therefore occur in these perturbed conditions, explicitly involving the O 2p orbitals as variables independent from the Cu 3d ones (Friedel 1988b): *the tJ models are not generally compatible with covalency*.

As has been pointed out above, a weak Mott localisation is also made possible in a delocalisation picture, owing to Umklapp processes in the three-quarter-filled Cu 3d–O 2p bands; but again doping would destroy this effect, even if this Mott gap was larger than the Slater one.

3.2.3. Covalent (heavy fermion) models. The development of 2p holes on O by doping (reported above) has strongly reinforced various electron transfer models which rely on the following assumptions (Varma *et al* 1987, Emery 1987, Emery and Gleiter 1988, Emery and Reiter 1989, Hirsch *et al* 1988a, b, Hirsch 1989, Hirsch and Marsiglio 1989, Newns *et al* 1988, Newns 1988, Zaanen and Olès 1988):

(i) The electron interaction U_{dd} is large enough to prevent more than one electron per Cu $3d_{x^2-y^2}$ orbital. As a result, undoped compounds such as La_2CuO_4, $YBa_2Cu_3O_6$, have full O 2p shells and one electron per Cu orbital.

(ii) When doping, electrons are preferentially taken from the antibonding O $2p_\sigma$ orbitals of the CuO_2 planes (or in Feinberg *et al* (1988), from the non-bonding ones). They are not taken from the Cu orbitals, as assumed in the ionic models.

(iii) Because of a direct transfer between O $2p_\sigma$ orbitals on neighbouring Cu–O bonds, the 2p states broaden into a 2p band of delocalised electrons, more-or-less correlated through their interaction U_{pp}.

(iv) Finally, a slight covalency between the Cu 3d and O 2p orbitals on the Cu–O bonds of CuO_2 planes mixes the localised moments on the Cu atoms with the band of 2p holes on the O atoms.

The energy conditions for this situation read

$$E_d < E_p^F < E_d + U_{dd} \tag{58}$$

where E_p^F is the Fermi level of the p band. Condition (58) is apparently met in a number of transition metal oxides (Zaanen and Sawatzki 1987, Sawatzki 1988, Eskes and Sawatzki 1989, Eskes *et al* 1989). If

$$|t_{pp}| > |t_{dp}| \tag{59}$$

the model is equivalent to those developed to describe heavy fermions in rare earth or actinide compounds (da Rosa Simoes *et al* 1988, Tournier 1988). The same type of discussion could then be developed, with distinction between cases of antiferromagnetism and of non-magnetic Kondo lattices for the Cu atoms, and possibly of electron–electron interactions driving superconductivity.

One of the most elaborate descriptions along those lines has been made by Gorkov and Sokol (1989). It gives the possibility of sudden changes when a condition such as (58) no longer holds, where E_d is renormalised for its interactions with p states. Thus the emptying of d states when $E_d > E_p^F$ is proposed to explain the sudden change of Hall number observed at $x > 0.13$ in $La_{2-x}Sr_xCuO_4$.

Two main objections can be raised against this type of picture. The first and main one, is that it is unlikely that the direct pp transfers produce a broad band. Band computations do not agree with a condition such as (59).

If now t_{dp} dominates, the d electrons are just as *delocalised* as the p ones. And this is indeed coherent with the observation of Knight shifts on Cu and Y as well as on O in $YBa_2Cu_3O_{7-\delta}$, as reported above.

The covalent models then boil down to a *Hubbard* model for delocalised Cu 3d and O 2p electrons, with electron interaction U_{dd}, but probably also U_{pp} and transfer integrals t_{dp}, building a strongly correlated Fermi liquid (Papoular 1988). In their most elementary form, they correspond to a Hamiltonian

$$H = \sum_i U_{dd} a_i^+ a_i + \sum_l U_{pp} b_l^+ b_l + \sum_{il} t_{il}(a_i^+ b_l + b_l^+ a_i) \tag{60}$$

where $t_{il} = \pm t_{dp}$, depending on the bond considered (Olès *et al* 1987, Olès and Zaanen 1988, 1989, Zaanen and Olès 1988, Becker and Fulde 1988, Spalek and Wojcek 1988). From the experimental evidence reported above on satellite lines, and from what is known generally about effective values of the U, taking into account intraatomic correlations (Friedel 1980), U_{dd} and U_{pp} cannot be much larger than the band width due to t_{dp} and are therefore far from infinite. Corrections due to t_{pp} or U_{dp} (Mayou *et al* 1988) are expected to play a small role.

In such Hubbard models and other related electronic exciton models, various direct electron–electron interactions are short or long range and can be considered as the origin of superconductivity (cf Hirsch 1989 for a review, also Hirsch and Tang 1989, Zawadowski 1989, Martin *et al* 1988a). The main argument against such coupling schemes is, as stressed above, the form of the phase diagrams of T_c and T_N, where the superconductive and antiferromagnetic instabilities seem detrimental to each other.

4. Conclusions

The problems discussed in this review centre on three questions.

(i) The *quasi-2D* structure of the oxides considered leads to specific anisotropy and friction of the vortex lines; they should not produce large 2D superconductive fluctuations above T_c, which should be near mean-field values.

(ii) The electronic structure and physical properties can be usefully discussed in terms of conduction electrons *delocalised* along Cu–O antibonds of CuO_2 planes (and on Cu–O bonds of CuO chains in $YBa_2Cu_3O_{7-\delta}$), making slower jumps between these planes. A tight-binding Hubbard model taking into account the Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals, the inter-orbital transfer integral t_{dp} and the on-site electron interactions U_{dd} and U_{pp} seems sufficient. A question which is still open is the relative amplitude of these U with respect to the band width due to t_{dp}. But the greater number of orbitals (3d and 2p) than hole carriers in the antibonding CuO band makes the La_2CuO_4 and $YBa_2Cu_3O_6$ magnetic (Slater) insulators, and not Coulomb (Mott) ones.

(iii) The large values of *superconductive* T_c observed can be explained in a standard BCS weak coupling scheme for delocalised electrons, if one takes into account the presence of large van Hove anomalies in the density of states near the Fermi level, due to the quasi-2D structure of the oxides. The origin of such a weak coupling could be the electron–electron repulsion via the antiferromagnetic fluctuations observed in some of these oxides. This is indeed what is thought to happen in quasi-low-dimensional organic conductors (Emery 1986, Bourbonnais and Caron 1988, Bourbonnais 1989); a possible mechanism would be Schrieffer's 'spin bag' scheme of weak magnetic polarons, where

electrons attract by lowering locally the amplitude of antiferromagnetic fluctuations and thus the width of the magnetic pseudo-gap that destabilises the electron hole (Schrieffer *et al* 1988). The existence of such a pseudo-gap due to non-vanishing electron interactions U_{dd} and antiferromagnetic fluctuations is necessary to explain the transport and Knight shift properties of conduction electrons in the metallic range; the whole picture can be connected to that of domain walls as discussed above (Schulz 1989c). But the decrease of T_c when approaching an antiferromagnetic region in the phase diagrams strongly suggests that, in contrast to organic superconductors, and analogous to normal transition metal alloys, superconductivity is due to *electron–phonon* couplings and weakened by antiferromagnetic fluctuations and the ensuing pseudo-gap. It might be that some specific phonon mode plays a dominant role (Barisic *et al* 1987, Barisic and Batistic 1989b, Baeriswyl and Bishop, 1987, Weber *et al* 1988, Besson 1989). But the values of λ required to explain the observed T_c, of order 0.1, can be obtained by coupling via many phonon modes, as in transitional metals and alloys (Barisic *et al* 1970).

Some final remarks can be made.

First, the discussion between localised and delocalised schemes in these oxides is reminiscent of the corresponding discussions for d electrons in transition metals. As in that case (Friedel 1980), there is no clear-cut evidence that treating U_{dd} as a perturbation to a band scheme is insufficient to describe the physical properties of these oxides. As in transition metals, careful studies of the Fermi surface, of the kind started by positron annihilation for $YBa_2Cu_3O_7$ (Peter *et al* 1988, Peter 1989) but also by de Haas–van-Alphen effect and of dispersion curves of conduction electron states E_k by angular resolved photoemission (Sakisaka *et al* 1989, Takahashi *et al* 1988) will be of great value. This was stressed by the author (Friedel 1988a); preliminary results seem in favour of the delocalised electron picture. It might well be however that U_{dd} (and U_{pp}) are somewhat too large to be treated in perturbation and that some variational scheme derived from the delocalised picture should be used. Contrary to simple Gutzwiller techniques, this should take into account antiferromagnetic fluctuations and their thermal statistics explicitly (Spalek and Wojcek 1988, Fazekas 1989). But one expects *a priori* a simple extrapolation of properties already met for small values of U_{dd} where the negative role of such antiferromagnetic fluctuations on superconductivity has not been properly studied.

Second, superconductivity of the oxides is reminiscent of that in other low-dimensional compounds such as transitional dichalcogenides, V_3Si or organic superconductors, in that the superconductive instability is in competition with other structural or magnetic instabilities affecting the Fermi electrons. Indeed, from that point of view, a maximum of T_c is obtained when the couplings responsible for T_c are optimised without optimising those of other instabilities. For BCS-type weak coupling, quasi-two-dimensionality can optimise T_c by producing large van Hove anomalies near the Fermi level without developing sizeable 2D fluctuations. From that point of view, there is no gain in increasing the number n of CuO_2 planes in the multisandwich structures, which decrease the amplitude of each van Hove anomaly. But there is no gain either in splitting the van Hove anomalies by an orthorhombic distortion as in $YBa_2Cu_3O_7$, nor in having the Fermi level too near a midband filling situation, where antiferromagnetism prevails as in La_2CuO_4 or $YBa_2Cu_3O_6$. This can explain the optimum values of T_c observed in the Bi and Tl families for $n = 3$ or 4 (Ihara *et al* 1989). If this interpretation is correct, it might be of interest to try and kill magnetism by using Ag or Au instead of Cu.

More generally, two ways of developing low dimension compounds seem promising *a priori*:

(i) *Multiple quasi-1D compounds* with nearly empty or full bands. Here detrimental 1D fluctuations could be reduced by sufficiently strong 3D couplings between interpenetrating chains. This was essentially the case of the V_3 Si family (Labbé *et al* 1967); it might be that of the cubic perovskite compounds Ba (Pb, Bi) O_3 (Sleight *et al* 1975) and (Ba, K) BiO_3 (Cava *et al* 1988a).

(ii) More probably *quasi-2D compounds* with partly filled bands so that the Fermi level is near a van Hove anomaly. From that point of view, the BCS coupling scheme makes no difference (for the CuO_2 base oxides) between doping by electrons or holes from the half filled band situation. It is therefore no surprise to observe sizeable T_cs for 'electron' compounds such as $Nd_{2-x}Ce_xO_4$ (Tokura *et al* 1988, Takagi *et al* 1989) where the band structure for the CuO_2 planes is very similar to that in $La_{2-x}Sr_xCuO_4$ (Gupta and Gupta 1989). It would be of interest to check whether, as expected, such compounds are antiferromagnetic when undoped and show an electron-like Hall effect due to small dopings, going over to positive hole behaviour for larger dopings. Other lamellar structures should be explored or revisited, with the aim of placing the Fermi level near a van Hove anomaly. Besides systematic dopings of transitional dichalcogenides, organic conductors seem a very flexible and thus a promising field. Indeed K (BEDT-TTF)$_3$ $Cu(SCN)_2$, the organic compound with the highest T_c observed so far (10.4 K, Urayama *et al* 1988) is a quasi-2D compound with van Hove anomalies near to E_F (Oshima *et al* 1988) and transport properties very sensitive to pressure (Kang 1989). In contrast to the oxides, this compound shows a Fermi surface very far from flat between the saddle points of the van Hove singularities: this might usefully decrease the stability of competitive 1D spin or charge modulations.

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