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A two-phase charge-density real-space-pairing model of high-T_c superconductivity

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Dedicated to Professor A. F. Moodie on the occasion of his 75th birthday

Abstract

It is usually assumed that high-T_c superconductors have a periodic band structure and a periodic charge density, although amorphous low-T_c superconductors are known. In this paper, it is suggested that the CuO_2 conduction planes of cuprate superconductors consist of regions of two different charge densities which do not normally repeat periodically. It is suggested that the pairing of holes occurs in real space in cuprate superconductors. It is proposed that the hole-pairing mechanism is magnetic exchange coupling and the pairing force is strong, the pairing energy being greater than kT at room temperature. The bound hole pair is essentially a bipolaron. A real-space model is very tentatively suggested in which the CuO_2 planes of $YBa_2Cu_3O_7$ contain nanodomains of a 3×3 hole lattice surrounded by interfaces one unit cell wide in which the holes are paired. In the superconducting state in this model, the existing hole pairs condense and move coherently and collectively around the insulating nanodomains, like trams running around blocks of houses, with one hole on each tramline. The hole pairs move in an elegant manner with hole pairs hopping from oxygen to oxygen *via* adjacent copper sites. The model explains the superconducting current being in the *ab* plane and it also explains the very short coherence lengths. Because the pairing force is strong, the model suggests that room-temperature superconductivity might be possible in carefully designed new oxide materials.

1. Introduction

As Moodie & Whitfield (1988) have pointed out, a study of the microstructure of high-T_c superconductors 'is essential in unravelling the factors determining both intrinsic and extrinsic properties'. In the present paper, we consider in detail the microstructure of cuprate superconductors, in particular the real-space distribution of the holes and of the hole pairs in the CuO_2 superconducting planes.

We suggest that this real-space distribution is the foundation on which to build a more detailed theory of high-T_c superconductivity, and that existing theories fail because they do not take into account the real-space distribution of the holes. This is the first time that the detailed distribution in real space of the charge carriers in cuprate superconductors has been considered and we suggest that it is of fundamental importance to high-T_c superconductivity. In this paper, we also suggest a pairing mechanism, and give a tentative model for how the hole pairs move coherently and collectively in the superconducting state.

A striking structural feature of all materials that exhibit the phenomenon of superconductivity at any temperature above 35 K is that they contain planes of Cu and O atoms in the ratio 1:2 that are arranged in the square structure shown in Fig. 1. In most cases, the lattice parameter a is slightly different from b (*i.e.* the three-dimensional lattice is orthorhombic instead of tetragonal), and the Cu atoms lie slightly out of the plane of the oxygen atoms so that the plane is slightly buckled. Nevertheless, these sheets of atoms are known as the CuO_2 planes, which lie in the *ab* plane of the structure. It is known that the electrical conductivity in both the normal and superconducting states is largely or entirely confined to these layers.

There are a large number of different cuprate superconductors, for example compounds of Y–Ba–Cu–O,

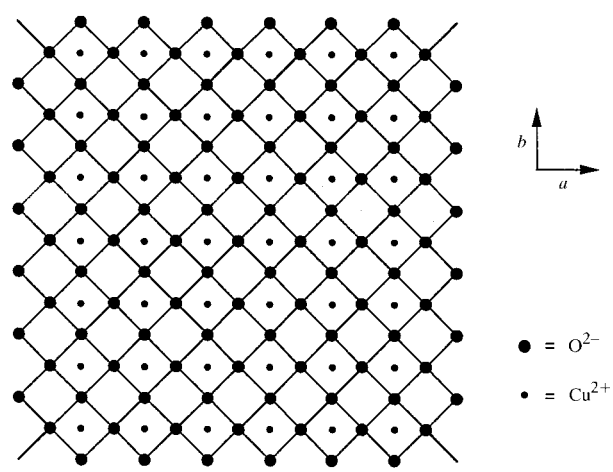

Fig. 1. The CuO_2 plane of cuprate superconductors.

La–Ba–Cu–O, Pr–Ce–Cu–O, Sm–La–Sr–Cu–O, Tl–Ba–La–Cu–O, Hg–Ba–Cu–O, Bi–Sr–Cu–O *etc.* Again, the characteristic common feature is that they all contain CuO_2 layers. To a first approximation, it appears that the other atoms in the crystal merely provide a structural framework and a charge reservoir for the CuO_2 planes. Given the obvious importance of the CuO_2 planes, and the huge number of papers on high-T_c superconductivity, it is curious that the real-space microstructure of the CuO_2 planes has not previously been studied, in particular the spatial distribution of the charge carriers in these planes.

2. The nature of the charge carriers

We will consider specifically $YBa_2Cu_3O_7$ in this paper, but we suggest that our conclusions will broadly apply to all cuprate superconductors because we are focusing on the hole structure of the CuO_2 planes (we exclude from our analysis the few cuprate superconductors which are *n*-type, although the mechanism proposed here for *p*-type superconductors may also be relevant to *n*-type if suitably modified).

Initially, we assume a simple ionic model for $YBa_2Cu_3O_7$ and take the ions to have their normal charge: Y^{3+}, Ba^{2+}, Cu^{2+} and O^{2-} (Cu^{1+} is unlikely in the O_7 form of $YBa_2Cu_3O_7$). Hence the net ionic charge in a unit cell containing one formula unit of $YBa_2Cu_3O_7$ is -1. Thus for charge neutrality each unit cell must on average contain one electron hole. Confirmation that the charge carriers in the normal state are holes is provided by Hall-effect measurements, and in the superconducting state the charge carriers are hole pairs (Gough *et al.*, 1987). Calculations (Temmerman *et al.*, 1988; Oles & Grzelka, 1991) show that it requires less energy to create a hole on an oxygen site (so that its valency is effectively O^-) than on a copper site, and experiments (Krol *et al.*, 1992; Nücker *et al.*, 1996; Alloul *et al.*, 1989) confirm that the holes are on oxygen sites and that they occur not only in the CuO_2 planes but on some other oxygen sites throughout the structure.

Various authors have determined the average number of holes, p, per CuO_2 unit in the conduction plane. For a wide range of cuprate superconductors, as the hole concentration p increases from zero, T_c increases and has a maximum value for $p \simeq 0.15$–0.25. As p increases further, T_c decreases and at $p \simeq 0.3$ the material becomes a metal (Uchida, 1993; Zhang & Sato, 1993). These values of p should be treated with caution since they assume a uniform hole density in the CuO_2 plane, which is not the case if the model presented in this paper is correct. Nevertheless, they provide a useful rough guide.

3. The arrangement of holes in the CuO_2 planes

We assume initially that the holes in the CuO_2 plane are at oxygen sites and form an ordered array so as to minimize their Coulomb repulsive energy. A number of possible 'hole lattices' are shown in Fig. 2. Fig. 2(*a*) gives a value of p of 0.5, Fig. 2(*b*) and its variant Fig. 2(*c*) a value of 0.25 and Fig. 2(*d*) a value of 0.22. We reject the hole lattice of Fig. 2(*a*) since its density is too high for the superconducting state. In Fig. 2(*b*), the holes will repel the adjacent Cu^{2+} ions along the *a* direction, but there are no adjacent Cu^{2+} ions along the *b* direction (and *vice versa* in Fig. 2*c*). This will introduce additional anisotropy into the lattice and may be energetically unfavourable. In Fig. 2(*d*), on the other hand, the holes on the oxygen sites will repel the adjacent copper ions in both *a* and *b* directions as shown in Fig. 3. Fig. 3 shows the expected static displacements of planar Cu^{2+} ions due to Coulomb repulsion by the holes on the oxygen sites. A key feature of Fig. 3 is that Cu^{2+} ions two unit

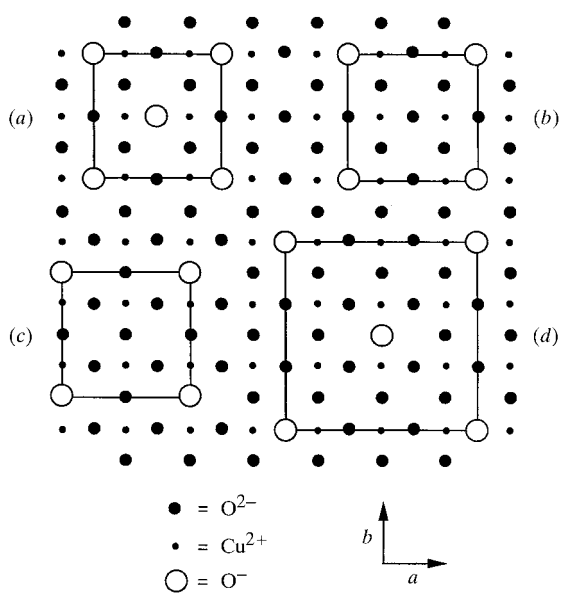

Fig. 2. The CuO_2 plane of cuprate superconductors. (*a*), (*b*), (*c*) and (*d*) show possible arrangements of holes on oxygen sites.

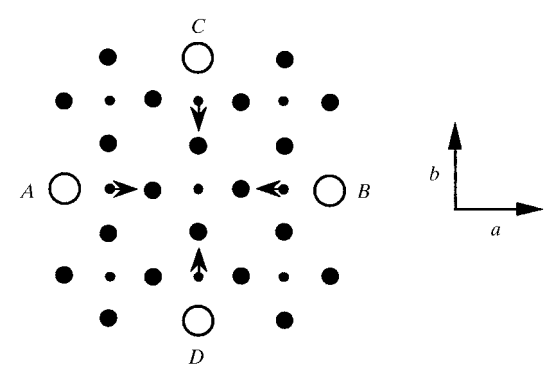

Fig. 3. The static displacement of Cu^{2+} ions due to Coulomb repulsion by holes on oxygen sites on the 3×3 lattice of Fig. 2(*d*).

cells apart are statically displaced towards each other, one pair of ions being displaced along **a** and the other pair along **b**. It is interesting to note that diffuse streaks have been observed in electron diffraction patterns of $YBa_2Cu_3O_7$ (Etheridge, 1996). An analysis of these shows them to be consistent with coupled static displacements of the planar copper ions and apical oxygen ions two unit cells apart along the ⟨28,0,3⟩ and ⟨091⟩ directions. Our model that planar copper ions two unit cells apart are statically displaced is consistent with this experimental evidence, except that the directions of the displacements in our model are along ⟨100⟩ and ⟨010⟩. However, these are the principal components in the *ab* plane of the observed displacements and it must be borne in mind that our model is a simple two-dimensional model, which inherently neglects any displacements along the *c* axis. On a more sophisticated three-dimensional model, we would expect to have a component of the displacement along [001] because of the Coulomb attraction between a displaced planar Cu^{2+} ion and an apical oxygen ion. There is therefore experimental evidence of static displacements of Cu ions two unit cells apart. However, if the 3×3 hole lattice of Fig. 2(*d*) exists throughout the crystal, this would give rise to weak superlattice diffraction spots in addition to the diffuse streaks. Such superlattice spots are not observed and we therefore deduce that the 3×3 hole lattice cannot repeat periodically through the crystal. One possibility is that the crystal consists of a 'two-phase' hole structure with small domains of the 3×3 hole lattice separated by regions in which there is a different density of holes. We explore this model in §5 below.

4. The hole-pairing mechanism

The holes at *A* and *B* in Fig. 3 may be weakly paired because the associated lattice distortions will minimize their energy. Similarly, the holes at *C* and *D* may be weakly paired. Detailed calculations are required to determine the pairing energy. However, it is clear that if the holes at *A* and *B* move as a hole pair then the associated lattice distortions will be large and they will involve a large number of atoms, hence the effective mass of the bipolaron will be very large. It seems highly unlikely that this will lead to superconductivity. We therefore explore a different pairing mechanism.

Consider the magnetic state of CuO_2 units in the *ab* plane containing zero, one and two holes. Fig. 4(*a*) shows the situation with zero holes. Each Cu^{2+} ion has a localized spin $S = 0.5$, and spins on nearest-neighbour Cu ions couple antiferromagnetically *via* the adjacent O^{2-} ion through the superexchange interaction J_{dd} (∼0.1 eV) (Emery & Reiter, 1988; Harony *et al.*, 1988) to produce the antiferromagnetic array of spins shown. Consider now a single hole on the oxygen site *A* (Fig. 4*b*). The spin on the O^- ion will couple antiferromagnetically with the spins on the neighbouring Cu sites 1 and 2 through the exchange interaction J_{pd} (∼1 eV) (Emery & Reiter, 1988; Harony *et al.*, 1988). Since $J_{pd} \gg J_{dd}$, the net effect is ferromagnetic coupling between copper ions 1 and 2 which destroys the antiferromagnetic coupling and results in spin frustration (Fig. 4*b*). Fig. 4(*c*) shows the situation with a pair of holes one lattice parameter *a* apart on oxygen sites *A* and *C*. The spin on *A* antiferromagnetically couples to the Cu^{2+} ions at 1 and 2, giving ferromagnetic coupling between them. Similarly, the spin on C gives ferromag-

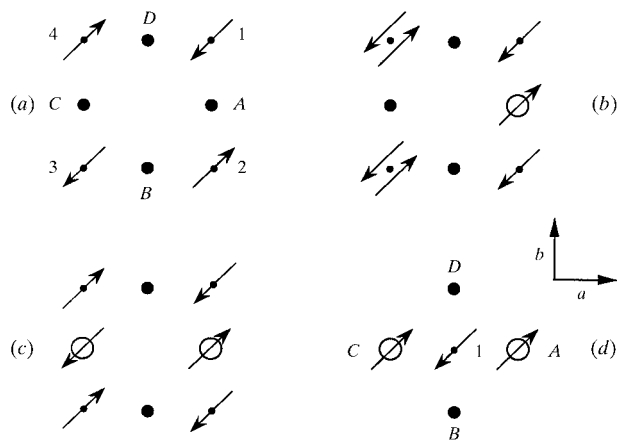

Fig. 4. Spin configurations for copper ions (at 1, 2, 3 and 4) and oxygen ions (at *A*, *B*, *C* and *D*): (*a*) no holes; (*b*) one hole on the oxygen at *A*; (*c*) holes on the oxygen atoms at *A* and *C*; (*d*) an alternative arrangement of ions in the CuO_2 plane with holes on the oxygen ions at *A* and *C*.

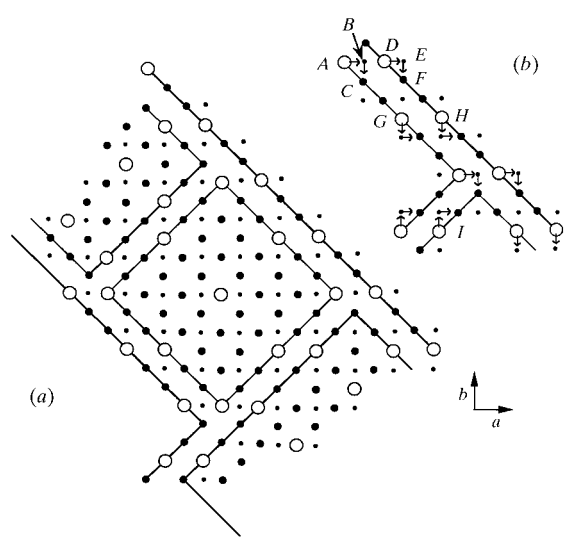

Fig. 5. (*a*) Schematic hole structure of the CuO_2 plane showing a nanodomain with a 3×3 hole structure surrounded by channels in which the holes are paired along **a** and along **b**. (*b*) Collective and coherent motion of hole pairs along channels. The hole pair on oxygen sites at *A* and *D* hops to *C* and *F* *via* copper sites *B* and *E*. Simultaneously, the hole pair at *G* and *H* advances one unit cell by hopping *via* copper ions, and so on.

netic coupling between copper ions 3 and 4. There is no frustration of spins and calculations of the binding energy of the $O^- - O^-$ pair show that nearest-neighbour pairing is indeed energetically favourable with a binding energy of 0.12 eV (Zhang & Catlow, 1991) (which is significantly greater than kT at room temperature). Similarly, holes on oxygen sites B and D, one lattice parameter b apart, will have a binding energy of 0.12 eV. In Fig. 4(c), the hole spins on the oxygen sites are antiparallel, leading to a singlet state. From the arrangement of atoms in the CuO_2 plane (see Fig. 1), an alternative arrangement of holes on oxygen sites one lattice parameter apart is shown in Fig. 4(d), in which the holes on the oxygen sites have parallel spins, leading to a triplet state. The binding energy of this triplet state has not yet been calculated, but inspection suggests that it will be lower than that of the singlet state. Hence we would expect singlet and possibly also triplet hole pairs to exist, with the holes one lattice parameter (a or b) apart. Thus we suggest that the hole pairing mechanism is due to magnetic exchange coupling and we note that this is a strong force.

5. A tentative model for the nanodomain structure of the CuO_2 planes

As shown above, we have evidence for a 3×3 hole structure and we also expect hole pairs to form with the holes separated by the lattice parameters a and b. We can reconcile these statements if the hole structure in the CuO_2 planes consists of nanodomains of a 3×3 hole structure separated by interfaces one unit cell wide in which the holes are paired along [100] or [010] directions. Fig. 5(a) shows schematically a possible structure that is very tentatively proposed. For simplicity, we show only one nanodomain with a 3×3 structure, together with some interfaces in which the holes are paired and parts of adjacent nanodomains. We emphasize that the periodic arrangement of atoms continues across the interfaces, which are not structural interfaces like grain boundaries or stacking faults, but are channels in which the hole density increases, and in which the holes are paired. Thus we have electronic phase separation in the CuO_2 planes. We emphasize that Fig. 5 is presented as a tentative model of real-space pairing. In this model, although the static displacements of Cu^{2+} ions are predominantly along **a** and **b**, we expect a component displacement along **c** due to the attraction of the apical oxygen ions (see §3).

We note that Phillips (1990) has suggested that some properties of $YBa_2Cu_3O_7$ are consistent with a microdomain structure. In addition, high-resolution electron microscopy reveals a 'cell' structure in $YBa_2Cu_3O_7$ in which the 'cells' have dimensions of typically 10–20 Å in the ab plane. The cell interfaces lie parallel to the {449} planes (Etheridge, 1996). [A nanodomain structure is also just visible on the high-resolution electron micrographs of $YBa_2Cu_3O_7$ in Moodie & Whitfield (1988) and on a number of other published high-resolution electron micrographs of $YBa_2Cu_3O_7$.] The {449} planes of the observed cell interfaces intercept the (001) ab plane along the [110] and [1$\bar{1}$0] directions. In our very tentative two-dimensional model of Fig. 5(a), in which the nanodomain shown has dimensions 16×16 Å, the channels run along [110] and [1$\bar{1}$0] directions and the channel width is about 3 Å. The smallest 3×3 nanodomain would have dimensions 8×8 Å. We would expect the abrupt charge-density changes in the CuO_2 plane proposed here to affect also the charge density in the CuO chains of $YBa_2Cu_3O_7$ and note that scanning tunelling microscopy (STM) reveals 13 Å period corrugations in the CuO chains, interpreted as a charge-density wave (Edwards *et al.*, 1994), and neutron scattering yields a modulation of 16.65 Å in the CuO chains (Mook *et al.*, 1996). We emphasize that our model of Fig. 5(a) is tentative and schematic, for example the nanodomains may contain a mixture of 3×3 and 2×2 hole lattices as shown in the nanodomains adjacent to the main nanodomain in Fig. 5(a). However, we also emphasize that most theories of high-T_c superconductivity assume a periodic crystal potential and hence a periodic band structure. According to our model, the usual assumption of periodicity is incorrect for cuprate superconductors. To a first approximation, our model has a periodic array of atomic nuclei, but there are nonperiodic static displacements of ions as shown in Fig. 3 and nonperiodic charge-density changes as shown in Fig. 5(a). Thus our model explains why existing theories of high-T_c superconductivity, based on a periodic potential, cannot be correct. We agree that it would seem from neutron and X-ray diffraction that cuprate superconductors have a periodic structure and hence a periodic potential. However, as Phillips (1990) has pointed out, it is extremely difficult for X-ray and neutron diffraction to detect a nanodomain structure in which the domains have an identical and coherent orientation relationship. Thus it is difficult for X-ray and neutron diffraction to detect the nanodomain structure of Fig. 5(a). We note that for low-temperature superconductivity a periodic structure is not essential and that amorphous superconductors exist with short-range electron–phonon interactions. Our proposed model of short-range real-space pairing in high-temperature superconductors is conceptually somewhat similar.

6. Conductivity in the normal state

Our model suggests that both in the normal state and in the superconducting state the CuO_2 planes of cuprate materials have a 'two-phase' structure of strongly bound hole pairs (which are present at room temperature), which lie in one-dimensional channels forming a two-dimensional network surrounding nanodomains that contain isolated holes (Fig. 5a). Above T_c, conductivity

in the normal state in principle could occur by the movement of free holes, by the hopping of holes in the nanodomains (with the associated lattice distortions, *i.e.* polaronic conductivity) and also by the bipolaronic movement of the hole pairs in the channels. There is increasing evidence that polaronic and/or bipolaronic charge carriers are present in cuprate superconductors (Alexandrov & Mott, 1994; Bi & Eklund, 1993; Mihailowic *et al.*, 1994; Zhao *et al.*, 1997; Edwards *et al.*, 1998; Devreese, 1997). For $T > T_c$, the bipolarons in the channels will dissociate into polarons and the localized holes will be ionized to free holes giving reasonable conductivity.

7. The superconducting state

For $T < T_c$, we tentatively propose that the existing hole pairs in the channels condense, mediated by phonons, and move collectively and coherently in a two-dimensional network around the nanodomains, which essentially form insulating blocks around which the supercurrent flows. When a current flows, the hole pairs move coherently and collectively in the elegant manner shown in Fig. 5(*b*). In particular, a hole on the oxygen site at *A* hops to the oxygen at *C via* the copper at *B*. Simultaneously, the hole at *D* moves to *F via E*. Thus the hole pair at *A* and *D* advances by one unit cell along [110]. Simultaneously, the hole pair at *G* and *H* advances by one unit cell along [110], and so on for all hole pairs along the quasi-one-dimensional channel. All hole pairs move together along the channel, collectively and coherently. Hole pairs in connecting channels, for example at *I* in Fig. 5(*b*), may have to wait until there is a suitable 'gap' for them to move into another channel by percolation. The hole pairs drawn are 3 unit cells apart along ⟨110⟩, but other separations may be possible. The essentially one-dimensional nature of the channels may increase the stability of the bound hole pairs, which are essentially bipolarons. Thus, at $T = T_c$, the existing bipolarons formed by magnetic spin coupling condense to move in the coherent manner shown in Fig. 5(*b*) mediated by phonons. Hence, high-T_c superconductivity involves a delicate interplay of magnetic spin coupling, Coulomb forces, lattice distortions and phonons. For $T < T_c$, we note that there are essentially two different types of holes in the CuO_2 planes: those that form mobile hole-pair states and the single holes in the nanodomains, which are immobile. Although in our model the hole pairs (bipolarons) move along one-dimensional channels, the channels form a two-dimensional connected network and there will be some overlap of the hole-pair wavefunctions in adjacent CuO_2 planes. Hence, the Bose condensation at $T = T_c$ may be essentially three-dimensional even though the hole pairs move in one-dimensional channels.

Our model not only accounts for the superconducting current flowing essentially in the *ab* plane, it also accounts for the very short coherence lengths, which we equate to either the separation of hole pairs along ⟨110⟩, *i.e.* $3 \times 2.7 \simeq 8$ Å, or to the length of a superconducting channel before it turns a corner, *i.e.* about 10 or 20 Å, depending on the size of the nanodomains.

8. Room-temperature superconductivity?

If the model proposed in this paper is correct, then it may be possible to use this model to design new materials with higher values of T_c. It is encouraging that the magnetic spin coupling energy which we suggest is responsible for hole pairing is large, being greater than kT at room temperature. Superconductivity then occurs at a critical temperature T_c at which the hole pairs condense and move collectively and coherently.

A very large number of 'trial-and-error' experiments have been performed on a wide variety of cuprate superconductors. It may be possible to use the present model to achieve higher values of T_c than 150 K in cuprate superconductors, but very much higher values would seem unlikely given the large number of empirical experiments that have already been performed on these materials.

To achieve substantially higher values of T_c than 150 K, it is suggested that a new materials system is needed that is not a cuprate material. If the pairing mechanism in cuprate materials is magnetic spin coupling as shown in Fig. 4, then a starting point for a new material would be to select a material which when undoped is antiferromagnetic as in Fig. 4(*a*), but which when doped produces spin coupling of the hole pairs as in Fig. 4(*c*) or (*d*). By analogy with the cuprate superconductors, a starting point would be to design a new material that has MO_2 planes, where *M* is a transition element, which has the magnetic properties referred to above, so that when the material is doped the coupling between hole pairs is strong and occurs above room temperature. For room-temperature superconductivity, we require the hole pairs to condense at room temperature. Whether or not this can be achieved is an open question, but since the pairing itself occurs above room temperature, according to the model in this paper, then it is suggested that we have grounds for optimism.

9. Summary and conclusions

(i) It is suggested that a knowledge of the real-space distribution of the holes in the CuO_2 planes of cuprate superconductors is important for understanding superconductivity mechanisms.

(ii) The CuO_2 planes have regions of two different charge densities. It is tentatively suggested that in $YBa_2Cu_3O_7$ nanodomains with a 3×3 hole lattice are surrounded by interfaces one unit cell wide in which the holes are paired.

(iii) It is suggested that the hole-pairing mechanism is magnetic exchange coupling and the pairing force is strong. The pairing energy is greater than kT at room temperature.

(iv) Most existing theories of high-T_c superconductivity assume a periodic band structure, which is incorrect according to the model in this paper.

(v) In the normal state, conductivity can occur by the movement of free holes, by the hopping of holes in the nanodomains and by the hopping of hole pairs in the channels.

(vi) In the superconducting state, our tentative model suggests that the existing hole pairs condense and move collectively and coherently around the insulating nanodomains. The hole pairs hop from oxygen to oxygen sites *via* adjacent copper sites.

(vii) The model explains the superconducting current being in the *ab* plane and it also explains the very short coherence lengths.

(viii) Because the magnetic pairing force is very strong, the model suggests that it may be possible to design new oxide materials, in which copper is replaced by a different transition element, which exhibit superconductivity at room temperature.

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References

Alexandrov, A. S. & Mott, N. F. (1994). *High Temperature Superconductors and other Superfluids.* London: Taylor and Francis.

Alloul, M., Ohno, T. & Mendels, P. (1989). *Phys. Rev. Lett.* **63**, 1700–1703.

Bi, X. X. & Eklund, P. C. (1993). *Phys. Rev. Lett.* **70**, 2625–2628.

Devreese, J. T. (1997). *Z. Phys. B*, **104**, 601–604.

Edwards, H. C., Barr, A. L., Markert, J. T. & de Lozanne, A. L. (1994). *Phys. Rev. Lett.* **73**, 1154–1157.

Edwards, P. P., Mott, N. F. & Alexandrov, A. S. (1998). *J. Supercond.* **11**, 151–154.

Emery, V. J. & Reiter, G. (1988). *Phys. Rev. B*, **38**, 4547–4556.

Etheridge, J. (1996). *Philos. Mag.* A**73**, 643–668.

Gough, C. E., Colclough, M. S., Forgan, E. M., Jordan, R. G., Keene, M., Muirhead, L. M., Rae, A. I. M., Thomas, N., Abell, J. S. & Sutton, S. (1987). *Nature (London)*, **326**, 855.

Harony, A. A., Birgeneau, R. J., Coniglio, A., Kastner, M. A. & Stanley, H. E. (1988). *Phys. Rev. Lett.* **60**, 1330–1333.

Krol, A., Ming, Z. H., Kao, Y. H., Nücker, N., Roth, G., Fink, J., Smith, G. C., Park, K. T., Yu, J., Freeman, A. J., Erb, A., Müller-Vogt, G., Karbinski, J., Kaldisand, E. & Schönmann, K. (1992). *Phys. Rev. B*, **45**, 2581–2584.

Mihailowic, D., Ruani, G., Kaldis, E. & Müller, K. A. (1994). *Proc. Int. Workshop on Anharmonic Properties of High-T_c Cuprates*, pp. 118–146. Singapore: World Scientific.

Moodie, A. F. & Whitfield, H. (1988). *Ultramicroscopy*, **24**, 329–338.

Mook, H. A., Dai, P., Salama, K., Lee, D., Dogan, R., Aeppli, G., Boothroyd, A. T. & Mostoller, M. E. (1996). *Phys. Rev. Lett.* **77**, 370–373.

Nücker, N., Pellegrin, E., Schweib, P., Fink, J., Molodtsov, S. L., Simmons, C. T., Kaindl, G., Frontrup, W., Thomson, C., Erb, A. & Müller-Vogt, G. (1996). *Phys. Rev. B*, **53**, 14761–14764.

Oles, A. M. & Grzelka, W. (1991). *Phys. Rev. B*, **44**, 9531–9540.

Phillips, J. C. (1990). *Phys. Rev. Lett.* **64**, 1605–1608.

Temmerman, W. M., Szotec, Z. & Guo, G. Y. (1988). *J. Phys. C*, **21**, L867–L874.

Uchida, S. (1993). *Jpn J. Appl. Phys.* **32**, 3784–3798.

Zhang, H. B. & Sato, H. (1993). *Phys. Rev. Lett.* **70**, 1697–1699.

Zhang, X. & Catlow, C. R. A. (1991). *J. Mater. Chem.* **1**, 233–238.

Zhao, E.-M., Hunt, M. B., Keller, H. & Müller, K. A. (1997). *Nature (London)*, **385**, 236–239.