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Abstract. We have calculated the electronic structure of the high-temperature super-conductors $Bi_2Sr_2CuO_6$ and $Tl_2Ba_2CuO_6$. We find that the Tl–O layers are mainly covalently bonded, whereas the Bi–O layers also have an ionic component. These materials have very similar crystal structures, but radically different superconducting properties, $T_c = 12$ K and 90 K respectively. We focus on how 'metallic' the Bi/Tl layers are and the degree to which the CuO_2 layers are doped by charge transfer as possible reasons for this difference, arguing that the latter is dominant.

1. Introduction

Since the discovery of high-temperature superconductivity in La–Ba–Cu–O compounds [1] there has been a vast amount of work directed towards elucidating the mechanism underlying the superconductivity, and to discovering materials with even greater values of T_c. A knowledge and understanding of the electronic structure of these materials is of central importance in both these endeavours. In this context we have embarked upon a comparative study of the electronic structure of $Tl_2Ba_2CuO_6$ and $Bi_2Sr_2CuO_6$.

Recently, high-temperature superconductivity has been discovered in several bis-muth- [2] and thallium- [3] based compounds (for an overview see [4]). Their crystal structure has been determined [5, 6] and they are found to have several structural similarities to the earlier high-T_c materials $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$. Specifically, the CuO_2 planes where the superconductivity is believed to occur are present in both these new materials. The compounds $Bi_2Sr_2CuO_6$ and $Tl_2Ba_2CuO_6$ are the simplest members of the new families of compounds. They have almost the same crystal structure and very similar unit cell volumes. However, the measured superconducting transition temperatures vary enormously, with T_c for the bismuth compound being about 12 K [4] and for the thallium compound $T_c = 90$ K [4].

The origin of the superconductivity seems to lie in the common structural feature of all known superconductors with $T_c > 50$ K: the CuO_2 (and perhaps NiO_2) planes. Thus the difference between the T_cs of the various compounds can come from three sources: the CuO_2 planes are slightly altered from compound to compound; they are doped away from half filling to differing degrees; or the material between the layers allows differing

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degrees of 'Josephson coupling' between the superconducting order in neighbouring planes—noting that an isolated (necessarily two-dimensional) CuO_2 plane will have a zero T_c. In the pair of compounds that we will investigate, the CuO_2 layers are essentially identical, so our calculations will yield information on the latter two possibilities.

In this paper we perform self-consistent density functional calculations of the electronic structure of these materials, focussing in particular on the role of the Bi/Tl–O layers as intermediaries for 'Josephson coupling' and as reservoirs of carriers for doping the CuO_2 plane. Many electronic structure calculations have been performed for the high-T_c materials ([7–11] for example) and for these two materials we are aware of one calculation of the electronic structure of each [12, 13]. In general these calculations have told us a lot about the bonding and structural characteristics of these materials. However, this type of calculation averages out the effect of electron correlations and fails to shed much light on the specific mechanism for superconductivity. As mentioned above, it is now generally accepted that the superconductivity takes place in the CuO_2 planes and it is here that there seems to be strong correlations so that the local density approximation will fail to describe the physics fully. One manifestation of this is that it seems impossible to obtain the insulating ground state of the 'parent' compounds, La_2CuO_4 and $YBa_2Cu_3O_6$, within the local density approximation, although the antiferromagnetism in the $YBa_2Cu_3O_6$ compound (but not La_2CuO_4) has been demonstrated [14].

However, away from CuO_2 planes, where the correlations are not so strong, we hope that the local density approximation will be a sufficient description of the electrons behaviour. In this paper the emphasis will be on the Bi/Tl–O and Sr/Ba–O layers, both in terms of how metallic the Bi/Tl–O planes are (and hence how easily they allow the superconducting order to spread up the c axis) and to what extent both types of layer act as acceptors, producing holes in the CuO_2 planes. We assume that the degree of charge transfer is a sufficiently crude measure of the electronic structure in the CuO_2 planes that the LDA will yield the correct answer.

2. Method

The crystal structure of these two materials is body-centred tetragonal with two formula units per unit cell. (We neglect the recently discovered small orthorhombic distortion of the Tl layers [15].) The crystal structure is shown in figure 1. In this calculation we have used the experimentally observed lattice, with one modification: we place the bismuth ions directly above each other, i.e. we move the top formula unit in figure 1 by $(\frac{1}{2}, \frac{1}{2}, 0)$, neglecting the body-centred nature of the tetragonal structure. In the real structure bismuth atoms in one Bi/Tl–O layer lie above oxygen atoms in the adjacent Bi/Tl–O layer. The reason for doing this is that it leads to a large saving in computer time used, making the calculation tractable. We expect the effect of this to be small, as the separation of the atoms between the Tl/Bi–O layers is sufficiently large (indeed in the Bi case, this is the largest interatomic distance in the structure) that the misalignment of these layers is unlikely to affect the bonding. The structural data put into the calculation are shown in table 1.

We have performed standard density functional [16] calculations for these two materials. The local approximation of Hedin and Lundqvist [17] was used to describe the exchange–correlation energy. The calculations were semi-relativistic in that the relativistic mass–velocity and Darwin corrections were included however spin–orbit coupling was neglected. The calculation was performed using the LMTO method [18, 19].
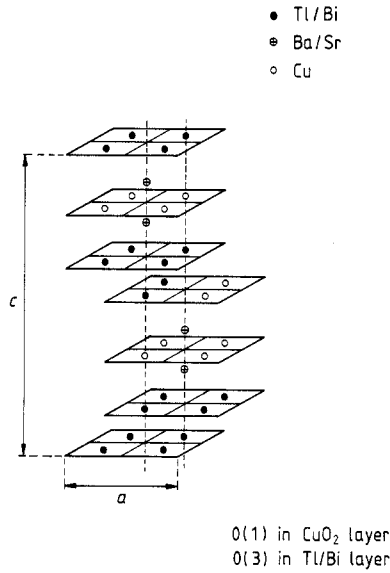
• Tl / Bi
⊕ Ba / Sr
○ Cu

O(1) in CuO_2 layer
O(3) in Tl/Bi layer

Figure 1. The crystal structure of $Tl_2Ba_2CuO_6$ and $Bi_2Sr_2CuO_6$.

Table 1. Table showing atomic sphere radius (S) and axial ratios for each of the materials examined. Also shown are the densities of states at the fermi energy ($n(E_F)$) and the total charge on each ion (n). The numbers in brackets are the charge on the single atom which are included to facilitate the readers perception of the degree of charge transfer. Note that n is dependent on the size of the inscribed sphere and thus can only be used for comparative purposes.

Atomic site	$Tl_2Ba_2CuO_6$			$Bi_2Sr_2CuO_6$		
	SS	$n(E_F)$	n	S	$n(E_F)$	n
Tl/Br	4.127	23.84	81.03 (81)	4.121	5.48	82.14 (83)
Ba/Sr	3.357	2.90	55.59 (56)	3.352	0.80	37.44 (38)
Cu	2.404	13.58	28.35 (29)	2.400	10.26	28.52 (29)
O(1)	2.003	6.26	8.16 (8)	2.000	7.25	8.23 (8)
O(2)	2.203	6.96	8.59 (8)	2.200	2.10	8.92 (8)
O(3)	2.203	62.10	7.94 (8)	2.200	2.98	8.50 (8)
Axial ratio		6.459			6.011	

To enable us to make a comparison of the charge transfers involved, in each material the ratio of atomic sphere volume to unit cell volume was kept constant for equivalent atoms.

To converge this calculation to a realistic solution it was necessary to allow an $l = 3$ degree of freedom around the Cu and Ba/Sr sites and $l = 2$ around the Tl/Bi and O sites. Our results vary markedly from those of Gupta and Gupta [20] for $Bi_2Sr_2CaCu_2O_8$ although we would expect some similarity. This may well be due to their neglect of these higher degrees of freedom. There was a small dependence of the results on the arbitrarily chosen atomic sphere radius. This has been observed previously, and is due to the open nature of the layered crystal structure. We have chosen the sphere radius so as to
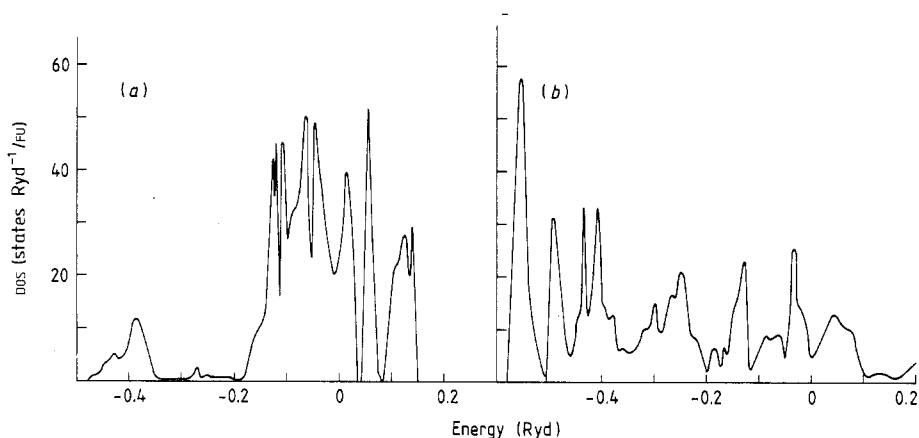
Figure 2. (*a*) The density of states on the thallium site in $Tl_2Ba_2CuO_6$; (*b*) the density of states on the bismuth site in $Bi_2Sr_2CuO_6$.

minimise the charge transfer (within reasonable limits) in $Tl_2Ba_2CuO_6$ case. This procedure has been found to give the best agreement with experiment in the past [21]; however, it means the calculation cannot rigorously be described as being of first principles. The charge density in the regions not included in the atomic spheres was not included in the determination of the self-consistent potential. (Computational constraints did not allow us to explore the possibility of the insertion of extra spheres in the spaces between the atoms, which would have allowed self-consistent calculation of their contribution.)

3. Results

In this section we display the results of the calculation and point out features that may be relevant to the discussion of the properties of the materials that we explore more fully in the next section. We will concentrate on the local density of states at the various sites, as this readily lends itself to interpretation. (Previous calculations [12, 13] have shown diagrams of the energy bands of $Bi_2Sr_2CuO_6$ and $Tl_2Ba_2CuO_6$.) Figures 2–7 show the densities of states for each inequivalent atom for each material. (In these figures the Fermi energy is set equal to zero.) These diagrams exhibit several noteworthy features.

Firstly consider the Bi/Tl–O layers (figures 2 and 3). Here there is a profound difference in the density of states between the two compounds. In the bismuth compound the density of states at the Fermi energy ($n(E_F)$) is rather low. However, in the Tl–O layer in $Tl_2Ba_2CuO_6$ $n(E_F)$ is very large. Furthermore, the bandwidth for the oxygen p bands is about 0.25 Ryd in $Tl_2Ba_2CuO_6$ compared with more like 0.65 Ryd in $Bi_2Sr_2CuO_6$. Similar discrepancies in the bandwidth occur on the metallic ion in this layer. This difference may be ascribed to there being a closer degeneracy of the Bi and O atomic levels than the Tl and O levels. This is consistent with the proximity and discrepancy in the energies at which the densities of states peak on the Bi and O sites, and the Tl and O sites, respectively. We find that the O bands are roughly three quarters full in both cases, implying that the Fermi level lies in the anti-bonding bands formed from the O 2p levels and the Bi/Tl 6p levels. Indeed it is interesting to note that the Tl
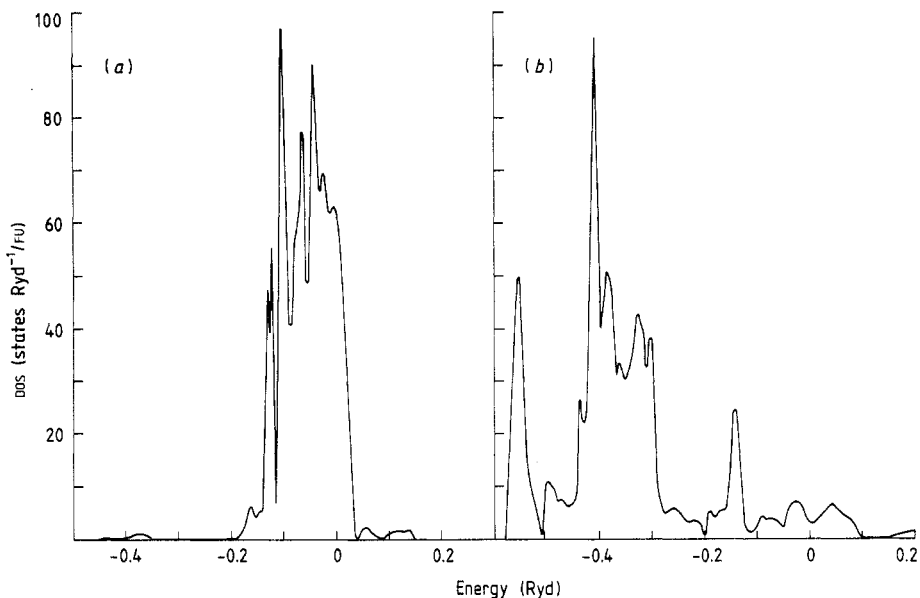
Figure 3. (*a*) The density of states on the O(3) site in Tl$_2$Ba$_2$CuO$_6$; (*b*) the density of states on the O(3) site in Bi$_2$Sr$_2$CuO$_6$.
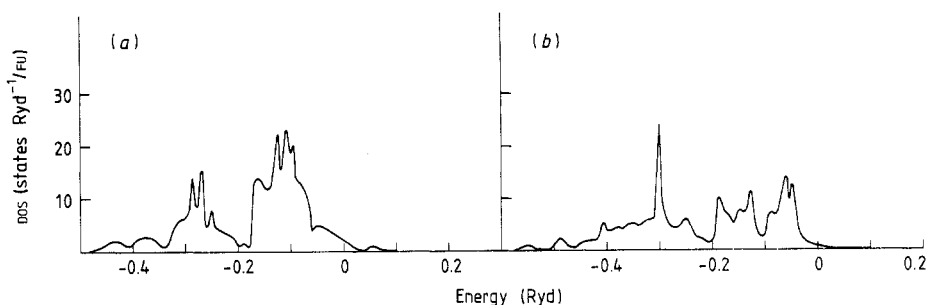

Figure 4. (*a*) The density of states on the barium site in Tl$_2$Ba$_2$CuO$_6$; (*b*) the density of states on the strontium site in Bi$_2$Sr$_2$CuO$_6$.

6p levels are partially occupied due to their capacity to bond to the O p states, whereas the Tl 6s states are empty. This is not true in the Bi case, where the 6s band lies below the Fermi energy.

Secondly we examine the Sr/Ba–O layers. Strontium and barium are in the same column of the periodic table. The densities of states for these sites are shown in figures 4 and 5. Again we observe that the density of states at E_F is fairly low, with some very sharp peaks below E_F. A point to note is that in Tl$_2$Ba$_2$CuO$_6$ there is a peak in the p density of states above the Fermi energy that is absent in Bi$_2$Sr$_2$CuO$_6$.

Finally we look at the CuO$_2$ layers, figures 6 and 7. We note that the density of states in these layers displays very comparable band widths, and similar, fairly low, values of the density of states at the Fermi level. The states around the Fermi energy are Cu(d$_{x^2-y^2}$)–O(p$_x$, p$_y$) states. The oxygen bonding levels are filled and the antibonding
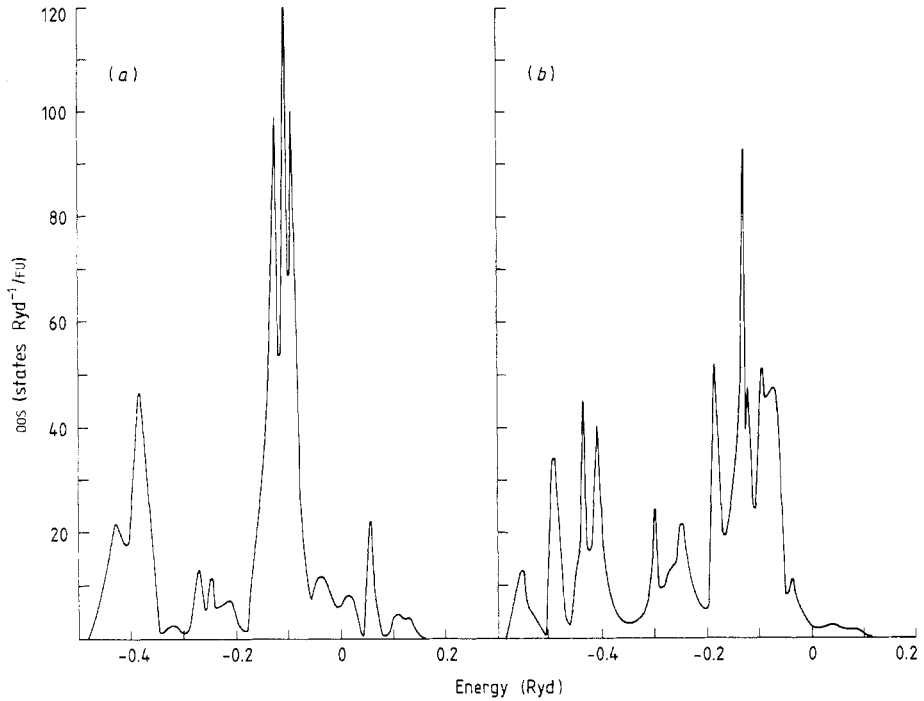
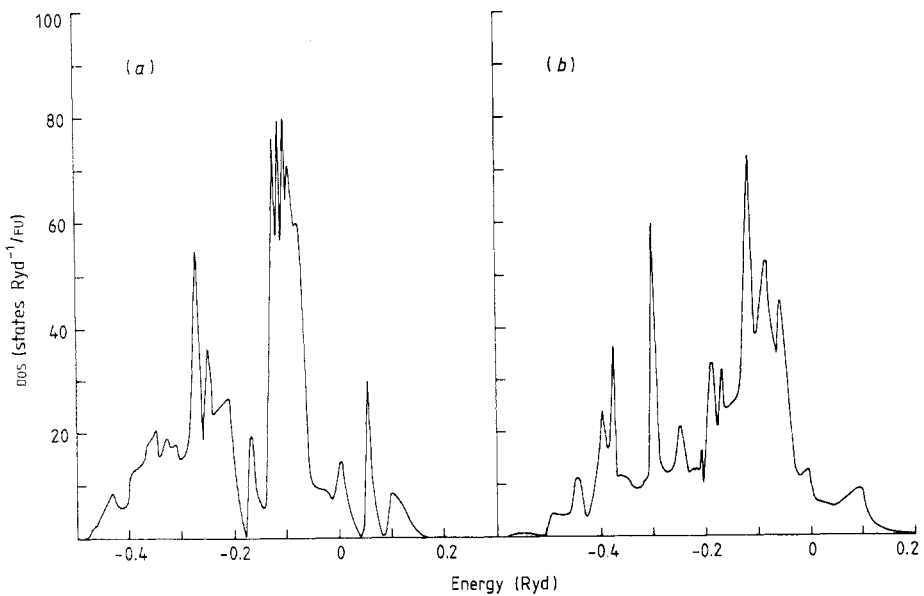**Figure 5.** (*a*) The density of states on the O(2) site in $Tl_2Ba_2CuO_6$; (*b*) the density of states on the O(2) site in $Bi_2Sr_2CuO_6$.

Figure 6. (*a*) The density of states on the copper site in $Tl_2Ba_2CuO_6$; (*b*) the density of states on the copper site in $Bi_2Sr_2CuO_6$.
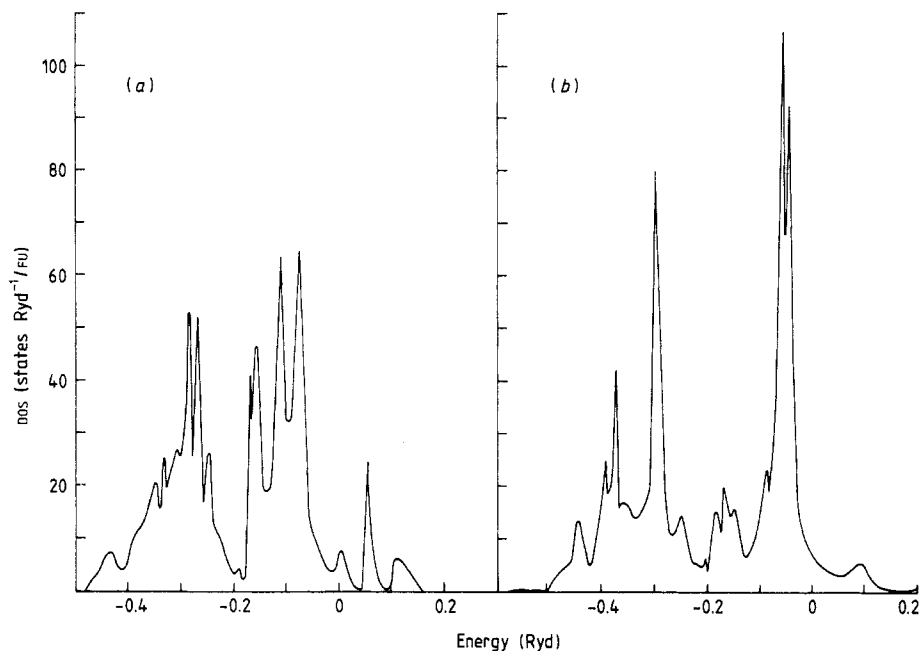
Figure 7. (*a*) The density of states on the O(1) site in Tl$_2$Ba$_2$CuO$_6$((*b*) the density of states on the O(1) site in Bi$_2$Sr$_2$CuO$_6$.

levels are approximately half filled. There are also some notable differences in the electronic structure of the CuO$_2$ layer between these materials. In the bismuth compound the O(1) peaks are taller and narrower than in the thallium compound. The opposite is true for the peaks on the copper site. The apical oxygen atoms have their 2p bands at different amounts beneath the Fermi surface: in the Tl case at -0.142 Ryd and in the Bi case at -0.232 Ryd.

One test of the effects of our assumption of a different structure from the experimentally observed one is the electronic pressure. This can be calculated in the usual way [19]. For the equilibrium lattice constant this should be zero. In Bi$_2$Sr$_2$CuO$_6$ the pressure at the equilibrium lattice constant takes on a small positive value. Further analysis of the pressure shows this arises from an electronic repulsion between the Bi ions on adjacent layers. We note that such a calculated electronic pressure is exactly what may be expected given our approximation to the experimentally observed crystal structure. This effect does not occur in Tl$_2$Ba$_2$CuO$_6$, indicating that the nature of the interlayer bonding in the two materials is rather different.

The degree of charge transfer tells us about doping of the CuO$_2$ planes, amongst other things, and we now turn to it. It is important to recall that the charge transfer is an arbitrary quantity, dependent on the size of the enscribed atomic sphere. As we have taken equivalent sphere sizes for corresponding ions in each material we are able to make comparisons of the amount of charge transfer, though the absolute values are meaningless. The results are summarised in table 1. From this we observe that there is a qualitative difference between the two materials. In Tl$_2$Ba$_2$CuO$_6$ the Tl–O layers remain more or less neutral. However, each Ba–O layer gains about 0.2 of an electron from the CuO$_2$ layer. In Bi$_2$Sr$_2$CuO$_6$ each Bi–O layer loses about 0.4 electrons and

donates it to the Sr–O layer. This ties in nicely with the peak seen above E_F in the p density of states in Ba but which is absent in Sr. The CuO_2 layer remains more or less neutral although there is about 0.25 electrons donated to each oxygen ion from copper within the layer.

4. Discussion

We now consider the effect on the superconducting properties of the similarities and differences between the electronic structures of the two materials. There are two different aspects to this: whether the Bi/Tl–O planes are metallic (i.e. how well they couple the CuO_2 planes); and the degree of charge transfer into the CuO_2 planes (i.e. how strong we expect the superconductivity to be).

Implicitly we have a view of superconducting CuO_2 planes 'Josephson-coupled' by the Bi/Tl–O planes. This is justified as long as the superconducting coherence length up the c axis, $\xi^{\parallel}$, is comparable or small compared to the c-axis lattice parameter (i.e. normal to the planes). (One should then think of the Cooper pair as a single entity in considering its motion in that direction.) Experimentally, $\xi^{\parallel}$ *is* smaller than the c-axis lattice parameter in the $YBa_2Cu_3O_{7-\delta}$ [22] and $Bi_2Sr_2CaCu_2O_8$ [23] materials, but it has not been measured, to our knowledge, in the cases of interest here. At finite temperatures, superconducting order in an isolated Cu–O plane would be destroyed at large distances by thermal fluctuations, but a 'Kosterlitz–Thouless' phase would still exist up to a temperature, T_{KT}, of the order of the mean-field T_c. Any interplanar coupling would be expected to raise the Kosterlitz–Thouless phase to the status of one with genuine long-range order. The argument for this is familiar from the theory of anisotropic magnets: as the temperature is lowered, towards T_{KT}, the correlation length, ξ, grows. This causes the coupling between the planes to grow. The reason for this is that the coupling is, in effect, between *blocks* of spins of area ξ^2. Thus once the Josephson coupling multiplied by $(\xi^2)^2$ is greater than $k_B T$, we expect three-dimensional order to set in. The important point is that the three-dimensional T_c is bounded *from below* by the Kosterlitz-Thouless transition temperature, T_{KT}, as that is where ξ diverges. (Here we assume that the three-dimensional transition occurs before the finite size of the London penetration depth influences the vortex configurations, which is probably accurate in these cases.)

Our results imply that $Tl_2Ba_2CuO_6$ has metallic Tl–O planes and hence should give a good proximity-effect coupling of the CuO_2 planes. However, in the case of $Bi_2Sr_2CuO_6$ the Bi–O planes are insulating, and hence one expects much less robust superconductivity. (Sterne and Wang [12] have also noted the importance of a metallic layer between the superconducting layers, in the context of $Bi_2Sr_2CuO_6$.) The argument about finite temperature fluctuation effects above imply that T_c is unlikely to be much affected by the degree of metallicity; however, measurements of the strength of the coupling of the superconducting state along the c axis, such as the size of the gap and H_{c1} (for H parallel to the ab plane) should be strongly influenced.

The insulating nature of the Bi–O planes may also imply that the material will be sensitive to any doping due either to O non-stoichiometry or impurities, which might lead to the Bi–O plane being doped and hence to an enhancement of T_c; indeed this may underlie the variability of the experimental results on the T_c of $Bi_2Sr_2CuO_6$. A final effect on the ease of communication between the CuO_2 planes is the difference of the energies of the apical O p bands: they are further below the Fermi energy in the Bi case

than in the Tl case, and hence are of less use as a means for tunnelling between the planes.

Let us turn to the issue of charge transfer and doping of the CuO_2 planes. This is radically different in the two materials, as can be seen from table 1. This table shows that the major difference in the two materials is in the Bi/Tl–O layer. In the thallium compound the Tl–O layer is more or less electrically neutral with very little intralayer charge transfer. In the bismuth compound the Bi loses nearly a whole electron and only half of this resides on the oxygen in the Bi–O layer. The rest is donated to the Sr–O layer. The upshot of this is that in $Tl_2Ba_2CuO_6$ the Ba–O layer dopes holes into the CuO_2 layer. This does not happen in $Bi_2Sr_2CuO_6$ because electrons on the Sr–O layer are attracted back to the Bi–O layer. This has profound consequences for the superconductivity in these materials. The difference in charge transfer into the CuO_2 planes means there is a different number of holes in this plane. Given the importance of the density of holes in determining T_c (see for instance [24] for a discussion in the case of $La_{2-x}Sr_xCuO_4$), the differing degree of doping of the CuO_2 planes correlates well with the observed T_c in these materials.

The relative robustness of the superconductivity in the two materials is also affected by the structure in a rather straightforward way namely the larger spacing (along the c axis) of the Bi–O layers than the Tl–O layers. This difference in the structures is initially surprising, given the ionic nature of the Bi–O layers which one would expect to lead to the Bi–O layers being *closer* to each other than the Tl–O layers. (Here one must note that in the correct crystal structure the (positive) Bi ions are above the (negative) O ions.) Our calculations yield a partial check on one suggestion as to why the converse is true. Sleight [4] has suggested that the lone-pair Bi 6s electrons may hybridise with the 6p to some extent and form a lobe pointing toward the O ion below/above the Bi ion. The electrostatic repulsion of the lone pair and the negative O ion leads to the counter-intuitive larger separation of the Bi–O layers. In the Tl case he predicted that there would not be a Tl lone pair, and hence the Tl–O layers would be closer together. Our result that the Tl 6s states are above the Fermi energy agrees with this assertion; however, we should note that we find largely covalent bonding in the Tl–O layers, and do not agree with his charge assignments (which would leave the Tl 6p states empty as well).

Finally let us note that there is *direct* experimental evidence on the validity of that our conclusions from recent photoemission experiments on $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2CuO_6$ ($T_c = 90$ K and 12 K, respectively). These show that both these materials have Bi(6p)–O(2p) character around E_F and that this dominates $n(E_F)$ in $Bi_2Sr_2CaCu_2O_8$ [25]. These results are wholly consistent with the picture of the electronic structure and its influence on the superconductivity we have erected.

5. Conclusions

We have performed self-consistent density functional calculations for $Tl_2Ba_2CuO_6$ and $Bi_2Sr_2CuO_6$, finding that the Tl–O layers are predominantly covalently bonded whereas the Bi–O layers also have an ionic component. We have highlighted two differences in the electronic structure which, in combination, are likely to explain their contrasting T_c values. Firstly there is the high density of states at the Fermi energy in the Tl–O plane in the thallium compound in contrast to the Bi–O layer in the bismuth compound. We argue that this facilitates the communication of the superconducting order parameter

perpendicular to the planes. The differing energies of the apical O p bands also contributes to this difference. Secondly, and probably more importantly, the degree of charge transfer to the superconducting CuO_2 planes is much larger in the Tl compound than in the Bi compound, implying a higher level of doping of the CuO_2 planes in that case.

Acknowledgments

Note added in proof. In the present work we have examined materials where the crystal structure remains nearly constant, but the chemical species changes. After submission of our paper the work of Massidda, Yu and Freeman [26, 27] was brought to our attention. They have performed accurate band calculations on $Tl_2Ba_2CaCu_2O_8$ and $Bi_2Sr_2CaCu_2O_8$. Further insight may be gained by a detailed comparison with their work where the crystal structure is changed but the chemical species involved remains as constant as possible.

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