

Bond-valence analysis of charge distribution in the spin ladders of $[M_2Cu_2O_3]_m[CuO_2]_n$ -type cuprates with $m = n = 1$

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[Received 16 December 1998 and accepted 15 February 1999]

ABSTRACT

The bond-valence-sum method is used to calculate the hole distribution in the spin ladders of $[M_2Cu_2O_3]_m[CuO_2]_n$ -type cuprates with $m = n = 1$ (where M are divalent or trivalent cations). It is shown that the appearance of superconductivity in this system is related to hole transfer from chain planes to the spin-ladder plane. The role of the valency and size of the M atoms is discussed in detail.

§ 1. INTRODUCTION

Among various spin-ladder compounds, the $[M_2Cu_2O_3]_m[CuO_2]_n$ cuprates (where M are divalent or trivalent cations) have attracted most attention because they consist of both simple chains and two-leg ladders of copper ions. This system consists of Cu_2O_3 spin-ladder planes as well as CuO_2 chains. Four phases of this family (for m/n ratios equal to 1/1, 5/7, 7/10 and 9/13) have been successfully synthesized and a superconducting phase has been shown to exist in the 1/1 (Leonyuk *et al.* 1998), 5/7 (Szymczak *et al.* 1999) and 7/10 (Uechara *et al.* 1996) phases.

To understand the appearance of superconductivity in the $[M_2Cu_2O_3]_m[CuO_2]_n$ system, it is crucial to clarify the distribution of the self-doped holes between the chain and ladder planes. It was suggested previously (Uechara *et al.* 1996, Szymczak *et al.* 1999) on the basis of experiments that superconductivity is related to the hole concentration transferred from the chain planes to the spin-ladder planes. In this letter we examine this problem by means of the bond-valence-sum (BVS) method. We decided to analyse the $[M_2Cu_2O_3]_m[CuO_2]_n$ system with $m = n = 1$ because of the detailed positional atom parameters (Leonyuk *et al.* 1998) that are available for both superconducting (SC) and non-superconducting (NSC) single crystals. Similar BVS calculations for $m = 7$ and $n = 10$ system have recently been performed (Kato

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et al. 1996; Isobe and Takayama-Muromachi 1998). Unfortunately, detailed structural parameters are not available for the 5/7 system. Hence, a BVS analysis could not be performed for this family. Therefore, the results presented in this letter cannot give direct comparison for all crystals belonging to the $[\text{M}_2\text{Cu}_2\text{O}_3]_m [\text{CuO}_2]_n$ system. It is worth mentioning that the BVS method was previously successfully used to analyse the distribution of holes in standard high-temperature superconductors (see Yamauchi and Karppinen (1998) and references therein).

§ 2. CONCEPT OF THE BOND-VALENCE CALCULATIONS

In order to interpret the charge distribution in an inorganic crystal, one may utilize the bond-valence methodology that has been derived from Pauling's rules for crystal chemistry. This can most easily be achieved by using the equation of Brown and Altermatt (1985) and Brown (1989) for the bond strength s_{ij} between ions i and j :

$$s_{ij} = \exp \left[\frac{R_0 - R_{ij}}{B} \right],$$

where R_{ij} is the bond length between the two ions, R_0 is the reference bond length for this pair and B is a constant approximately equal to 0.37. The valence V_i of any atom is thus the sum of the contributions from each bond:

$$V_i = \pm \sum_j s_{ij},$$

where the valence is negative for an anion and positive for a cation. For most inorganic crystals, the valence of any atom is very close to the formal oxidation valence. If, however, the BVS yields a valence which exhibits a significant departure from the formal oxidation state, this can be taken to represent the presence of a hole or an electron.

For an ionic crystal M_xN_y , where M is a cation with formal valence i and N is an anion with formal valence j , and assuming that the true valence of M is V_{M} and the true valence of N is V_{N} , the concentration $p(\text{M}_x\text{N}_y)$ of carriers can be found through the equation

$$p(\text{M}_x\text{N}_y) = x(V_{\text{M}} - i) + y(V_{\text{N}} + j).$$

A positive value for $p(\text{M}_x\text{N}_y)$ suggests the presence of holes, while a negative value is indicative of electrons.

§ 3. RESULTS AND DISCUSSION

The crystals studied in this paper have the chemical formulae $\text{Ca}_{0.48}\text{Sr}_{0.49}\text{Bi}_{0.03}\text{Cu}_{1.69}\text{O}_{2.99}$ (for the SC sample) and $\text{Sr}_{0.56}\text{Pr}_{0.29}\text{Y}_{0.12}\text{Ba}_{0.03}\text{Cu}_{1.91}\text{O}_3$ for the NSC sample). The presence of bismuth and barium in the SC and NSC samples respectively is simply the result of impurities in the growing process. The lattice constants for both crystals are within 2% of each other, and the atomic coordinates are also extremely similar. Each crystal contains alternating layers of cuprate chains and spin-ladder sublattices in the a - c plane. The major differences between the two crystals occur in the copper occupancy of the chain plane and, more obviously, the chemical composition of the atom defined by M .

As the spin-ladder planes are the only superconducting structure in the crystals, they are of primary interest. Hence, in this study, only the hole concentration in this plane will be considered.

The oxygen atoms that comprise the spin-ladder plane can be divided into two groups, namely leg oxygen and rung oxygen. These are defined as O(1) and O(2) respectively. A computer program was used to calculate the distances to each oppositely charged ion within several coordination spheres. The same program also calculated the bond strength to each oppositely charged ion, and the valence sum for the O(1), O(2) and copper atoms. The results are listed table 1.

The valence sum for the rung oxygen was substantially different from that of the leg oxygen. This presented a problem when considering the hole concentration on the spin-ladder planes. By weighting the relative abundances of O(1) and O(2), it was possible, however, to obtain an average value for the valence of the spin-ladder oxygen systems. The simple relation

$$V_A = \frac{2V_1 + V_2}{3}$$

where V_1 is the obtained valence for O(1), V_2 the valence for O(2) and V_A the average valence for oxygen in the spin-ladder plane, was therefore used. Thus, the hole concentration was calculated using the formula

$$p(Cu_2O_3) = 2(V_{Cu} - 2) + 3(V_A + 2),$$

where $p(CuO_2)$ is the hole concentration on the spin-ladder plane, V_{Cu} is the valence obtained for copper and V_A is again the average valence for oxygen.

The computer program was also used to calculate another set of data, namely the percentage contribution of each bond to the total valence of the atom studied. This can serve as a good indicator of bond strength, and perhaps as a check of position as well. The result are presented in table 2.

The results obtained for both samples obey the valence sum rule and are in line with conventional theory, that is more hole carriers reside on SC spin-ladder system than on the similar NSC system.

Table 1. Electronic properties of the spin-ladder systems in the SC and NSC samples.

Property	Value	
	SC	NSC
V_{Cu}	+ 2.1468	+ 2.0906
$V_{O(1)}$	-2.0832	-2.0822
$V_{O(2)}$	-2.1244	-2.1398
V_A	-2.0970	-2.1014
$p(CuO_2)$	+ 0.0026	-0.1230

Table 2. Relative importance of different bond types for the spin-ladder oxygen atoms in the samples. The figures are expressed as a percentage of the total bond valence for the oxygen atoms.

	Relative importance (%) in SC samples		Relative importance (%) in NSC samples	
	M	Cu	M	Cu
O(1)	25.9	74.1	29.0	71.0
O(2)	45.6	54.5	46.5	53.5

As noted before, the structural properties of the two crystals are very similar. There are, however, some differences which could conceivably have an effect upon their electronic properties. The most striking difference between the SC and the NSC crystals is in the chemical composition of the atom defined by M. Whereas the SC crystal has a large percentage of relatively small ions, the NSC sample is made up almost entirely of large-radius cations, such as strontium, praseodymium and yttrium. This difference could have several effects. The larger-radius ions may be able to connect the chain and spin-ladder planes better, perhaps facilitating the transfer of charge between the two sublattices. This charge transfer could conceivably account for the difference in $\rho(\text{CuO}_2)$ for the two crystals.

Perhaps more importantly, the large-radius cations which dominate the NSC system could heavily distort the lattice structure, causing a significant deviation from the spin-ladder structure in the SC system. This observation is supported by the fact that the lattice constants are effectively very similar; yet the average M radius is much larger in the NSC crystal. It is not inconceivable that the large M atoms compress the spin-ladder structure to such an extent that the distances between successive rungs are so great that superconductivity becomes impossible. This would suggest that the spin-ladder systems are very sensitive to even the smallest structural perturbations. In the NSC system, the distances between the rungs seems to be greater than in the SC system. Also, the copper and oxygen atoms which make up the leg of the ladder are closer together. The differences in distance, however, are only very small, never exceeding $\pm 2\%$ of the other's value.

It is worth noting that the O(2) (rung oxygen) atoms have about 45% of the total bond-valence attachment to the M atoms, compared with about 25% for the O(1) (leg oxygen) atoms. Referring to table 1, it becomes apparent that there may be some correlation between the bond strength and the distribution of charge. Of the three atoms that make up the spin-ladder system in the $m/n = 1/1$ crystal, the greatest change in valence occurs for the O(2) and Cu(1) atoms. Indeed, the O(1) atom hardly changes its valence at all. Although the alteration of the O(2) valence is much smaller than for the Cu(1), this suggests a redistribution of charge from the spin-ladder system to the M atoms, accounting for the minor change in both the O(1) and the O(2) atoms. Perhaps this suggests that charge transfers into and out of the spin-ladder system via the M atoms, in which case the rung oxygen would be very important to this process.

§ 4. CONCLUSIONS

It has been shown using the BVS approach that the charge transfer from chain planes to the ladder planes is responsible for superconductivity in the $m/n = 1/1$ systems. It seems that similar mechanisms exist in the $7/10$ systems. To make general conclusions on superconductivity in the $[\text{M}_2\text{Cu}_2\text{O}_3]_m [\text{CuO}_2]_n$ systems, a theoretical analysis of the charge distribution in the $5/7$ systems should be made

ACKNOWLEDGEMENTS

We would like to thank Dr A. Bledowski for the time that he so generously donated to us. One of us (P. Brydon) is grateful to the Kronenberg Foundation and the National Youth Science Forum for supporting his stay in Poland. This work was partly supported by the Polish State Committee for Scientific Research (grant 2P03B10214).

REFERENCES

- BROWN, I. D., 1989, *J. solid-st. Chem.*, **82**, 122.
- BROWN, D. I., and ALTERMATT, D., 1985, *Acta crystallogr. B*, **41**, 244.
- ISOBE, M., and TAKAYAMA-MUROMACHI, E., 1998, *J. phys. Soc. Japan.*, **67**, 311.
- KATO, M., SHIOTA, K., and KIOKE, Y., 1996, *Physica C*, **258**, 284.
- LEONYUK, L., RYBAKOV, V., SOKOLOVA, E., MALTSEV, V., SHVANSKAYA, L., BABONAS, G.-J., SZYMCZAK, R., SZYMCZAK, H., and BARAN, M., 1998, *Z. Kristallogr.*, **213**, 406.
- SZYMCZAK, R., SZYMCZAK, H., BARAN, M., MOSINIEWICZ-SZABLEWSKA, E., LEONYUK, L., BABONAS, G.-J., MALTSEV, V., and SHVANSKAYA, L., 1999, *Physica C*, **311**, 187.
- UECHARA, M., NAGATA, T., AKIMITSU, J., TAKAHASHI, H., and KINOSHITA, K., 1996, *J. phys. Soc. Japan*, **65**, 2764.
- YAMAUCHI, H., and KARPPINEN, M., 1998, *Mater. Sci. Engng.* **B54**, 92.