Physica C 206 (1993) 70–74
North-Holland

Electron spin resonance evidence for the role of copper ions in interlayer coupling in layered copper oxycarbonates

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Received 2 October 1992;
Revised manuscript received 1 December 1992

Electron spin resonance (ESR) studies have been carried out on the layered copper oxycarbonates (alternating layers of CuO_2 and CO_3^{2-}) with the nominal composition $Ba_3SrCu_2O_6.2CO_2$ and their reaction products with ammonium slats. The ESR signals typical of copper ions in square-planar geometry with a slight orthorhombic distortion presumably arise from the copper ions being incorporated in the carbonate layer. A simple grinding procedure at room temperature using $(NH_4^+)_nX^{n-}$ ($X=F^-$, $(NO_3)^-$, $(VO_3)^-$, $(HPO_4)^{2-}$) incorporates X^{n-} anions in the structure with the liberation of ammonia. The environment of the copper ion in the carbonate layer is thus changed without altering the structure. The g_3 values are most affected by this reaction showing that the filled e_g orbitals are oriented in the plane of the carbonate layer. The half-filled e_g orbitals (transforming as $d_{x^2-y^2}$ orbitals) are oriented out of the plane. This suggests that the copper ions in the carbonate layers are probably involved in introducing magnetic coupling between the CuO_2 layers.

The recent discovery of layered copper oxycarbonates derived from $Sr_2CuO_2.CO_3$ [1–3], and the discovery [2,4] of superconductivity in them, have raised important questions. The parent $Sr_2CuO_2.CO_3$ may be regarded as being derived from the infinite layer $ACuO_2$ compounds [5] with an alternation of CuO_2 layers and CO_3 layers and with Sr ions being sandwiched in between these layers as shown in fig. 1. It is becoming apparent that an essential ingredient for the high-temperature superconductivity is the magnitude of the inter-CuO_2-planar transfer integral [6]. In order that the carbonate layer acts as a charge reservoir or introduces interlayer exchange coupling it is necessary that a soft, polarisable or multivalent ion is incorporated in this layer. The carbonate ions by themselves do not fit such a description. Izumi et al. [2] find evidence from neutron diffraction studies that nearly ten percent of the C sites in the carbonate layer are occupied by copper ions. These copper ions could then serve as the medium through which inter-CuO_2-plane exchange or hole transport could take place. The second important feature of these compounds is the potential of exploiting the high reactivity of the carbonate group to make new layered compounds. Matacotta et al. [3] have given evidence to suggest that the carbonate ion may be replaced by the formate ion by reaction with formic acid.

In this communication we report the results of our electron spin resonance studies on compounds with the nominal composition $Ba_3SrCu_2O_6.2CO_2$. When there are Cu^{2+} ions in the carbonate layer, they are expected to be isolated and have a well defined ESR signal corresponding to its local environment. Advantage is taken of the fact that the carbonates react in a facile manner with salts of weak bases and strong acids, such as the ammonium salts. In this manner the carbonate group may be replaced by other anionic groups. We thus have control over the environment of the copper ions which would be reflected in the ESR signals. The systematics of the changes in the ESR signals on the substitution in the carbonate

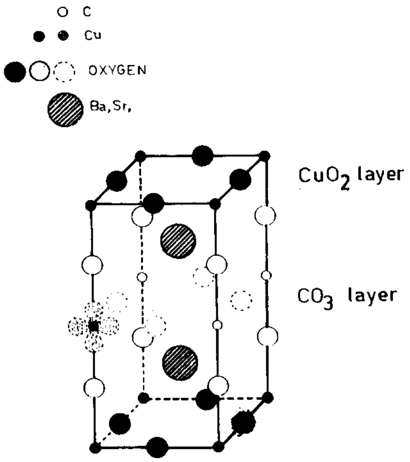

Fig. 1. Structure of the prototype layered oxycarbonate, $Sr_2CuO_3.CO_2$ (from ref. [1]) based on which the structure of $Ba_3SrCu_2O_6.2CO_2$ is given. The CuO_2 layer and the carbonate layers are shown. The dashed circles correspond to oxygen sites which are fifty percent occupied. The orientation of the half-filled e_g orbital (transforming as $d_{x^2-y^2}$ orbital) of the copper ions in the carbonate layer is also shown.

Table 1
Weight loss on grinding and the lattice parameters of the reaction products of $Ba_3SrCu_2O_6.2CO_2$ and $(NH_4)_nX^{n-}$

X^{n-}	Weight loss [b]	Lattice parameters ($\pm$0.005 Å)	
		a	c
–		3.997 [a]	7.908
$(VO_3)^-$	69	4.006	7.914
$(SO_4)^{2-}$	27	3.974	7.954
Cl^-	5	3.984	7.934
$H(PO_4)^{2-}$	66	4.003	7.978
$(NO_3)^-$	28	3.991	7.937
F^-	67	4.005	7.911

[a] The lattice parameters were orthorhombic with $a=4.004$ and $b=3.990$.

[b] The percent weight loss as expected from eq. (1) is given.

layers then gives an idea of the nature of the local distortion and hence of the orientation of the e_g orbitals of the copper ions. This would give an idea of the mechanism of the interlayer coupling.

We have carried out solid phase reactions of the oxycarbonates with ammonium salts, $(NH_4)_nX^{n-}$, of various acids. This has been done by simple grinding procedures and the extent of the reaction has been followed by classical gravimetric methods. We find considerable reactivity in this case with retention of the basic structure. We have examined the polycrystalline reaction products by simple electron spin resonance studies. The results of our investigations are reported below.

The layered copper oxycarbonates that are most easily prepared in air [3] as a single phase by reaction of CuO with $BaCO_3$ and/or $SrCO_3$ at 880°C have a composition corresponding closely to $Ba_3SrCu_2O_6.2CO_2$ with an idealised structure similar to that shown in fig. 1. The refined lattice parameters as obtained by us are given in table 1. The lattice parameters are comparable to those reported by Izumi et al. [2] in the dimensions of the a and b parameters but are significantly smaller in the c parameter. It has been noted by Matacotta et al. [3] that the a–b-plane lattice parameters of the orthorhombic 213 phase [5] (containing Cu–O–Cu chains) in the Ba–Sr–Cu–O system become tetragonal when the Ba:Sr ratio is close to 3. At this value the system becomes nearly tetragonal with the basal a parameter being nearly 4.00 Å. This seems to be the reason for the facile formation of the layered copper oxycarbonates with CuO_2 planes at the composition used by us.

The parent phase has been reacted with various ammonium salts, $(NH_4)_nX^{n-}$, by grinding in a pestle and mortar for a prolonged period (1 h) at room temperature and if necessary keeping the ground mixture at 100°C for a few hours. The reaction is expected to proceed as follows:

$$Ba_3SrCuO_6.2CO_2+(2/n)(NH_4)_nX^{n-}$$
$$\rightarrow Ba_3SrCu_2O_6.2HX_{1/n}+2NH_3\uparrow+2CO_2\uparrow\,. \quad (1)$$

The reaction mixture of $Ba_3SrCu_2O_6.2CO_2$ was taken in the ratio of 1:(2/n) as required in eq. (1) above. The extent of the reaction as calculated from the weight loss is given in table 1. Infra-red spectra of these compounds (to be reported later) showed substantial changes with a prominent decrease in the intensity of the carbonate band and the appearance of some new bands associated with the X anions. There were no features due to ammonium ions in the infrared spectra. Except in the case in which

$X^{n-} = (NO_3)^-$, the reacted products were found to retain their structure as long as the temperature was not increased beyond 100°C during the preparation stage. The formation of the layered oxycarbonates may thus be regarded as an intercalation of CO_2 molecules between $(Ba,Sr)CuO_3$ layers [7]. When $X^{n-} = (NO_3)^-$ we find a substantial presence of $Ba(NO_3)_2$ in the X-ray pattern. Typical diffraction patterns of the mixture after grinding with ammonium fluoride are shown in fig. 2. The lattice parameters obtained from the refinement of the X-ray diffraction patterns for various X anions are given in table 1. We do not observe a significant change in the lattice parameters. This is also not expected.

The room temperature ESR spectra of these compounds are shown in fig. 3. There is a marked change in the nature of the ESR signal after reaction with the ammonium salt. The spectra in all cases are characteristic of orthorhombic symmetry. The g values are given in table 2. The parent compound is closest to tetragonal symmetry. The average g values in these compounds are close to 2.1 which is the typical value found in oxides [8]. In more ionic complexes such as $[Cu(H_2O)_6]^{2+}$ or $[Cu(NO_3)_6]^{2+}$ complexes, the average g value [7] is ≥ 2.2. Only in the case of $X^{n-} = F^-$ is there a marked increase in the g_3 value which is again consistent with the more ionic nature of the Cu–F linkage compared to that of the Cu–O linkage. The changes as observed by us cannot thus be attributed to a simple reaction of the parent layered copperoxycarbonate to give different impurity phases of the copper salts.

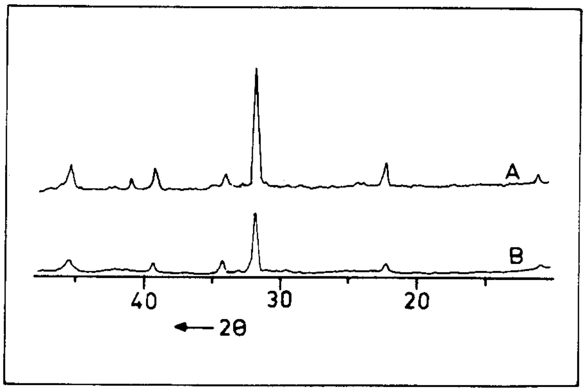

Fig. 2. X-ray diffraction patterns of $Ba_3SrCu_2O_6$(A) and the reaction product after grinding with ammonium fluoride (B).

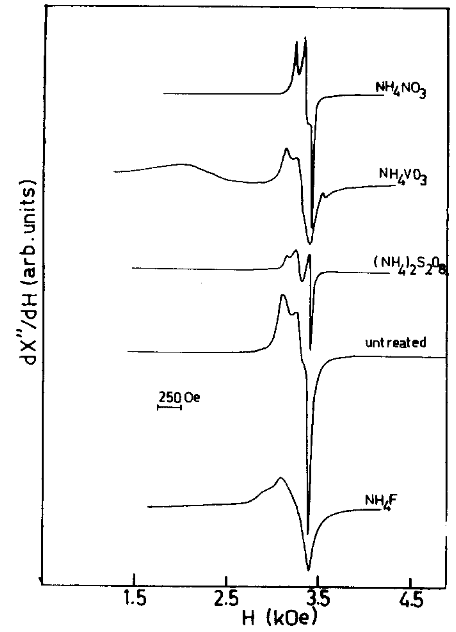

Fig. 3. Electron spin resonance spectra from the reaction products of $Ba_3SrCu_2O_6.2CO_2$ after grinding with various ammonium salts as indicated against the spectra.

Table 2
g values of ESR lines of $Ba_3SrCu_2O_6.2CO_2$ and the reaction products with $(NH_4)_nX^{n-}$

X^{n-}	g values [a]		
	g_3	g_2	g_1
–	2.24	2.10	2.045
$(NO_3)^-$	2.18	2.09	2.046
$(S_2O_8)^{2-}$	2.22	2.09	2.050
$(VO_3)^-$	2.23	2.12	2.054
F^-	2.31	2.13	2.053

[a] The ESR lines have been analysed on the basis of an orthorhombic symmetry.

In most cases the spectra are completely changed with little or no contribution from the original unreacted compound. Since the reaction is not complete (table 1) this would indicate that the regions which react most strongly with the ammonium salts are those that are associated with the copper ions responsible for the ESR signal. The ESR lines are unlikely to be associated with impurity phases [8] such as unreacted CuO or $BaCuO_2$. The antiferromagnetically coupled copper ions in the CuO_2 planes are not likely to give rise to an ESR signal as experiments with model systems [8] have shown. The g values of the ESR lines as well as the line shape are somewhat similar to the weak signal obtained [8] with the 213 phases such as Sr_2CuO_3. Our signals are too strong to be attributed to such phases.

The changes in the ESR spectra attest to the presence of some copper ions in the carbonate layers as first proposed by Izumi et al. [2]. The intensity has been compared with that from $CuSO_4.5H_2O$. In all cases the ESR intensity corresponds to a contribution from about 6 to 10 percent of all the copper ions present. The changes in the g values of the lines reflect the changes in the environment of these copper ions when the carbonate anionic group is replaced by the new anionic group X^{n-}. The most considerable changes are found in the value of g_3. The local coordination axis of the copper–oxygen pseudo-octahedron is determined with the axis of elongation being taken as the axis parallel to the g_3 axis. Since the changes are brought about by reaction with the carbonate groups which are predominantly in the *a–b*-plane, it would seem that the g_3 axis is in the *a–b*-plane or carbonate layer. The basal square-planar CuO_4 unit of the elongated pseudo-octahedron of the isolated copper ion in the carbonate plane is thus oriented [9,10] perpendicular to this layer (to the *a–b*-plane). The filled e_g orbitals (d_{z^2} orbitals) of the Cu^{2+} ion are therefore oriented parallel to the plane. The plane of the half-filled e_g orbitals of the Cu^{2+} ions transforming as $d_{x^2-y^2}$ is therefore oriented perpendicular to the *a–b*-plane. In this case the CuO_2 *layers* would be coupled through the half-filled orbitals of the isolated Cu^{2+} ions incorporated in the carbonate layer. This provides the mechanism for the interlayer coupling which is now expected to be magnetic in origin [6].

The presence of some Cu^{2+} ions in the carbonate layer would require the presence of extra copper ions as proposed by Izumi et al. [2]. On the other hand the pseudo-cubic nature of the structure for the composition $Ba_3SrCu_2O_6.2CO_2$ suggests that its origin is a cubic perovskite. In this case there is likely to be a scrambling between the copper and carbon atoms. Some carbonate groups may thus also be incorporated in the CuO_2 layer. These carbonate groups may be less reactive. We find that the percentage yield of the product never exceeds 70 per cent. This aspect is being investigated. Such a scrambling would also explain the infra-red spectra of Matacotta et al. [3] which show the persistence of the carbonate group even after the reaction is complete. Our preliminary infra-red data also support this conclusion.

The compounds prepared by us are not superconducting, having a resistivity nearly two orders of magnitude higher at room temperature. The magnitude of the resistivity at the onset of superconductivity is not only a good indicator of the quality of the specimen but also gives an indication of whether the T_c may be increased or not. It has been pointed out [11] that, in single phase layered cuprate oxides, superconductivity appears when the resistivity of polycrystalline samples is less than 10–20 mΩ cm while T_c in a given family is a maximum when the onset resistivity in polycrystalline samples is close to 500 μΩ cm. The sample measured by Kinoshita and Yamada [4] has a resistivity less than 15 mΩ cm at room temperature and a resistivity of ~8 mΩ cm at the onset T_c. The high value of the resistivity in this case would indicate that there could be some CuO_2 layers which have carbonate ions incorporated in them. In our compositions, the nearly cubic nature of the unit cell leads to an increased scrambling which besides increasing the unit-cell c parameters (which reduces the interlayer coupling), also reduces the conductivity in the plane so as to destroy superconductivity. The possibility of incorporating novel X^{n-} anions by reaction now highlights the exciting possibility of introducing a reducing or electron donating charge reservoir in the layers proximate to the CuO_2 layers. This would serve the dual purpose of increasing the interlayer coupling and increasing the conductivity. Thiocarbamate or thiols may be the proper choice in this regard. Experiments are being planned with this in mind.

Another point is that the basal lattice parameters are too large for hole superconductors [4]. Instead we expect n-type conductivity as in the electron-doped $Nd_{2-x}Ce_xCuO_{4-d}$ compounds. The presence of excess oxygen is not necessarily to be identified with hole conduction since there may be an equilibrium of the kind

$$2(1-x)Cu^{1+}+(1-x)(O_2)^{2-}+(2x+d)O^{2-} +2xCu^{2+}\rightleftarrows 2CuO+dO\,. \qquad (2)$$

The mixed valence of the copper ions may now yield n-type conductivity. Thermopower measurements on our samples [12] of $Ba_3SrCu_2O_{6+d}.2CO_2$ show a negative sign for the Seebeck coefficient at room temperature.

Acknowledgement

One of us (NS) is grateful to the Council of Scientific and Industrial Research, New Delhi, India, for financial support.

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