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EPR Study of Triplet Defects in $SrCuO_2$

Cesare Oliva,[a] Lucio Forni*[a] and Anatoli V. Vishniakov[b]

[a] *Dipartimento di Chimica Fisica ed Elettrochimica, Universitá di Milano e Centro C.N.R., 20133 Milano, Italy. Fax: +39 270 638129*

[b] *Mendeleev Institute of Chemical Technology, 125820 Moscow, Russian Federation. Fax: +7 095 200 4204*

The EPR spectrum of $SrCuO_2$ is explained by means of a model based on the formation of defects involving two neighbouring copper ions.

In a previous paper[1] we reported that two samples of $SrCuO_2$, prepared in exactly the same way, showed distinctly different X-ray diffractograms when calcined in air or *in vacuo*. Additional lines were observed in the former case, indicating the presence of a different phase or a polyphasic material. We also observed that the $g \simeq 2$ room temperature (r.t.) EPR spectrum is composed of a single line, 800 G broad for the sample calcined *in vacuo*, while that of the sample calcined in air is more intense and is just 600 G broad.† This suggested that the interaction of our solid with oxygen favours spin–spin exchange between unpaired electrons belonging to different copper ions. A 'half-field' $\Delta M_s = 2$ line was also observed at r.t. for both samples, calcined either in air or *in vacuo*. Furthermore, the catalytic behaviour of $SrCuO_2$ for the decomposition of NO to $N_2 + O_2$ was analysed through pulse-reactor experiments, but neither adsorption of NO nor catalytic activity was observed.[1] Finally, temperature-programmed desorption (TPD) studies on the sample prepared *in vacuo* have shown[2] that part of the oxygen formed after interaction with the $NO + N_2$ gas mixture desorbs very quickly at low temperature, and this amount rapidly decreases to zero with increase in the reaction temperature, while another part of the oxygen desorbs only at high temperature. In addition, the sample exhibits consumption instead of formation of oxygen during injection of the $NO + N_2$ gas pulses.[2] With the aim of obtaining a better insight into this topic, in the present work the EPR study of the $SrCuO_2$ sample calcined in air has been repeated at various temperatures after exposing the sample to atmospheric air for a few months at r.t.

The new EPR spectrum (Fig. 1) showed a second narrower line in addition to the previous single line in the $g \simeq 2$ region [Fig. 1(*b*)]. At higher temperatures [Fig. 1(*a*)], this line prevails over the broader one. Furthermore, the intensity of the half-field line decreases and almost disappears. At the same time a new EPR line (about 300 G broad) appears at *ca.* 2350 G [Fig. 1(*a*)]. On the contrary, at lower temperatures the half-field line can still be detected and a very strong signal (about ten times as intense as that at 200°C) is observed at $g \simeq 2$ [Fig. 1(*c*)], probably due to the overlapping of the two lines, which were better resolved at r.t.

These EPR results seem to confirm what was suggested by the previous TPD analysis, namely the formation on the surface of the sample of essentially two different paramagnetic species containing oxygen. In fact, at lower temperatures a triplet species is observed, characterized by a dipolar constant D less than the Zeeman interaction $h\nu$. In this case, which involves rather small dipolar interactions, the half-field line is observed, as in Fig. 1(*b*) and (*c*). However, it is well known[3] that this line is not observable with very strong dipolar interactions, *i.e.* when $D > h\nu$. This is what we encountered at higher temperatures [Fig. 1(*a*)], when a different species is formed with a very large dipolar constant D, and as a consequence the half-field line is no longer detectable.

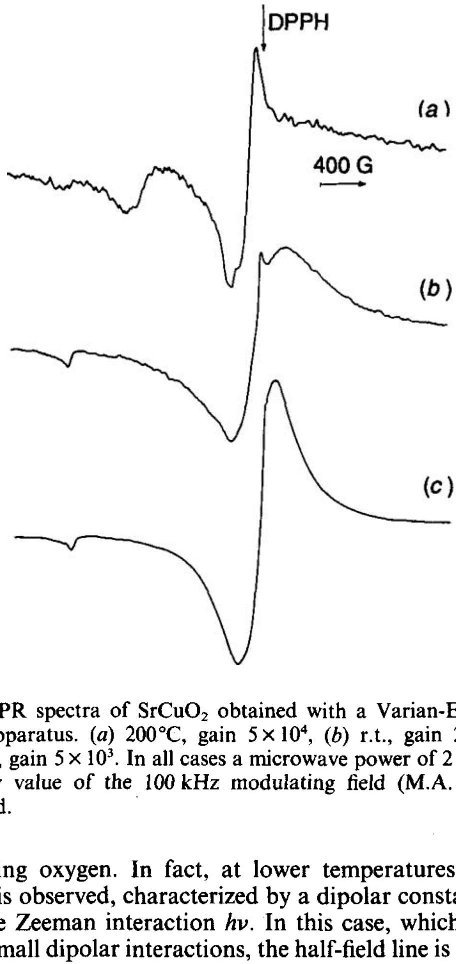

Fig. 1 EPR spectra of $SrCuO_2$ obtained with a Varian-E9 Century Series apparatus. (*a*) 200°C, gain 5×10^4, (*b*) r.t., gain 2×10^4, (*c*) −130°C, gain 5×10^3. In all cases a microwave power of 2 mW and a very low value of the 100 kHz modulating field (M.A. 0.8) were employed.

This instance of strongly interacting dipoles (SID) is commonly found for many dimers or clusters formed by copper ions.[4–8] Hence, the formation of defects involving two neighbouring copper ions can be hypothesized in the present case at

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† 1 G = 10^{-4} T.

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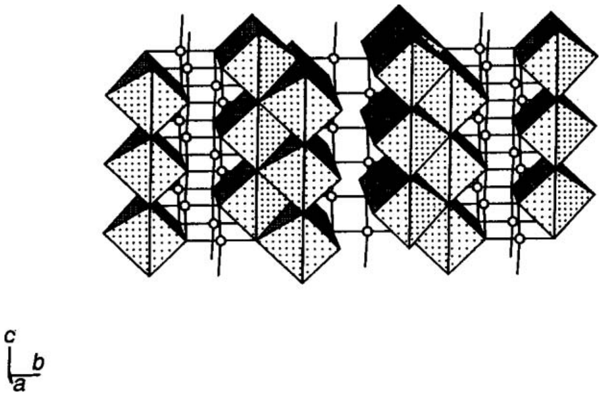

Fig. 2 The crystal structure of $SrCuO_2$ as obtained using the X-ray data reported in ref. 9. Open circles represent Cu ions, Sr ions are within the 'boxes', the vertices of which represent the oxygen ions.

higher temperatures, in analogy with what we have already observed, within a relatively wide temperature range, with Ca_2CuO_3.[1,8] In fact, in the presence of SID, the $\Delta M_s = \pm 2$ line can no longer be observed and the line shapes exhibit severe distortion. Furthermore, the low-field z_1 line would also disappear, being replaced, in the low-field region, by a strong new z_2' line. The latter is due to a $W_{-1}' = W_0 + h\nu$ transition between the same levels of z_2 (high field) line, which is therefore due to the $W_{-1} = W_0 - h\nu$ transition. Indeed, the new line measured at *ca.* 2350 G at higher temperatures [Fig. 1(*a*)] can be attributed to the z_2' SID line. The z_2 line should still be detectable at about 8000 G, but with very low intensity, and we were unable to observe it, within the limits of our apparatus. The x_1 and y_1 (low fields) lines could be merged into the narrower line appearing in the $g \simeq 2$ region. On the other hand, it is well known[9] that in $SrCuO_2$ the copper ions are present essentially as interstitial copper(II) oxide. The X-ray structure of $SrCuO_2$ is shown in Fig. 2: the CuO particles are not strongly linked to the crystal framework. On the contrary, they can move, more easily the higher the temperature, forming dimers containing two oxygen ions. This could be the origin of the oxygen consumption observed at higher temperatures under our reaction conditions. In this situation $SrCuO_2$ could also catalyse the decomposition of NO, but with a catalytic activity so low that it would be masked by the oxygen consumption.

References

1 L. Forni, C. Oliva, F. P. Vatti, N. A. Sinitsina, S. V. Sorochkin, A. Moev and A. V. Vishniakov, *J. Chem. Soc., Faraday Trans.*, 1992, **7**, 1041.

2 L. Forni, F. P. Vatti, C. Oliva, N. A. Sinitsina, A. Moev and A. V. Vishniakov, *Zh. Fiz. Khim.*, submitted for publication.

3 J. E. Wertz and J. R. Bolton, *Electron Spin Resonance. Elementary Theory and Practical Applications*, McGraw-Hill, New York, 1972, p. 223; N. M. Atherton, *Electron Spin Resonance. Theory and Applications*, Wiley, New York, 1973, p. 150.

4 J. A. Barnes, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 144.

5 J. Kohout, M. Liska and M. Hvastijova', *Inorg. Chim. Acta*, 1977, **25**, L71.

6 R. C. Dickinson, F. T. Helm, W. A. Baker, Jr., T. D. Black and W. H. Watson, Jr., *Inorg. Chem.*, 1977, **16**, 1530.

7 J. R. Wasson, C. I. Shyr and C. Trapp, *Inorg. Chem.*, 1968, **7**, 469.

8 C. Oliva, L. Forni, A. Ponti and A. V. Vishniakov, *Appl. Magn. Res.*, in the press.

9 Chr. L. Von Teske and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.*, 1970, **379**, 234.

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