Acta Chemica Scandinavica, 1993: 47: 1041–1042
Printed in Belgium – all rights reserved

Copyright © Acta Chemica Scandinavica 1993
ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Short Communication

Magnetic Properties of $YBaCuCoO_5$

P. Karen and A. Kjekshus*

Department of Chemistry, University of Oslo, Blindern, N-0315 Oslo, Norway

Karen, P. and Kjekshus, A. 1993. Magnetic Properties of $YBaCuCoO_5$. – Acta Chem. Scand. 47: 1041–1042.

The present authors have earlier, as a part of a larger collaboration,[1] reported a powder neutron diffraction (PND) study of the nuclear and magnetic structures of the oxygen-deficient, ordered perovskite $YBaCuCoO_5$. The work forms a part of a program on the substitution of a transition metal for Cu in the $YBa_2Cu_3O_7$ family (cf. the survey in Ref. 2). In the continued[3] examination of the magnetic properties of another member of the $YBa_2Cu_3O_7$ family, $YBa_2Fe_3O_8$, we have (much to our surprise) found that the antiferromagnetism[4] is no longer observed when the sample is cooled after having been brought above the Néel temperature ($T_N = 650 \pm 2$ K). The present magnetic susceptibility study of $YBaCuCoO_5$ was undertaken in order to check whether the latter compound also exhibits a similar phenomenon.

Samples were prepared and characterized as described in Ref. 1. Magnetic susceptibilities were measured between 80 and 1000 K by the Faraday method (maximum field 8 kOe, samples of 10–20 mg). Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) measurements were made between 20 and 600°C (1000°C for DTA) with a Mettler TA 3000 and a Netzsch 404 EP system, respectively, using 50 mg specimens and a heating/cooling rate of 5°C min^{-1}.

The inverse magnetic susceptibility versus temperature characteristic of $YBaCuCoO_5$ (Fig. 1) is fully reproducible and reversible with respect to heating/cooling. The $\chi^{-1}(T)$ relationship in Fig. 1 is quite typical for an antiferromagnet which transforms to paramagnetism at higher temperatures, and the present value of 540 ± 10 K for T_N is in complete agreement with $T_N = 536 \pm 3$ K obtained by PND in Ref. 1. The fact that $\Theta = -1700 \pm 100$ K differs appreciably from the molecular field relation, $\Theta = -T_N$, for a simple antiferromagnet, is not alarming, and places $YBaCuCoO_5$ in a good company with similar magnetic materials. According to the behaviour above T_N, the paramagnetic moment $\mu_P = 4.2 \pm 0.2\ \mu_B$ per 0.5Cu + 0.5Co corresponds (spin-only approximation) to 3.3 ± 0.2 unpaired electrons per transition metal ion. Remarkably, the moment derived from least-squares fitting of observed (room temperature) and calculated PND intensity data indicates only 1.49 ± 0.02 unpaired, antiferromagnetically ordered electrons per transition metal ion. Such, and even larger, discrepancies are sometimes observed between magnetic susceptibility and neutron diffraction measurements (our results have, e.g., revealed[4] that $YBa_2Fe_3O_8$ is in a similar situation). However, to complete the 'tales of the unexpected', we also record that, only with good faith and knowing where to look, T_N could be located as a rather indistinct peak on DSC/DTA curves of $YBaCuCoO_5$. (A similar observation has been made for the $YBa_2Fe_3O_8$ phase.)

This leaves us with at least three strange aspects of the magnetism of $YBaCuCoO_5$ which demand explanation:

(i) The exchange mechanism which carries the message from one $(Co/CuO_2)(BaO)(Co/CuO_2)$ antiferromagnetic 'double-layer' to the next (cf. Ref. 1). As for $YBa_2Cu_3O_6$ and $YBa_2Fe_3O_8$, the Y atoms must be involved, but the question is how.

(ii) The negligible magnetic specific heat anomaly as compared with the expected ~ 20 J mol^{-1} according to the molecular field approximation.

(iii) The appreciably different number of unpaired electrons observed by magnetic susceptibility and neutron diffraction measurements. The actual numbers make it tempting to wonder whether a low- to high-spin conversion takes place in $YBaCuCoO_5$. In the low-spin case, the three unpaired electrons per $YBaCuCoO_5$ formula unit seen by neutron diffraction would be compatible with the expected electron configurations for, say, Cu^{2+} and Co^{3+} in their actual square-pyramidal coordination in the structure.[1] A schematic illustration of the evolution in the d-orbital energy splitting from the situation for an unperturbed atom/ion to square-planar coordination is

* To whom correspondence should be addressed.

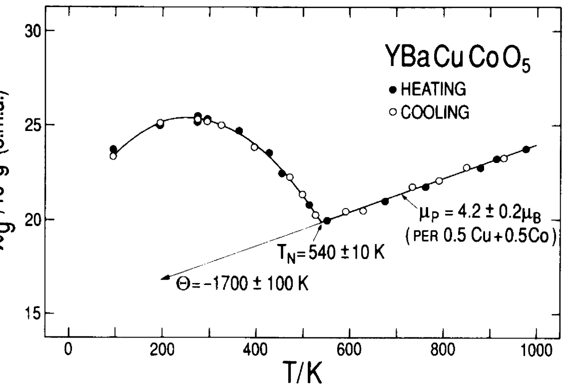

Fig. 1. Inverse magnetic susceptibility as function of temperature for $YBaCuCoO_5$.

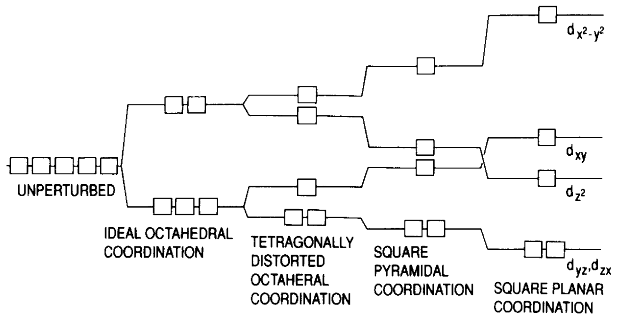

Fig. 2. Schematic illustration of d-orbital energy splittings in octahedral, square-pyramidal and square-planar coordinations. (Note that the scale of the energy splittings is left unspecified.)

provided in Fig. 2. The filling of nine and six d-electrons for, say, Cu^{2+} and Co^{3+}, respectively, into the energy scheme appropriate to the pyramidal coordination in Fig. 2 would lead to just three unpaired electrons per $YBaCuCoO_5$ formula unit. In the high-spin case, distribution of the overall 15 d-electrons of Cu and Co per $YBaCuCoO_5$ formula unit gives five unpaired electrons. To comply with the paramagnetic moment, there would accordingly have to be an orbital contribution.

References

1. Huang, Q., Karen, P., Karen, V. L., Kjekshus, A., Lynn, J. W., Mighell, A. D., Natali-Sora, I., Rosov, N. and Santoro, A. *J. Solid State Chem.* (1993). *In press.*
2. Karen, P., Braaten, O. and Kjekshus, A. *Acta Chem. Scand.* *46* (1992) 805.
3. Huang, Q., Karen, P., Karen, V. L., Kjekshus, A., Lynn, J. W., Mighell, A. D., Natali-Sora, I., Rosov, N. and Santoro, A. *To be published.*
4. Huang, Q., Karen, P., Karen, V. L., Kjekshus, A., Lynn, J. W., Mighell, A. D., Rosov, N. and Santoro, A. *Phys. Rev. B 45* (1992) 9611.

Received February 24, 1993.