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Magnetic structure of the uranium–copper double perovskite UBa_2CuO_6

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Abstract

The uranium–copper double perovskite UBa_2CuO_6 exhibits antiferromagnetic ordering below $T_N = 11$ K. The magnetic structure was determined from Rietvelt refinements of neutron powder diffraction data. It is characterized by a propagation vector $\boldsymbol{k} = [1/2, 1/2, 0]$ and can be described as alternating $+ - + -$ (110) ferromagnetic planes. The copper magnetic moments lie in the basal plane along the [110] direction, and their amplitude is 0.88(3) μ_B at 1.4 K.

1. Introduction

Many of the high temperature oxide superconductors have perovskite-type derived structures or contain perovskite-like building blocks. They are also characterized by the existence of copper–oxygen planes which play a key role in the onset of superconductivity, and, in the most famous compound $YBa_2Cu_3O_{7-x}$, superconducting properties disappear for $x > 0.4$, with the setting up of antiferromagnetic correlations in the Cu–O2 planes [1, 2].

The crystal chemistry of uranium, when in the tetravalent state, is quite similar to that of the rare earth elements, and it was tempting to introduce uranium in the high T_c structural types where rare earth elements are present, the more as the ternary uranium perovskite $BaUO_3$ forms rather easily. In fact, we could not achieve any substitution of uranium for rare earth, even with partial replacement of divalent Ba (or Sr) by monovalent alkaline elements to take into account the charge balance. It appears that the thermodynamic equilibria do not allow the stabilization of U^{4+} together with Cu^{2+} in oxide systems, and even in mild reducing conditions uranium was found to oxidize up to the hexavalent state with a concomitant reduction of the copper ion. The only mixed oxide which could form in air is the double perovskite UBa_2CuO_6, a compound already reported many years ago [3, 4], in which hexavalent uranium has the same ionic radius as divalent copper (0.73 Å in an octahedral environment [5]). This compound was reported to undergo an antiferromagnetic transition at low temperature [4]. In this paper, we present its magnetic structure determined by powder neutron diffraction.

2. Sample preparation and magnetic behaviour

UBa_2CuO_6 was prepared by heating in air at 1200 °C appropriate amounts of U_3O_8, $BaCO_3$ and CuO. Two intermediate grindings and annealings were necessary to eliminate fully the barium uranate $BaUO_4$ which always appeared as a secondary phase. The X-ray powder pattern has been successfully indexed using the lattice parameters given in ref. 4.

The magnetic properties of our sample were determined using a superconducting quantum interference device magnetometer, in the temperature range 2–300 K. The susceptibility was found to exhibit a pronounced maximum at $T = 11$ K indicating antiferromagnetic ordering (Fig. 1). In the paramagnetic range, the susceptibility was fitted according to the Curie–Weiss law $\chi = c/(T - \theta)$, giving an effective paramagnetic moment of $1.91\mu_B$ and a paramagnetic Curie temperature $\theta = -2$ K. These results are in agreement with previously published data [4].

3. Neutron diffraction and magnetic structure

3.1. Data collection and analysis

Neutron powder diffraction data were collected on the G41 multidetector, installed in the guide hall of the Orphée reactor (Saclay). Seven diffraction patterns

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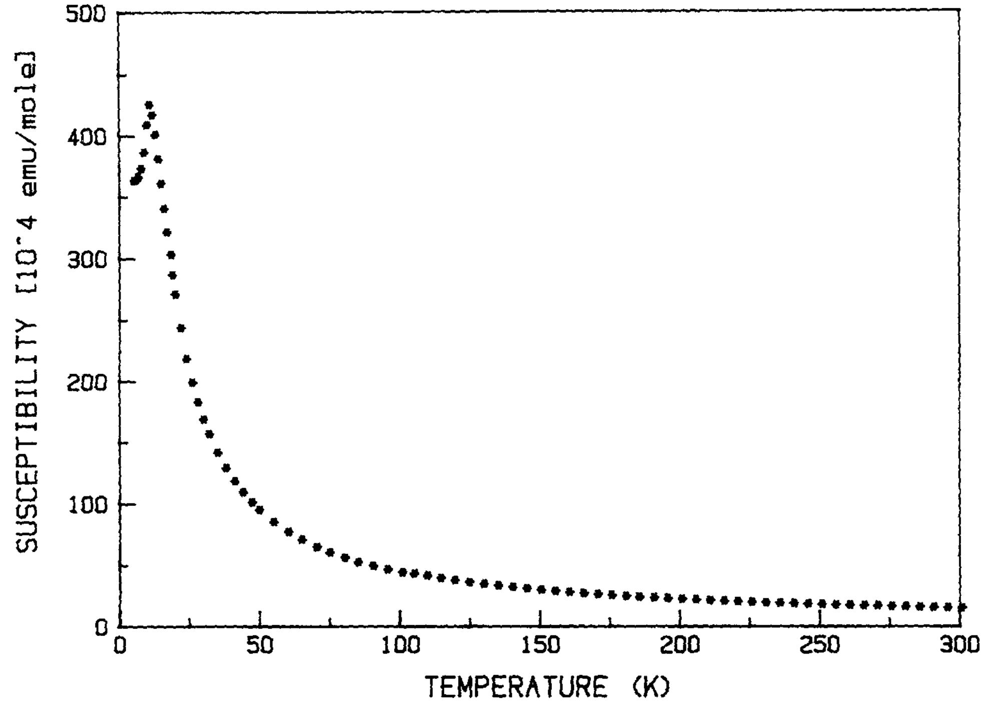

Fig. 1. Magnetic susceptibility *vs.* temperature for UBa_2CuO_6.

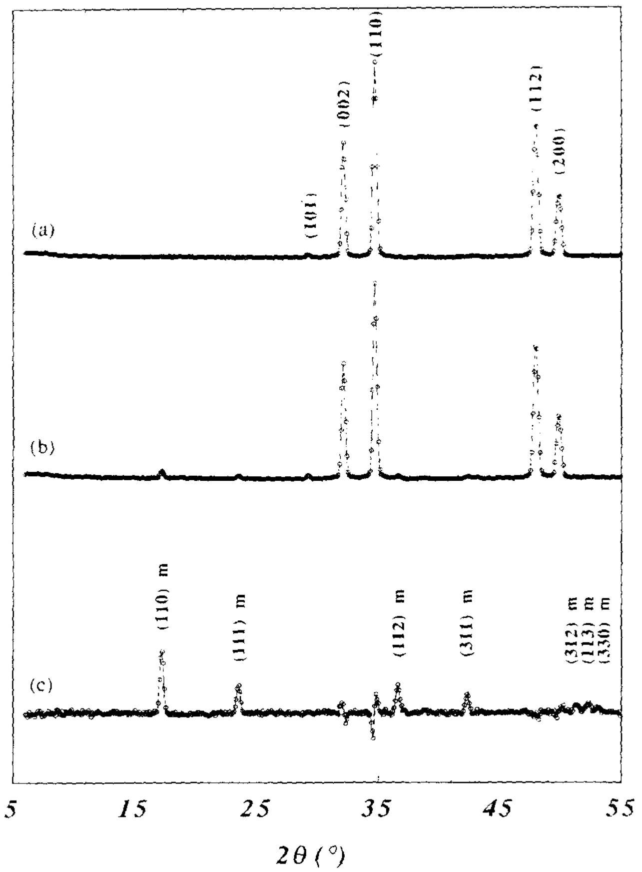

Fig. 2. Neutron powder diffraction patterns at 15 K (spectrum a) and 1.4 K (spectrum b) and difference spectrum (spectrum c; ×10).

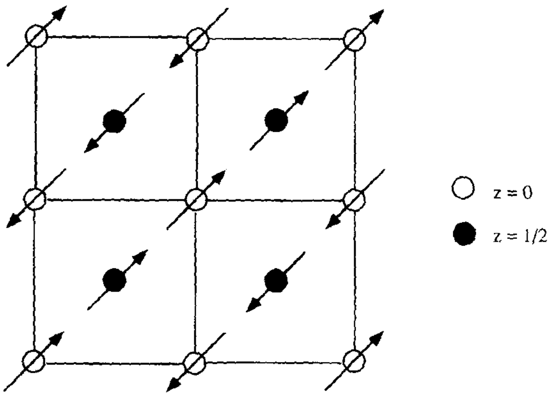

Fig. 3. Projection of the magnetic structure (Cu atoms only) on the basal plane.

($6° < 2\theta < 86°$) were recorded at temperatures of 1.4, 4.0, 7.0, 9.0, 9.5, 10 and 15 K with a wavelength of 2.4275 Å. Analysis and refinements were performed using the Rietvelt-modified program FULLPROF [6].

3.2. *Nuclear structure*

At 15 K, all diffraction lines (Fig. 2, spectrum a) could be indexed using the lattice parameters given in ref. 4, with the space group *I4/mmm*. Least-squares refinements gave the values $a = b = 5.773(5)$ Å, $c = 8.805(6)$ Å, in good agreement with the previous values [4]. The positional parameters deduced from X-ray powder data [4] were introduced for preliminary structure factors calculations: Cu in 2a (0, 0, 0), U in 2b (0, 0, 1/2), Ba in 4d (0, 1/2, 1/4), O(1) in 4e (0, 0, z)

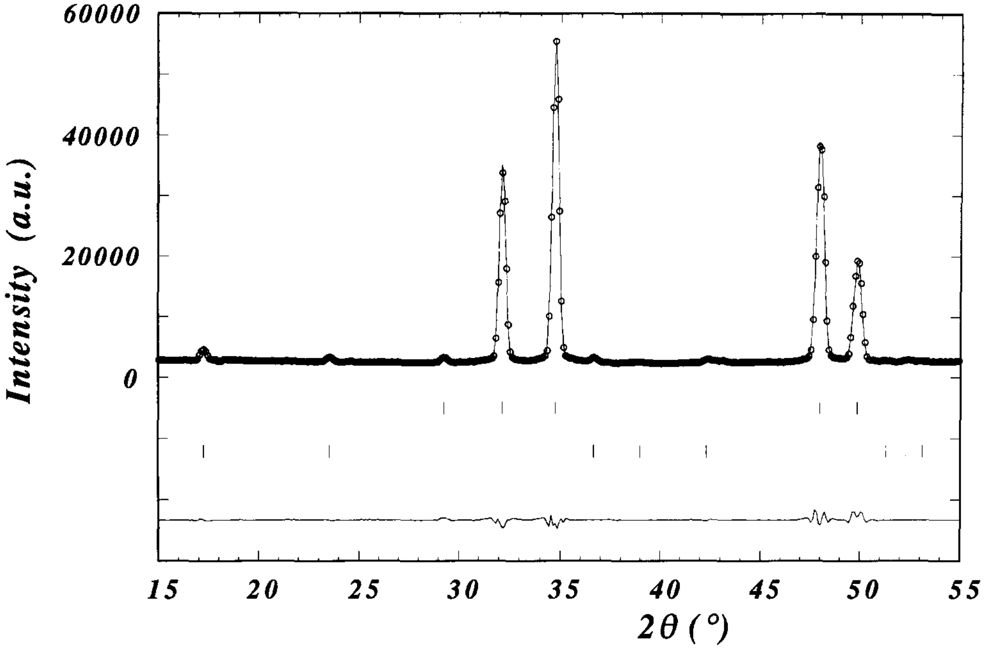

Fig. 4. Observed (●), calculated (upper full line) and difference (lower full line) profiles at $T = 1.4$ K.

and O(2) in 8h (x, x, 0). Refinements of the variable parameters gave $z[O(1)] = 0.2709(8)$ and $x[O(2)] = 0.2413(6)$, which are more reliable values than those determined from X-ray powder data (0.263 and 0.255 respectively). The final Bragg R factor was 0.043.

3.3. Magnetic structure

Figure 2 shows the powder diffraction patterns recorded at 15 K (Fig. 2, spectrum a) and 1.4 K (Fig. 2, spectrum b) and the difference spectrum (Fig. 2, spectrum c). The extra magnetic peaks which appear below 10 K have been indexed with a propagation vector $\boldsymbol{k} = [1/2, 1/2, 0]$. As expected, the analysis of their intensities showed that the magnetic moments are located on the copper sites only, since uranium is in the hexavalent state and has no more 5f electrons. The magnetic arrangement consists of ferromagnetic ($1\ \bar{1}\ 0$) planes coupled antiferromagnetically according to the sequence $+-+-$. The copper magnetic moments lie in the tetragonal basal plane along the [110] direction (Fig. 3). The refined data at $T = 1.4$ K (Fig. 4) lead to $M_x = M_y = 0.62(2)\ \mu_B$, $M_z = 0$, giving a magnetic moment modulus $M = 0.88(3)\mu_B$ for the copper atoms.

The magnetic structure of UBa_2CuO_6 is more closely related to that of La_2CuO_4 [7] than to that of $YBa_2Cu_3O_6$ [1, 2]. All of them exhibit antiferromagnetic interactions in the basal plane. In $YBa_2Cu_3O_6$, two consecutive planes are coupled antiferromagnetically, while in La_2CuO_4 the copper moments also form alternating ferromagnetic sheets perpendicular to the basal plane.

In UBa_2CuO_6, the presence of non-magnetic hexavalent uranium in the (a, b) plane (crystallographic positions (0, 0, 0) for copper and (1/2, 1/2, 0) for uranium) reduces considerably the in-plane interaction. There is a large decrease in the ordering temperature ($T_N = 420$ K for $YBa_2Cu_3O_6$, 220 K for La_2CuO_4 and 11 K for UBa_2CuO_6) but the ordered copper magnetic moment is the largest in the uranium compound ($0.6\mu_B$, $0.5\mu_B$ and $0.88\mu_B$ respectively).

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