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Magnetic structure of Sr_2CuWO_6

S Vasala[1], M Avdeev[2], S Danilkin[2], O Chmaissem[3,4] and M Karppinen[1]

[1] Department of Chemistry, Aalto University, PO Box 16100, FI-00076 AALTO, Finland
[2] Australian Nuclear Science and Technology Organisation, Bragg Institute, Lucas Heights, NSW 2234, Australia
[3] Department of Physics, Northern Illinois University, DeKalb, IL 60115, USA
[4] Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

E-mail: maarit.karppinen@aalto.fi

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Abstract

Magnetic structure of the double perovskite Sr_2CuWO_6 was determined from neutron powder diffraction data. At 3 K the material is magnetically long-range ordered into a collinear antiferromagnetic structure described by a propagation vector $k = (0, 1/2, 1/2)$ with the Cu^{II} moments of 0.57(1) μ_B parallel to the a-axis. The result is in agreement with our previous prediction (Vasala *et al* 2014 *Phys. Rev.* B **89** 134419) based on electronic structure calculations, showing that the three-dimensional magnetic long-range order is caused by relatively strong antiferromagnetic next-nearest-neighbor interactions.

Keywords: double-perovskite oxide, magnetic structure, neutron powder diffraction

(Some figures may appear in colour only in the online journal)

1. Introduction

Low-dimensional magnetism is of great interest in solid-state physics, as for example in the parent phases of high-T_c copper-oxide superconductors which are two-dimensional antiferromagnets (AFM). Moreover, superconductivity in the cuprates is believed to be strongly correlated with their magnetic properties [1–3]. These compounds have a square lattice of $S = 1/2$ Cu^{II} ions, which is considered to be responsible for their magnetic and superconducting behavior. Thus, studying other similar square-lattice compounds could help in advancing our understanding of the magnetic interactions in this kind of compounds.

The B-site ordered double-perovskite oxides $A_2CuB''O_6$, where A = Sr or Ba and B'' is a diamagnetic hexavalent ion Mo, Te or W, have been found to exhibit quasi-low-dimensional magnetic properties characterized by broad magnetic susceptibility maxima with no clear indication of long-range magnetic order [4–9]. This low dimensionality is due to the cooperative Jahn–Teller (JT) effect of the octahedrally coordinated Cu^{II}, which results in a distorted tetragonal structure with short Cu–O_{ab} bonds in the ab-plane and long Cu–O_c bonds along the c-axis. The half-filled Cu $3d_{x2-y2}$ orbitals are ordered in the ab-plane, whereas the d_{z2}, d_{yz} and d_{zx} orbitals of Cu^{II} pointing in the c-direction are all filled. This effectively creates a square lattice of Cu^{II} with relatively strong magnetic interactions between the neighboring Cu ions within the ab-planes, but with weaker interactions in the c direction, making the magnetic interactions quasi-two-dimensional. Despite the apparent low-dimensionality, such compounds tend to have three-dimensionally long-range ordered ground states mediated by weak inter-layer interactions.

Magnetic long-range order in the B-site ordered double perovskites is of interest in itself. In an ideal cubic B-site ordered double-perovskite $A_2B'B''O_6$, the B' (or B'') cation forms a face-centered cubic (FCC) lattice, and few common types of magnetic orderings are found for such an FCC array of cations where the magnetic interactions are mainly AFM, namely type I, II and III orderings [10–12]. Which of these orderings is favored depends on the nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions between the magnetic ions: type-I is favored where the NN interactions are stronger than the NNN interactions, whereas type-II is found where the NN interactions are weak compared to the NNN interactions. Type-III order is an intermediate form where the NN interactions are relatively strong, but the NNN interactions are still significant. What is interesting in case of the $A_2B'B''O_6$ double perovskites is that both type-I and type-II orderings are commonly seen, indicating that the relative strength of the NN and NNN interactions in these compounds can be tuned as a function of composition [13, 14].

While magnetic long-range order is not obvious in the magnetic susceptibility of the quasi-low-dimensional $A_2CuB''O_6$ perovskites, Todate *et al* [9] found a three-dimensional ordered state in Ba_2CuWO_6 below $T_N = 28$ K using muon spin rotation/relaxation (μSR). Additionally, neutron powder diffraction (NPD) showed the long-range ordered state of this compound to be of type-II, with a magnetic propagation vector of $k = (0, 1/2, 1/2)$ with respect to the tetragonal unit cell ($I4/m$, $a = 5.564$ Å, $c = 8.636$ Å, from [6]) [9]. On the other hand, Ba_2CuUO_6 has been reported either as a quasi-two-dimensional compound [15, 16] or as a typical antiferromagnet [17, 18]. Either way, the compound shows long-range order at $T_N \approx 10$ K and a propagation vector of $k = (1/2, 1/2, 0)$, indicating relatively strong AFM NN interactions and ferromagnetic (FM) NNN interactions. This is despite the fact that Ba_2CuUO_6 exhibits a JT-distorted structure closely resembling those of other $A_2CuB''O_6$ compounds, with diamagnetic U^{VI} ions at the B'' site. It is therefore clear that similar to the $A_2B'B''O_6$ perovskites in general, in this family of compounds the magnetic properties are also strongly affected by their composition, making them a relatively simple model system for studying the various magnetic interactions. Thus, determining their magnetic structures is of interest in the study of the borderline between quasi-low-dimensional and three-dimensional magnetic properties.

We have previously studied the structural and magnetic properties of one member of this $A_2CuB''O_6$ family, namely Sr_2CuWO_6 [4, 5]. High-resolution NPD measurements verified the cooperative JT distortion of the CuO_6 octahedra, with Cu–O_{ab} and Cu–O_c bond lengths of 1.97 Å and 2.29 Å, respectively. μSR measurements evidenced a long-range ordered magnetic state below $T_N = 24$ K. Magnetic exchange-interaction constants derived from electronic-structure calculations indicated significant AFM 180° Cu–O–W–O–Cu NNN interactions (−7.47 meV) and weaker AFM 90° Cu–O–(W)–O–Cu NN interactions (−1.20 meV) within the *ab*-plane; the relative strength of the NNN interaction compared to the NN interactions is expected due to the half-filled, σ-bonded Cu^{II} $3d_{x2-y2}$ orbitals. The interplanar 90° Cu–O–(W)–O–Cu NN interactions were found to be negligible (−0.03 meV), but surprisingly, the interplanar 180° Cu–O–W–O–Cu NNN interactions along the *c*-axis were found to be relatively strong (−4.21 meV). These computational results predicted the long-range order in this compound to be a type-II AFM ordering, the same as for Ba_2CuWO_6.

We also attempted to determine the nature of the long-range ordered state of Sr_2CuWO_6 with NPD at 10 K, i.e. below T_N, but the high-resolution data showed no magnetic reflections. This was assumed to be due to weak reflections from the $S = 1/2$ system, possibly weakened still by the low dimensionality and slight magnetic frustration suggested by our previous results [4, 5], as such quasi-low-dimensional and/or frustrated magnetic systems have been found to exhibit decreased values of ordered magnetic moment [19–21]. Based on the high-resolution NPD data the upper limit on the ordered Cu^{2+} magnetic moment in Sr_2CuWO_6 was estimated to be ∼0.5 μB. The same problem of detecting the long-range magnetic order was also observed in the case of Ba_2CuWO_6,

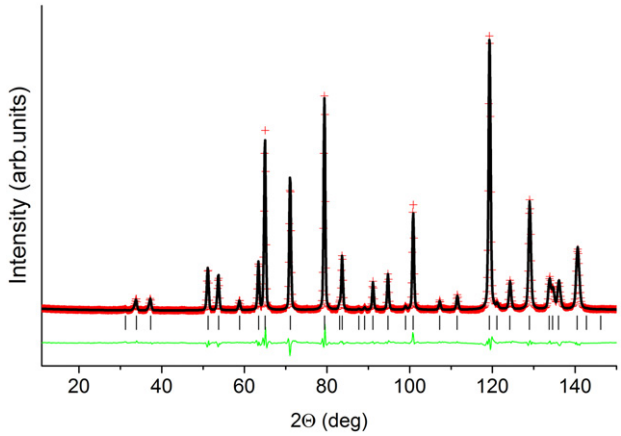

Figure 1. Final Rietveld fit for Sr_2CuWO_6 to neutron powder diffraction data collected at 30 K. The red crosses and black and green solid lines indicate the observed and calculated patterns and their difference, respectively. The tick marks indicate the position of the diffraction peaks. $R_p = 5.11\%$, $R_{wp} = 6.95\%$, $R_{Bragg} = 2.78\%$.

but the magnetic structure was ultimately determined in a high-flux NPD experiment [8, 9]. In this work we use high-flux NPD to verify the long-range three-dimensional magnetic order in Sr_2CuWO_6. The magnetic order is found to be of type-II as predicted by our calculations [5], with an ordered magnetic moment of 0.57(1) μ_B.

2. Experimental details

A 5 g sample of Sr_2CuWO_6 was synthesized by solid-state reaction of a stoichiometric mixture of $SrCO_3$, CuO and WO_3 powders. The powders were thoroughly ground in an agate mortar together with ethanol and then calcined for 12 h in air at 900 °C. The sample was then reground, pressed into pellets and sintered twice in air at 1000 °C for 24 h with an intermediate grinding.

Neutron powder diffraction (NPD) data were collected at the OPAL reactor (ANSTO, Lucas Heights, Australia) at 3 and 30 K on the Echidna diffractometer by using neutron wavelength of 2.4395 Å. Since magnetic scattering signals proved to be very weak, additional high flux data were also collected on the triple-axis spectrometer Taipan in a diffraction mode with the neutron wavelength of 2.345 Å. Taipan's high flux was achieved by a double focusing pyrolytic graphite monochromator. The high order reflections from the monochromator were suppressed by a graphite filter installed upstream to the sample and background was reduced using an analyzer adjusted to the incident wavelength. Rietveld analysis of the data was performed using the Fullprof Software Suite [22], with default neutron scattering lengths and Cu^{II} magnetic form-factor.

3. Results and discussion

Neutron powder diffraction data collected on Echidna for Sr_2CuWO_6 at 30 K (i.e. above the transition temperature of $T_N = 24$ K) were successfully analyzed using the crystal structural model reported previously [4]. The final Rietveld fit for Sr_2CuWO_6 at 30 K is shown in figure 1, and the refined

Table 1. Crystal structural parameters for Sr_2CuWO_6 based on Rietveld refinement using Echidna neutron powder diffraction data collected at 30 K and 3 K (top and bottom line in the relevant rows, respectively). Space group $I4/m$ (#87), $a = 5.4115(1)$ Å, $c = 8.4125$ (1) Å, $V = 246.36$ (1) Å^3 (30 K) and $a = 5.4112$ (1), $c = 8.4125$ (1) Å, $V = 246.33$ (1) Å^3 (3 K).

Atom	Wyckoff site	x	y	z	U_{iso}, $\times 100$, (Å^2)	BVS[a]
Sr	4*d*	0	1/2	1/4	0.28(9)	2.10(1)
					0.25(5)	2.10(1)
Cu	2*b*	0	0	1/2	0.04(12)	2.19(1)
					−0.01(1)	2.17(1)
W	2*a*	0	0	0	0.05(18)	6.09(2)
					0.30(10)	6.12(1)
O1	8*h*	0.2899(6)	0.2021(5)	0	0.55(7)	2.12(1)
		0.2890(3)	0.2015(3)		0.43(4)	2.13(1)
O2	4*e*	0	0	0.2270(4)	0.54(11)	2.01(9)
				0.2277(2)	0.55(6)	2.00(1)

[a] Bond valence sums (BVS) calculated with Fullprof using the constants published in [23] and distance cut-off 3.5 Å.

crystallographic information at both 3 and 30 K are presented in table 1. The results are in good agreement with our previous results at 10 K.

Examination of the Echidna NPD data collected at 3 K revealed an additional diffraction peak due to long-range magnetic ordering. The peak position was found consistent with a $k = (0, 1/2, 1/2)$ propagation vector (equivalent to $k = (1/2, 0, 1/2)$ due to tetragonal symmetry), but its low intensity and subsequent refinements allowed us only to estimate the magnetic moment value of 0.5(1) μ_B with a relatively large standard deviation, consistent with the established limit proposed in our previous study [5]. Therefore, additional high neutron flux data were collected at the same two temperatures using the triple-axis spectrometer Taipan. The data are shown in figure 2. High counting statistics helped distinguish from the background several more but weaker magnetic diffraction peaks (inset of figure 2). All of the magnetic peaks unambiguously confirmed the $k = (0, 1/2, 1/2)$ propagation vector. Representational group theory analysis performed with BasIReps [22] for the Cu (2*b*; 0,0,1/2) site of the I 4/*m* space group revealed a single one-dimensional irreducible representation Γ2 with three possible basis vectors corresponding to the direction of magnetic moment along *a*, *b* or *c* axes.

Rietveld analysis of the magnetic structure was done on the difference of the Taipan NPD data collected at 3 and 30 K, i.e. purely magnetic contribution, with the crystal structural parameters fixed to the values determined from the Echidna NPD data and peak shape and scale parameters fixed to the values obtained from the Taipan NPD data collected at 30 K. Examination of the magnetic intensities produced by different models suggested the alignment of the Cu^{II} magnetic moments along the *a*-axis, as shown in figure 3. This model (equivalent to the P_{2_s}-1 magnetic space group, Opechowski-Guccione #2.4.7) produced the best agreement factors between the experimental and calculated powder diffraction patterns. Agreement factors $R_{mag} = 19\%$, 80% and 61% for the models with the moments along *a*, *b* and *c* axes, respectively (inset of figure 3). Refinements of either *b*- or *c*-axis magnetic-moment components in addition to the *a*-axis component were unsuccessful as the process rapidly diverged. Thus, we

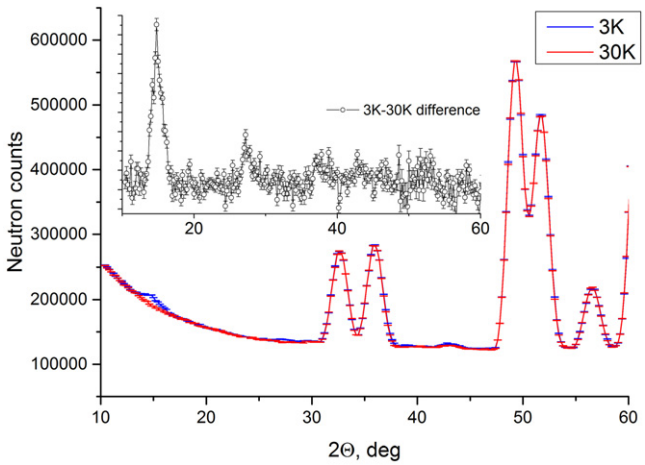

Figure 2. NPD data collected at 3 and 30 K on the Taipan triple-axis spectrometer. Inset shows the difference of the two data sets, i.e. magnetic scattering contribution only.

conclude that our experimental data are best described by the model with Cu^{II} magnetic moments along the *a*-axis with a value of 0.57(1) μ_B. Figure 4 shows a representation of the magnetic structure. The three-dimensional magnetic order is the so-called type-II ordering of the double-perovskite lattice, as predicted by electronic-structure calculations.

4. Conclusions

A three-dimensional long-range magnetic order was determined for Sr_2CuWO_6 from neutron powder diffraction data at 3 K, as was expected based on our previous muon spin rotation/relaxation experiment [5]. The magnetic structure was found to be an antiferromagnetic type-II ordering of the double-perovskite lattice, with a propagation vector $k = (0, 1/2, 1/2)$ with respect to the tetragonal double-perovskite lattice. The results are in agreement with our previous prediction based on electronic structure calculations [5]. The Cu^{II} moments of 0.57(1) μ_B were found to be aligned parallel to the *a*-axis. The value of the magnetic moment is smaller than what might be expected for the $S = 1/2$ Cu^{II} ions, most probably due to the quasi-two-dimensional nature

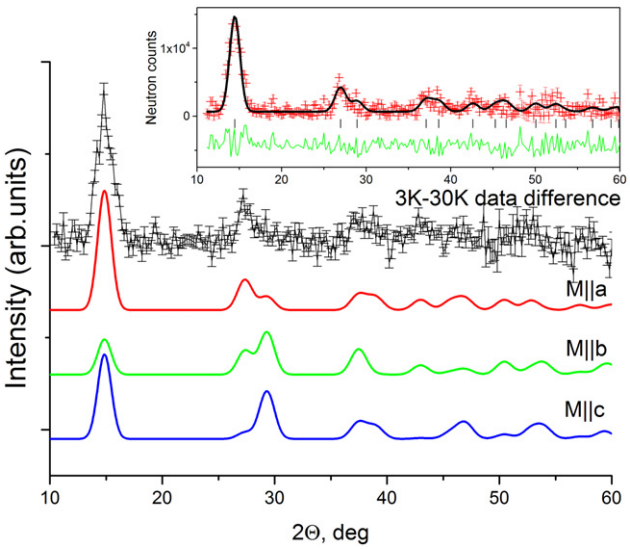

Figure 3. Experimental magnetic diffraction data (black) and simulated patterns for the models with Cu^{II} magnetic moment along *a*, *b* or *c* axes (red, green and blue, respectively). Inset shows the Rietveld fit using the model with the magnetic moments along *a*-axis ($R_{mag} = 19\%$).

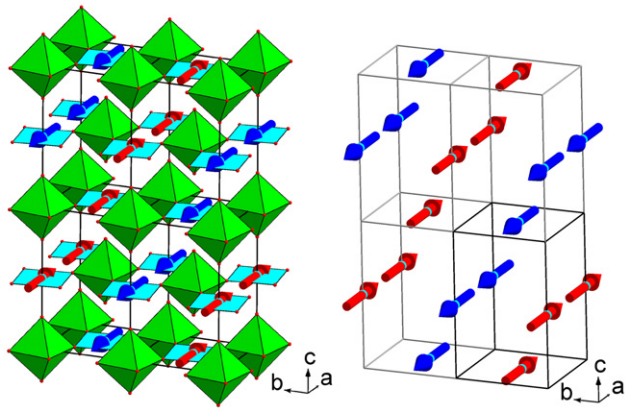

Figure 4. Left: general view of Sr_2CuWO_6 crystal structure. Right: magnetic structure with diamagnetic atoms omitted; black and gray solid lines outline chemical and magnetic unit cells, respectively.

and/or magnetic frustration of the compound, as discussed in the introduction.

The magnetic properties of the $A_2CuB''O_6$ double perovskites depend notably on their composition. Thus far, for these compounds the magnetic ground state has only been determined for Sr_2CuWO_6, Ba_2CuWO_6 and Ba_2CuUO_6. This still leaves the magnetic structure of the quasi-low-dimensional compounds Sr_2CuMoO_6, Sr_2CuTeO_6 and Ba_2CuTeO_6 open for investigation. The full determination of this model system is of great interest for the proper understanding of the magnetic interactions and magnetic order parameters in this class of square-lattice Cu^{II} compounds.

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