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Investigation on the Influence of Particular Structure Parameters on the Anisotropic Spin-Exchange Interactions in the Distorted Wolframite-Type Oxides $Cu(Mo_xW_{1-x})O_4$

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A spin-dimer analysis of the anisotropic spin-exchange interactions in the distorted wolframite-type oxides $CuWO_4$, $CuMoO_4$-III, and $Cu(Mo_{0.25}W_{0.75})O_4$ was performed by Koo and Whangbo (*Inorg. Chem.* **2001**, *40*, 2161–2169). For $Cu(Mo_{0.25}W_{0.75})O_4$, a magnetic structure with a magnetic unit cell doubled along the *a* and *b* axes has been predicted, but neutron powder diffraction on $Cu(Mo_{0.25}W_{0.75})O_4$ did not confirm such a magnetic structure. In the present work, a detailed spin-dimer analysis, considering the influence of particular atomic structure parameters, finally revealed that a wrong coordinate transformation of the Cu *z* coordinate of the $Cu(Mo_{0.25}W_{0.75})O_4$ structure is responsible for the prediction of the new, hypothetical magnetic structure. The deviation from the correct value is too small to be recognized by unreasonable bond lengths or angles but is sufficient to change one specific calculated value that is responsible for the prediction of the hypothetical magnetic structure.

$CuWO_4$ crystallizes in a triclinic, distorted wolframite-type structure and can approximately be described as a hexagonal close packing, with the cations occupying half of the octahedral sites. CuO_4 and WO_4 zigzag chains consisting of cis-edge-sharing CuO_6 and WO_6 octahedra, respectively, are corner-connected and run along the *c* direction.[1] At 23.0(2) K, the magnetic moments of the Cu^{2+} ions order three-dimensionally antiferromagnetic (AFM), with the magnetic unit cell doubled along the *a* axis.[2,3] $CuMoO_4$-III is a metastable modification that is isostructural with $CuWO_4$ and also undergoes three-dimensional AFM ordering at low temperatures, but with the magnetic unit cell doubled along the *c* axis, in contrast to $CuWO_4$. Ehrenberg et al. compared the crystallographic and magnetic structures of $CuWO_4$ and $CuMoO_4$-III in order to gain insight into the model of spin-exchange interactions.[4] Their analysis was restricted to geometrical considerations of the exchange paths. Koo and Whangbo developed that model further based on spin-dimer analysis in the frame of the extended Hückel theory. For a detailed description of the content of the following part and a description of the strength and weakness of the extended Hückel method, the reader is referred to the publication of Koo and Whangbo.[5] There are two different superexchange paths (Cu−O−Cu coupling) within the CuO_4 chains (Figure 1). The corresponding spin dimers representing a coupling path are two edge-sharing CuO_6 octahedra that form a $(Cu_2O_{10})^{16-}$ cluster ion. A spin dimer that represents a super-superexchange path (Cu−O···O−Cu coupling) between two Cu atoms belonging to two different CuO_6 chains is represented by two $(CuO_6)^{10-}$ ions that form a $(Cu_2O_{12})^{20-}$ cluster ion. For each cluster ion, an extended Hückel calculation is performed and the difference of energy Δe between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is determined. The spin-exchange parameter J of a spin dimer is the sum of a ferromagnetic term J_F and an AFM term J_{AF}, and it is assumed that the latter can be expressed approximately by $J_{AF} \approx -(\Delta e)^2$. The ferromagnetic part J_F of the exchange parameter is assumed to be comparably small and not so sensitive to the geometry of the coupling paths. It is therefore

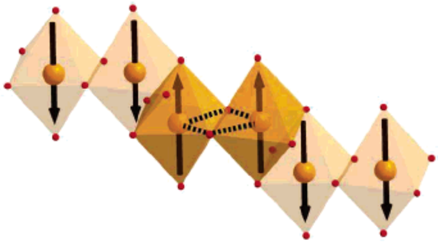

Figure 1. Section of a CuO_4 chain in $CuMoO_4$-III. The $(Cu_2O_{10})^{16-}$ cluster ion representing the J_1 (A) superexchange coupling path (dashed lines) is darkened. Arrows represent magnetic moments.

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Table 1. Δe Values (in meV) for Spin Dimers (a) in $CuWO_4$[1] As Published in Reference 5, (b) in $CuMoO_4$-III[4] As Published in Reference 5, (c) in $Cu(Mo_{0.25}W_{0.75})O_4$[6] As Published in Reference 5, and (d) As Calculated for Corrected Crystal Structure Published in Reference 6

	exchange path			
	a	b	c	d
	Superexchange			
J_1(A)	48	47	82	49
J_1(B)	13	22	22	15
	Super-superexchange			
J_6(B)	49	47	40	47
J_8	77	73	74	75
J_9(A)	204	214	214	197

possible to calculate the qualitative trends in the J parameter of extended AFM solids by extended Hückel theory. Koo and Whangbo used the single-crystal X-ray structures of the isostructural compounds $CuWO_4$ and $CuMoO_4$-III and the mixed crystal $Cu(Mo_{0.25}W_{0.75})O_4$ and calculated the Δe values for a variety of spin dimers within the extended Hückel theory. The Δe values were used to deduce, in a qualitative manner, the three-dimensional magnetic structures. The magnetic structure of $Cu(Mo_{0.25}W_{0.75})O_4$ has not been determined experimentally and should be predicted. The calculations of the Δe values showed that for all compounds there are three important super-superexchange paths, namely, J_9(A), J_8, and J_6(B), and two superexchange paths, namely, J_1(A) and J_1(B). All other coupling paths had Δe values smaller than that of J_1(B) and were not listed. For $CuWO_4$ as well as for $CuMoO_4$-III, the Δe values decrease in the following order: $J_9(A) \gg J_8 > J_6(B), J_1(A) > J_1(B)$ (parts a and b of Table 1). Koo and Whangbo deduced that J_9(A) and J_8 build "two-leg AFM ladder chains" that are coupled by J_6(B) to form two-dimensional AFM sheets (Figure 2). J_1(A), J_8, and J_6(B) form a triangular arrangement, leading to magnetic frustration. Because J_6(B) is a super-superexchange path, whereas J_1(A) is a superexchange path, J_1(A) has a stronger ferromagnetic term that is not represented in the Δe value so that J_1(A) finally couples ferromagnetically in the triangular arrangement. The two-dimensional AFM sheets exist in $CuWO_4$ and $CuMoO_4$-III, but the way the magnetic sheets are coupled via J_1(B) is different. J_1(B) is smaller in $CuWO_4$ ($\Delta e \approx 13$ meV) than in $CuMoO_4$-III ($\Delta e \approx 20$ meV), and it is concluded that the two-dimensional AFM sheets couple ferromagnetically in $CuWO_4$ and antiferromagnetically in $CuMoO_4$-III, leading to the two different magnetic propagation vectors. For $Cu(Mo_{0.25}W_{0.75})O_4$, the Δe values are all comparable in size with those for $CuWO_4$ or $CuMoO_4$-III except the Δe value representing the J_1(A) coupling path calculated about twice as big as for the end members (Table 1c). The preceding analysis predicts a magnetic unit cell of $Cu(Mo_{0.25}W_{0.75})O_4$ doubled along the a axis as well as along the b axis.[5] This prediction of a new magnetic structure was not confirmed by neutron powder diffraction experiments![7]

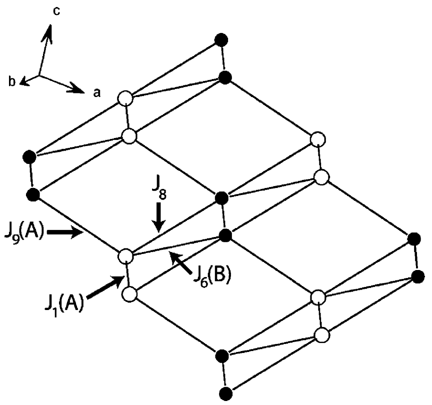

Figure 2. Two-dimensional AFM sheet present in $CuWO_4$ and $CuMoO_4$-III. J_9(A), J_8, and J_6(B) are super-superexchange paths, and J_1(A) is a superexchange path. Black and white circles represent Cu^{2+} sites with up and down spins, respectively.

As a consequence of the contradiction between the prediction of theory and the experimental results, the calculations of the Δe values are extended. The aim is the verification, whether the change of the Δe values, comparing those for $CuWO_4$ with those of $Cu(Mo_{0.25}W_{0.75})O_4$, can be ascribed mainly to the change of a particular structural parameter. Therefore, the Δe values for the most important coupling paths in $CuWO_4$ are calculated as described above using the *CAESAR* package.[8] Then, a single structural parameter (e.g., the x coordinate of the Cu atom) is changed stepwise from the value it has in $CuWO_4$ to the value it has in $Cu(Mo_{0.25}W_{0.75})O_4$, and for each step, all Δe values are calculated, respectively. Consequently, here the absolute change of the Δe values caused by the partial change of a single structure parameter is the product of the sensitivity of that Δe value to the change of the particular structural parameter (partial derivation) and the absolute change of the parameter from one structure to the other. The linear interpolated, stepwise change of the structural parameters is simply done for more clarity. The crystal structure of the end member as well as that of the "mixed crystal" are described by the six metric parameters a, b, c, α, β, and γ and three spatial coordinates for each of the six atoms on general sites in the asymmetric unit. There are one Cu site, four O sites, and one common W/Mo site. Figure 3 shows, for example, how Δe values change when the x coordinate of the Cu atom is changed stepwise from the coordinate it has in $CuWO_4$ (completeness of displacement = 0) to the coordinate it has in $Cu(Mo_{0.25}W_{0.75})O_4$ (completeness of displacement = 1): There is no considerable change of any of the Δe values. The same holds approximately for the change of all other structural parameters but is different when the Cu z coordinate is changed (Figure 4). When the Cu z coordinate is changed from the value it has in $CuWO_4$ to the value it has in $Cu(Mo_{0.25}W_{0.75})O_4$ and all other structural parameters are kept constant, the Δe value representing J_1(A) changes from 48 to 82 meV. This dramatic change of that particular Δe value is responsible for the prediction of a new magnetic structure, different from those of the end

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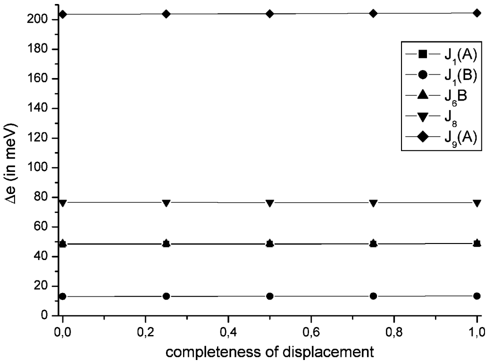

Figure 3. Evolution of Δe values starting with the structure parameters of $CuWO_4$ (completeness of displacement = 0) when the Cu x coordinate is changed stepwise to the value it has in $Cu(Mo_{0.25}W_{0.75})O_4$ (completeness of displacement = 1).

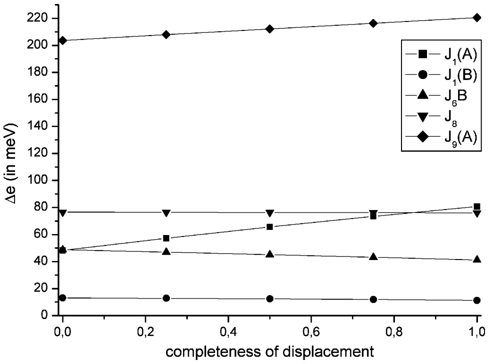

Figure 4. Evolution of Δe values starting with the structure parameters of $CuWO_4$ (completeness of displacement = 0) when the Cu z coordinate is changed stepwise to the value it has in $Cu(Mo_{0.25}W_{0.75})O_4$ (completeness of displacement = 1).

members.[5] As stated above, the dramatic effect of the partial displacement of the Cu z coordinate on the J_1(A) Δe value can be caused by either a high sensitivity of that Δe value to this structural parameter, a large change of that structural parameter itself, or both. Thus, the next step is the investigation into whether the published Cu z coordinate of $Cu(Mo_{0.25}W_{0.75})O_4$, and with it the magnitude of the change of the structural parameter, is really correct. The original structural data of the measurement (′) was refined in a certain triclinic setting: $a' = 4.714(2)$ Å, $b' = 5.848(2)$ Å, $c' = 4.879(2)$ Å, $\alpha' = 88.49(2)°$, $\beta' = 82.35(2)°$, and $\gamma' = 87.52(2)°$. In order to present the crystal structure in the triclinic setting common for the wolframite-type structures (Table 2), the basis transformation $a = a'$, $b = c'$, and $c = -b'$ has to be made. Furthermore, the so-obtained z coordinates have to be modified in order to end in the common basis and origin (see further information). It was actually missed in ref 6 to carry out this calculation instruction for the Cu and W/Mo z coordinates, but the deviation is very small and does not result in obvious wrong bond lengths or angles. Table 1d shows the results of the calculation of the Δe values of $Cu(Mo_{0.25}W_{0.75})O_4$ using the correct values. There is a dramatic change in the Δe value representing the J_1(A) superexchange path from 82 to 49 meV. Because the correct Δe value for J_1(A) and all other values are comparable in size with those calculated for $CuWO_4$ and $CuMoO_4$-III, there is no reason for the prediction of a new magnetic structure for $Cu(Mo_{0.25}W_{0.75})O_4$ differing from those of the end members. By a comparison of the Δe values, it is most serious to predict for $Cu(Mo_{0.25}W_{0.75})O_4$ a $CuWO_4$-type magnetic structure.

Table 2. Corrected Crystal Structure of $Cu(Mo_{0.25}W_{0.75})O_4$ with Wrong Transformed Parameters in Square Brackets

space group $P\bar{1}$	$a = 4.714(2)$ Å	$b = 5.848(2)$ Å	$c = 4.879(2)$ Å
$V_{UC}/Z = 66.56$ Å^3	$\alpha = 91.51(2)°$	$\beta = 92.48(2)°$	$\gamma = 82.35(2)°$
$Z = 2$			

atom	x	y	z
Cu	0.4940(2)	0.6588(1)	**0.2446(1)** [0.2554]
Mo/W	0.0244(1)	0.1735(1)	**0.2548(1)** [0.2452]
O1	0.2502(10)	0.3534(9)	0.4263(9)
O2	0.2145(9)	0.8792(8)	0.4281(8)
O3	0.7344(10)	0.3806(8)	0.0984(9)
O4	0.7829(10)	0.9076(8	0.0518(8)

Koo and Whangbo[5] used the crystal structure, obtained by single-crystal X-ray diffraction, to calculate Δe values that represent the magnetic coupling strengths with the extended Hückel theory. Thus, for $Cu(Mo_{0.25}W_{0.75})O_4$, a new magnetic structure was predicted. In this work, more detailed extended Hückel calculations, in the sense that the influence of particular structure parameters on the Δe values was considered, even gave the hint that a structure parameter is supposed to be incorrect. Following investigations on the structure parameters indeed revealed that the Cu z coordinate was wrong. The remarkable point is that the deviations were too small to be recognized by obvious incorrect bond lengths or angles. However, because extended Hückel calculations of the spin dimers are so sensitive to small structural changes, the prediction of a different magnetic structure, in contrast to experimental results, allowed one to detect even marginally wrong structure parameters for the reported structure.[6]

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Supporting Information Available: Partial derivation of Δe values to the Cu z coordinate, linear interpolation of "mixed" crystal atomic coordinates, transformation of metric and atomic coordinates, and definition of superexchange and super-superexchange spin dimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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