Supporting Information

Partial derivation of Δe-values to the Cu-z-coordinate

Figure 1 shows the partial derivation of the Δe-values in $CuWO_4$ when the Cu-z-coordinate is varied. Especially the Δe-value representing the J_1(A)-coupling path has a strong dependence on the partial change of the Cu-z-coordinate. Thus, the large deviation of the J_1(A)-Δe-value, that is by mistake responsible for the prediction of a new magnetic structure for the $Cu(Mo_{0.25}W_{0.75})O_4$-crystal, is caused by the use of an incorrect atomic parameter and the fact that especially this coupling path shows a strong dependence on this structure parameter.

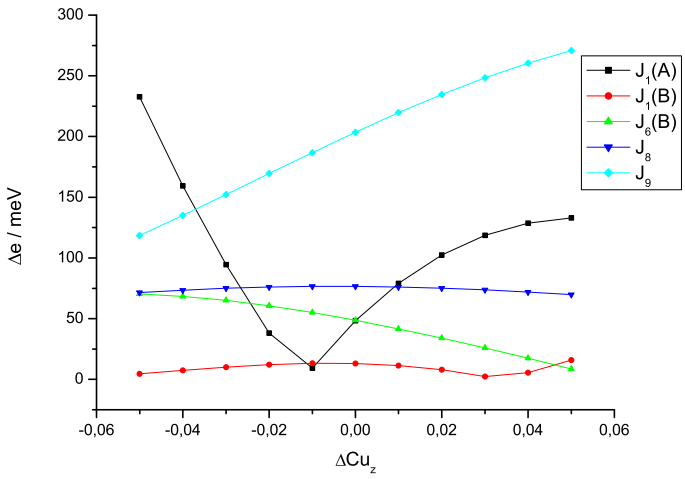

Figure 1: Δe-values as a function of partial change of the Cu_z-parameter.

Linear interpolation of "mixed" crystal atomic coordinates

Figure 2 shows differences of atomic coordinates. The black line ($CuWO_4$ − $CuMoO_4$-III) represents the differences of the atomic coordinates of the end members. If the atomic coordinates of the "mixed" crystal with 75% W could be obtained by a linear interpolation of the coordinates of the end members, then the red line ($Cu(Mo_{0.25}W_{0.75})O_4$ − $CuMoO_4$-III) should fall together with the green line ($CuWO_4$ − $CuMoO_4$-III)·0.75. It is obvious that this holds for nearly all coordinates, but not for the W/Mo-z- and the Cu-z-coordinate. Figure 3 shows the corresponding differences of the corrected

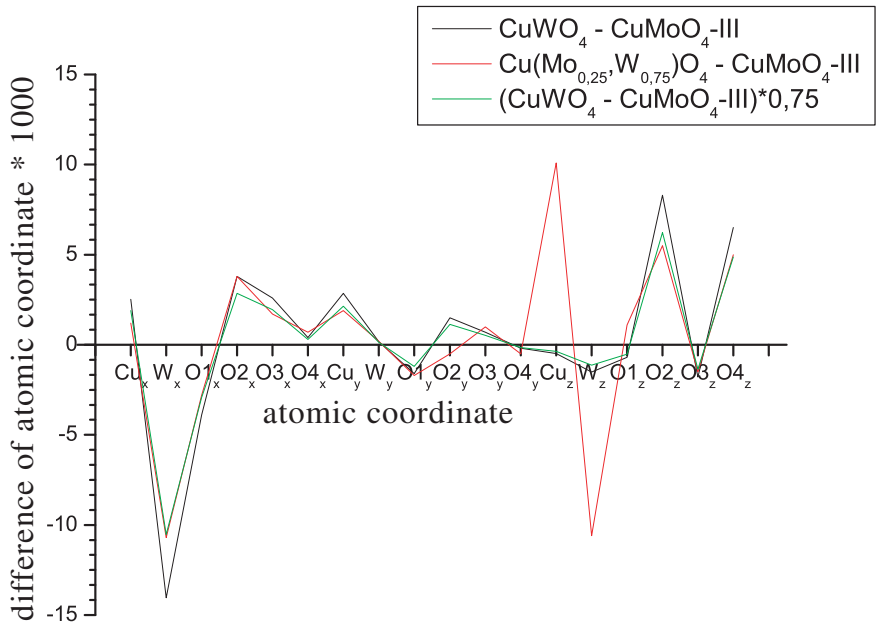

Figure 2: Differences of atomic coordinates. $Cu(Mo_{0.25}W_{0.75})O_4$ coordinates as published in [1].

structure of the "mixed" crystal. The large difference of the W/Mo-z- and the Cu-z-coordinate is no longer existent.

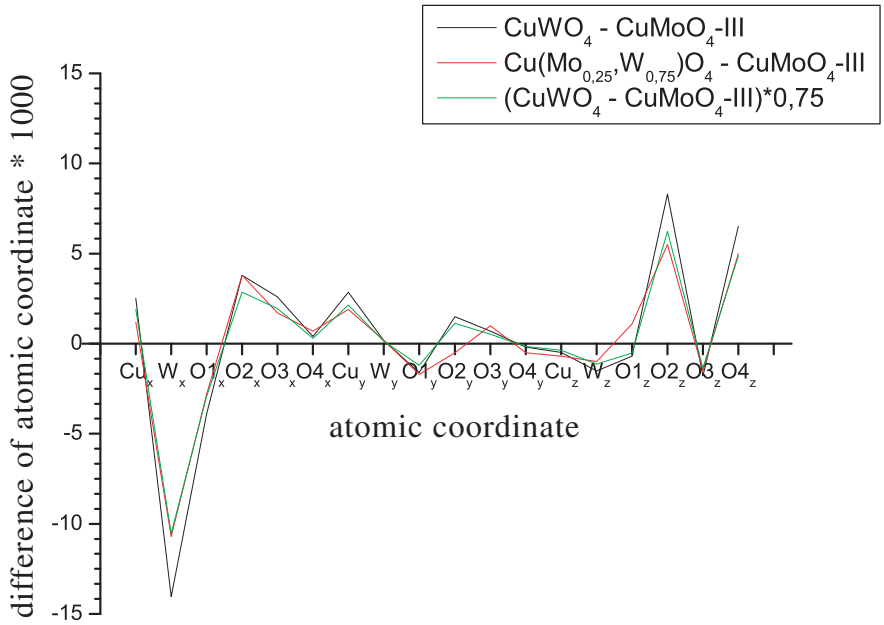

Figure 3: Differences of atomic coordinates. Corrected W/Mo-z- and Cu-z-coordinates for $Cu(Mo_{0.25}W_{0.75})O_4$ were used.

Transformation of metric and atomic coordinates

Figure 4 shows the original SHELXL-datasheet of the structure refinement of the $Cu(Mo_{0.25}W_{0.75})O_4$-crystal with the original metric (see also table 1). In order to present the data in the metric setting commonly used for wolframates, the metric setting has to be transformed according to the instructions shown in the last line of table 1. This metric transformation implies the atomic coordinate transformation shown in table 2.

	a/Å	b/Å	c/Å	α/°	β/°	γ/°
original metric (′)	4.71400	4.87900	5.84800	88.49000	82.35000	87.52000
wolframite metric	4.71400	5.84800	4.87900	91.51000	92.48000	82.35000
metric transformation	$\vec{a} = \vec{a}\,'$		$\vec{b} = \vec{c}\,'$		$\vec{c} = -\vec{b}\,'$	

Table 1: Original metric used in refinement of the $Cu(Mo_{0.25}W_{0.75})O_4$-crystal (first line), metric commonly used for the wolframite structure (second line) and transformation instruction from one to the other (third line).

atom	x	y	z	atom notation in original data (table 4)
Mo/W	(x)	(z)	(−y)+0,5	Mo1/W1
Cu	(x)	(z)	(−y)+0,5	Cu2
O1	(x)	(z)	(−y)+0,5	O4
O2	(x)	(z)+1	(−y)+0,5	O5
O3	1+(x)	(z)	(−y)+0,5	O3
O4	1−(x)	1−(z)	−1−(−y)+0,5	O6

Table 2: Instruction to transform the atomic positions from the original refinement to the metric setting commonly used for the wolframite structure given in table 1 (second line).

```
TITL wie15
CELL 0.71069  4.71400  4.87900  5.84800 88.49000 82.35000 87.52000
ZERR 2   0.00200   0.00200   0.00200   0.02000   0.02000   0.02000
LATT 1
SFAC CU MO O W
UNIT  2 .5 8 1.5
PLAN -10
FMAP 2
L.S. 8
MORE 2
BOND
CONF
ACTA
EXYZ MO1 W1
EADP MO1 W1
WGHT      0.0352     1.0152
EXTI    0.061776
FVAR      0.52240   0.25225
MO1     2   0.02437   0.24521   0.17345  21.00000   0.00577   0.01034 =
        0.00878   0.00117  -0.00060  -0.00049
W1      4   0.02437   0.24521   0.17345  21.00000   0.00577   0.01034 =
        0.00878   0.00117  -0.00060  -0.00049
CU2     1   0.49400   0.25537   0.65879  11.00000   0.00807   0.01240 =
        0.01163   0.00313   0.00182   0.00015
O3      3  -0.26562   0.40162   0.38055  11.00000   0.00835   0.01308 =
        0.01015   0.00245   0.00128   0.00150
O4      3   0.25016   0.07372   0.35343  11.00000   0.00950   0.01502 =
        0.01068   0.00214  -0.00080  -0.00130
O5      3   0.21454   0.07194  -0.12076  11.00000   0.00654   0.01211 =
        0.00992  -0.00065   0.00220  -0.00305
O6      3   0.21714   0.55180   0.09237  11.00000   0.00982   0.01369 =
        0.00871   0.00212  -0.00192  -0.00044
HKLF 4 END
```

Figure 4: Original dataset of the refinement of the $Cu(Mo_{0.25}W_{0.75})O_4$-crystal used for publication in [1].

Definition of superexchange and super-superexchange spin dimers.

	x	y	z
	J_1(A)		
Cu1	-Cu1$_x$	-Cu1$_y$	-Cu1$_z$
Cu2	-1+Cu1$_x$	-1+Cu1$_y$	Cu1$_z$
O1	-O1$_x$	-O1$_y$	1-O1$_z$
O2	-O1$_x$	-O1$_y$	-O1$_z$
O3	-1+O1$_x$	-1+O1$_y$	O1$_z$
O4	-1+O1$_x$	-1+O1$_y$	-1+O1$_z$
O5	-O2$_x$	-O2$_y$	-O2$_z$
O6	-1+O2$_x$	-1+O2$_y$	O2$_z$
O7	-O3$_x$	-O3$_y$	-O3$_z$
O8	-1+O3$_x$	-1+O3$_y$	O3$_z$
O9	-O4$_x$	-O4$_y$	-O4$_z$
O10	-1+O4$_x$	-1+O4$_y$	O4$_z$
	J_6(B)		
Cu1	1-Cu1$_x$	-Cu1$_y$	-Cu1$_z$
Cu2	-1+Cu1$_x$	-1+Cu1$_y$	-1+Cu1$_z$
O1	1-O1$_x$	-O1$_y$	-O1$_z$
O2	O1$_x$	-1+O1$_y$	-1+O1$_z$
O3	-O1$_x$	-O1$_y$	-O1$_z$
O4	-1+O1$_x$	-1+O1$_y$	-1+O1$_z$
O5	1-O2$_x$	-O2$_y$	-O2$_z$
O6	-1+O2$_x$	-1+O2$_y$	-1+O2$_z$
O7	1-O3$_x$	-O3$_y$	-O3$_z$
O8	O3$_x$	-1+O3$_y$	O3$_z$
O9	-O3$_x$	-O3$_y$	-1-O3$_z$
O10	-1+O3$_x$	-1+O3$_y$	-1+O3$_z$
O11	1-O4$_x$	-O4$_y$	-O4$_z$
O12	-1+O4$_x$	-1+O4$_y$	-1+O4$_z$
	J_9(A)		
Cu1	-Cu1$_x$	1-Cu1$_y$	-Cu1$_z$
Cu2	Cu1$_x$	-1+Cu1$_y$	-1+Cu1$_z$
O1	-O1$_x$	1-O1$_y$	-O1$_z$
O2	1-O1$_x$	-O1$_y$	-O1$_z$
O3	-1+O1$_x$	O1$_y$	-1+O1$_z$
O4	O1$_x$	-1+O1$_y$	-1+O1$_z$
O5	-O2$_x$	1-O2$_y$	-O2$_z$
O6	O2$_x$	-1+O2$_y$	-1+O2$_z$
O7	1-O3$_x$	-O3$_y$	-1-O3$_z$
O8	-O3$_x$	1-O3$_y$	-O3$_z$
O9	-1+O3$_x$	O3$_y$	O3$_z$
O10	O3$_x$	-1+O3$_y$	-1+O3$_z$
O11	-O4$_x$	1-O4$_y$	-O4$_z$
O12	O4$_x$	-1+O4$_y$	-1+O4$_z$

	x	y	z
	J_1(B)		
Cu1	-Cu1$_x$	-Cu1$_y$	-Cu1$_z$
Cu2	-1+Cu1$_x$	-1+Cu1$_y$	-1+Cu1$_z$
O1	-O1$_x$	-O1$_y$	-O1$_z$
O2	-1+O1$_x$	-1+O1$_y$	-1+O1$_z$
O3	-O2$_x$	-O2$_y$	-O2$_z$
O4	-1+O2$_x$	-1+O2$_y$	-1+O2$_z$
O5	-O3$_x$	-O3$_y$	-O3$_z$
O6	-1+O3$_x$	-1+O3$_y$	O3$_z$
O7	-1+O3$_x$	-1+O3$_y$	-1+O3$_z$
O8	-O3$_x$	-O3$_y$	-1-O3$_z$
O9	-O4$_x$	-O4$_y$	-O4$_z$
O10	-1+O4$_x$	-1+O4$_y$	-1+O4$_z$
	J8		
Cu1	Cu1$_x$	-1+Cu1$_y$	Cu1$_z$
Cu2	-1+Cu1$_x$	-1+Cu1$_y$	-1+Cu1$_z$
O1	1-O1$_x$	-O1$_y$	1-O1$_z$
O2	O1$_x$	-1+O1$_y$	O1$_z$
O3	-O1$_x$	-O1$_y$	-O1$_z$
O4	-1+O1$_x$	-1+O1$_y$	-1+O1$_z$
O5	O2$_x$	-1+O2$_y$	O2$_z$
O6	-1+O2$_x$	-1+O2$_y$	-1+O2$_z$
O7	1-O3$_x$	-O3$_y$	-O3$_z$
O8	O3$_x$	-1+O3$_y$	O3$_z$
O9	-O3$_x$	-O3$_y$	-1-O3$_z$
O10	-1+O3$_x$	-1+O3$_y$	-1+O3$_z$
O11	O4$_x$	-1+O4$_y$	O4$_z$
O12	-1+O4$_x$	-1+O4$_y$	-1+O4$_z$

Table 3: Definitions of the cluster-ions representing the correponding magnetic exchange paths.

References

[1] Wiesmann, M.; Ehrenberg, H.; Miehe, G.; Peun, T.; Weitzel, H.; Fuess, H. *J. of Solid State Chemistry* **1997**, 132, 88-97.