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The crystal and magnetic structure relationship in $\text{Cu}(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ compounds with wolframite-type structure

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Abstract

The magnetic structures of $\text{Cu}(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ compounds with wolframite-type structure at 1.5 K have been determined by neutron powder diffraction for average composition $\langle x \rangle = 0.15, 0.25$ and 0.35 . For $\langle x \rangle = 0.15$ the magnetic structure is antiferromagnetic with a magnetic unit cell doubled along the a -axis, $\vec{k} = (\frac{1}{2}, 0, 0)$, i.e. the same magnetic structure as for CuWO_4 . For $\langle x \rangle = 0.25$ and 0.35 two magnetic structures are observed: one is identical to that for $\langle x \rangle = 0.15$, while the other is doubled with respect to the c -axis, $\vec{k} = (0, 0, \frac{1}{2})$, i.e. the same magnetic structure as for the high-pressure modification CuMoO_4 III. The coexistence of these two magnetic arrangements is interpreted as reflecting a slightly inhomogeneous contribution of Mo and W in different crystallites together with a sharp transition between the stability ranges of the two types of magnetic structure with respect to x . The specific Mo:W distributions in the grains of the powdered samples were deduced from a profile analysis based on high-resolution synchrotron powder diffraction data. No additional, intermediate magnetic phase with $\vec{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ was found in $\text{Cu}(\text{W}_{0.75}\text{Mo}_{0.25})\text{O}_4$, in contrast to predictions in the framework of extended Hückel calculations based on the precise crystal structure.

1. Introduction

Prediction of magnetic properties based on chemical composition and underlying crystal structure is one of the goals of solid-state physics. Theoretical approaches are challenged by mag-

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netic model systems, where structural degrees of freedom can be varied continuously, and tiny changes in these parameters result in magnetic phase transitions with very different properties of the magnetic phases involved. A suitable model system for the investigation of the relationship between magnetic exchange couplings in copper oxides and geometrical details of the exchange paths such as bond lengths and angles is $\text{Cu}(\text{W}, \text{Mo})\text{O}_4$. The high-pressure modification CuMoO_4 III is metastable at ambient conditions if cooled down to room temperature before pressure is released and can also be obtained by chemical pressure due to the partial replacement of Mo by W without external pressure being applied [1]. This high-pressure phase CuMoO_4 III and CuWO_4 are isomorphous and crystallize in the wolframite-type structure (space group $P\bar{1}$, $Z = 2$). In spite of very similar structure parameters for the two phases, different antiferromagnetic structures are observed: in CuMoO_4 III the magnetic unit cell is doubled with respect to the c -axis, i.e. $\vec{k}_c = (0, 0, \frac{1}{2})$, instead of the a -axis, $\vec{k}_a = (\frac{1}{2}, 0, 0)$, as in CuWO_4 [2]. The small deviations in the geometry of the exchange paths affect the magnetic coupling parameters sufficiently to result in different magnetic ground states. Therefore, the comparison between CuMoO_4 III and CuWO_4 provides a severe test for calculations of magnetic superexchange couplings based on the underlying crystal structure. Recently, the magnetic exchange interactions have been calculated for CuMoO_4 III and CuWO_4 in the framework of extended Hückel theory, and the results can explain their different magnetic structures [3]. Furthermore, a third magnetic structure type with simultaneous doubling of the a - and b -axes, $\vec{k} = (\frac{1}{2}, \frac{1}{2}, 0)$, is predicted for $\text{Cu}(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ with $x = 0.25$ [3], based on the crystal structure parameters as obtained from an x-ray single-crystal structure refinement for a sample with this W:Mo ratio [1]. This theoretical work has inspired the experimental studies presented here on mixed compounds $\text{Cu}(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ for compositions x close to the transition from $\vec{k}_a \rightarrow \vec{k}_c$, carried out to elucidate the evolution of magnetic structure types with respect to x .

Diffraction techniques always provide averaged structural parameters, although bond lengths and angles vary on the atomic scale in mixed crystals, depending on the specific site occupation. The description of magnetic properties based on averaged structural parameters might fail when small changes in geometry change the resulting coupling strength significantly, so variations in the coupling parameters have to be taken into account versus averaged values. Local variations will result in spin dimers or short-range order at intermediate temperature. Such a behaviour has been discussed in detail for CuWO_4 [4], but in this contribution we will focus on the magnetic ground state of $\text{Cu}(\text{W}, \text{Mo})\text{O}_4$ compounds at low temperature only.

2. Experimental details

The samples were prepared by subsolidus reaction from the educts CuO (Aldrich, 99.99%), WO_3 (99%) and MoO_3 . Appropriate amounts for $\text{Cu}(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ with $x = 0.15, 0.25$ and 0.35 were intimately mixed in an agate mortar under acetone and placed in a platinum crucible. The samples were heated in flowing oxygen at a rate of 180 K h^{-1} to 973 K and after 72 h cooled down to room temperature at a rate of 120 K h^{-1} . X-ray powder diffraction confirmed a pure phase with wolframite-type structure for $x = 0.15$, while traces of an additional α - CuMoO_4 impurity were found in the products with $x = 0.25$ and 0.35 .

The temperature dependence of the magnetization was measured for all samples at a constant field strength of 0.1 T using a superconducting interference device from Quantum Design. The neutron powder diffraction study was performed at the Paul-Scherrer Institute (Switzerland) using the diffractometer DMC with a wavelength of 2.565 \AA and a pyrolytic graphite filter to reduce high-order contamination [5].

The beamline B2 at the Hamburger Synchrotron Strahlungslabor (Germany) was used for high-resolution synchrotron powder diffraction to analyse the homogeneity of the Mo:W

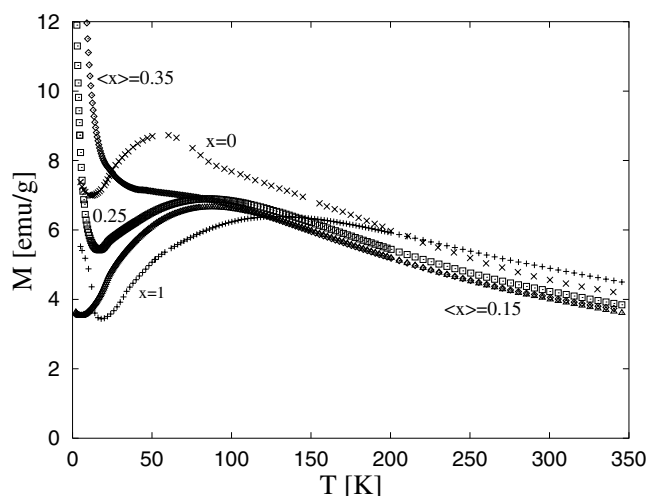


Figure 1. The temperature dependence of the magnetization for Cu(W_{1-x}Mo_x)O₄ compounds with an applied field strength of 0.1 T.

Table 1. Results from Curie–Weiss fits to the data from 200 to 350 K.

x	μ (μ_B)	Θ (K)	T_N (K)
0.00	2.20	-125.5	22.5(1.0)
0.15	2.03	-131.5	21.5(1.0)
0.25	2.10	-148	21.5(1.0)
0.35	2.04	-158	22.0(1.0)
1.00	2.20	-256	32.0(1.0)

distribution in the crystallites on a macroscopic scale. A difference in the Mo:W ratio will result in slightly different lattice parameters and, therefore, the diffraction peak half-widths increase. This broadening depends strongly on the indices (hkl), as all lattice parameters change in a different way with the Mo:W ratio x and, thereby, allow us to separate variations in composition from particle size and stress effects. The observed reflection profiles are compared to a CuWO₄ reference standard. Data have been collected in the range $10^\circ \leq 2\Theta \leq 48.5^\circ$ in steps of 0.004° using photons with 1.12436 \AA wavelength, selected by a Ge(111) double-crystal monochromator and with an additional Ge(111) analysing crystal between the sample and scintillation counter. A pneumatically bent mirror was used to reduce vertical divergence and, thereby, to optimize instrumental resolution to ensure that sample effects are as clearly detectable as possible [6].

3. Results and discussion

The temperature dependence of the magnetization is given in figure 1 for five Cu(W_{1-x}Mo_x)O₄ compounds. All compounds show significant deviations from a Curie–Weiss paramagnetic behaviour at about 200 K, indicating short-range or low-dimensional magnetic order in an intermediate-temperature region. The local maxima are shifted to higher temperature for increasing Mo content. The Néel temperatures are determined as the local maxima of the slopes dM/dT ; see table 1. This procedure is supported by the good agreement with reported values for the Néel temperature of CuWO₄ $T_N = 24(1) \text{ K}$, from the disappearance of the

EPR line [7], and $T_N = 23.0(2)$ K, based on the temperature dependence of the magnetic $(\frac{1}{2}00)$ reflection [8]. The magnetization data between 200 and 350 K have been fitted by the Curie–Weiss law

$$M(T) = \frac{C}{T - \Theta}$$

and are compared with those for the end-members CuWO_4 ($x = 0$) and CuMoO_4 III ($x = 1$) in table 1. The magnetic moment per Cu ion is constant ($2.1(1) \mu_B$) while the paramagnetic Curie–Weiss temperature decreases linearly according to

$$\Theta(x) = -116(5) \text{ K} - x \times 137(10) \text{ K},$$

indicating a slightly stronger antiferromagnetic coupling for increasing x in agreement with the observed shift of the local maximum in $M(T)$ and the highest Néel temperature for CuMoO_4 III. However, the evolution in the temperature dependence $M(T)$ with Mo content x does not follow a simple interpolation between those of the end-members. In particular, the samples with $\langle x \rangle = 0.25$ and 0.35 show a pronounced increase in magnetization at low temperature, perhaps due to effectively free spins which might contribute to a further Curie term.

The neutron powder diffraction results confirm antiferromagnetic ordering. Two diffraction patterns of $\text{Cu}(\text{W}_{0.85}\text{Mo}_{0.15})\text{O}_4$, recorded at $T = 86$ K, well above the Néel temperature, and at 1.5 K, below T_N , are shown in figure 2. The one significant additional reflection at low temperature is $(\frac{1}{2}00)$, and the ordered magnetic moment is refined to $0.78(3) \mu_B$ on the basis of the same magnetic structure model as for CuWO_4 . For the two other mixed compounds with higher Mo content, both the magnetic structure types, CuWO_4 and CuMoO_4 III, coexist at 1.5 K; see figure 3. The amount of CuMoO_4 III-type material with a doubled c -axis increases from 40% for $\langle x \rangle = 0.25$ to 70% for $\langle x \rangle = 0.35$. This behaviour can be explained by a varying Mo:W ratio in different crystallites and a sharp transition between the two magnetic structure types at a certain value x_c . On the basis of a Gaussian distribution

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp -\frac{1}{2} \frac{(x - \langle x \rangle)^2}{\sigma^2}$$

for the Mo:W ratio with centres at $\langle x \rangle = 0.25$ and 0.35 , $\sigma = 0.128$ and $x_c = 0.28$ can be determined from the relative ratios of the two magnetic structure types. Neither diffuse nor Bragg scattering is observed at those scattering angles, where reflections would be expected for $k = (\frac{1}{2}, \frac{1}{2}, 0)$. Furthermore, we could not detect any kind of diffuse scattering in the diffraction pattern at 1.5 K, which would result from short-range or low-dimensional order. We only found Bragg scattering at 1.5 K.

An energy-dispersive x-ray analysis with a Philips CM20 transmission electron microscope of 15 crystallites from the $\text{Cu}(\text{W}_{0.75}\text{Mo}_{0.25})\text{O}_4$ sample gave an average value $\langle x \rangle = 0.25$ with $\sigma = 0.05$ and specific relations $x_i < x_c$ for 10 crystallites in agreement with about 60% of the sample ordering in the CuWO_4 -type magnetic structure. A representative analysis of the cation distribution in the sample was obtained by Rietveld refinement based on the high-resolution synchrotron diffraction data. Sections of observed and calculated diffraction patterns are shown in figure 4. The distribution function has been approximated by refining the scale factors for 11 phases in steps of $\Delta x = 0.05$ from $x = 0$ to 0.5 , on the basis of the half-width and profile parameters deduced from undoped CuWO_4 as a reference and with specific lattice parameters obtained from the linear interpolation between those for CuMoO_4 III and those for CuWO_4 ; see table 2. The same atomic parameters have been used for all 11 phases; only the Mo and W site occupation factors were adapted to x for each phase individually and kept fixed during the refinement. The observed half-width of the reflections is mainly determined by the variations of the angles γ and α , and the combination

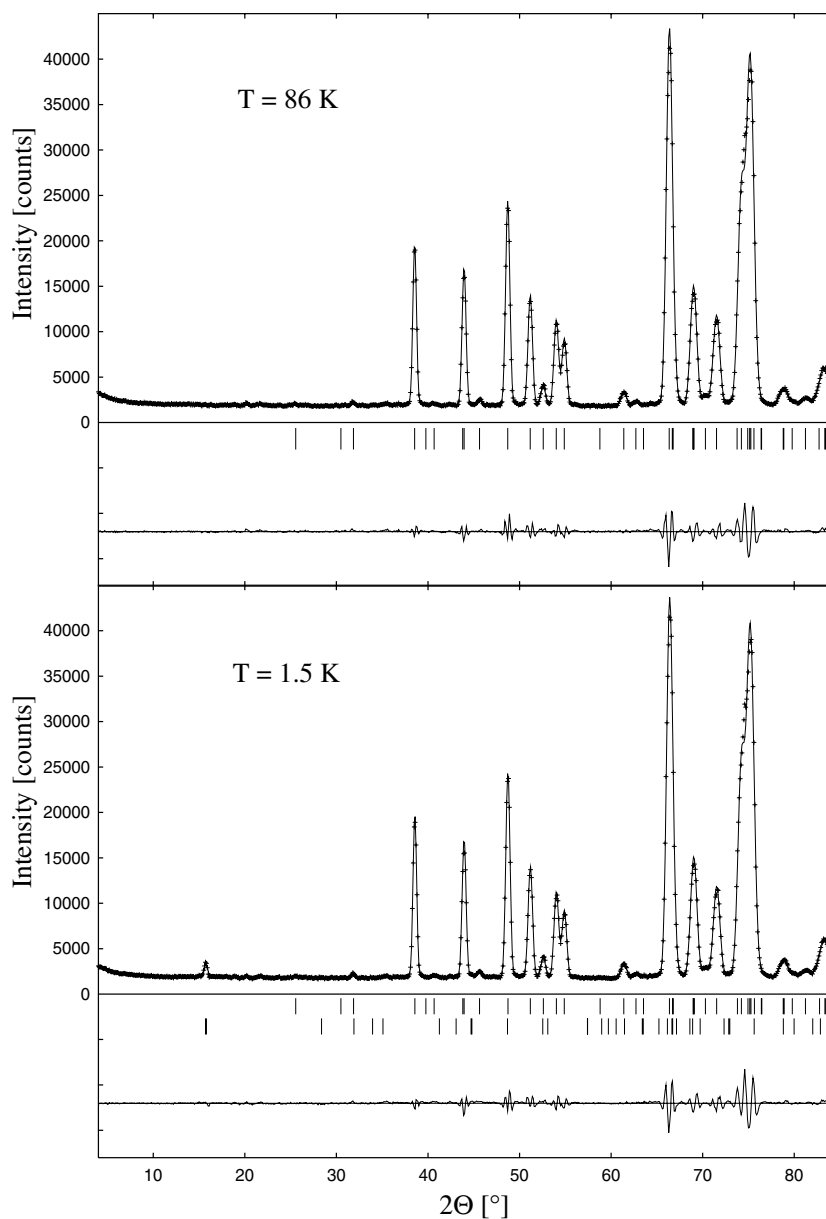


Figure 2. Neutron diffraction patterns of Cu(W_{0.85}Mo_{0.15})O₄ below and above the Néel temperature. The lower line of reflection marks in the 1.5 K pattern corresponds to the additional magnetic reflections for $\vec{k} = (\frac{1}{2}, 0, 0)$.

of Rietveld refinement with constrained structure parameters gives an excellent agreement between observed and calculated profiles. Therefore, the distribution functions shown in figure 5 can be determined very reliably. Other contributions to the observed half-width such as particle size and stress follow a characteristic dependence on 2Θ and can be clearly distinguished from a broadening caused by a specific distribution of lattice parameters. For the sample with $\langle x \rangle = 0.25$, 40% of the crystallites should have more Mo than $x_c = 0.28$,

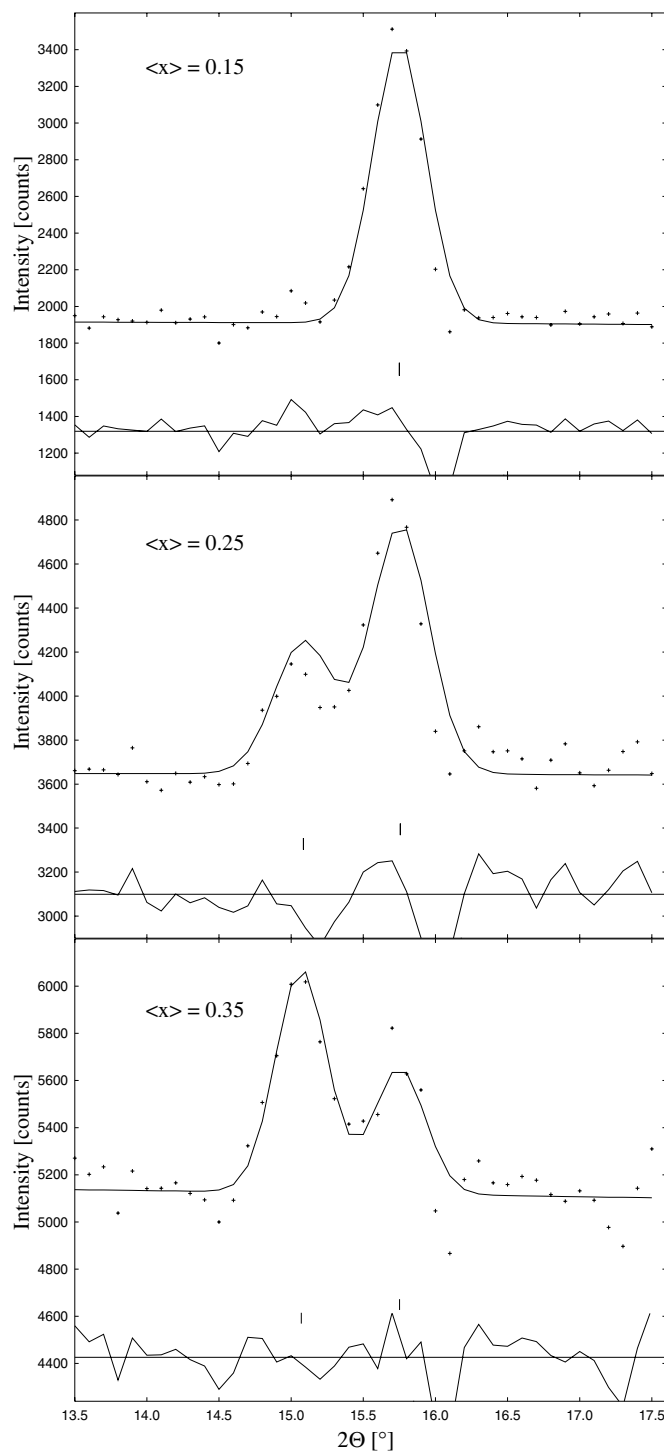


Figure 3. The dominant magnetic reflections $(\frac{1}{2}, 0, 0)$ of the CuWO_4 -type magnetic structure (upper marks) and $(0, 0, \frac{1}{2})$ of the CuMoO_4 III-type structure (lower marks) in $\text{Cu}(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ for $\langle x \rangle = 0.15, 0.25$ and 0.35 , at 1.5 K. The amount of CuMoO_4 III-type material increases with Mo content.

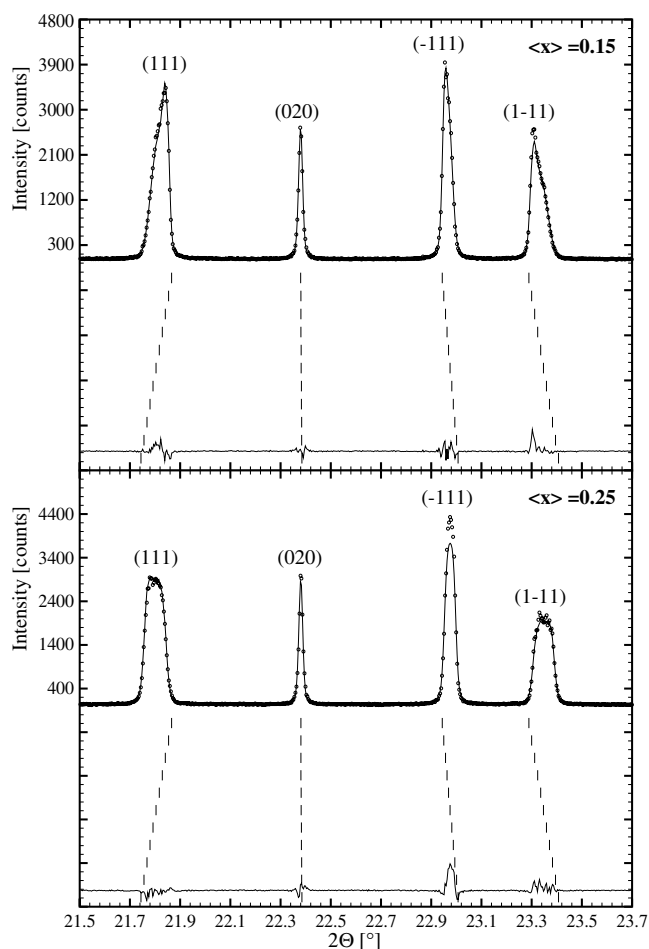


Figure 4. Sections of high-resolution synchrotron diffraction patterns for Cu(W_{1-x}Mo_x)O₄ for the two different averaged Mo contents $\langle x \rangle = 0.15$ and 0.25. The asymmetry of the Mo distribution for the $\langle x \rangle = 0.15$ sample is clearly reflected in the peak shape.

Table 2. Lattice constant dependence on x , $p(x) = p_0 + x dp/dx$.

Lattice parameter p	p_0	$\frac{dp}{dx}$
a	4.706 40(6) Å	0.0213(3) Å
b	5.841 55(4) Å	0.0162(2) Å
c	4.880 96(2) Å	-0.0124(9) Å
α	91.658(2)°	-0.503(12)°
β	92.498(1)°	-0.080(4)°
γ	82.782(2)°	-1.443(12)°

in very good agreement with the observed magnetic intensities. However, for the sample with $\langle x \rangle = 0.15$, still about 15% of the material should order in the magnetic structure type CuMoO₄ III. Probably this level is too low to be detected in the diffraction pattern.

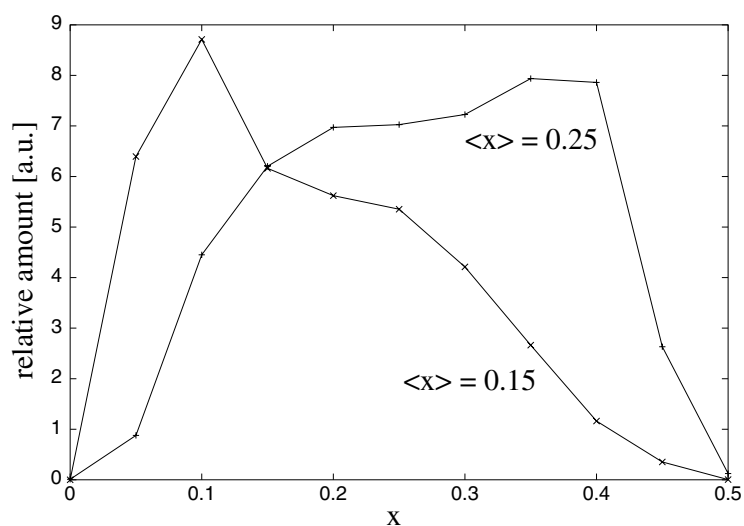


Figure 5. Cation distribution functions for two samples with averaged compositions $\langle x \rangle = 0.15$ and 0.25 , as deduced from high-resolution synchrotron diffraction. The relative amounts are proportional to the scale factors of the eleven discrete compositions used to approximate the continuous distribution function.

4. Conclusions

For the mixed series $\text{Cu}(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ with $\langle x \rangle = 0.15$ and 0.25 , the distribution function for the Mo:W ratios in the crystallites could be determined very reliably from a profile analysis based on high-resolution synchrotron diffraction data. This distribution is spread over a wide enough range of compositions for both magnetic structure types with doubled a - and c -axes, respectively, to be observed in the samples with $\langle x \rangle = 0.25$ and 0.35 . There is no indication of any intermediate phase with a different magnetic structure type. However, a very narrow stability range cannot be excluded, as only a very low amount of material could order in such an arrangement and, therefore, the resulting magnetic reflections might be too weak to be detected. However, it is more probable that the use of averaged atomic positions in mixed crystals—as provided by diffraction, even from a ‘single’ crystal—is not sufficient for the explanation of resulting physical properties. The magnetic supersuperexchange couplings will be different even for Cu–O–O–Cu paths, which are crystallographically equivalent in the averaged structure, depending on the specific occupation of neighbouring $[(\text{W}, \text{Mo})\text{O}_6]$ octahedra either with Mo or with W. In the case of mixed crystals the prediction of magnetic properties from the underlying crystal structure has to take such local variations into account.

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References

- [1] Wiesmann M, Ehrenberg H, Mieke G, Peun T, Weitzel H and Fuess H 1997 *J. Solid State Chem.* **132** 88–97
- [2] Ehrenberg H, Wiesmann M, Garcia-Jaca J, Weitzel H and Fuess H 1998 *J. Magn. Magn. Mater.* **182** 152–60

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- [3] Koo H J and Whangbo M H 2001 *Inorg. Chem.* **40** 2161–9
 - [4] Lake B, Cowley R A and Tennant D A 1997 *J. Phys.: Condens. Matter* **9** 10 951–75
 - [5] Fischer P, Keller L, Schefer J and Kohlbrecher J 2000 *Neutron News* **11** 19–21
 - [6] Knapp M, Ehrenberg H, Fuess H, Hahn U, Hesse M, Schulte-Schrepping H and Wroblewski T 2001 *Nucl. Instrum. Methods A* **467–468** 291–3
 - [7] Anders A G, Zvyagin A I, Kobets M I, Pelikh L N, Khats'ko E N and Yurko V G 1972 *Sov. Phys.–JETP* **35** 934–6
 - [8] Forsyth J B, Wilkinson C and Zvyagin A I 1991 *J. Phys.: Condens. Matter* **3** 8433–40