

## Scientific Report Dirk Wulferding (2127)

**Duration** 15.09.2008 – 17.10.2008

**Location** Department of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, 106 91 Stockholm, Sweden

**Host** Associate Professor Dr. Mats Johansson

### **Purpose of the visit**

Oxohalogenides, comprising transition metals and elements having an asymmetric coordination due to the presence of stereochemically active lone pairs, such as  $\text{Te}^{\text{IV}}$ ,  $\text{Se}^{\text{IV}}$ ,  $\text{As}^{\text{III}}$  or  $\text{Sb}^{\text{III}}$ , have proven to be a very interesting family of compounds in which there is a high probability of finding novel host-guest compounds, frustrated quantum spin systems and low-dimensional compounds (Johansson et al., 2000, 2003, 2004)<sup>1</sup>.

In the past, the collaboration between our group in Braunschweig and Dr. Johansson's group in Stockholm has led to a large number of scientific results and publications. Magnetic properties of novel low-dimensional materials developed in his workgroup have been investigated by means of inelastic light scattering in our group and in many other groups of the ESF-HFM network. Due to their low-dimensionality, these systems exhibit often strong effects of magnetic frustration.

The purpose of the visit was my interest in learning the techniques of synthesizing such systems, producing new and possibly low-dimensional compounds and performing characterization measurements on them.

### **Description of the work carried out during the visit**

Different sets of samples (see tables 1-3) were prepared by mixing the starting chemicals MnO,  $\text{MnCl}_2$ ,  $\text{TeO}_2$ , CuCl, CuO and  $\text{SnCl}_2$  in a defined molar ratio and grinding the powder mixture in a mortar. The resulting powder was then equally distributed into six quartz tubes ( $d = 4$  mm,  $l = 15$  cm). These tubes were evacuated and sealed, and subsequently placed into six furnaces (each at a different temperature ranging from 400°C to 550°C) for about 90 hours. After cooling down, the quartz tubes were opened and the resulting substances were examined through a microscope. Small crystals of each composition were picked for EDS analysis and finally, XRD measurements were performed on one crystal piece.

*Table 1: Batch D1*

Starting chemicals	MnO	$\text{MnCl}_2$	$\text{TeO}_2$
Molar ratio	1	1	1
Formula weight	70.94	125.844	159.60
Used amount (g)	0.3561	0.6299	0.7997
Manufacturer	Sigma Aldrich (99 %)	Alfa Aesar (97 %)	Sigma Aldrich (99 %)

*Table 2: Batch D2*

Starting chemicals	MnO	$\text{CuCl}_2$	$\text{TeO}_2$
Molar ratio	1	1	1
Formula weight	70.94	134.45	159.60

Used amount (g)	0.3560	0.6739	0.8001
Manufacturer	Sigma Aldrich (99 %)	AVOCADO Research Chemicals (98 %)	Sigma Aldrich (99 %)

Table 3: Batch D3

Starting chemicals	SnO	MnCl <sub>2</sub>	TeO <sub>2</sub>
Molar ratio	1	1	1
Formula weight	134.69	125.844	159.60
Used amount (g)	0.6753	0.6310	0.7999
Manufacturer	ABCR (98 %)	Alfa Aesar (97 %)	Sigma Aldrich (99 %)

Table 4: Batch D11

Starting chemicals	MnCl <sub>2</sub>	MnO	CuO	TeO <sub>2</sub>	CuCl
Molar ratio	2	2	3	7	1
Formula weight	125.844	70.94	79.54	159.60	99.00
Used amount (g)	0.2696	0.1522	0.2565	1.1995	0.1060
Manufacturer	Alfa Aesar (97 %)	Sigma Aldrich (99 %)	Sigma Aldrich (98 %)	Sigma Aldrich (99 %)	ABCR (97 %)

## Description of the main results obtained

Except for D3, all tubes already contained numerous, albeit very small, crystalline phases with typical edge lengths of several  $\mu\text{m}$ . Therefore, a Sn containing composition was not further investigated.

EDS measurements confirmed all starting elements in the D1 and D2 tubes. However, the crystals of the D1 batch (which contained the starting chemicals Mn-Te-O-Cl) were of poor quality, that is, they only occurred as very thin, brittle and transparent plates. Such crystals are especially difficult to handle as they tend to break apart as soon as one tries to work with it. Thus, the main focus was shifted to Cu-Mn-O-Te compositions. Still, future investigations on this composition could be of interest, since it might show a low temperature ferromagnetic / antiferromagnetic behaviour.

The next step was to adjust the molar ratio of the starting chemicals and to synthesize new samples according to the EDS results. Unfortunately, it turned out rather difficult to obtain tubes with only a single phase as well as larger crystals. We succeeded nevertheless in synthesizing needle shaped crystals with a length of some 100  $\mu\text{m}$ , which is an acceptable size for XRD and possibly large enough for further Raman measurements back in Braunschweig.

The EDS results on those needles are given below (see page 5). The crystals were grown from the starting mixture given in table 4 (batch D11). As one can see from the table of the EDS results, this sample no longer contains Mn; the measurements point to the formula sum  $\text{Cu}_6\text{Te}_2\text{O}_5\text{Cl}_4$  (containing  $\text{Cu}^{1+}$  ions). There were, however, multiple needles of this stoichiometry in different sets of batches, which proves that this phase is a stable one. Unfortunately, we only discovered it during the last week of my stay so there was no time to improve the size and the amount of the crystals by varying the ratio of the starting chemicals.

As a by-product, we got large amounts of green needles with the formula sum  $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$ , making it probably the most stable phase. This compound was first reported by Dr. Johnsson et al.<sup>2</sup>.

Due to the limited amount of time it was only possible to determine the structure of one small crystal piece via XRD. Still, the crystal gave a good enough signal. The corrected formula sum according to the XRD measurements results in  $\text{Cu}_4\text{CuTe}_2\text{O}_6\text{Cl}_5$  (with a mixture of  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$ ; space group P21/c and the cell parameters  $a = 6.4007(4) \text{ \AA}$ ,  $b = 9.3504(5) \text{ \AA}$ ,  $c = 20.9645(11) \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 90.017(5)^\circ$ ). In fig. 1 and 2 we can already make out some constricted structural features as the chlorine ions act as terminating species.

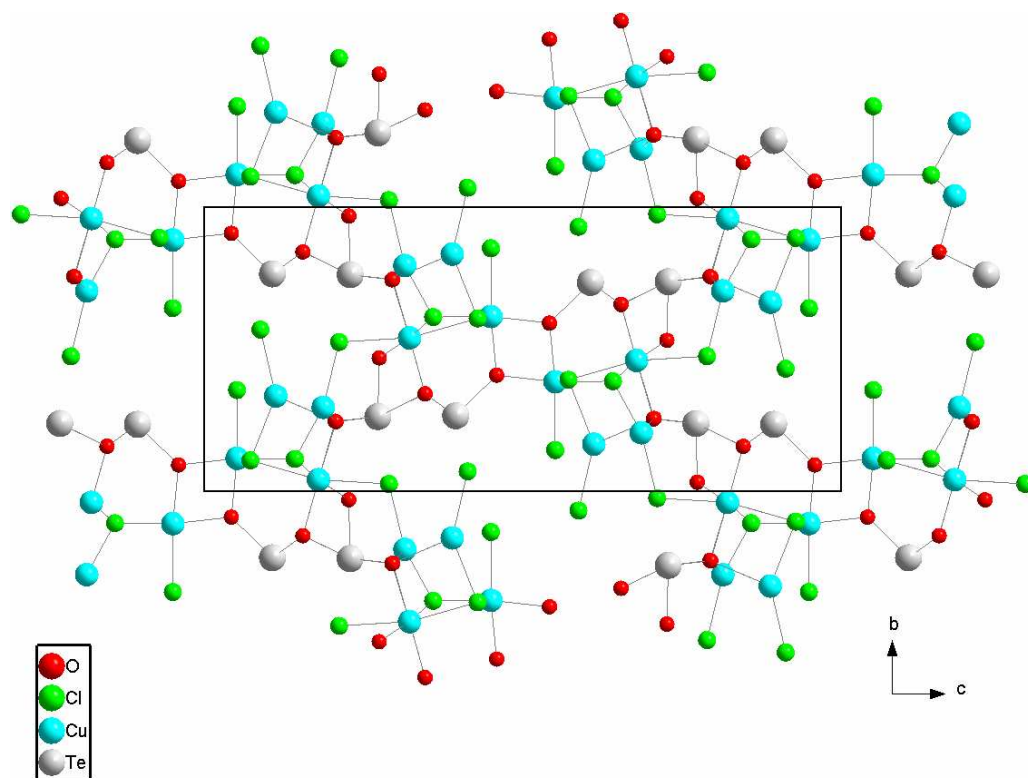


Fig. 1: bc-plane of the  $\text{Cu}_4\text{CuTe}_2\text{O}_6\text{Cl}_5$  compound.

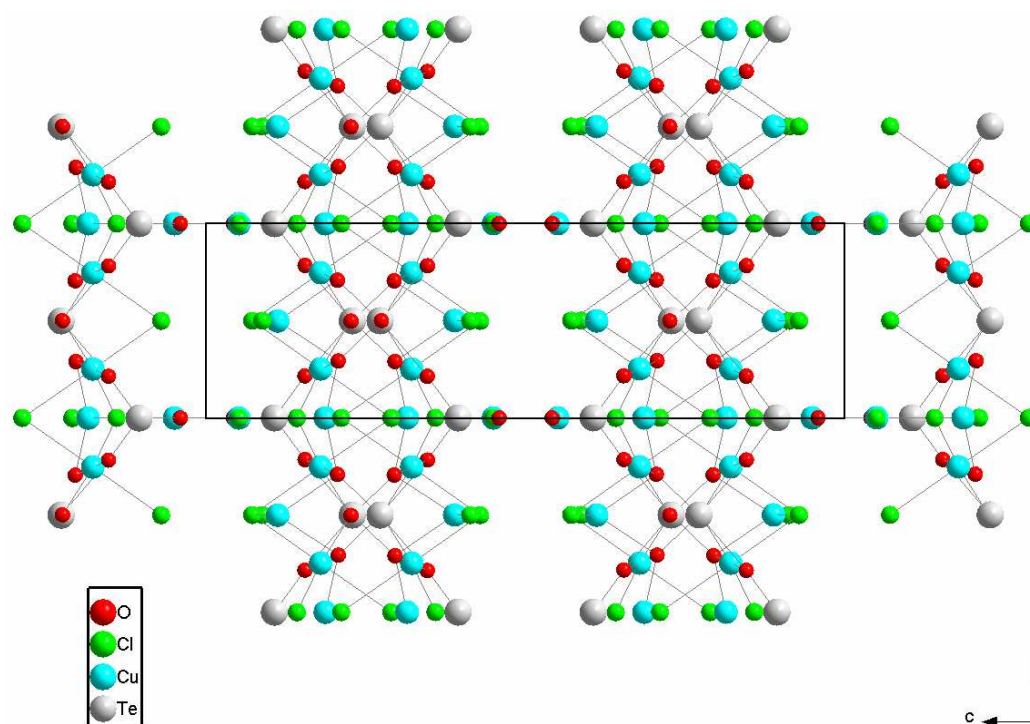


Fig. 2: ac-plane of the  $\text{Cu}_4\text{CuTe}_2\text{O}_6\text{Cl}_5$  compound.

### **Future collaboration with host institution (if applicable)**

As a future collaboration we will try to increase the size of the crystals by adding chlorine gas as a reaction agent to the quartz tubes before sealing them. Also, we will shift the focus completely to the  $\text{Cu}_4\text{CuTe}_2\text{O}_6\text{Cl}_5$  composition.

In addition to that, our group in Braunschweig will continue to perform Raman measurements on similar compounds synthesized by Dr. Johnsson's Group.

### **Projected publications/articles resulting or to result from your grant**

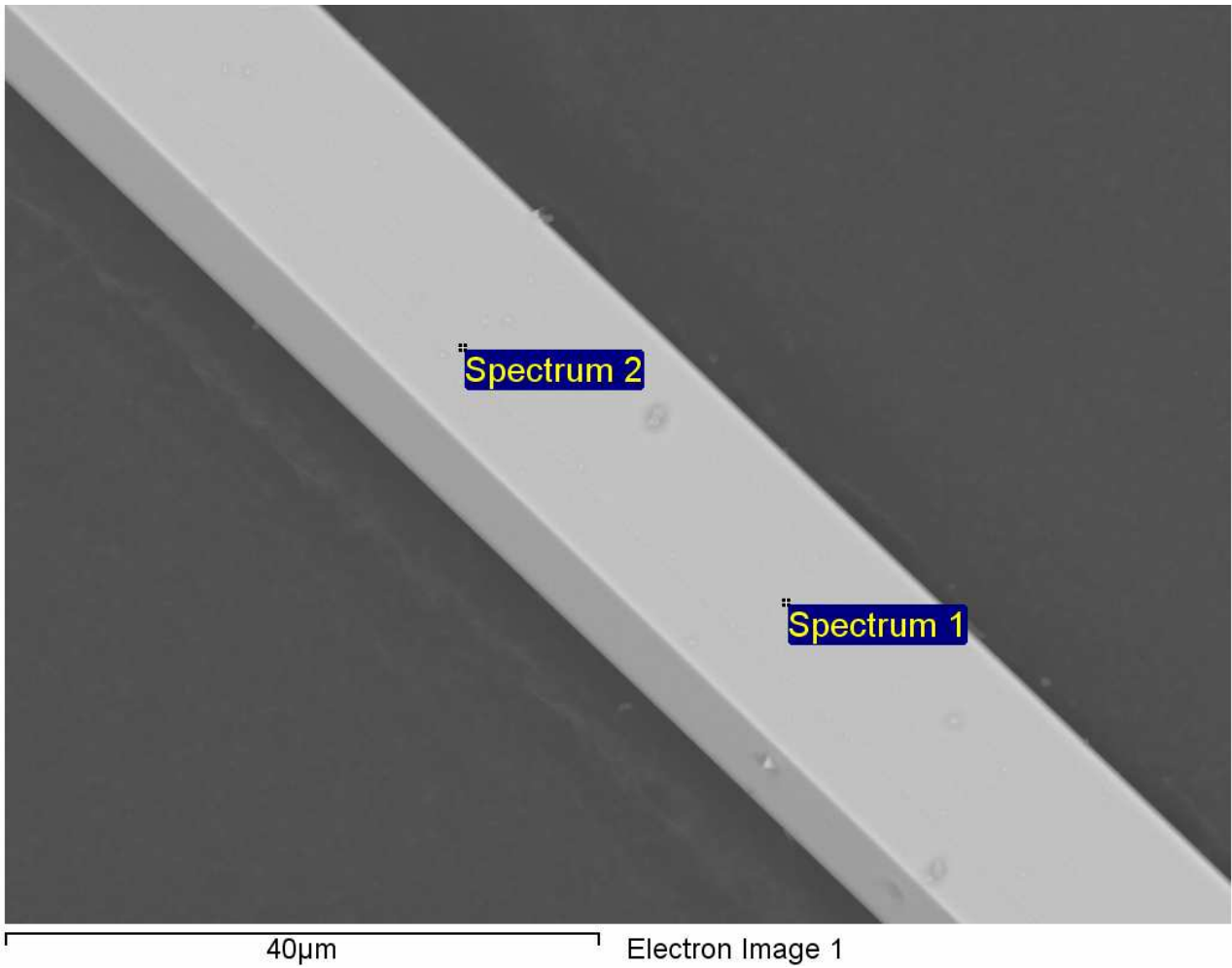
Raman measurements are still to be performed on the large enough crystal needles in Braunschweig. Furthermore, SQUID measurements are a likely addition. Depending on the final outcome and quality of these measurements, a publication of our results is to be expected.

### **Other comments**

I would like to thank Dr. Johnsson very much for making my visit to his group possible and for giving me an insight into crystal growth and the chemical aspect of low dimensional systems. Furthermore, many thanks are due to Dr. Zhang who spent much of his time assisting me with my experiments and teaching me sample characterization techniques.

### **References**

- [1] Rie Takagi, Mats Johnsson; Crystal Structure Communications; **2005**, C61, i106-i108.
- [2] Mats Johnsson, K. W. Törnroos, F. Mila, P. Millet; Chem. Mater. **2000**, 12, 2853-2857.



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	Cl	Cu	Te
Spectrum 1	Yes	35.09	47.82	17.08
Spectrum 2	Yes	34.81	48.71	16.48
Mean		34.95	48.27	16.78
Std. deviation		0.20	0.63	0.43
Max.		35.09	48.71	17.08
Min.		34.81	47.82	16.48

All results in atomic%