



	Experiment title: Chemical disorder on the mixed atomic sites in the ternary μ -phase $Zr_{30}Nb_{20}Al_{50}$ determined by resonant X-ray powder diffraction.	Experiment number: 01-01-620
Beamline: BM01B	Date of experiment: from: 9-april-03 to: 11-april-03	Date of report: 30-september-03
Shifts: 6	Local contact(s): Hermann EMERICH	<i>Received at UNIL:</i>

Names and affiliations of applicants (* indicates experimentalists):

*Radovan Černý

Laboratoire de Cristallographie, Université de Genève, 24, quai Ernest-Ansermet
CH-1211 Genève 4, Suisse

* Jean-Marc Joubert

Laboratoire de Chimie Métallurgique des Terres Rares – CNRS, 2-8 rue Henri Dunant
F- 94320 THIAIS CEDEX, France

μ -phases are intermetallic compounds belonging to the Frank-Kasper family. They are formed between transition metal elements at compositions close to A_6B_7 ($A=Nb, Ta, Mo, W$; $B=Fe, Co, Ni, Zn$). The fully ordered crystal structure of the μ -phases is: space group $R-3m$, $a \sim 5 \text{ \AA}$, $c \sim 29 \text{ \AA}$, A in $6c1, 6c2, 6c3$; B in $3a, 18h$. However, non stoichiometry and large homogeneity domains characterize those phases. We are involved in the determination of the atomic occupancies in binary compounds as a function of the composition. Rare examples of pure ternary (i.e. not existing in any of the constituting binary systems) μ -phases exist, among which μ - Zr-Nb-Al is the unique example involving Zr. Aluminium distribution among the five sites can be obtained unambiguously from conventional powder X-ray diffraction data. But the determination of Nb and Zr distribution is only possible by using at least one additional diffraction data set with different diffraction contrasts between Nb and Zr. However, Nb and Zr have the particular feature of presenting both similar X-ray atomic scattering factors ($Z_{Zr} = 40$, $Z_{Nb} = 41$) and similar coherent scattering lengths for neutrons ($b_{Zr} = 7.16$, $b_{Nb} = 7.05$), preventing the use of neutron diffraction as a second diffraction data set. The resonant X-ray diffraction using the effect of anomalous dispersion is the only solution. By measuring a powder diffraction pattern at a wavelength close to the absorption edge of one element, this technique helps to enhance the diffraction contrast between neighboring elements in the periodic table. We have already successfully applied it to the determination of occupancy parameters in complicated cases [1,2].

Three powder diffraction data sets have been measured: one far above the Zr and Nb absorption K-edge (24 keV) and the others 8 eV below Zr (18 keV) and Nb (19 keV) K-edges. Measurements of the fluorescence signal has been performed allowing us to derive the exact value of f'' by the use of Kramers-Krönig relationships. The data analysis is performed by joint Rietveld refinement of the three data sets.

Figure 1 shows the values of f' and f'' of Zr and Nb around the two K-edges as a function of energy. Those data have been derived from the absorption data measured via the fluorescence signal. Kramers-Krönig transformation was obtained by using the program CHOOCH (<http://babinet.globalphasing.com/people/gwyndaf/Chooch.html>). The obtained values at the energy actually used are $f'_{\text{Zr}} = -7.4$ e at the Zr edge, $f'_{\text{Nb}} = -7.5$ e at the Nb edge. Detailed Rietveld analysis is underway. We will particularly consider the effects on the accuracy of refining together the three patterns compared to the refinement of two patterns which are normally sufficient to obtain the two occupancy factors on each site. The distribution of the atoms on the available atomic sites obtained for the μ -phase in the system Zr-Nb-Al will be compared to the results already obtained on binary compounds (Nb-Ni [3], Ta-Ni, Mo-Co, W-Fe) by conventional X-ray diffraction and to those which will be obtained by joint refinement from X-ray and neutron diffraction data measured on ternary compounds (Nb-Ni-V and Nb-Ni-Al). Occupancy factors will be correlated to the nature of the element, its valence, its atomic radius, interatomic distances and coordination number of the site. This knowledge yields a better understanding of the phenomena governing the occupancy of a given atomic site by a peculiar atom, not only for the μ -phases, but also generally for all Frank-Kasper phases.

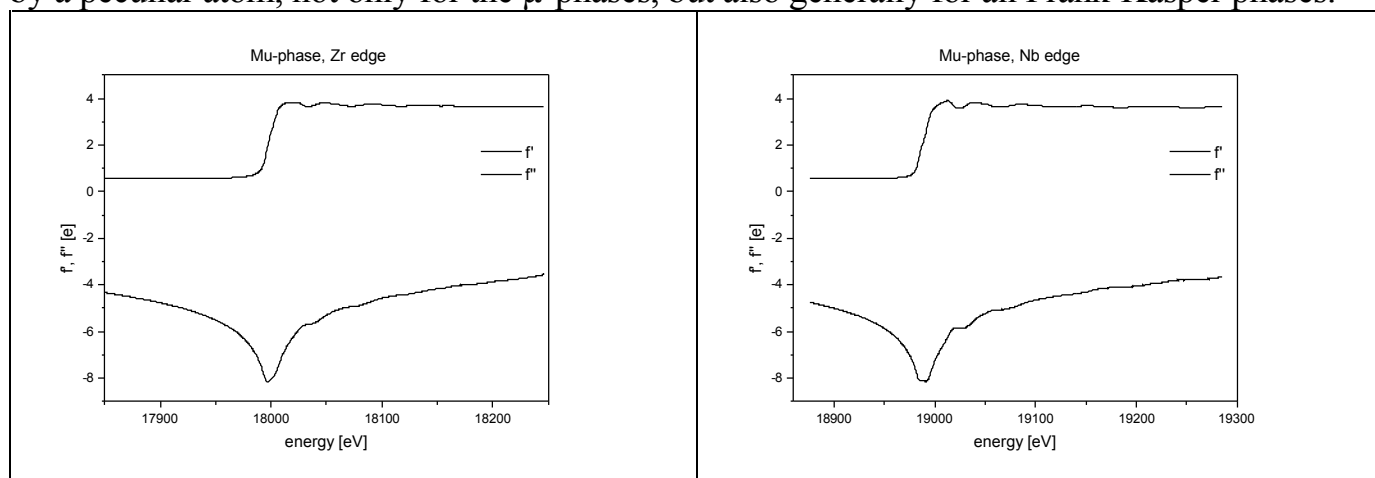


Figure 1: f' and f'' values derived from the Kramers-Krönig transformation of absorption data for Zr and Nb at their respective edges.

- [1] J.-M. Joubert, R. Černý, M. Latroche, A. Percheron-Guégan and K. Yvon, "Site occupancies in LaNi₅ three-substituted compound determined by means of multiwavelength X-ray powder diffraction.", *J. Appl. Crystallogr.*, **31** (1998) 327-332.
- [2] M. Latroche, J.-M. Joubert, A. Percheron-Guégan and P. H. L. Notten, "Crystal structure of non-stoichiometric copper substituted AB₅-type compounds studied by neutron and synchrotron anomalous powder diffraction", *J. Solid State Chem.*, **146** (1999) 313-321.
- [3] J.-M. Joubert and Y. Feutelais, "Contribution of the Rietveld method to non-stoichiometric phase modeling. Part II: γ -Ti₅Te₃ and μ Nb-Ni as experimental examples", *Calphad*, **26** (3) (2002) 427-438.