ESRF	Experiment title: **Electronically-induced structural changes across the metal-to-insulator transition** of $RNiO_3$ (R=Sm, Eu, Gd, Dy)	Experiment number: **CH-422**
Beamline: **BM16**	Date of experiment :from: **31-Jan-98** to: **5-Feb-98**	Date-rep: **27-Aug-98**
Shifts: **1 2**	Local contact(s): **Eric DOORYHEE**	*Received at ESRF:* 3 1 AOUT 1998

Names and affiliations of applicants (* indicates experimentalists):

Dr. Miguel A. G. Aranda" Universidad de Malaga, Spain **g_aranda@uma.es**
Dr. Jose A. Alonso* ICMM - CSIC, Madrid, Spain **jalonso@fresno.csic.es**
Dr. Xavier Turrillas* IETCC - CSIC, Madrid, Spain **turrillas@ietcc.csic.es**

Report:

The main objective of this study is to characterise the very subtle structural changes in $RNiO_3$ materials across the metal-to-insulator transition. To do that, several powder diffraction patterns at selected temperatures (standard heated air furnace) in capillaries (borosilicate, ϕ =0.5 mm) with a short wavelength (0.518056(3) A) to minimise the absorption (due to the lanthanide cations) were collected. For high-T patterns the beam was 4 mm wide to avoid temperature gradients on the samples. For RT patterns (16 ºC) a wider beam (8 mm) was used to collect the patterns quicker.

There were no problems with the beam, optic, diffractometer and furnace (!) and many extremely good patterns were collected. **Si** to calibrate λ; **R=Sm: rt***; **R=Eu: rt***, 155, 165, 170*, 175, 185, 193, 200*, 205, 215, 225, 350"; **R=Gd: rt",** 180, 200, 220*, 225, 235, 240*, 245,270,290; **R=Dy: rt*; R=Ho: rt", 200,265,285,295,300,305,315,335,400;** and **R** = Y: rt*, 240, 270,280*, 290,300,310,320,330*, 340,360. The marked patterns were recorded with good statistics to carry out full structural Rietveld refinements (3 h at RT and 6.5 h at high-T). The other patterns were collected for 30 min to study the evolution of the unit cell parameters with T. The patterns were initially analysed with GSAS on site (at "almost" real time) to check the transition temperatures. Very good agreement between our T_{MI} from DSC and the T_{MI} from the powder data with the calibrated furnace was found (always inside 5 ºC).

We have observed for *the* first time, a *symmetry change* at the M-I transition in $RNiO_3$ materials **(R=Ho** and Y). These samples are orthorhombic when metallic but changes to monoclinic when insulator (Figure 1). Two powder patterns for R=Ho (above and below T_{MI}) are presented in Figure 1 and the unit cell parameters vs. T in Figure 2. Furthermore, previously unsuspected *changes in microstructructure are* also observed across M-I transition as shown in Figure 1 for R=Gd. The Rietveld fits for most of the patterns are finished, and we are in the process to write up the publications.

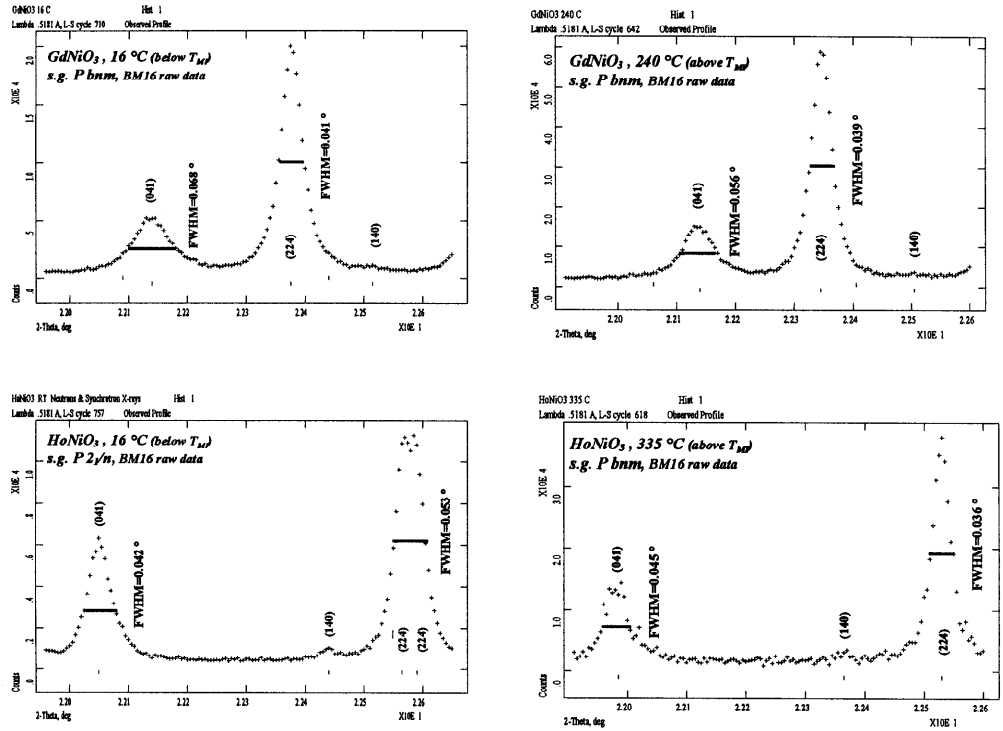

Figure 1. Selected raw data of $RNiO_3$ (R=Gd, Ho) showing the changes across the M-I transition in symmetry (R=Ho) and in microstructure (R=Gd)

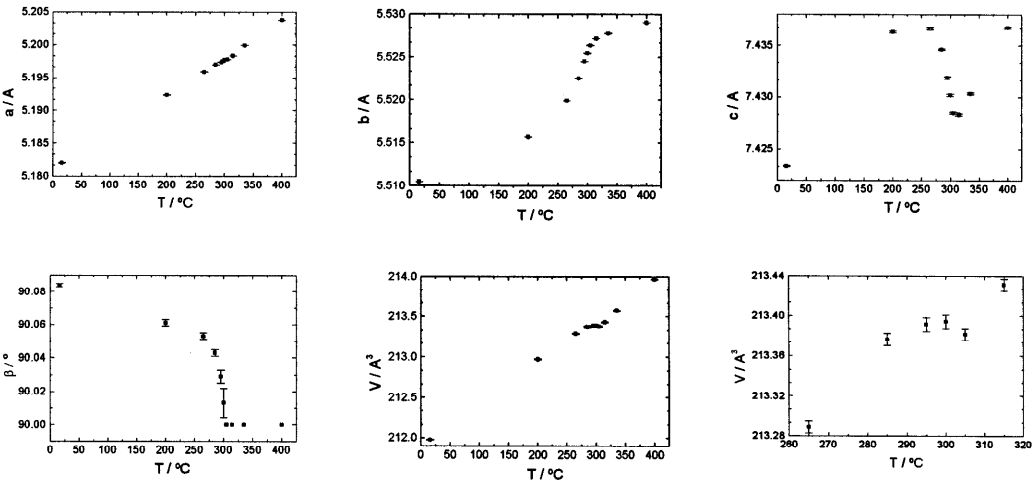

Figure 2. Unit cell parameters vs. T for **$HoNiO_3$** across the M-I transition. To be noted that the *overall change* in c-axis is smaller than 0.001 *Å*, and in β angle than 0.09 *°* !!!

The high resolution from BM16 has been essential to determine these very subtle changes