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Gabriela Aurelio^a

^a CONICET, Laboratory of Magnetic Resonances, Centro Atómico Bariloche, Av. Bustillo 9500, S. C. de Bariloche, Argentina

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Studies in materials science and magnetism at Centro Atómico Bariloche using neutron powder diffraction

GABRIELA AURELIO

CONICET, Laboratory of Magnetic Resonances, Centro Atómico Bariloche, Av. Bustillo 9500, S. C. de Bariloche, Argentina

Introduction

Neutron powder diffraction (NPD) has been a fundamental tool in our group's research for the past 15 years. It has provided insight into various crystallographic and thermodynamic aspects of metastable phases in physical metallurgy problems, which were not possible to assess using more traditional methods such as X-ray or electron diffraction. After joining the Laboratory of Magnetic Resonances, NPD turned fundamental to study the magnetic order in the complex magnetic oxides that were being studied, complementing other *in-house* techniques such as magnetometry, magneto-transport, ESR and microscopies. In the following, the main results of our research based on NPD will be over-viewed, and our perspectives for the project of a regional Neutron Scattering Facility will be outlined.

Crystallography of metastable phases in Zr-Nb and Ti-V alloys

The transition metals Ti, Zr and Hf crystallize at high temperature in the bcc (β) phase, which transforms upon cooling into an hcp (α) phase. When alloys of these elements are quenched from high temperature, three metastable phases may be formed, *viz.*, a martensitically formed α phase, the untransformed β phase and the so-called Ω phase (Figure 1). Since its first observation in 1954 [1], the Ω phase has been one of the most intensively studied metastable phases, due to its profound influence over the physical properties of alloys. Whereas in some cases the formation of Ω is to be avoided because it may cause hardening and embrittlement upon aging [2], in some other cases the phase may act as a nucleation point finely dispersed in the α matrix, improving the thermo-mechanical properties of β -alloys [3]. Omega has also been reported to influence the superconductor properties

in Ti and Zr alloys [4]. The applications of Ti and Zr alloys range from surgical and other medical applications, to components in nuclear reactors, in which the operation conditions may result in the formation of unwanted metastable phases [5]. It is therefore of fundamental interest to study the structural properties and relative stability of metastable phases in these alloys. In our group, the Zr-Nb and Ti-V systems were intensively studied. Neutron diffraction experiments were conducted over several years, studying the atomic ordering in the Ω phase, the composition dependence of interatomic distances in the

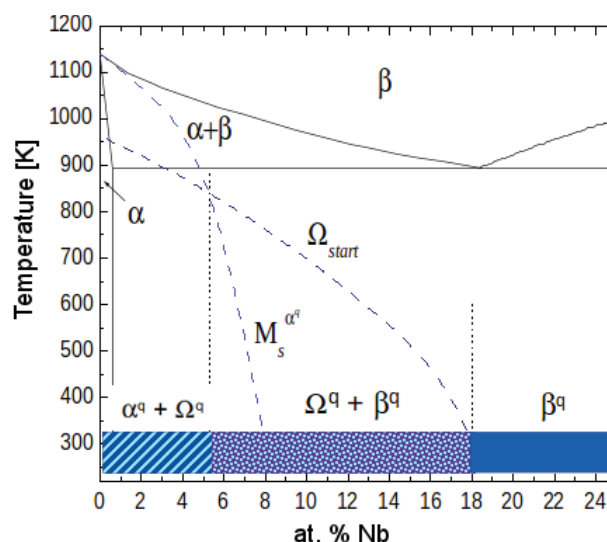


Figure 1. Zr-rich range of the binary phase diagram of Zr-Nb [13]. Solid lines correspond to the equilibrium phase diagram, whereas dashed lines represent the temperatures of the martensitic transformation $\beta \rightarrow \alpha$ (M_s^{α}) and the $\beta \rightarrow \Omega$ (Ω_{start}) transformation. The coloured regions indicate the constitution of alloys quenched ("q") from the high-temperature β phase, studied in our work (from Reference [12]). Image courtesy of Gabriela Aurelio.

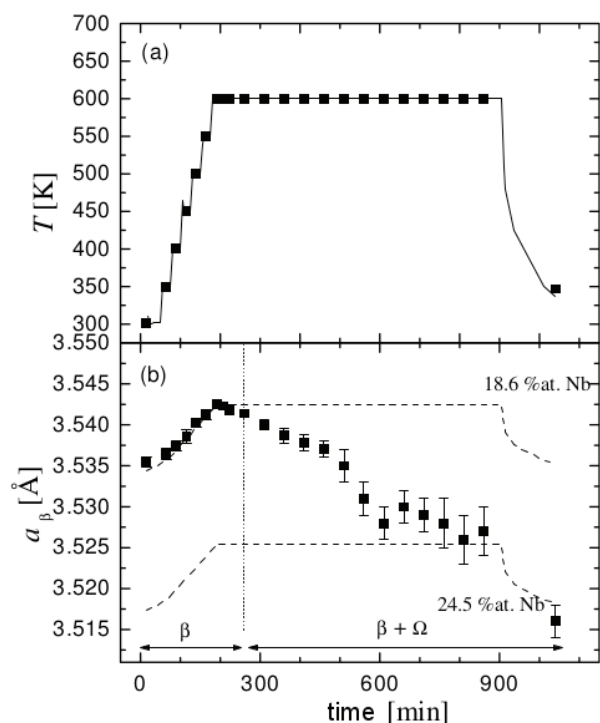


Figure 2. (a) *In situ* thermal treatment for a sample with 18.6 at.% Nb. Symbols represent the temperature of the sample every 5 min. intervals. Diffractograms were summed up every 5 minutes to improve statistics. (b) Lattice parameter of the β phase from NPD, as a function of the elapsed time. The dashed lines represent a reference behaviour established in our work, relating cell constants and composition of the metastable phases. The initial and final Nb content of the 18 at.% Nb alloy aged at 600 K for 15 h was thus determined (from Reference [12]). Image courtesy of Gabriela Aurelio.

metastable phases, and generating a reliable experimental database which is a valuable tool for the modelling of binary, ternary and higher-order alloy phase diagrams. With such data, a series of issues were analysed related to the structure, relative stability, and phase relations in the alloys and its constitutive elements [6–12].

The effect of composition upon the lattice parameters of the metastable phases was combined in a consistent way with a critical analysis of structural and thermophysical data on the metastable phases of the pure elements Ti and Zr. The relative stability of the metastable quenched phases in Zr-Nb alloys, and its evolution towards thermodynamic equilibrium, were studied combining neutron thermodiffraction and analytical electron microscopy techniques. Structural properties of the alloys were determined as a function of temperature, time and composition. A method of analysis was applied to the data involving a reference behaviour based on the composition

and temperature dependence of the lattice parameters, leading to a consistent picture of the isothermal reactions occurring at high temperature which involve composition changes both in the Ω and β phases (Figure 2). To sum up, the results obtained using a state-of-the-art technique never applied before to study the Ω phase, proved the advantages of using neutron diffraction experiments to gain insight into the stable and metastable phase diagrams in alloys. Over the years, we extended these studies to explore the martensitic Fe-Mn-Si system [14] and lead-free solder candidate Cu-Sn-In [15,16].

Crystallography and magnetism in cobalt oxides

Cobalt-oxide based materials attracted considerable interest in the last decades because they were expected to exhibit similar properties to those in the manganites and cuprates. Indeed, it was found that they present additional tunable features, as the cobalt spin state that add to their complexity but also make them even more fascinating and challenging. Among cobalt oxides, the layered compounds $R\text{BaCo}_2\text{O}_{5+d}$ (R = rare earth, $0 < d < 1$) with a perovskite-based structure were studied by our group since 2006. The oxygen non-stoichiometry in these compounds (d) controls the mixed valence state of Co ions. Several factors strongly influence their physical properties: the nonstoichiometry, the R -cation size, the vacancies order, and the structural disorder introduced by doping with small quantities of smaller cations.

As a part of a long-term research project, we synthesized and studied the cobaltites $\text{YBaCo}_2\text{O}_{5.5}$, $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)\text{Co}_2\text{O}_{5.5}$ and $\text{Y}(\text{Ba}_{1-x}\text{Ca}_x)\text{Co}_2\text{O}_{5.5}$. We observed that even a small addition of Sr and Ca in the Ba-site (10%) produces a dramatic effect on the magnetization of the samples, on the Seebeck coefficient and on the electrical resistivity [17]. We performed very detailed neutron diffraction experiments at the ILL [18] from which we found that in samples substituted with Ca, the magnetic arrangements of Co ions are drastically modified: the AFM (antiferromagnetic) long-range order is destroyed, and a ferrimagnetic phase with spin-state-order (SSO) is stabilized below 290 K. For the sample with $x_{\text{Ca}} = 0.05$ a fraction of AFM phase coexists with the ferrimagnetic one below 190 K, whereas for $x_{\text{Ca}} = 0.10$ the AFM order is completely lost. Our systematic neutron diffraction studies led us to propose for the parent compound ($x = 0$) a two-phase scenario, consisting of a ferrimagnetic SSO phase transforming to an AFM phase at 250 K, accompanied by a second phase showing no ferrimagnetic order

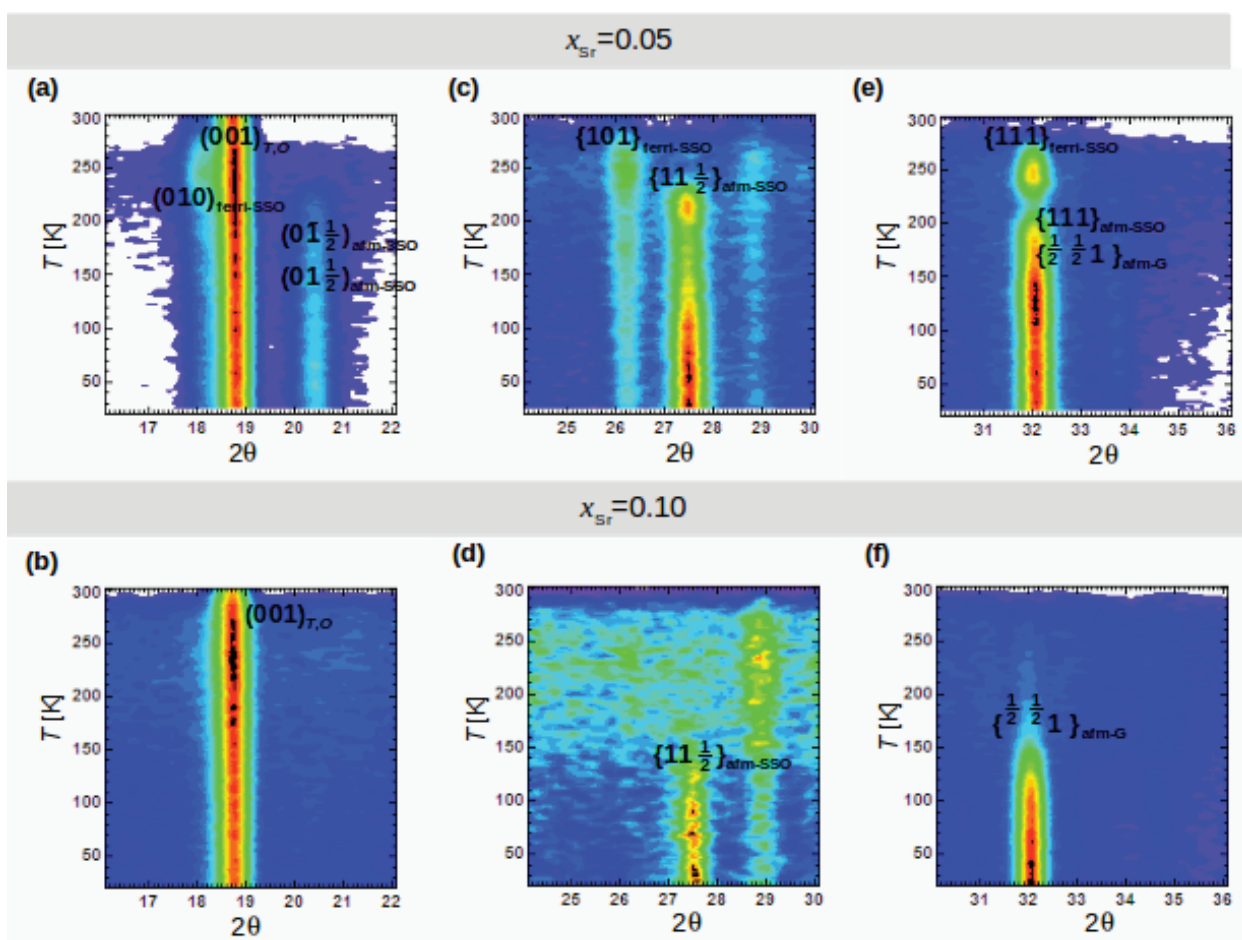


Figure 3. Projection of three selected sections of the thermodiffractograms corresponding to samples with $x_{\text{Sr}} = 0.05$ (upper panels) and $x_{\text{Sr}} = 0.10$ (bottom panels). The panels show the major magnetic reflections. Data were collected at ILL (D20) with $\lambda \sim 2.42 \text{ \AA}$ in the temperature range 20–310 K (adapted from [19]).

but a paramagnetic to AFM transition at 200 K, meaning that below 200 K the system presents the coexistence of two different AFM arrangements [18].

The study on samples substituted with Sr at the Ba-site confirmed the phase-separation scenario [19,20]. We found that Sr addition destabilizes the ferrimagnetic SSO phase, as well as the “122” order, favoring instead a tetragonal and less ordered structure (Figure 3). A key contribution of our work has been to disentangle each of the phases that coexist in the parent compound, and show how they can actually be stabilized by the local disorder introduced by Ba-site substitution. We complemented our neutron diffraction experiments with the study of local order using chemical selective tools such as synchrotron radiation XAS experiments [21].

More recently a new family of Co-rich oxides was discovered—closely related in composition—called R-114 cobaltites (the RBaCo_4O_7), which soon gained attention due to its unique topology leading to magnetic frustration. Moreover, the member with $R = \text{Ca}$ was recently found to be multiferroic [22]. Our most recent study on Sr-substituted “Ca-114” cobaltites reveals that the addition of Sr greatly influences the stability of the magnetic arrangements. It is only through NPD experiments that the identity of these arrangements could be revealed (Figure 4), giving us a clue on the relevant magnetic interactions in the system, and unveiling how their stability may be tuned using variables such as composition, magnetic field and temperature.

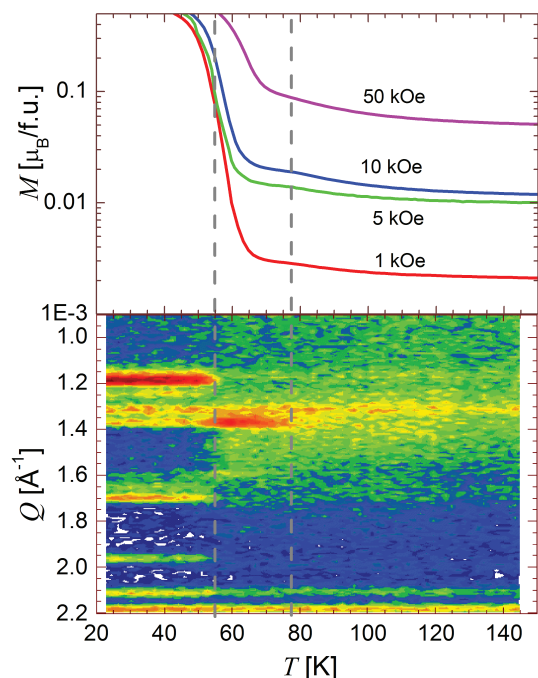


Figure 4. The upper panel shows a region of the DC magnetization curves for a sample of CaBaCo₄O₇ doped with 2at.% Sr. The different colours represent the different applied magnetic fields during a field-cooled measurement in a SQUID magnetometer. The lower panel corresponds to a projection on the Q - T space of the thermodiffractiongram for the same sample collected at ILL (D20 data @ 1.3 Å). The dashed vertical lines represent the magnetic transitions observed. Data collected by G. Aurelio, J. Curiale, G. J. Cuello, R. Sánchez in 2013, proposal #5-24-530, to be published.

Summary and perspectives

The sustained experience gained over the past decade using NPD at the D1B, D1A, D2B and D20 diffractometers of the ILL has turned us into key actors in the scenario of a possible national/regional Neutron Scattering Facility, a project to which we are strongly committed.

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