Heavy crystals: structural crystallography of heavy-element compounds

Co-Chairs: Olga V. Yakubovich (RU), Marie Colmont (FR)

Examples of Ordered or Disordered Ternary Intermetallics Containing Rare-earth Elements and Transition Metals

E. Gaudin, J.L. Bobet, S. Tencé, S. Couillaud and B. Chevalier

CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
E-mail: gaudin@icmcb-bordeaux.cnrs.fr

In the first part of the presentation, the structural and magnetic properties of a new series of intermetallics with the general formula \( \text{RE}_6 \text{M}_{1.67} \text{Si}_3 \) (\( \text{RE} = \text{Ce}-\text{Tb}, \text{M} = \text{Co}, \text{Ni} \)) [1-4] will be discussed. In these series \( \text{Gd}_6 \text{Ni}_{1.67} \text{Si}_3 \) and \( \text{Gd}_6 \text{Co}_{1.67} \text{Si}_3 \) exhibit very interesting magnetocaloric effect with the existence of an important magnetic entropy variation \( \Delta S_m \) around room temperature [3]. All these compounds crystallize with the \( \text{Ce}_6 \text{Ni}_{1.67} \text{Si}_3 \) structure type [2]. This structure type is closely related to the \( \text{Ho}_6 \text{Co}_{3.07} \) (or \( \text{Ho}_6 \text{Co}_{4.61} \)) structure type [5] with a perfect ordering between silicon and cobalt/nickel atoms. This hexagonal structure (S.G. P\( \overline{6} \)3/m) is characterized by infinite chains of face-shared trigonal prisms [\( \text{RE}_6 \)] filled by Si or M atoms. Theses chains are running along the c-axis and extend as triangular columns by sharing rectangular faces in the (a, b)-plane. Between these columns infinite chains of face-shared [\( \text{RE}_6 \)] octahedra are partially filled by M-atoms (Fig. 1). The strong delocalization of the electron density of M-atoms observed in these latter chains has been attributed to strong steric strains (Fig 1). This behavior was also observed in the homologous binary compound \( \text{Gd}_6 \text{Co}_{4.85} \) [6].

In the second part, the discovery of two new Mg-rich phases in ternary systems RE-M-Mg (RE = La, Gd, and M = Ni, Cu) will be presented. \( \text{LaCuMg}_8 \) [7] crystallizes in the \( \text{La}_2\text{Mg}_{17} \) structure type (S.G. P\( \overline{6} \)3/mmc) with the lattice parameters \( a = 10.1254(2) \) and \( c = 10.0751(2) \) Å. A disordered structure is observed with a random distribution of Cu atoms on some La and Mg positions. The structure of the second phase, \( \text{Gd}_{13} \text{Ni}_9 \text{Mg}_{78} \) [8], was not fully determined because of a medium crystallinity. The structure was partially deduced using TEM and an average cubic structure with lattice parameter \( a = 4.55 \) Å could be assumed. A modulation along both \( a^* \) and \( b^* \) axis with vectors of modulation \( q_1 = 0.42a^* \) and \( q_2 = 0.42b^* \) was observed. Because of the high amount of magnesium, the hydrogen absorption properties of these new phases were studied.

Figure 1: Structure of Ce\( _6 \text{Ni}_{1.67} \text{Si}_3 \). Left: Projection along the c-axis. Right: Fourier-map showing the strong delocalization of the electron density within the chains of face-shared octahedra

Figure 2: Left: Structure of LaCuMg\( _8 \). Right: Electron diffraction pattern of Gd\( _{13} \text{Ni}_9 \text{Mg}_{78} \)

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