# RELATIONSHIP BETWEEN CHEMICAL COMPOSITION AND MAGNETIC ORDER IN THE Ce-Ni-Ge SYSTEM

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Unusual properties are often observed at low temperatures for intermetallic Ce compounds, leading to Kondo systems, either magnetic or not, Intermediate Valence and/or Heavy Fermion properties… These ground state properties are governed by the $J_{cf}$ interaction between spins of localized 4f(Ce) electrons and conduction electrons, via a competition between Kondo and RKKY (Ruderman-Kittel-Kasuya-Yosida) interactions, resulting either in the quenching of the 4f (Ce) ion magnetic moment (Kondo interaction) or in the occurrence of long-range magnetic order for 4f (Ce) ion magnetic moments (RKKY interaction). A systematic study of magnetic properties was then investigated in the ternary Ce-Ni-Ge system, for which more than 20 stoechiometric compounds were known to exist, in order to connect chemical composition and magnetic properties. Both macroscopic (magnetic susceptibility, electrical resistivity, specific heat measurements) and microscopic techniques (X-ray and neutron diffraction, XANES) were used in order to characterise the magnetic state of the systems.

Structural similarities can be found in the series. A set of such similarities is illustrated in Figure 1 for $Ce_2NiGe_6$, $CeNiGe_3$, $CeNiGe_2$ and $Ce_3Ni_2Ge_7$ compounds: the orthorhombic crystal structures of $CeNiGe_3$ and $Ce_3Ni_2Ge_7$ for instance have identical stackings of a $[Ce_4Ge_4]$ antiprism, a $[Ce_6]$ trigonal prism and another $[Ce_4Ge_4]$ antiprism, along the longest crystallographic axis. These sequences are separated either by a $[Ge_8]$ cube in $CeNiGe_3$ or by a $[Ge_{12}]$ cubooctahedron in $Ce_3Ni_2Ge_7$. Going from $CeNiGe_3$ to $Ce_3Ni_2Ge_7$ is then due to the insertion into the $[Ge_8]$ cube of the $CeNiGe_3$ crystal structure of an atomic plane, containing Ce and Ge atoms. Let us notice then that if only one crystallographic site is available for Ce in $CeNiGe_3$, two are now available in $Ce_3Ni_2Ge_7$, adding a "new" Ce position (hereafter referred as Ce1) within the $[Ge_{12}]$ cubooctahedron to the Ce "initial" position (Ce2), common to $[Ce_6]$ and $[Ce_4Ge_4]$ polyhedra,



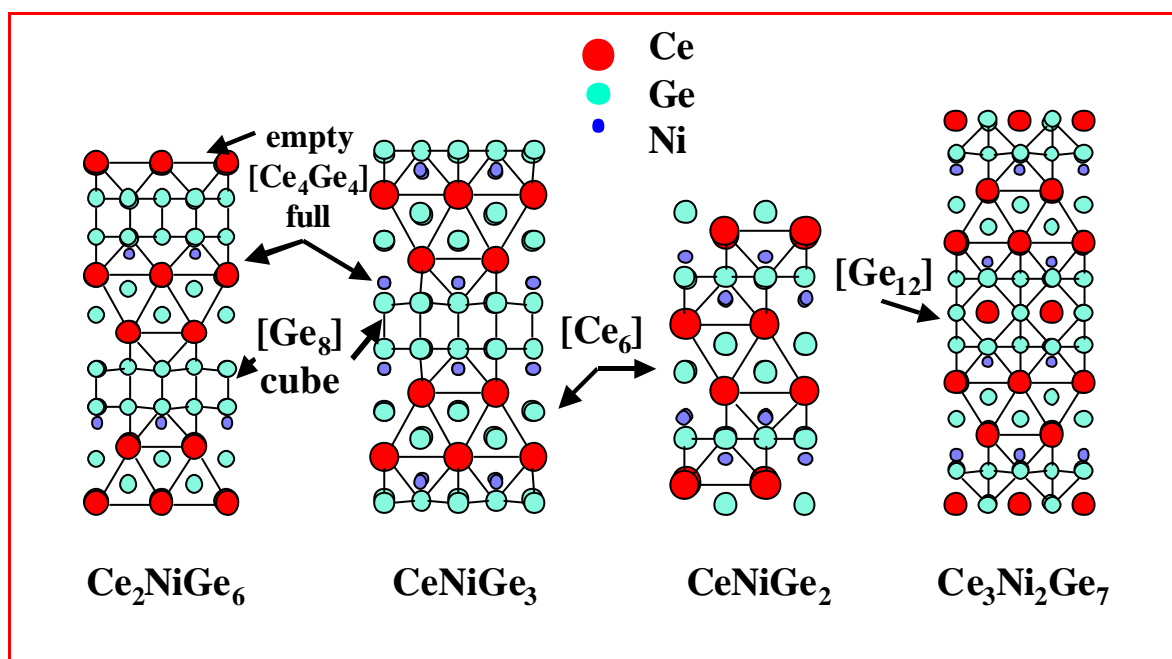Figure 1. Crystal structures of $Ce_2NiGe_6$, $CeNiGe_3$, $CeNiGe_2$ and $Ce_3Ni_2Ge_7$. The elementary polyhedra are shown: $[Ce_4Ge_4]$ antiprisms, $[Ce_6]$ trigonal prisms, $[Ge_8]$ cubes and $[Ge_{12}]$ cubooctahedrons.

From magnetic measurements we know that the Ce-Ni-Ge ternary germanides, with more 50 Ge-atomic %, are antiferromagnetic, with Néel temperatures $T_N$ decreasing with Ge-content: $Ce_2NiGe_6$ ($T_N$=10.4(2) K), $Ce_3Ni_2Ge_7$ ($T_N$=7.2(2) K), $CeNiGe_3$ ($T_N$=5.5(2) K), $Ce_2Ni_3Ge_5$ ($T_N$=4.8(2) K or 5.1(2) K and $CeNiGe_2$ ($T_N$=3.9 K). In this composition range however, $Ce_2NiGe_3$ exhibits spin glass properties, in connection with its hexagonal crystal structure ($AlB_2$-type), clearly different from the above described crystal structures.

All the corresponding magnetic structures have been obtained via neutron powder diffraction.

$Ce_2NiGe_6$, $Ce_3Ni_2Ge_7$ and $Ce_2Ni_3Ge_5$ show collinear antiferromagnetic structures, while $CeNiGe_3$ possesses more complex magnetic properties, with both commensurate and incommensurate magnetic structures coexisting at 1.4 K. The commensurate magnetic structure of $CeNiGe_3$ must be compared to that of $Ce_3Ni_2Ge_7$ (Fig. 2). In the latter compound, the Ce1 atoms do not carry any ordered magnetic moment. As a consequence, these two magnetic structures are identical and can be described by antiferromagnetic stacking of ferromagnetic layers of trigonal [$Ce_6$] prisms [2].



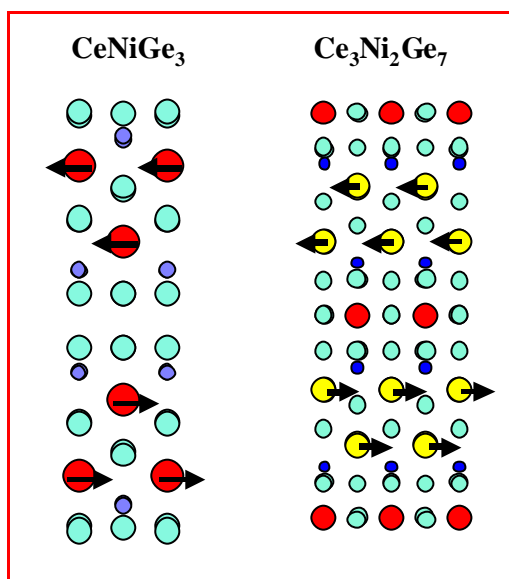Figure 2. Commensurate $Ce_3Ni_2Ge_7$ and $CeNiGe_3$ magnetic structures.

As the Néel temperatures $T_N$ are decreasing with Ge-content, so the value of the Ce-magnetic moments at 1.4K, with $M_{Ce} = 1.98(7)\mu_B$ in $Ce_3Ni_2Ge_7$, $M_{Ce} = 0.8(2)$ $\mu_B$ in $CeNiGe_3$ and $M_{Ce} = 0.4(1)\mu_B$ in $Ce_2Ni_3Ge_5$. This decrease of Ce-magnetic moment reflects the increasing strength of Kondo interaction, when going from $Ce_3Ni_2Ge_7$ to $Ce_2Ni_3Ge_5$, a result confirmed by specific heat measurements on $Ce_2Ni_3Ge_5$ showing that the Kondo temperature $T_K$ for this stoechiometry is of the same order of magnitude as $k_B T_N$.

On the contrary, the Ni-rich compounds ($\geq$ 50 Ni-at. %) don't show any long range magnetic order. $CeNi_{4.25}Ge_{0.75}$ is an intermediate valence compound. $CeNi_9Ge_4$ shows heavy fermion properties with $\gamma$=1.2 J/mol$^{-1}$K$^{-2}$.

The Ce-Ni-Ge germanides at the borderline between the two families, which have been described above, namely $CeNi_2Ge_2$, $Ce_3Ni_4Ge_4$ and CeNiGe, show an intermediate valence behaviour, which is more and more pronounced as we follow the sequence $CeNi_2Ge_2 \rightarrow Ce_3Ni_4Ge_4 \rightarrow CeNiGe$ [2].

The magnetic properties of intermetallic Ce-Ni-Ge compounds have then been investigated, in connection with the stoechiometry and the crystalline geometrical environment of Ce ions. The above work is associated to Laurence Durivault's PhD, defended at Bordeaux University, on November 2002, 4th.

## References

[1] L. Durivault et al., J. Phys.: Condens. Matter, 15 (2003) 77-90.
[2] L. Durivault et al., Acta Physica Polonica B, 34 (2003) 1393-1397.