# THE Ce–Ni–Ge SYSTEM: RELATIONSHIP BETWEEN CHEMICAL COMPOSITION AND MAGNETIC ORDERING*

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The investigation on Ce–Ni–Ge phase diagram indicates a relationship between the physical behavior of these ternary germanides and their chemical composition. Those with more than 50 % Ge-atomic percentage order antiferromagnetically, with Néel temperatures $T_{\rm N}$ decreasing with Ge-content. The Ce-magnetic moment at 1.4 K, determined by neutron powder diffraction, also decreases with Ge-content. As for the ternary germanides rich in Ni (≥33 %), they can be classified as intermediate valence compounds (CeNiGe, $Ce_3Ni_4Ge_4$ and $CeNi_{4.25}Ge_{0.75}$) or heavy-fermions systems ($CeNi_2Ge_2$ and $CeNi_9Ge_4$).

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## 1. Introduction

A lot of investigations were reported on a series of intermetallic compounds $Ce_xT_yX_z$ (with T, a transition metal and X, a $p$ element), which crystallize often in the same type structure, where the occurrence of unusual behaviors (heavy fermion behavior, valence fluctuation, non-Fermi liquid behavior, superconductivity, Kondo systems, ...) is caused by change of elements in the composition (series with different transition metals and/or with different elements $p$). Recently Salamakha *et al.*, have identified 20 ternary germanides in the Ce–Ni–Ge system [1]. This paper summarizes our investigation devoted to the physical properties of these ternary germanides in order to determine the influence of chemical composition on the

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Ce-magnetic ground states. In particular, we present some Ce–$L_{III}$ edge X-ray absorption spectroscopy measurements.

## 2. Experimental procedures

The samples synthesis and their checking by microprobe analysis and X ray powder diffraction were described previously [2]. Excepted $Ce_2NiGe_6$ sample which contains some traces of $Ce_3Ni_2Ge_7$, all the others are single phase. The structural characterization agrees with that reported by Salamakha *et al.*, [1] but two new germanides were found: $CeNi_9Ge_4$ (tetragonal $CeNi_{8.5}Si_{4.5}$-type with $a = 0.7971(2)$ nm and $c = 1.1773(4)$ nm) and $CeNi_{4.25}Ge_{0.75}$ (hexagonal $CaCu_5$-type with $a = 0.49155(4)$ nm and $c = 0.40732(4)$ nm).

## 3. Results and discussion

For the Ce–Ni–Ge system, two chemical composition domains were determined according to the criterions that given compound exhibit magnetic ordering or not (Fig. 1).

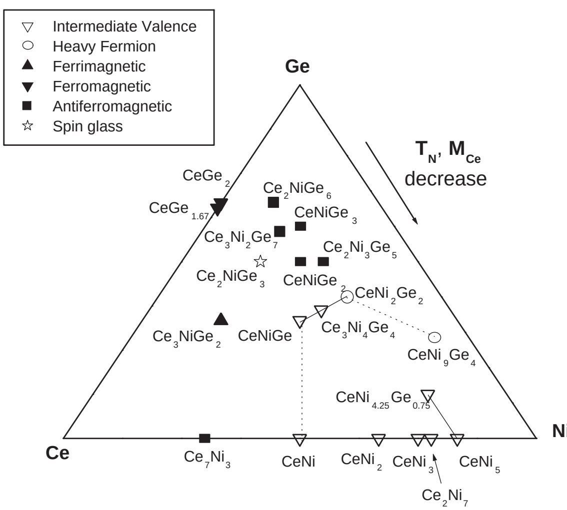


Fig. 1. Relationship between chemical composition and physical properties in the Ce–Ni–Ge system.

The magnetization measurements reveal, that the compounds containing 50 % or more of Ge order antiferromagnetically, with Néel-temperature $T_N$ decreasing practically with Ge-content: $Ce_2NiGe_6$ ($T_N = 10.4(2)$ K) [3], $Ce_3Ni_2Ge_7$ ($T_N = 7.2(2)$ K) [2], $CeNiGe_3$ ($T_N = 5.5(2)$ K) [4], $Ce_2Ni_3Ge_5$ ($T_{N1} = 4.8(2)$ [5] K or 5.1(2) K [6]) and $CeNiGe_2$ ($T_{N1} = 3.9$ K) [7]. $Ce_2NiGe_3$ is an exception in this composition range since it is considered as a Kondo lattice compound showing spin glass behavior [8]. By neutron powder diffraction, we have determined some of their magnetic structures. $Ce_3Ni_2Ge_7$ and $Ce_2Ni_3Ge_5$ present a simple collinear antiferromagnetic structure [2, 5] while $CeNiGe_3$ shows a complex magnetic behavior where commensurate and incommensurate magnetic structures coexist at 1.4 K [4]. The Ce-magnetic moment at 1.4 K decreases with Ge-content $M_{Ce} = 1.98(7)\ \mu_B$ for $Ce_3Ni_2Ge_7$, $M_{Ce} = 0.8(2)\ \mu_B$ for $CeNiGe_3$ and $M_{Ce} = 0.4(1)\ \mu_B$ for $Ce_2Ni_3Ge_5$. The magnetic properties of these compounds are connected to the valence instability displayed by Ce. It is well known that the magnetic properties of these compounds are governed by the competition between the Kondo and RKKY interactions. In this case, the Ce magnetic moment is reduced by the strength of the Kondo effect which increases from $Ce_3Ni_2Ge_7$ to $Ce_2Ni_3Ge_5$. This is confirmed by specific heat measurements on $Ce_2Ni_3Ge_5$ which suggest that the Kondo energy scale $k_B T_K$ is of the order of $k_B T_N$ [6].

On one side, $Ce_3NiGe_2$ is announced to be antiferromagnetic below 6.2 K and then ferromagnetic below 5.2 K [9]. Our results of the temperature dependence of magnetization ($M$) characterize two Curie points at 6.2(2) K and 5.7(2) K (derivative curve $dM/dT$, Fig. 2).

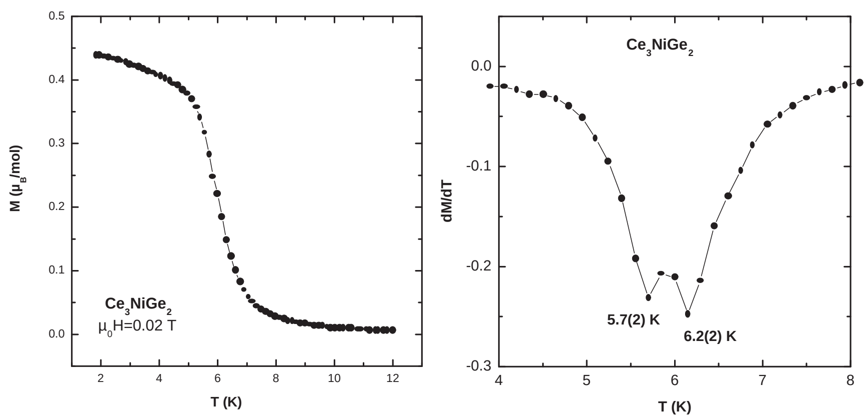


Fig. 2. Thermal dependence of the magnetization of $Ce_3NiGe_2$ (left) and the corresponding derivative curve (right).

On the other side, the compounds richer in Ni ($\geq$33 % Ni) present no magnetic ordering. The heat capacity data for $CeNi_9Ge_4$ show heavy fermion behavior with $\gamma = 1.2\,\mathrm{Jmol}^{-1}K^{-2}$ [10].

Figs. 3(a) and 3(b) show $L_{III}$ X ray absorption spectra of Ce in different ternary germanides. For $CeNi_{4.25}Ge_{0.75}$ and $CeNi_2Ge_2$, two resolved peaks at 5725 eV and 5733 eV are observed which is consistent with an intermediate valence state. Moreover, the peak at 5733 eV is less pronounced in $CeNi_2Ge_2$ than in $CeNi_{4.25}Ge_{0.75}$ and this demonstrates a more delocalized state of the $4f$ electronic shell in $CeNi_{4.25}Ge_{0.75}$ than in $CeNi_2Ge_2$. The analysis of the average valence gives $v = 3.30(1)$ for $CeNi_{4.25}Ge_{0.75}$ and 3.07(1) for $CeNi_2Ge_2$. The spectra of Fig. 3(b) have a two-peak structure, with the secondary peak becoming more and more important as we proceed along the sequence $CeNi_2Ge_2 \rightarrow Ce_3Ni_4Ge_4 \rightarrow$ CeNiGe ($v = 3.07(1)$ for $CeNi_2Ge_2$, $v = 3.08(1)$ for $Ce_3Ni_4Ge_4$ and $v = 3.18(1)$ for CeNiGe). On the contrary, the spectra of $Ce_2Ni_3Ge_5$ and $CeNi_9Ge_4$ show only one peak at 5725 eV, corresponding to a trivalent state for Ce atoms.

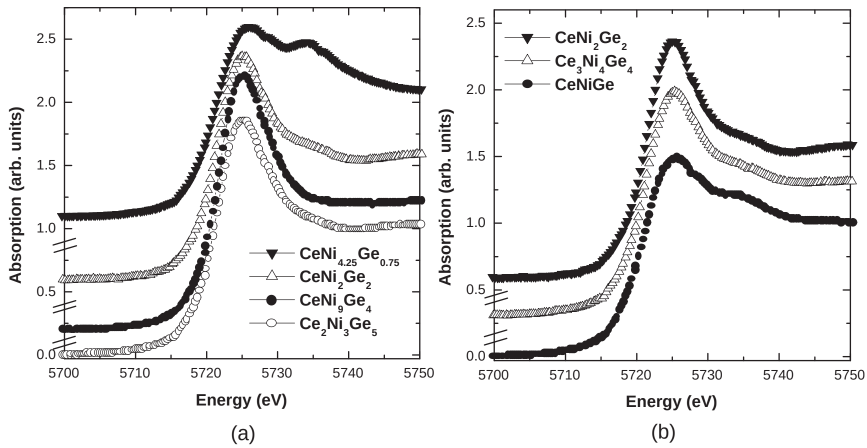


Fig. 3. Ce $L_{III}$ absorption edge at 300 K for (a) $CeNi_{4.25}Ge_{0.75}$, $CeNi_2Ge_2$ $CeNi_9Ge_4$ and $Ce_2Ni_3Ge_5$; (b) $CeNi_2Ge_2$, $Ce_3Ni_4Ge_4$ and CeNiGe (for clarity the spectra are shifted vertically).

## 4. Conclusion

We have proposed a Ce–Ni–Ge phase diagram indicating the physical behavior of ternary germanides as a function of their chemical composition. Our investigations lead to several tendencies; the compounds on the Ni-rich side ($\geq 33\,\%$ Ni) exhibit an intermediate valence state ($CeNi_{4.25}Ge_{0.75}$, CeNiGe and $Ce_3Ni_4Ge_4$) or are heavy fermion systems ($CeNi_9Ge_4$); on the Ge-rich side ($\geq$50 % Ge) ($Ce_2NiGe_6$, $Ce_3Ni_2Ge_7$, $CeNiGe_3$, $Ce_2Ni_3Ge_5$ and $CeNiGe_2$) have a trivalent Ce with a Ce ordered magnetic moment which decreases with the Ge content. The germanides at the borderline between these two domains show an intermediate valence behavior which is more and more pronounced as we follow the sequence $CeNi_2Ge_2 \rightarrow Ce_3Ni_4Ge_4 \rightarrow$ CeNiGe. These observations show a large Ce-ground states in the Ce–Ni–Ge system.

## REFERENCES

[1] P. Salamakha *et al.*, *J. Alloy. Compd.* **236**, 206 (1996).
[2] L. Durivault *et al.*, *J. Magn. Magn. Mater.* **232**, 139 (2001).
[3] B. Chevalier *et al.*, *J. Magn. Magn. Mater.* **196-197**, 880 (1999).
[4] L. Durivault *et al.*, *Appl. Phys.* **A74** [Suppl.], S677 (2002).
[5] L. Durivault *et al.*, *J. Magn. Magn. Mater.* **246**, 366 (2002).
[6] Z. Hossain *et al.*, *Phys. Rev.* **B62**, 88950 (2000).
[7] Dexuan Hua *et al.*, *Phys. Rev.* **B64**, 224405 (2001).
[8] V.K. Pecharsky *et al.*, *Phys. Rev.* **B43**, 10906 (1991).
[9] A.P. Pikul *et al.*, *Physica B* **312**, 422 (2002).
[10] P. Rogl, private communication.