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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_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 ($\geq 33\%$), they can be classified as intermediate valence compounds (CeNiGe, Ce₃Ni₄Ge₄ and CeNi_{4.25}Ge_{0.75}) or heavy-fermions systems (CeNi₂Ge₂ and CeNi₉Ge₄).

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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).

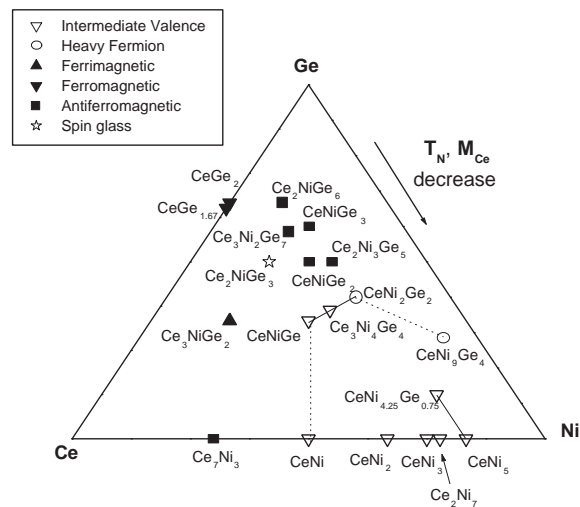


Fig. 1. Relationship between chemical composition and physical properties in the Ce-Ni-Ge system.

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. $\text{Ce}_3\text{Ni}_2\text{Ge}_7$ and $\text{Ce}_2\text{Ni}_3\text{Ge}_5$ 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 $M_{\text{Ce}} = 1.98(7) \mu_{\text{B}}$ for $\text{Ce}_3\text{Ni}_2\text{Ge}_7$, $M_{\text{Ce}} = 0.8(2) \mu_{\text{B}}$ for CeNiGe_3 and $M_{\text{Ce}} = 0.4(1) \mu_{\text{B}}$ for $\text{Ce}_2\text{Ni}_3\text{Ge}_5$. 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 $\text{Ce}_3\text{Ni}_2\text{Ge}_7$ to $\text{Ce}_2\text{Ni}_3\text{Ge}_5$. This is confirmed by specific heat measurements on $\text{Ce}_2\text{Ni}_3\text{Ge}_5$ which suggest that the Kondo energy scale $k_{\text{B}} T_{\text{K}}$ is of the order of $k_{\text{B}} T_{\text{N}}$ [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).

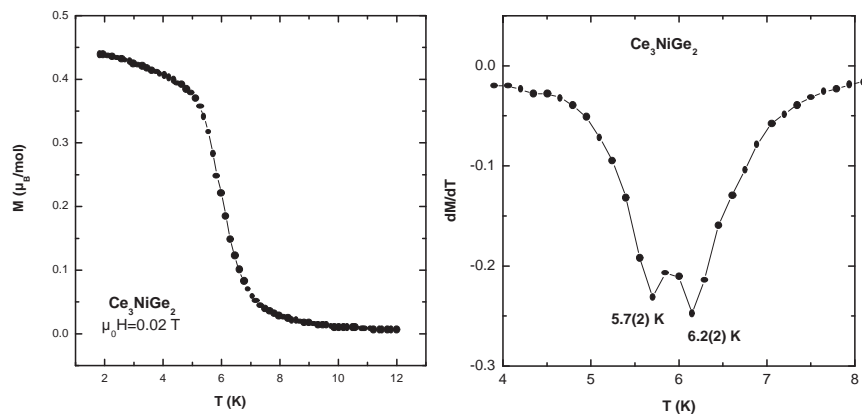


Fig. 2. Thermal dependence of the magnetization of Ce_3NiGe_2 (left) and the corresponding derivative curve (right).

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

Figs. 3(a) and 3(b) show L_{III} X ray absorption spectra of Ce in different ternary germanides. For $\text{CeNi}_{4.25}\text{Ge}_{0.75}$ 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 $\text{CeNi}_{4.25}\text{Ge}_{0.75}$ and this demonstrates a more delocalized state of the 4f electronic shell in $\text{CeNi}_{4.25}\text{Ge}_{0.75}$ than in CeNi_2Ge_2 . The analysis of

the average valence gives $v = 3.30(1)$ for $\text{CeNi}_{4.25}\text{Ge}_{0.75}$ 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 $\text{CeNi}_2\text{Ge}_2 \rightarrow \text{Ce}_3\text{Ni}_4\text{Ge}_4 \rightarrow \text{CeNiGe}$ ($v = 3.07(1)$ for CeNi_2Ge_2 , $v = 3.08(1)$ for $\text{Ce}_3\text{Ni}_4\text{Ge}_4$ and $v = 3.18(1)$ for CeNiGe). On the contrary, the spectra of $\text{Ce}_2\text{Ni}_3\text{Ge}_5$ and CeNi_9Ge_4 show only one peak at 5725 eV, corresponding to a trivalent state for Ce atoms.

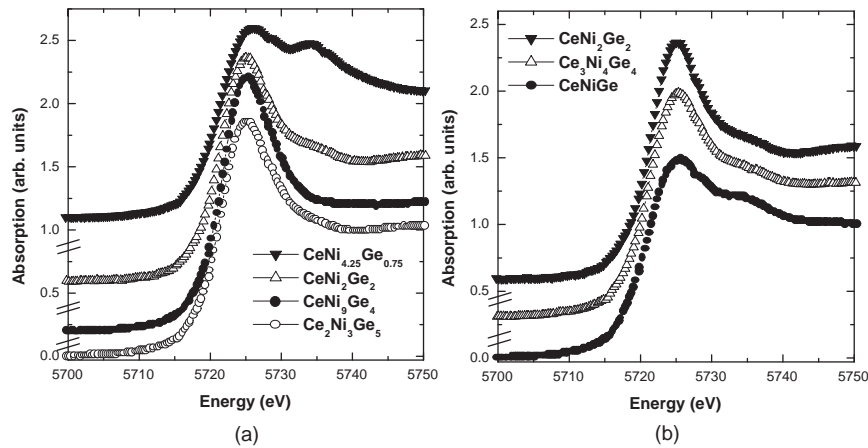


Fig. 3. Ce L_{III} absorption edge at 300K for (a) $\text{CeNi}_{4.25}\text{Ge}_{0.75}$, CeNi_2Ge_2 , CeNi_9Ge_4 and $\text{Ce}_2\text{Ni}_3\text{Ge}_5$; (b) CeNi_2Ge_2 , $\text{Ce}_3\text{Ni}_4\text{Ge}_4$ and CeNiGe (for clarity the spectra are shifted vertically).

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 ($\text{CeNi}_{4.25}\text{Ge}_{0.75}$, CeNiGe and $\text{Ce}_3\text{Ni}_4\text{Ge}_4$) or are heavy fermion systems (CeNi_9Ge_4); on the Ge-rich side ($\geq 50\%$ Ge) (Ce_2NiGe_6 , $\text{Ce}_3\text{Ni}_2\text{Ge}_7$, CeNiGe_3 , $\text{Ce}_2\text{Ni}_3\text{Ge}_5$ 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 $\text{CeNi}_2\text{Ge}_2 \rightarrow \text{Ce}_3\text{Ni}_4\text{Ge}_4 \rightarrow \text{CeNiGe}$. These observations show a large Ce-ground states in the Ce–Ni–Ge system.

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