MAGNETIC PROPERTIES OF THE NEW NpX_{2-x} (X= Si, Ge) WITH THE AlB_2 TYPE STRUCTURE*

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We report on the magnetic and electronic properties of AlB_2-type structure $NpSi_{2-x}$ and $NpGe_{2-x}$ as inferred from SQUID magnetisation and ^{237}Np Mössbauer spectroscopy. $NpGe_{2-x}$ orders ferromagnetically below $T_C \approx 157.4$ K with an ordered moment $\mu_{Np} \approx 2.01\ \mu_B$, whereas $NpSi_{2-x}$ exhibits three different ordered magnetic phases respectively below 110 K, 105 K and 90 K. The average ordered moment amounts to $\mu_{Np} \approx 1.51\ \mu_B$ at 4.2 K.

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1. Introduction

The recent discovery of compounds that are simultaneously ferromagnetic and superconducting has attracted much attention in the correlated electron phenomena community. The stoichiometric compound UGe_2 represents the first system where such properties were observed [1]. The crystallochemistry of the binary systems An-X (X=Si,Ge) is more complex as one may expect. Indeed a careful analysis of these systems shows that around the 1:2 composition several phases with defect stoichiometry (UGe_{2-x}) are forming, crystallising either in the tetragonal $ThSi_2$-type (low defect) or hexagonal AlB_2-type (large defect) phases and exhibiting a rich range of magnetic properties [2, 3]. We have undertaken the study of the An-X binary systems with An = Np, Pu and have indicated that for transuranium elements the defect phases were preferentially obtained [4]. In this contribution, we report on the magnetic and electronic properties of AlB_2-type $NpSi_{2-x}$ and $NpGe_{2-x}$ as inferred from SQUID magnetisation and ^{237}Np Mössbauer spectroscopy.

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2. Experimental

The Polycrystalline samples were prepared as explained in [4]. The tetragonal AlB_2-type structures were determined by X-ray single crystal diffraction. The occupancy was found to be $x = 0.41(1)$ for both compounds and the lattice parameters $a = 3.969(1)$ Å and $c = 4.171(1)$ Å for $NpGe_{2-x}$ and $a = 3.838(1)$ Å and $c = 4.092(1)$ Å for $NpSi_{2-x}$. Magnetic susceptibility measurements were performed on bulk samples using a SQUID magnetometer in the temperature range 2–300 K and in magnetic fields up to 7 T. The ^{237}Np Mössbauer investigations were conducted on powder absorbers, with a thickness of ∼100 mg of Np/cm^2 using a transmission spectrometer calibrated with the standard absorber $NpAl_2$. The Mössbauer source of ∼100 mCi of ^{241}Am was kept around 4.2 K and the temperature of the absorber was varied from 4.2 K up to 140 K.

3. Results

3.1. $NpGe_{2-x}$

The susceptibility and magnetisation curves of $NpGe_{2-x}$ clearly show the onset of ferromagnetic order at low temperature with a saturation moment $\mu_{sat} \approx 1.1\ \mu_B$/Np. The Curie temperature $T_C \approx 157.4$ K was determined using Arrott plots. In the paramagnetic region, the susceptibility follows a modified Curie–Weiss law with $\mu_{eff} \approx 1.93\ \mu_B$, $\theta_p \approx 152$ K and $\chi_0 \approx 737 \times 10^{-6}$ emu/Np mole. The Mössbauer spectrum recorded at $T = 4.2$ K exhibits a clear magnetic hyperfine splitting which confirms the occurrence of magnetic order. From the hyperfine field value $H_{hf} = 432(4)$ T, we deduce an ordered Np moment $\mu_{ord} \approx 2.01(4)\ \mu_B$. This value is approximately twice higher than the saturated moment which suggests that the Np magnetic moments are aligned along the *c*-axis. The value of the isomer shift ($\delta_{IS} \approx 11.2$ mm/s *vs* $NpAl_2$) suggests the occurrence of a Np^{3+} charge state (configuration $5f^4$). Due to the high Curie temperature, no spectrum could be recorded in the paramagnetic phase.

3.2. $NpSi_{2-x}$

$NpSi_{2-x}$ exhibits a more intricate magnetic phase diagram: The onset of magnetic order occurs at $T_{c1} \approx 110$ K where a ferromagnetic-type phase is observed in a very narrow range of temperature. $NpSi_{2-x}$ then undergoes a magnetic phase transition to a ferrimagnetic-type order below $T_{c2} \approx 105$ K. Finally, an antiferromagnetic-type phase appears below $T_{c3} \approx 90$ K. This latter phase is metamagnetic and transforms into the ferrimagnetic phase at relatively low fields, as illustrated on Fig 1. Such successive magnetic phase transitions (Ferro → Ferri → AF) are rather unusual but a similar magnetic

phase diagram was observed *e.g.* in $NpIn_3$ [5]. As Fig. 1 shows, there is a higher induced moment at 100 K than at low temperature.

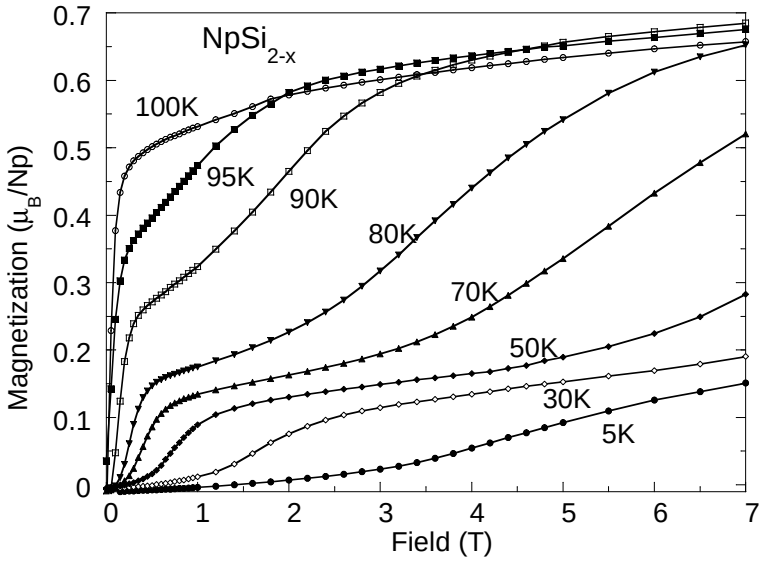

Fig. 1. Magnetisation curves of $NpSi_{2-x}$ at different temperatures.

The magnetic susceptibility above 150 K obeys a modified Curie–Weiss law with $\mu_{\rm eff} \approx 2.08\ \mu_{\rm B}$, $\theta_p \approx 128$ K and $\chi_0 \approx 345.10^{-6}$ emu/Np mole. The positive value of θ_p quite close to $T_{\rm C}$ confirms the ferromagnetic nature of the first ordering phase.

The Mössbauer spectrum at 140 K consists of a pure quadrupolar splitting ($|e^2qQ| \approx 14.3$ mm/s), as expected in the paramagnetic state. This shows, in agreement with the crystal structure determination, that there is only one Np crystallographic site experiencing the same surrounding. The isomer shift ($\delta_{\rm IS} \approx 6.4$ mm/s *vs* $NpAl_2$) suggests the occurrence of a Np^{3+} charge state. At 110K, the spectrum lines begin to broaden, indicating the onset of magnetic order, in close agreement with the magnetisation data. At 105 K, *i.e.* in the "ferromagnetic" phase according to magnetisation data, the spectrum exhibits a rather complex pattern consisting of the superposition of a paramagnetic subspectrum and a magnetic splitting with a population ratio 1:2. At 100 K, the paramagnetic contribution is still present but the ratio is strongly reduced. From 90 K down to 4.2 K, *i.e.* in the "AF" phase suggested by the magnetisation data, the Mössbauer spectra display a fully magnetic splitting, increasing with decreasing temperature. However, this splitting consists of two magnetic subspectra of comparable population and respective hyperfine fields $H_{\rm hf} = 337(2)$ T ($\mu_{\rm ord} \approx 1.57(2)\ \mu_{\rm B}$) and $H_{\rm hf} = 309(2)$ T ($\mu_{\rm ord} \approx 1.44(2)\ \mu_{\rm B}$). This shows that the AF-phase is

actually ferrimagnetic (with an antiferromagnetic coupling of the two sublattices). Moreover, the comparison of quadrupolar interaction parameters, of both sites and in the ordered and paramagnetic phase, suggests that Np moments are collinear and make an angle of 40 to 60° with the c axis. It is worth mentioning that the magnetic moments in the uranium isotypic ferromagnetic compound UGe_{2-x} are aligned in a direction oriented at 38° from the c axis [6].

4. Conclusion

$NpGe_{2-x}$ and $NpSi_{2-x}$ (x $\approx$ 0.41) are isotypes to the UX_{2-x}. Whereas UGe_{2-x} orders ferromagnetically at $T_c = 94$ K [6] and USi_{2-x} is a paramagnet [2], the neptunium counterparts show a stronger magnetic character: $NpGe_{2-x}$ orders ferromagnetically at $T_C \approx 157.4$ K with an ordered moment $\mu_{Np} \approx 2.01\ \mu_B$. $NpSi_{2-x}$ exhibits a complex magnetic phase diagram with three distinct magnetic phases appearing respectively below 110 K, 105 K and 90 K. The Mössbauer experiments suggest the Np magnetic moment to point at 40° from the c-axis (similar to UGe_{2-x}). The average ordered moment amounts to $\mu_{Np} \approx 1.51\ \mu_B$ at 4.2 K. In both $NpSi_{2-x}$ and $NpGe_{2-x}$, the value of the isomer shift suggests a Np^{3+} charge state. The magnetic and electronic properties of these different phases remain to be corroborated and complemented by further investigations.

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