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Magnetic ordering of $NdNiGe_2$ and $CeNiGe_2$ studied by neutron diffraction and magnetic measurements

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The magnetic properties of the compounds $CeNiGe_2$ and $NdNiGe_2$ were studied by means of magnetic measurements and neutron diffraction. Neutron diffraction experiments made in the paramagnetic regime confirmed the $CeNiSi_2$ structure reported earlier for these compounds. Refined atomic position parameters for both compounds are given. Neutron diffraction measurements performed in the magnetically ordered regime showed that the rare earth moments in $NdNiGe_2$ order ferromagnetic with the preferred moment direction along the *c*-axis. Long-range ferromagnetic ordering was not observed in $CeNiGe_2$. Its previously reported two-step antiferromagnetic ordering below $T < 4$ K can not be yet elucidated.

1. Introduction

In previous studies we have investigated the magnetic properties of several silicides of the type $RNiSi_2$ and showed that antiferromagnetic ordering occurs when R is a heavy rare earth element [1] while ferromagnetism is found for light rare earth elements [2]. In the present investigation we have focused our attention on two isostructural germanides. It forms an extension of an earlier study made on $TbNi_{0.4}Ge_2$, which compound has shown to order antiferromagnetically at low temperatures [3]. For the $CeNiGe_2$ compound a Néel-type double transition has been reported [4] to occur at $T = 4$ K and 3.2 K on the basis of specific heat data. The purpose of the present investigation is to establish whether changes from ferromagnetism (R light rare earth) to antiferromagnetism (R heavy rare earth) are a common feature of the $RNiGe_2$-type compounds.

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2. Experimental procedures and results

The samples $NdNiGe_2$ and $CeNiGe_2$ were prepared by arc-melting from starting materials of at least 99.9% purity, followed by vacuum annealing at 800°C for about 4 weeks. X-ray diffraction showed that after this treatment the samples were approximately single phase. All reflection lines were indexed on the basis of the orthorhombic $CeNiSi_2$ structure type [5].

Measurements of the temperature dependence of the inverse susceptibilities of $CeNiGe_2$ and $NdNiGe_2$ ($\mu_0 H = B = 0.1$ T) in the temperature range $2\ \text{K} \leqslant T \leqslant 350$ K and measurements of the field dependent magnetization of $NdNiGe_2$ at $T = 5$ K in the range $0 < B < 2.5$ T were carried out, utilizing a dc SQUID magnetometer. Results of the inverse susceptibilities χ^{-1} and $M(B)$ are shown in figs. 1–3. Curie and Néel-type transitions are seen to occur around 6 and 4 K for $NdNiGe_2$ and $CeNiGe_2$, respectively. The results displayed in figs. 1 and 2 show that in the range well above T_c and T_N the reciprocal susceptibility (χ^{-1}) behaves very closely according to the

Curie–Weiss law. The corresponding effective moments per rare earth ion are $3.37\mu_B$ for $NdNiGe_2$ and $2.3\mu_B$ for $CeNiGe_2$. Both effective moments are slightly below the corresponding free-ion values. The Curie–Weiss intercepts are equal to $\theta_p = 6$ K for $NdNiGe_2$ and $\theta_p = -46$ K for $CeNiGe_2$.

The neutron diffraction data were obtained with the DMC (double-axis multicounter system) at the Saphir Reactor, Würenlingen. The wavelength used for the data collection was $\lambda = 0.170012$ nm and the step increment of the diffraction angle 2θ was 0.10°. Measurements were made in the paramagnetic range as well as in the magnetically ordered range. All data were corrected for absorption and evaluated by means of the Rietveld line profile analysis method [6,7]. The scattering lengths and magnetic form factors used for the various elements are from refs. [8] and [9], respectively.

Neutron diffraction powder data obtained in the paramagnetic state are shown in the top parts of figs. 4 and 5 where the experimental intensities can be compared with intensities calculated on the basis of the $CeNiSi_2$-type structure. The good agreement between the two sets of data confirms the $CeNiSi_2$ structure for both compounds. Refined parameters can be found in table 1.

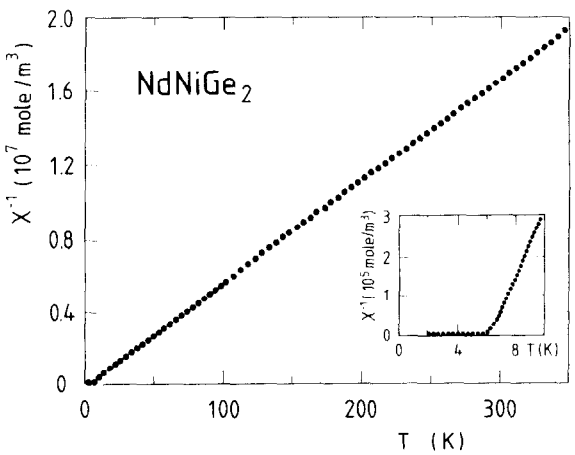

Fig. 1. Temperature dependence of the reciprocal susceptibility of $NdNiGe_2$. The inset shows the temperature dependence in the range 2–10 K measured in a field $\mu_0 H = 0.1$T.

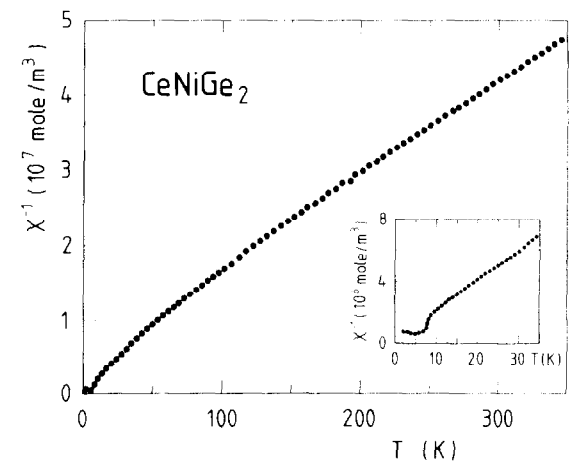

Fig. 2. Temperature dependence of the reciprocal susceptibility of $CeNiGe_2$. The inset shows the temperature dependence of the range 2–35 K measured in a field $\mu_0 H = 0.1$ T.

The low-temperature neutron diffraction patterns are shown in the bottom parts of figs. 4 and 5. It may be inferred from the 1.5 K data shown for $NdNiGe_2$ (collected with a counting rate three times that used for the nuclear data) that all magnetic reflections appear at reciprocal lattice positions of the chemical unit cell. The relative intensities of the first three observed magnetic reflections (020, 040 and 110) can be seen in a separate difference diagram (fig. 6). It follows from these data that the *b*-axis cannot be the easy axis of magnetization and that the intensity en-

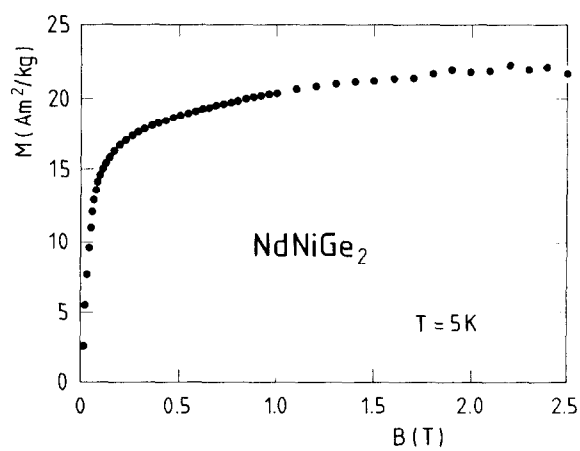

Fig. 3. Field dependence of the magnetization in the range 0–2.5 T for $NdNiGe_2$ measured at 5 K.

hancement is to be associated with ferromagnetic ordering. The calculated intensity ratio resulting from contributions of only the real part of the structure factor only (ferromagnetic mode F(+ + + +)) is 0.272, while the ratio resulting from the imaginary part (antiferromagnetic model G(+ − + −)) is 17.93. As seen from fig. 6, only the former value compares favourably with the observations. F and G refer to the relative moment signs of the R atoms: (0, y, 1/4); (0, $-y$, 3/4); (1/2, 1/2 + y, 1/4); (1/2, 1/2 − y, 3/4).

The refinement converged for magnetic moment directions along the c-axis for $NdNiGe_2$. The corresponding magnetic space group is $Cm'c'm$ (Sh_{63}^{462}) which allows for the 4c symmetry

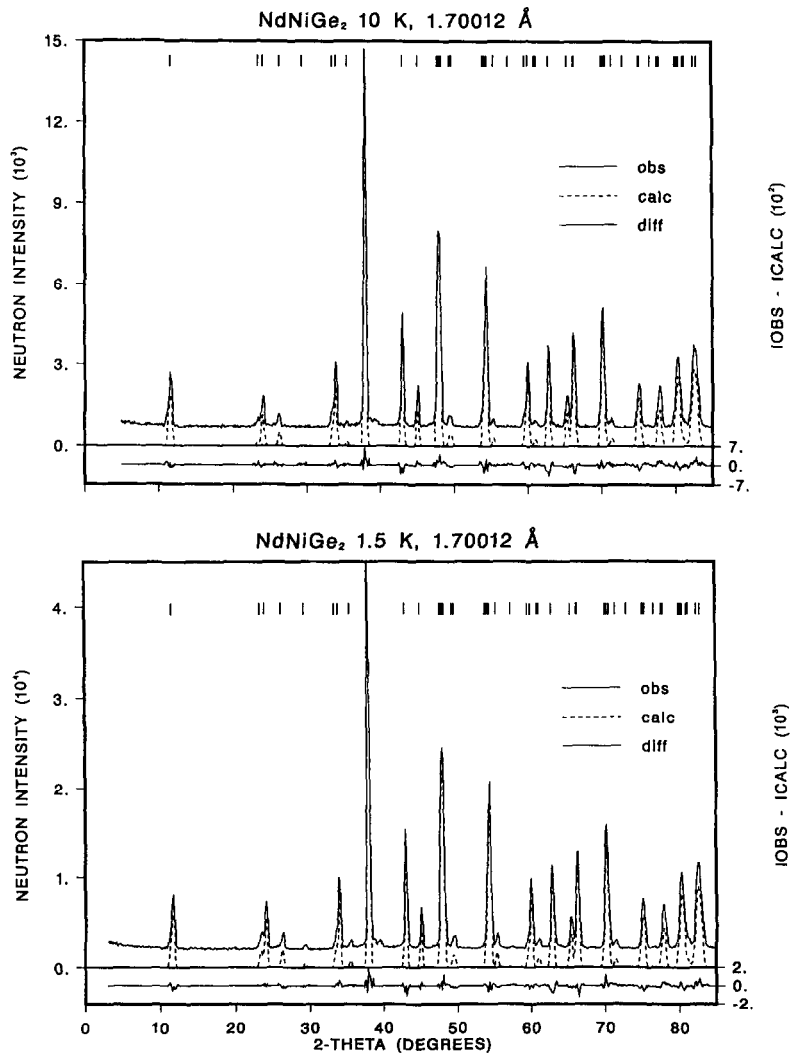

Fig. 4. Neutron diffraction pattern of the compounds $NdNiGe_2$ in the paramagnetic range (10 K, top part) showing observed intensities (full line), calculated curves (broken lines). Data obtained in the magnetically ordered regime (1.5 K) are shown in the bottom part. The differences between observed intensities (corrected for background) and calculated intensities are plotted at the bottom of the figure (right scale).

position only a F_z ferromagnetic contribution [1]. The refined parameters for magnetically ordered $NdNiGe_2$, listed in table 1, indicate that there is a satisfactory agreement between observed and calculated moment arrangements. The ordered moment of Nd ($2.32\mu_B$) is below the value expected for trivalent Nd ions ($gJ[\mu_B] = 3.27\ [\mu_B]$ for Nd^{3+}), which indicates a strong influence of crystal fields. The same conclusion can be reached from the results of the magnetic measurements. At 5 K and $\mu_0 H = 2.2$ T we found a magnetic moment equal to only $1.37\mu_B$/Nd (fig. 3).

A similar analysis as described above for $NdNiGe_2$ at 1.5 K was also made for $CeNiGe_2$. Contrary to the former compound the difference diagram I[1.5 K]–I[10 K] did not indicate long-range ferromagnetic ordering in $CeNiGe_2$ at 1.5 K. Instead the neutron diffraction data of $CeNiGe_2$ show the presence of only one very weak peak at $2\theta = 4.1°$, which most probably lies

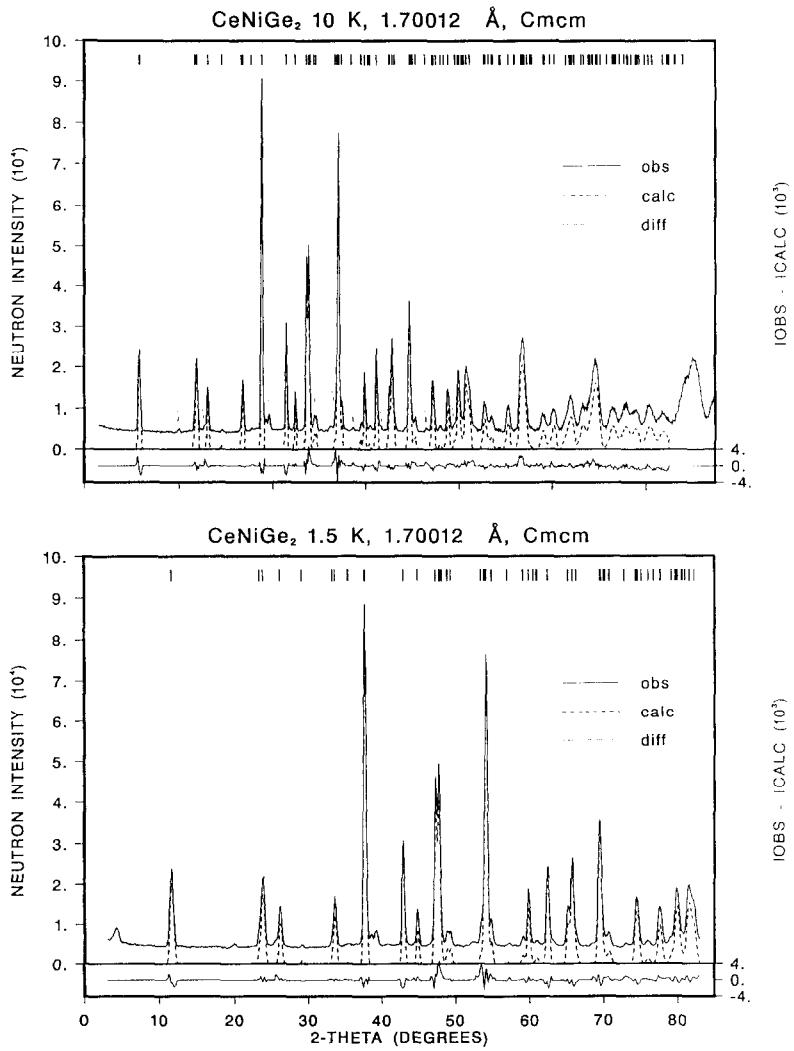

Fig. 5. Neutron diffraction pattern of the compounds $CeNiGe_2$ in the paramagnetic range (10 K, top part) showing observed intensities (full line), calculated curves (broken lines). Data obtained in the magnetically ordered regime (1.5 K) are shown in the bottom part. The differences between observed intensities (corrected for background) and calculated intensities are plotted at the bottom of the figure (right scale). Peaks marked i denote impurity lines.

Table 1
Refined structural parameters of $RENiGe_2$ (RE = Nd, Ce) compounds (a) in the paramagnetic state at 10 K, and (b) in the magnetically ordered state. Space group Cmcm (no. 63) all atoms at 4c (0, y, 1/4).

Parameter	$NdNiGe_2$		$CeNiGe_2$	
	10 K value	1.5 K value	10 K value	1.5 K value
y_{RE}	0.1080(3)	0.1082(3)	0.1081(3)	0.1087(4)
y_{Ni}	0.3190(2)	0.3182(1)	0.3182(1)	0.3179(2)
$y_{Ge(1)}$	0.4567(3)	0.4579(2)	0.4579(2)	0.4572(2)
$y_{Ge(2)}$	0.7487(3)	0.7489(2)	0.7489(2)	0.7483(2)
$\mu_z(\mu_B)$		2.32(6)	–	–
a (nm)	0.41959(3)	0.41958(2)	0.42409(3)	0.42392(3)
b (nm)	1.67365(13)	1.67363(11)	1.67619(11)	1.67546(15)
c (nm)	0.41710(3)	0.41713(3)	0.42020(3)	0.42005(3)
B (nm^2)	0.0025(5)	0.0021(5)	0.0031(3)	0.0020(6)
R_n, R_{wp}	7.7, 8.5	4.0, 7.2	6.9, 11.5	5.1, 9.7
R_m(%), R_{exp}(%)	–, 3.9	5.7, 2.2	–, 1.6	–, 1.40

in a general position in reciprocal space. We are therefore unable to determine the magnetic structure. All that can be stated is that the Ce moments order in a complex antiferromagnetic way and are fairly small. A small ferromagnetic contribution found in the magnetic measurements below 9 K (fig. 2, inset) is most likely related to the presence of some impurity.

3. Concluding remarks

In a previous investigation we reported on the magnetic structure of the compound $TbNi_{0.4}Ge_2$ and showed that this compound orders antiferromagnetically, the preferred moment direction being along the c-direction [3]. Similar results were obtained also for the compounds $TbNiGe_2$ and $HoNi_{0.64}Ge_2$ [10]. All these data indicate that the Ni concentration is of little influence in determining the magnetic ordering type. In contrast, both the Néel temperature and the ordered moment value of the rare earth ion are strongly dependent on the concentration of the transition metal (Ni). For the stoichiometric $TbNiGe_2$ [10] $T_N = 37$ K and μ/Tb ion $= 8.8\mu_B$ (100% Ni) whereas for

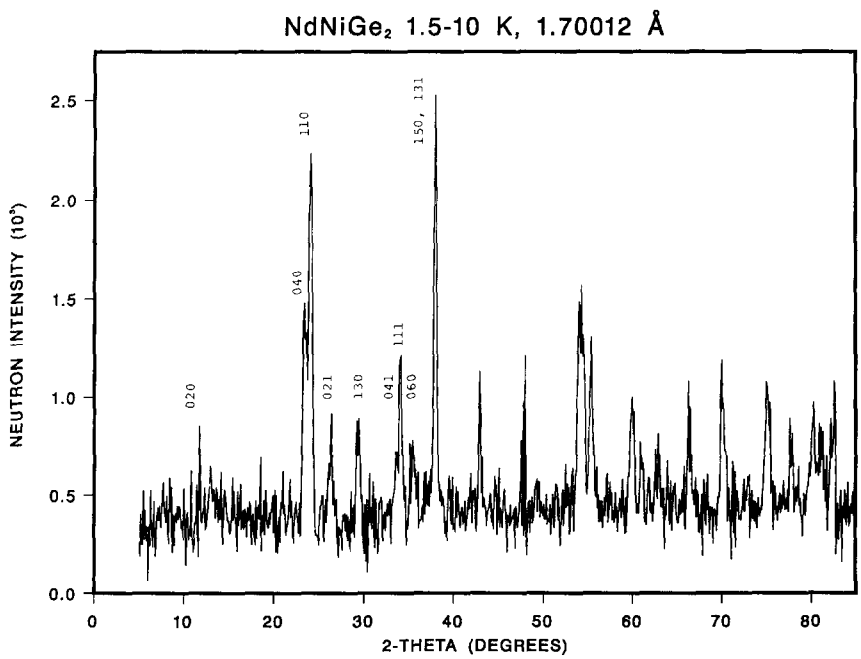

Fig. 6. Difference diagrams of $NdNiGe_2$ obtained by subtracting the nuclear contribution measured at the higher temperature in the paramagnetic regime from the intensities observed at the lower temperature in the magnetically ordered regime.

$TbNi_{0.4}Ge_2$ we have $T_N = 16$ K and μ/Tb ion = $5.6\mu_B$ [3].

Of considerable interest is the present observation that the magnetic ordering in $NdNiGe_2$ is ferromagnetic rather than antiferromagnetic. This suggests that the type of coupling between the rare earth spin moments changes when passing from the light rare earths to the heavy rare earths in $RNiGe_2$. Apparently the situation is similar to that in the series of $RNiSi_2$ compounds where we also observed [2] a change in magnetic coupling from ferromagnetic (R light rare earth) to antiferromagnetic (R heavy rare earth).

The behaviour of the compound $CeNiGe_2$ does not fit into this general picture. Here the antiferromagnetic ordering observed from magnetic measurements [11,12] may be associated with the valence instability of the Ce moment since specific heat measurements [4] showed that $CeNiGe_2$ falls into the class of heavy-fermion systems.

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