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MAGNETIC ORDERING IN $TbRh_2Si_2$ AND $CeRh_2Si_2$

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Magnetic measurements and a neutron diffraction study have been carried out on the ternary compounds $TbRh_2Si_2$ and $CeRh_2Si_2$ with a tetragonal structure of $ThCr_2Si_2$-type. $TbRh_2Si_2$ is found to order antiferromagnetically below $T_N = 92$ K with moments along the c-axis. The structure, of wave vector $\mathbf{k} = [001]$, consists of a stacking of ferromagnetic (001) planes with a $+ - + -$ sequence. $CeRh_2Si_2$ develops below $T_N = 36$ K a structure described by a wave vector $\mathbf{k} = [1/2\ 1/2\ 0]$ in which the coupling within a (001) plane is antiferromagnetic. This change of coupling together with the large negative value of $\theta_p = -61$ K has been attributed to a change of the sign of the first nearest neighbour in-plane interaction which would correspond to an exchange mechanism different from the usual *RKKY* one in $CeRh_2Si_2$.

1. INTRODUCTION

THE TERNARY SILICIDES RM_2Si_2 in which R is a rare earth metal and M is a $3d$, $4d$ or $5d$ transition element have been extensively studied during the past years. They crystallize in a simple structure of $ThCr_2Si_2$-type which is tetragonal of space group *I4/mmm* [1]. These ternary silicides allow us to study many interesting physical properties as the supraconductivity, the valence fluctuations, the Kondo effect or the magnetism [2–4].

The magnetic properties of the silicides with a $3d$ transition element (Mn, Fe, Co, Ni, Cu) have been studied in more detail than those with a noble metal as M = Ru, Rh, Ir. In a recent work we have shown that the RRh_2Si_2 (R = Ce, Nd, Sm, Gd, Tb, Dy, Ho, Er) exhibit at low temperatures an antiferromagnetic ordering [2]. In this paper we report the results of a more detailed study on the $CeRh_2Si_2$ and $TbRh_2Si_2$ silicides by means of neutron diffraction and magnetic measurements.

1.1. *Sample preparation*

$CeRh_2Si_2$ and $TbRh_2Si_2$ have been prepared by the direct melting of the elements in an arc furnace under a purified argon atmosphere. The obtained compounds were analyzed by X-rays using a Guinier camera and proved to have the quadratic structure of $ThCr_2Si_2$-type. The lattice parameters at room temperature of $CeRh_2Si_2$ ($a = 4.075$ Å, $c = 10.13$ Å) and of $TbRh_2Si_2$ ($a = 4.031$ Å, $c = 9.96$ Å) are in good agreement with the previously published values [5].

In the case of $TbRh_2Si_2$ a single crystal (3 mm diameter and 2 mm height) has been grown by using a Czochralski method developed at the University of Bordeaux [6].

2. MAGNETIC MEASUREMENTS

The magnetic measurements have been performed between 4.2 K and 300 K by using a balance of Faraday type and a magnetometer with a vibrating sample.

$CeRh_2Si_2$ orders antiferromagnetically at T_N = 36 K. The magnetic susceptibility follows a Curie–Weiss law (Fig. 1). The effective moment value $\mu_{\text{eff}} = 2.56\ \mu_B$ is in agreement with cerium in a trivalent state. The paramagnetic Curie temperature $\theta_p = -61$ K has a large negative value. These values differ significantly from the quite recent measurements of Godart *et al.* ($\theta_p = -72$ K, $\mu_{\text{eff}} = 2.9\ \mu_B$) [7].

$TbRh_2Si_2$ orders also antiferromagnetically at T_N = 94 K. The effective moment value $\mu_{\text{eff}} = 10.0\,\mu_B$ is slightly larger than the free ion value of a Tb^{3+} ion ($\mu_{\text{eff}} = 9.72\,\mu_B$) which may indicate a positive polarization of the conduction electrons. The paramagnetic Curie temperature $\theta_p = 43$ K has a positive value, as in most of the other RRh_2Si_2 ternaries [2], indicating that

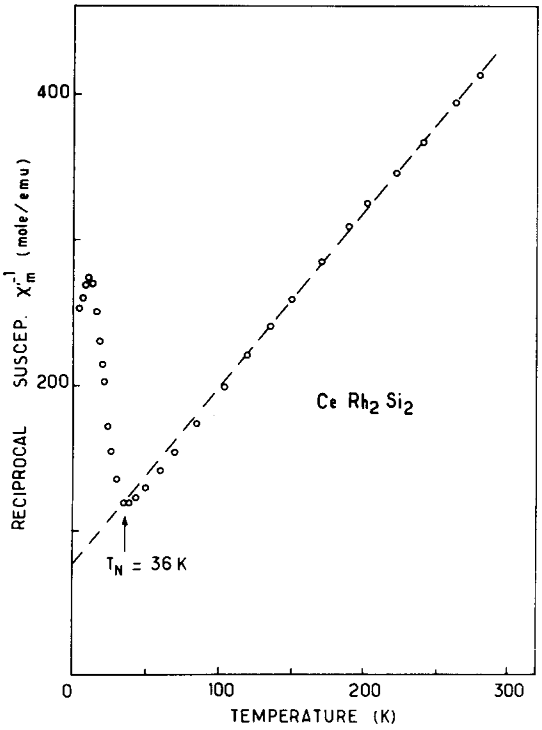

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of $CeRh_2Si_2$.

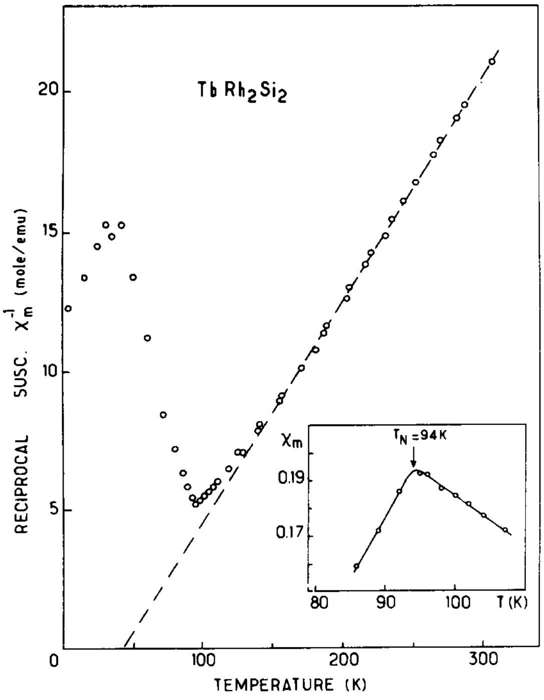

Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility of $TbRh_2Si_2$.

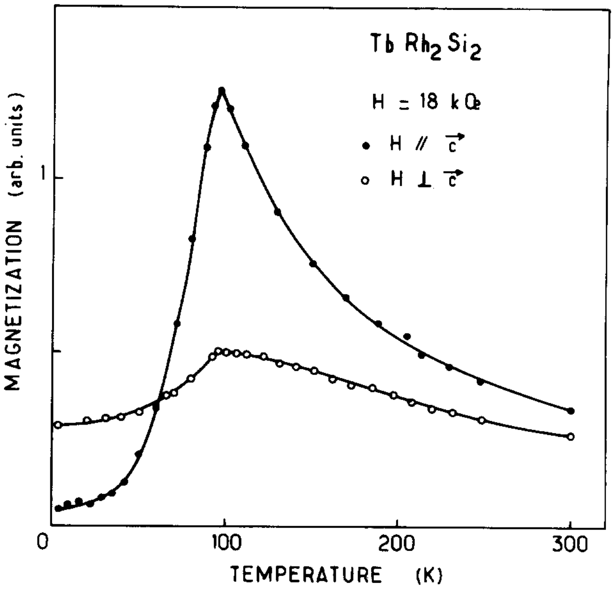

Fig. 3. Temperature dependence of the magnetization of a $TbRh_2Si_2$ single crystal measured with a magnetic field of 18 kOe applied along and perpendicularly to the c-axis.

the interactions have mainly a ferromagnetic character in $TbRh_2Si_2$ (Fig. 2). The magnetization measured on a single crystal, exhibits a large anisotropy depending on the magnetic field is applied along or perpendicularly to the c-axis (Fig. 3). The antiferromagnetic direction is along the c-axis.

3. NEUTRON RESULTS

Neutron experiments have been carried out at the Siloe reactor of the CEN-Grenoble. The diffraction patterns were recorded with a linear multidetector spectrometer [8] using a neutron wavelength of 2.483 Å.

The scattering by the nucleus gives rise to nuclear Bragg peaks which can be well accounted by the extinction condition $(h + k + l = 2n + 1)$ of the body centered-tetragonal space group $I4/mmm$. The crystal structure of $ThCr_2Si_2$-type contains:

one R atom in the site $2a$: (000) of D_{4h} symmetry;
two Rh atoms in the site $4d$: $(0\frac{1}{2}\frac{1}{4})$ and $(\frac{1}{2}0\frac{1}{4})$;
two Si atoms in the site $4e$: $(00z)$ and $(00\bar{z})$.

Then the structure can be described as a stacking of atomic planes perpendicular to the c-axis with the sequence R-Si-Rh-Si-R and located respectively at $z = 0$, $1/2 - z_{Si} = 0.125$, $1/4$, $z_{Si} = 0.375$ and $1/2$. The fit of the calculated and integrated intensities gives no evidence for any mixing between Rh and Si atoms in $4d$ and $4e$ sites. As an example a comparison between observed and calculated intensities of a few nuclear peaks are given in Table 1 in the case of $TbRh_2Si_2$. A quite good agreement ($R = 2.7\%$) is obtained for $z_{Si} = 0.375$, the intensities were calculated using

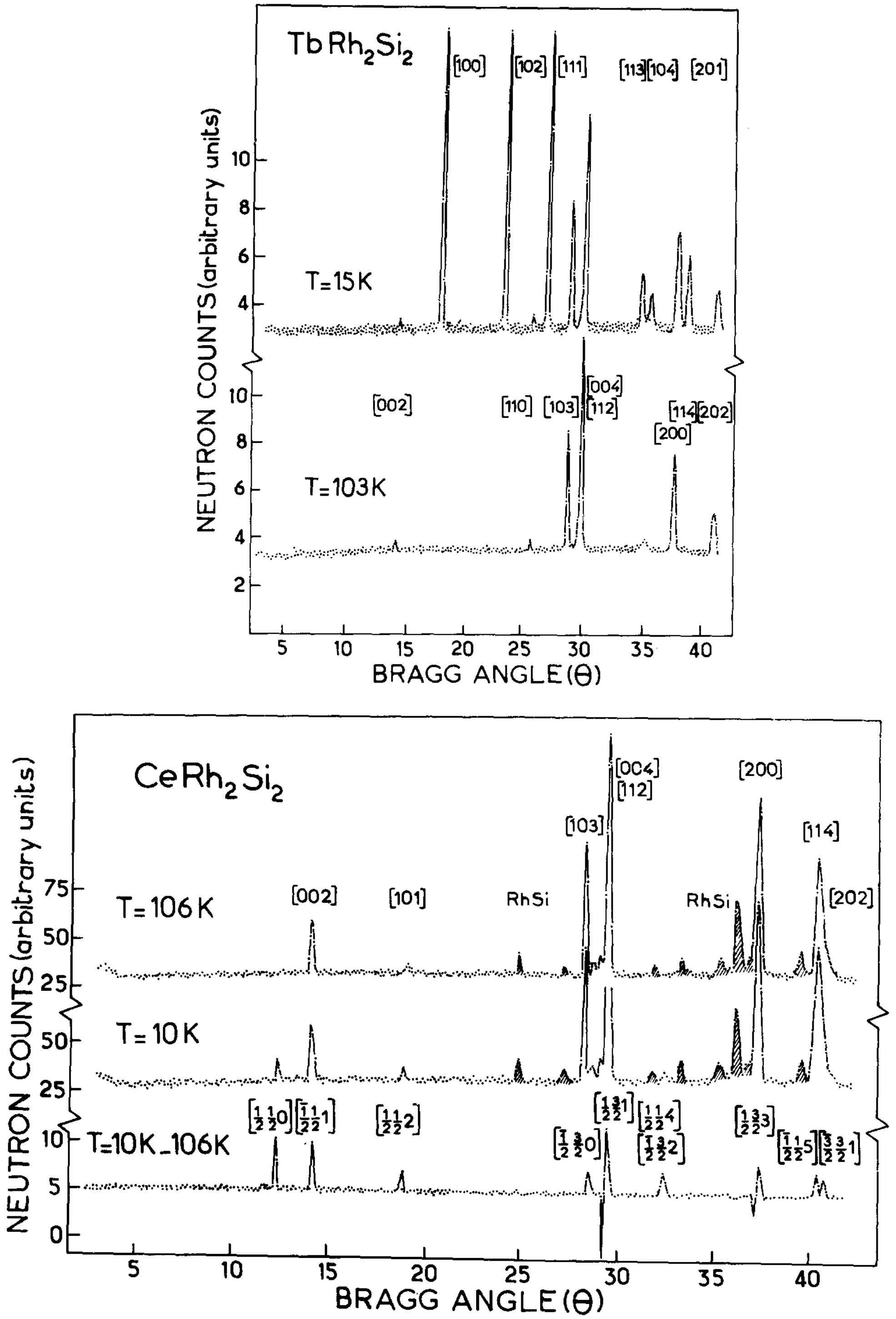

Fig. 4. (a) Neutron diffraction patterns from paramagnetic (103 K) and ordered (15 K) $TbRh_2Si_2$. Magnetic reflections are associated with a wave vector $\mathbf{k} = [0\,0\,1]$. (b) Neutron diffraction patterns from paramagnetic (106 K) and ordered (10 K) $CeRh_2Si_2$. Magnetic reflections are associated with a wave vector $\mathbf{k} = [1/2\;1/2\;0]$.

the following scattering lengths: $b_{Tb} = 0.756$, $b_{Rh} = 0.591$, $b_{Si} = 0.415 \times 10^{-12}$ cm. As far as the magnetic properties are concerned this structure is quite simple because the magnetic ions (rare earth) are located in one Bravais lattice.

$TbRh_2Si_2$

In the neutron diffraction diagrams given in Fig. 4 additional reflections can be identified at $T = 15$ K. These new reflections, due to the onset of the magnetic order, can be easily indexed on the basis of the

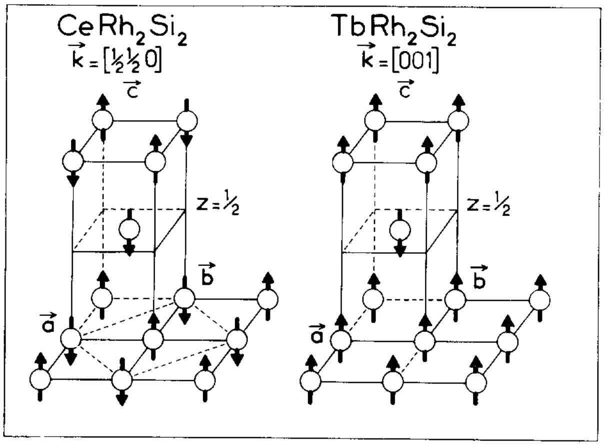

Fig. 5. Magnetic structures of $TbRh_2Si_2$ ($\mathbf{k}$ = [0 0 1]) and $CeRh_2Si_2$ ($\mathbf{k}_1$ = [1/2 1/2 0]).

Table 1. Calculated and observed intensities of the nuclear peaks in barn per $TbRh_2Si_2$ *molecule at* T = 15 K (a = 4.027 Å, c = 9.952 Å, z_{Si} = 0.375)

hklI	I_{obs}	I_{cal}
0 0 2	0.17	0.36
1 0 1	0.14	0.22
1 1 0	0.89	0.65
1 0 3	13.98	13.98
0 0 4 1 1 2	31.58	31.19
2 0 0	26.67	29.05
1 1 4 2 0 0	14.58	13.34

$R = 2.7\%$

Table 2. Calculated and observed intensities of the magnetic superlattice peaks of $TbRh_2Si_2$ *in barn/*Tb *atom at* T = 15 K.

hkl	I_{obs}	I_{cal}
0 0 1	*n*.0	0
1 0 0	17.2	17.8
0 0 3	*n*.0	0
1 0 2	18.7	18.6
1 1 1	29.5	26.5
1 1 3	12.4	13.1
1 0 4	6.0	6.1
0 0 5	*n*.0	0
2 0 1	22.1	19.7

$m_0 = 8.5 \pm 0.3\,\mu_B \quad R = 6.5\%$

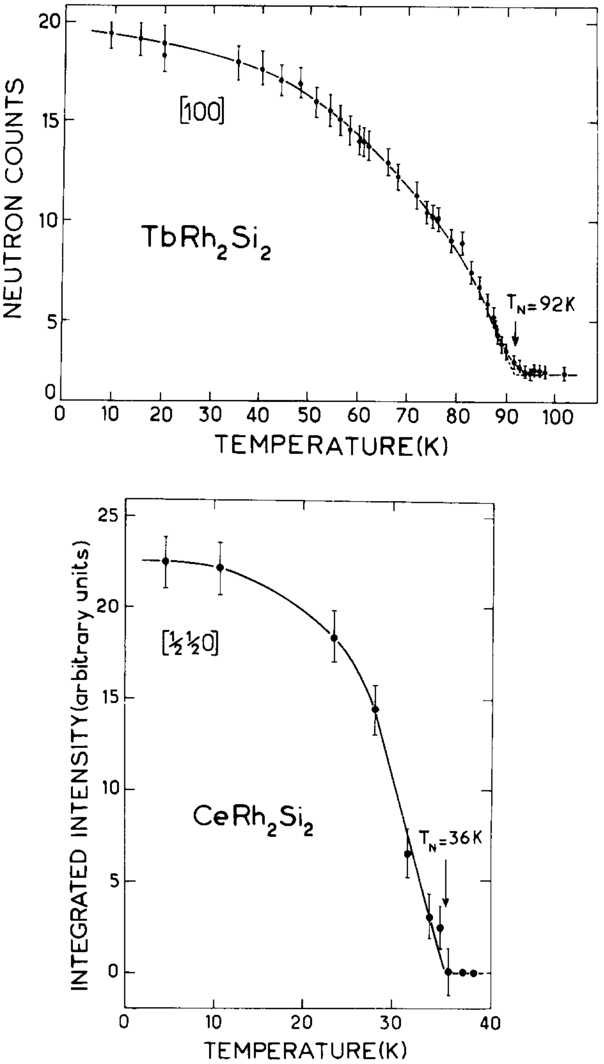

Fig. 6. (a) Temperature dependence of the magnetic intensity of the [1 0 0] reflection of $TbRh_2Si_2$. (b) Temperature dependence of the integrated intensity of the [1/2 1/2 0] magnetic reflection of $CeRh_2Si_2$.

crystallographic unit cell with the following rule $h + k + l = 2n + 1$. The magnetic scattering vectors $\mathbf{h}$ being defined by the relation $\mathbf{h} = \mathbf{H} + \mathbf{k}$, whre $\mathbf{H}$ spanned the different Brillouin zone centers i.e. the nuclear lattice vectors, the ordering is described by the wave vector $\mathbf{k}$ = [0 0 1]. This wave vector corresponds to a symmetry point of the Brillouin zone (for $c > a$) i.e. it describes a truly antiferromagnetic structure [9]. The structure consists of a stacking of ferromagnetic (0 0 1) planes with a $+-+-$ sequence along the c-axis (Fig. 5). The absence of the [0 0 1], [0 0 3] magnetic peaks indicates without any ambiguity that the moments are aligned along the c-axis. The observed intensities (Table 2) can be well accounted (R = 6.7%) by using the Tb^{3+} form factor given by [10]. A moment value $m_0 = 8.5 \pm 0.3\,\mu_B$ is found at T = 15 K indicating that the terbium magnetic moment is close to the free ion value ($g_J J = 9\,\mu_B$). Moreover there is no evidence of any magnetic moment on the rhodium atoms.

The temperature dependence of the [1 0 0] magnetic

Table 3 Calculated and observed intensities of the magnetic superlattice peaks of $CeRh_2Si_2$ *in barn/Ce atom at* T = 10 K. *Magnetic peaks are indexed in the domain associated with* $\mathbf{k}_1 = [1/2\ 1/2\ 0]$.

h k l	I_{obs}	I_{cal}
$\frac{1}{2}\frac{1}{2}0$	0.294	0.300
$\frac{\bar{1}}{2}\frac{1}{2}1$	0.405	0.438
$\frac{1}{2}\frac{1}{2}2$	0.240	0.236
$\frac{1}{2}\frac{1}{2}3$	*n*.0	0.123
$\overline{\tfrac{1}{2}}\frac{3}{2}0$	0.472	0.466
$\frac{1}{2}\frac{3}{2}1$	1.418*	0.855
$\overline{\tfrac{1}{2}}\frac{3}{2}2$	0.756	0.757
$\frac{1}{2}\frac{1}{2}4$		
$\frac{1}{2}\frac{3}{2}3$	0.622*	0.494
$\frac{3}{2}\frac{3}{2}0$	*n*.0*	0.186
$\overline{\tfrac{3}{2}}\frac{3}{2}1$	0.609*	0.390
$\overline{\tfrac{1}{2}}\frac{1}{2}5$		
$m_0 = 1.50 \pm 0.15\mu_B$ $R = 8\%$		

*The intensity of these peaks are affected by a large uncertainty because they are superimposed to nuclear peaks.

peak intensity is reported in Fig. 6(a) giving an ordering temperature $T_N = 92$ K which is a quite large value for rare earth ternary compounds of $ThCr_2Si_2$-type structure.

$CeRh_2Si_2$

The neutron diffraction diagrams given in Fig. 4(b) show that $CeRh_2Si_2$ develops, at low temperature, a magnetic order different from that found in $TbRh_2Si_2$. The superlattice magnetic peaks can be indexed by considering the structure to be associated with the wave vector $\mathbf{k} = [1/2\ 1/2\ 0]$ which corresponds also to a symmetry point of the Brillouin zone. It describes a simple antiferromagnetic ordering within (001) planes with a $+-+-$ stacking sequence along a [110] direction. The magnetic cell $(a\sqrt{2}, a\sqrt{2}, c)$ is actually two times larger than the crystallographic one.

The star of **k** contains two non-equivalent wave vectors $\mathbf{k}_1 = [1/2\ 1/2\ 0]$ and $\mathbf{k}_2 = [1/2\ \bar{1}/2\ 0]$ defining two *K*-domains. In both of them the magnetic order is the same within a (001) plane, it differs only by the coupling between adjacent (001) planes, i.e. by the coupling between the magnetic moments in (000) and (1/2 1/2 1/2). In the domain $\mathbf{k}_1 = [1/2\ 1/2\ 0]$ the coupling is antiferromagnetic (see Fig. 5) while it is ferromagnetic in domain $\mathbf{k}_2 = [1/2\ \bar{1}/2\ 0]$. Therefore the stacking sequence of (001) planes along the c-axis will not depend on the sign of the exchange interaction I' between nearest neighbouring planes.

The best fit ($R = 8\%$) between observed and calculated magnetic intensities (Table 3) indicates that the antiferromagnetic direction is along the c-axis and gives a moment value $m_0 = 1.50 \pm 0.15\,\mu_B$ at $T = 10$ K, close to the free ion value $g_J J = 2.14\,\mu_B$. The intensities were calculated by using the form factor given by [10] and the Fermi lengths: $b_{Ce} = 0.482$, $b_{Rh} = 0.591$ and $b_{Si} = 0.415$. The thermal variation of the intensity of the first magnetic peak [1/2 1/2 0], reported in Fig. 6(b), gives an ordering temperature $T_N = 36$ K.

4. DISCUSSION

The investigation of the magnetic ordering in $CeRh_2Si_2$ and $TbRh_2Si_2$ provides interesting information about the magnetic anisotropy and the exchange interactions in the RRh_2Si_2 ternary compounds.

The large value of the magnetic moment found in $TbRh_2Si_2$ indicates that the crystal field, of D_{4h} symmetry, acting on the Tb^{3+} ions must lead to a ground state with two very close singlets $1/\sqrt{2}\,(|6\rangle + |-6\rangle)$ and $1/\sqrt{2}\,(|6\rangle - |-6\rangle)$; then the magnetic moments are quenched along the c-axis giving rise to an Ising-like behaviour. However, in $CeRh_2Si_2$ a moment reduction exists which can be explained by a crystal field effect. Actually, a crystal field level scheme similar to that found in $CeCu_2Si_2$ [11] with a ground state doublet $|0\rangle = 0.9\,|\pm 5/2\rangle + 0.18\,|\mp 3/2\rangle$ explains quite well the observed moment value.

As far as the magnetic interactions are concerned, they are quite different in both compounds: in $CeRh_2Si_2$ the coupling is antiferromagnetic within (001) planes whereas it is ferromagnetic in $TbRh_2Si_2$. Actually, a ferromagnetic planar coupling was found in almost all compounds crystallizing with the structure of $ThCr_2Si_2$-type [12]. In the ternaries RM_2Si_2 or RM_2Ge_2 the $M = 3d$, $4d$ or $5d$ atoms are non-magnetic excepted with Mn [13] and the lanthanides or actinides order all with a ferromagnetic coupling in the (001) planes, but the coupling between planes has been found to be ferromagnetic ($\mathbf{k} = 0$), antiferromagnetic ($\mathbf{k} = [100]$), commensurate ($\mathbf{k} = [00\,1/2]$) or incommensurate ($\mathbf{k} = [00k_z]$) [12].

The only exception is $TbNi_2Si_2$ [14] in which the in-plane coupling was found to be antiferromagnetic as in $CeRh_2Si_2$.

Using a molecular field approximation, a simple analysis of the possible magnetic structures can be done in the structure of $ThCr_2Si_2$-type because magnetic ions are located in a single body-centered tetragonal Bravais lattice. An antiferromagnetic structure being defined by a wave vector corresponding to a symmetry point of the Brillouin zone ($\mathbf{k} = \mathrm{H}/2$) [2], the body-centered tetragonal Bravais lattice with $c > a$, allows, in addition to the ferromagnetic order ($\mathbf{k} = 0$), only three types of antiferromagnetic structures: AFI with $\mathbf{k} = [001]$, AFII with $\mathbf{k} = [1/2\ 1/2\ 0]$ and AFIII with $\mathbf{k} = [1/2\ 0\ 1/2]$.

By considering the in-plane interactions (I_1, I_2, . . .) as stronger than the inter-plane ones (I', I'', . . .), the ordering within a (001) plane can be only ferro or antiferromagnetic if only two exchange integrals I_1 and I_2 are taken into account. Actually, three exchange integrals are needed to get an incommensurate or a commensurate order within a (001) plane. The order will be ferromagnetic ($\mathbf{k} = 0$) or antiferromagnetic ($\mathbf{k} = [1/2\ 1/2\ 0]$) according to $I_1 > 0$ or $I_1 < 0$, at least if I_2 has not too large a negative value; in that case ($|I_2| > |I_1|/2$), the wave vector will be $\mathbf{k} = [1/2\ 0\ 0]$. Actually the coupling between planes of *RKKY*-type is not weak, an estimation can be done easily, when the in-plane coupling is ferromagnetic, by comparing the values of T_N and θ_p. For $TbRh_2Si_2$ we get $T_N = 92$ K and $\theta_p = 43$ K indicating that the inter-plane coupling ($\theta_p - T_N$) is antiferromagnetic and of the same order of magnitude than the in-plane ferromagnetic coupling. Then, in the case of large inter-plane couplings, incommensurate structures can be stabilized in addition to the antiferromagnetic ones. It must be pointed out that the in-plane component of the wave vector will depend on both the in-plane (I_1, I_2) and inter-plane (I', I'') exchange integrals. Up to now only the incommensurate structure with a wave vector $\mathbf{k} = [0\,0\,k_z]$ has been found in $PrCo_2Ge_2$, UPd_2Si_2 and UPd_2Ge_2, and a commensurate structure with $\mathbf{k} = [0\,0\,1/2]$ exists in UCu_2Ge_2 [12].

Coming back to the RRh_2Si_2 compounds, susceptibility measurements [2] have shown that they exhibit at low temperatures an antiferromagnetic order probably with a ferromagnetic in-plane coupling as, for all of them, θ_p has a large positive value like in $TbRh_2Si_2$, in particular in $NdRh_2Si_2$ the following values $\theta_p = 27$ K and $T_N = 57$ K [2] have been measured. The only exception in the series would be $CeRh_2Si_2$ where θ_p has an unusually large negative value ($\theta_p = -61$ K), but in comparison a rather small value of the ordering temperature ($T_N = 36$ K). The explanation of this unexpected result is only due to a change of sign of the first nearest neighbour exchange integral I_1 which has a positive value for normal rare earths and a negative value in the case of cerium. Actually, the ferromagnetic ($\mathbf{k} = 0$) and the antiferromagnetic coupling with $\mathbf{k} = [1/2\ 1/2\ 0]$ are dual by changing the sign of I_1. Moreover in this antiferromagnetic structure, imposed by the in-plane exchange integrals I_1 and I_2, the nearest neighbouring exchange integral between (001) planes (I') is not involved to determine the stacking sequence of (001) planes while it has a large value. Actually, in $CeRh_2Si_2$ as in $TbRh_2Si_2$, I' has a large negative value which explains the important difference between the values of T_N and θ_p. Then the large negative value of θ_p in $CeRh_2Si_2$ is the consequence that the main interactions are all antiferromagnetic ($I_1 < 0$, $I_2 < 0$ and $I' < 0$). A large negative value of θ_p has been found also in $CePd_2Si_2$ ($\theta_p = -75$ K), $CeAu_2Si_2$ ($\theta_p = -12$ K) and $CeAg_2Si_2$ ($\theta_p = -15$ K) [15] while these compounds order antiferromagnetically below 10 K. Therefore, these cerium compounds may develop a magnetic order similar to that found in $CeRh_2Si_2$, at least in $CePd_2Si_2$.

In normal rare earth ternary compounds the magnetic coupling is of the *RKKY*-type and it is quite important in the RRh_2Si_2 series probably due to a high density of states at the Fermi energy. However, the sudden change of the sign of I_1 in $CeRh_2Si_2$ indicates that the interactions are not only of the *RKKY*-type in this compound, in particular the usual intra-atomic 4*f*–5*d* exchange interaction is not the dominant mechanism. Actually, the dominant exchange interaction in $CeRh_2Si_2$ would be due to the large mixing between 4*f* and conduction electrons leading to a Kondo-like behaviour. Such a mixing process gives rise to anisotropic indirect interactions in which one part behave as *RKKY* ones [16] but the other part is always antiferromagnetic and decreases exponentially with the distance [17]. This latter contribution could explain the change of sign of I_1. A more extensive study of the magnetic properties of $CeRh_2Si_2$ and similar compounds as $CePd_2Si_2$ would be interesting to confirm this idea.

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