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MAGNETIC PROPERTIES AND MAGNETIC STRUCTURE OF $GdNi_2Si_2$ AND $GdCu_2Si_2$ COMPOUNDS

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The magnetic properties of the tetragonal $ThCr_2Si_2$-type compounds $GdNi_2Si_2$ and $GdCu_2Si_2$ have been investigated by resistivity, susceptibility and magnetization measurements. Their magnetic structure has been also determined by neutron diffraction at a very short wavelength where the absorption cross section of gadolinium is not too high. $GdNi_2Si_2$ orders in an amplitude modulated antiferromagnetic structure while a simple commensurate antiferromagnetic structure occurs in $GdCu_2Si_2$. All the properties are consistent with those of the other compounds of the corresponding series.

1. Introduction

In the last few years, a large number of studies were performed on the structural and magnetic properties of ternary RM_2Si_2 compounds (R = rare earth, M = 3d, 4d or 5d transition metals) [1,2]. Especially compounds with M = Ni or Cu crystallize in the tetragonal $ThCr_2Si_2$-type structure (I4/mmm space group) [3–5]; moreover these compounds order antiferromagnetically in a large variety of magnetic structures. Whereas the Cu based compounds have simple commensurate magnetic structures [6], the Ni based ones have complex incommensurate modulated structures [7]. Among these latter compounds $TbNi_2Si_2$ exhibits an incommensurate to commensurate transition at 9 K. The stability of these magnetic structures was discussed taking into account the RKKY interactions and crystal field effects.

No neutron diffraction studies have been performed in Gd based compounds due to the huge absorption cross section of natural gadolinium at usual wavelengths (≈ 1 Å). The Gd^{3+} ion being in an S state, crystal field effects are negligible and the study of $GdNi_2Si_2$ and $GdCu_2Si_2$ can give interesting information on the origin of the complex magnetic structures observed in this type of tetragonal compounds. In this paper we present a study of the magnetic properties of these compounds from resistivity (section 2), magnetization (section 3) and neutron diffraction experiments (section 4). Polycrystalline samples were prepared by a direct fusion of the stoichiometric amounts of constituents in a cold crucible induction furnace. The crystallographic structure was checked by X-ray analysis.

2. Resistivity measurements

Resistivity was measured by the ac four probe method between 1.5 and 40 K at the Laboratoire Louis Néel of Grenoble and between 15 and 300 K at the Laboratorio de Estado Solido of the Universidad de Cantabria (Santander).

Fig. 1 shows the thermal variation of the resistivity of the two studied compounds for temperatures ranging from 1.5 to 300 K. An almost linear

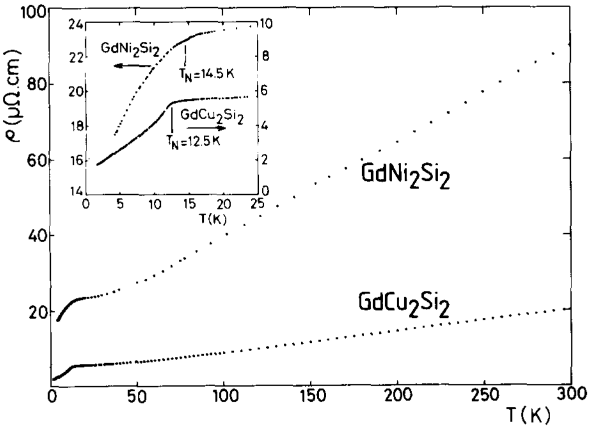

Fig. 1. Thermal variations of the resistivity of $GdNi_2Si_2$ and $GdCu_2Si_2$; the inset shows the low temperature behaviour.

behaviour is obtained at high temperatures. Changes in the slopes are observed at 14.5 and 12.5 K in the compounds with Ni and Cu, respectively (inset of fig. 1); they correspond to the antiferromagnetic ordering temperature T_N (see below). Below T_N the thermal variations of the resistivities are quite different for the two compounds.

The high temperature variations are characteristic of the phonon contribution to the resistivity which would be very similar for both compounds because of the same crystallographic structure with close cell parameters. The larger values and slope observed in $GdNi_2Si_2$ compared to $GdCu_2Si_2$ can be due to the larger brittleness of the Ni compound.

3. Magnetic properties

The bulk magnetic measurements were performed using the extraction method in magnetic field up to 80 kOe and in the temperature range 1.5–300 K, at the Laboratoire Louis Néel of Grenoble.

Fig. 2 shows the thermal dependences of the reciprocal susceptibility for $GdNi_2Si_2$ and

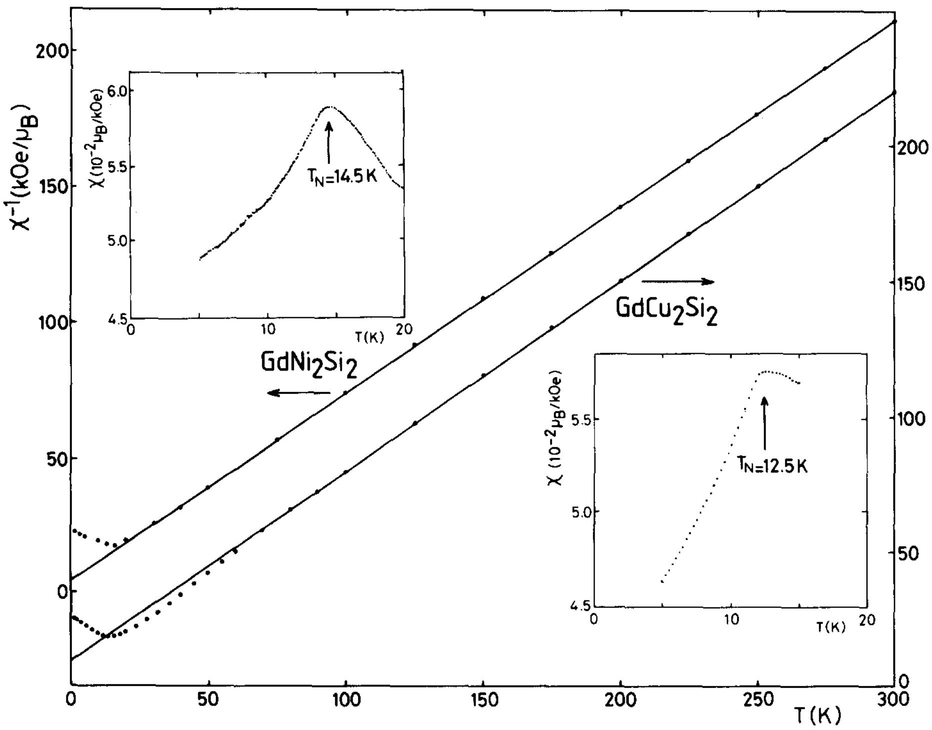

Fig. 2. Reciprocal susceptibilities in $GdNi_2Si_2$ and $GdCu_2Si_2$; the insets show the low temperature behaviour of the susceptibilities.

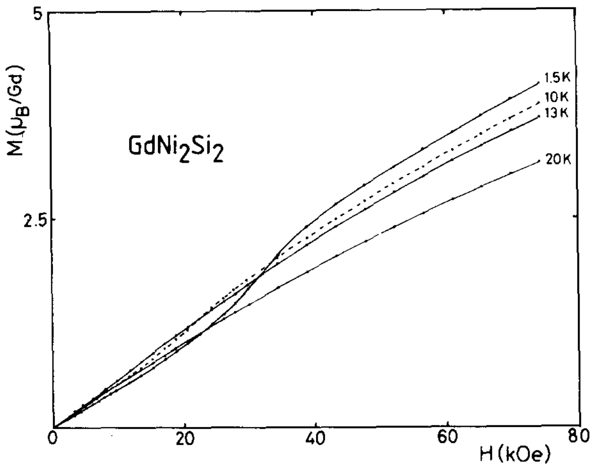

Fig. 3. Isothermal magnetization curves in $GdNi_2Si_2$; dashed and full lines are only guides for the eyes.

$GdCu_2Si_2$. Curie–Weiss laws are observed at temperatures above 60 K leading to paramagnetic effective moments of $8.05\mu_B$ and $8.01\mu_B$, respectively, very close to the free 3 + ion ($7.94\mu_B$). The deduced paramagnetic Curie temperatures are −7 K for $GdNi_2Si_2$ and −16 K for $GdCu_2Si_2$.

The insets of fig. 2 show the thermal variations of the low temperatures susceptibility. They exhibit a maximum at the Néel temperatures which are in agreement with those determined by electrical resistivity.

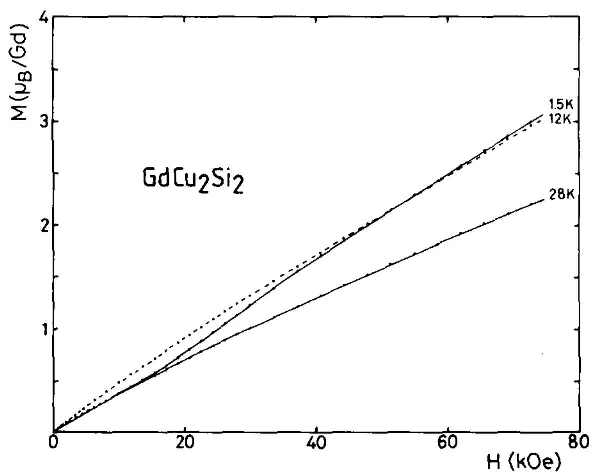

Fig. 4. Isothermal magnetization curves in $GdCu_2Si_2$; dashed and full lines are only guides for the eyes.

Field dependences of magnetization for both compounds are shown in figs. 3 and 4 at different temperatures. Below T_N metamagnetic transitions are observed which are most pronounced at 1.5 K. At this temperature they occur around 30 and 20 kOe for the Ni and Cu based compounds, respectively. The smoothness of the transitions can be associated with the weakness of the anisotropy.

4. Neutron diffraction

Elastic neutron scattering experiments were performed on the D4B diffractometer of the Institute Laue–Langevin, in Grenoble. The absorption cross section of natural gadolinium is prohibitively high (σ_a between 15000 and 55000 barn) at the neutron wavelengths generally used (λ = 1 to 2 Å). However, the absorption cross section is two

Table 1
Main crystallographic and magnetic data for $GdNi_2Si_2$ and $GdCu_2Si_2$

	$GdNi_2Si_2$	$GdCu_2Si_2$
lattice parameters (at ~ 20 K)		
a (Å)	3.973	3.922
c (Å)	9.583	9.993
c/a	2.412	2.503
Si position z	0.366	0.368
Néel temperature		
T_N (K)	14.5	12.5
paramagnetic Curie temperature		
θ_p (K)	−7	−16
effective moment		
μ_p (μ_B)	8.05	8.01
propagation vector		
Q (reduced units)	(0.207, 0, 0.903)	(1/2, 0, 1/2)
magnetic structure type	amplitude modulated	antiferromagnetic
magnetic moment value		
M_0 (μ_B)	8.9 (maximum)	7.2
moment direction	[0 1 0]	[0 1 0]
nuclear reliability factor		
R_N (%)	4.9	18.7
magnetic reliability factor		
R_m (%)	15	7

orders of magnitude smaller at $\lambda = 0.5$ Å ($\sigma_a = 250$ barn). This wavelength is available on the D4B diffractometer of the I.L.L. situated on the hot source of the reactor. The spectrometer was equipped with one 64 cell multidetector, situated at about 3 m of the sample to recover a reasonable angular resolution which was lowered by the use of the short wavelength. Typical counting time was 10 h per spectrum.

5. $GdNi_2Si_2$

Fig. 5 shows the neutron diffraction pattern obtained at 19 K and the difference between those obtained at 2 and 19 K which is characteristic of the magnetic scattering.

The 19 K pattern can be indexed in the tetragonal system respecting the extinction condition of the space group I4/mmm ($h + k + l = 2n + 1$ forbidden). The nuclear intensities were calculated for the following atomic positions of the space group I4/mmm: Gd in 2a: (0, 0, 0); Ni in 4d: (0, $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{2}$, 0, $\frac{1}{4}$); Si in 4e: (0, 0, z and 0, 0, $\bar{z}$). Using the Fermi lengths of Ni and Si given in ref. [8], the calibrating factor, the silicon position z and the Fermi length of Gd were refined by a least square procedure, leading to a satisfactory agreement between the calculated and observed intensities. The values of the cell parameters, in good agreement

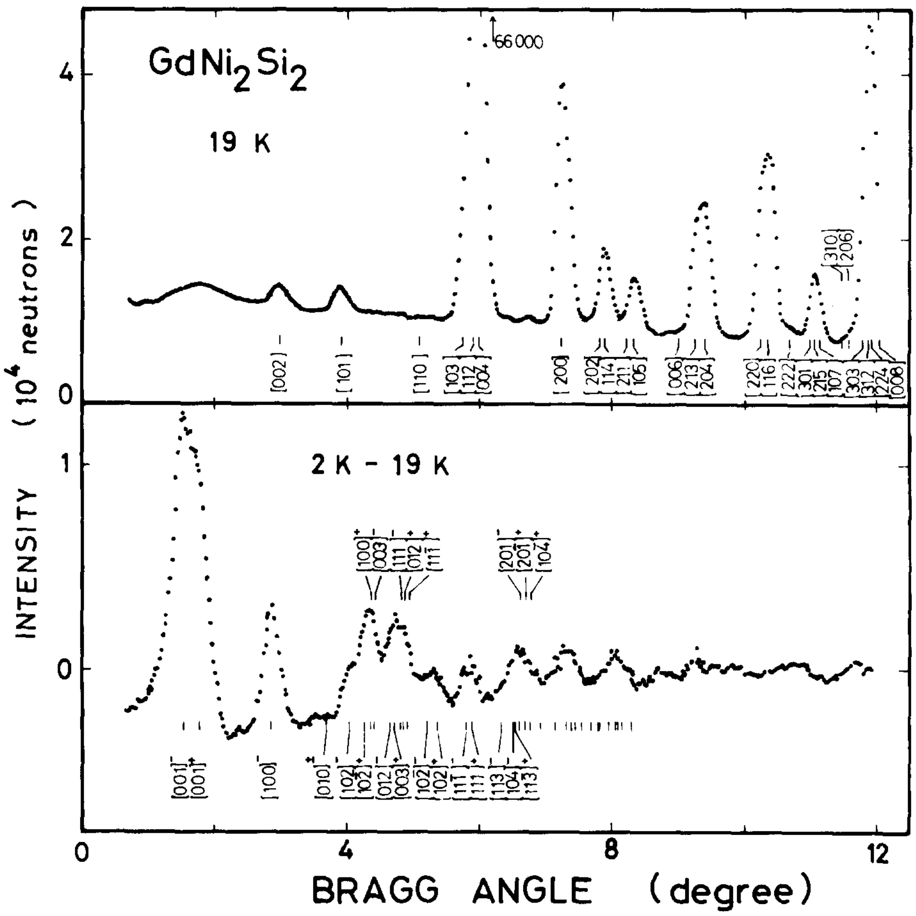

Fig. 5. Neutron patterns in $GdNi_2Si_2$. Upper part: diagram at 19 K. Lower part: difference between diagrams at 2 and 19 K; the notation $[h\,k\,l]^{\pm}$ refers to magnetic reflections with scattering vectors ($h \pm \tau_x$, k, $l \pm \tau_z$) with $\tau_x = 0.207$ and $\tau_z = 0.097$.

with those of the literature, are presented in table 1 as well as the z value and the reliability factor. Due to the proximity of an absorption peak, the Gd scattering amplitude b_{Gd} varies with the neutron wavelength [9]. Our refined value of b_{Gd} is $(1.2 \pm 0.1) \times 10^{-12}$ cm, not far from previous determinations with a comparable neutron wavelength [9,10].

The difference pattern shows a lot of magnetic peaks, especially at low Bragg angle an intense line appears, in which two magnetic peaks are present. It can be indexed with a complex incommensurate propagation vector $\boldsymbol{Q} = (0.207, 0, 0.903)$. The magnetic lines can be considered as satellites of forbidden nuclear lines. The modulation vector is out of a high symmetry axis. The refinement of the magnetic intensities (table 2) leads to a sine wave modulated structure with a moment direction along or very close to the [0, 1, 0] direction. In the refinement the magnetic intensities were calculated taking into account the magnetic form factor of the Gd^{3+} ions [11] and assuming that nickel is not magnetic (see ref. [12]). Due to symmetry considerations, the [0, 1, 0] direction is most probable. This moment direction is perpendicular to the $\boldsymbol{Q}$ vector as occurs in most of the other compounds of the series [7]. The deduced amplitude of the sine wave modulation is

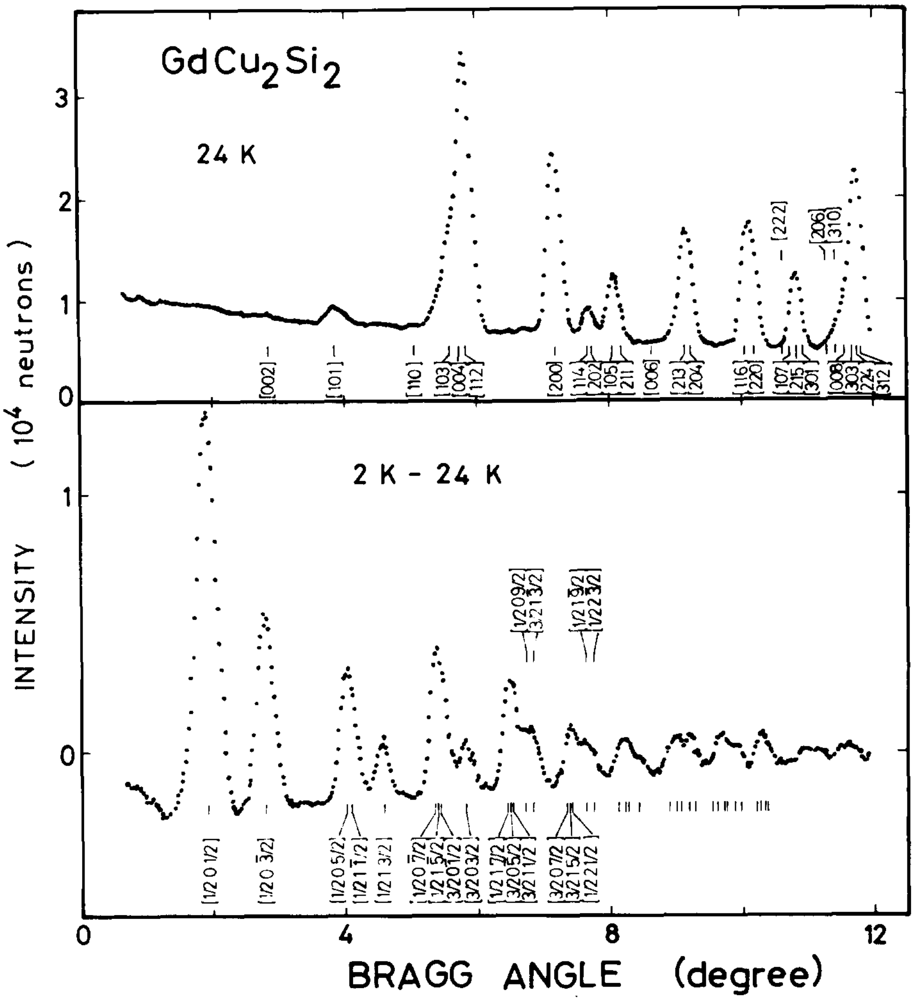

Fig. 6. Neutron patterns in $GdCu_2Si_2$. Upper part: diagram at 24 K. Lower part: difference between diagrams at 2 and 24 K.

Table 2
Position and intensities of the magnetic reflections in $GdNi_2Si_2$ (calc: calculated, obs: observed). The notation $[hkl]^{\pm}$ refers to reflections with scattering vector $(h \pm \tau_x,\ k,\ l \pm \tau_z)$ with $\tau_x = 0.207$ and $\tau_z = 0.097$

$h\ k\ l$	θ_{calc}	q_{obs}	I_{calc} (barn)	I_{obs} (barn)
$0\ 0\ 1^-$	1.54	1.57	11.0	11.4
$0\ 0\ 1^+$	1.80	1.83	10.9	5.5
$1\ 0\ 0^-$	2.86	2.87	10.0	12.8
$0\ 1\ 0^{\pm}$	3.69	–	0.8	~ 0
$1\ 0\ 2^-$	4.04	4.04	8.9	8.6
$1\ 0\ 2^+$	4.25			
$1\ 0\ 0^+$	4.36	4.33	25.6	23.8
$0\ 0\ 3^-$	4.41			
$0\ 1\ 2^-$	4.66			
$0\ 0\ 3^+$	4.69			
$1\ 1\ 1^-$	4.80	4.78	36.0	41.8
$0\ 1\ 2^+$	4.84			
$1\ 1\ 1^+$	4.89			
$1\ 0\ \bar{2}^-$	5.21	5.31	15.0	15.9
$1\ 0\ 2^+$	5.37			
$1\ 1\ \bar{1}^-$	5.82	5.85	17.0	20.0
$1\ 1\ 1^+$	5.89			
$1\ 1\ 3^-$	6.34			
$1\ 0\ 4^-$	6.51			
$1\ 1\ \bar{3}^+$	6.54			
$2\ 0\ 1^-$	6.62	6.63	49.3	35.4
$2\ 0\ \bar{1}^+$	6.68			
$1\ 0\ \bar{4}^+$	6.77			

Table 3
Position and intensities of the magnetic reflections in $GdCu_2Si_2$ (calc: calculated, obs: observed)

$h\ k\ l$	θ_{calc}	θ_{obs}	I_{calc} (barn)	I_{obs} (barn)
$\frac{1}{2}\ 0\ \frac{1}{2}$	1.93	1.93	28.6	29.3
$\frac{1}{2}\ 0\ \frac{3}{2}$	2.80	2.80	26.7	26.5
$\frac{1}{2}\ 0\ \frac{5}{2}$	4.01	4.04	33.9	34.9
$\frac{1}{2}\ 1\ \frac{1}{2}$	4.08			
$\frac{1}{2}\ 1\ \frac{3}{2}$	4.56	4.56	16.5	16.0
$\frac{1}{2}\ 0\ \frac{7}{2}$	5.34			
$\frac{1}{2}\ 1\ \frac{5}{2}$	5.39	5.40	60.7	64.1
$\frac{3}{2}\ 0\ \frac{1}{2}$	5.44			
$\frac{3}{2}\ 0\ \frac{3}{2}$	5.81	5.80	18.3	20.0
$\frac{1}{2}\ 1\ \frac{7}{2}$	6.44			
$\frac{3}{2}\ 0\ \frac{5}{2}$	6.48	6.48	61.3	54.6
$\frac{3}{2}\ 1\ \frac{1}{2}$	6.52			
$\frac{1}{2}\ 0\ \frac{9}{2}$	6.71	6.79	37.8	40.0
$\frac{3}{2}\ 1\ \frac{3}{2}$	6.83			
$\frac{3}{2}\ 0\ \frac{7}{2}$	7.38			
$\frac{3}{2}\ 1\ \frac{5}{2}$	7.42	7.40	36.5	28.1
$\frac{1}{2}\ 2\ \frac{1}{2}$	7.45			
$\frac{1}{2}\ 1\ \frac{9}{2}$	7.62	7.64	23.8	20.0
$\frac{1}{2}\ 2\ \frac{3}{2}$	7.73			

$(8.9 \pm 0.4)\mu_B$. This value corresponds to the first harmonic of an antiphase structure with a moment of $7.0\mu_B$ for the gadolinium ions. In such a structure, small higher order harmonics, especially third-order ones, are expected. Some of them may appear at low angle, where the Lorentz factor makes them observable. In $GdNi_2Si_2$, due to the particular propagation vector, the third-order satellites of the [001] peak are both situated at higher angle (2.48° and 2.96° for the $[001]^{3-}$ and $[001]^{3+}$, respectively). Their intensity is then expected to be very small and within the experimental resolution.

6. $GdCu_2Si_2$

In fig. 6 we present the neutron diffraction pattern obtained at 24 K and the difference between those obtained at 2 and 24 K.

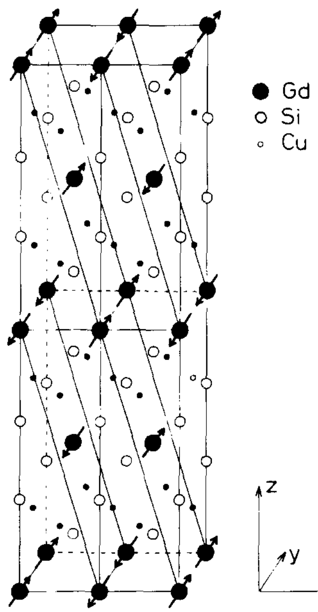

Fig. 7. Magnetic structure of $GdCu_2Si_2$.

The 24 K pattern corresponds to the only nuclear scattering as in the previous compound. The characteristics of our analysis are reported in table 1.

At low temperature, numerous magnetic lines appear, which may be well indexed with a commensurate propagation vector $Q = (\frac{1}{2}, 0, \frac{1}{2})$. The best fit between calculated and observed magnetic intensities (table 3) leads to a magnetic moment of $(7.2 \pm 0.4)\mu_B$ along the [0, 1, 0] direction.

This structure (fig. 7) is identical to that observed in $TbCu_2Si_2$ and $HoCu_2Si_2$ [6]. The characteristics of this structure are presented in table 1.

7. Discussion

Crystallographic and magnetic characteristics of $GdNi_2Si_2$ and $GdCu_2Si_2$ are summarized in table 1. For each compound the magnetic structure is of the same type as those of the other compounds of the series [6,7]. Especially all the compounds with Ni are incommensurate whereas the compounds with Cu have more simple commensurate antiferromagnetic structures. Our results on these S-ion compounds confirm that the exchange interactions in the Ni based compounds are intrinsically more complex that in the Cu based ones. This difference between the two series can be a little surprising due to the similarities in lattice parameters, atomic positions (especially of Si) and values of the Néel temperature. In fact the difference of the magnetic structures may be due to changes of band structure associated with the larger number of conduction electrons for the Cu compounds.

The main difference between gadolinium and the other rare earths concerns the magnetocrystalline anisotropy. The similarity between the magnetic structure of Gd compounds and the rest of each series shows the preponderant role of the exchange interactions on the propagation vector Q, the propagation vector corresponding to the extremum of the Fourier transform of the exchange interactions.

As in the other compounds of both series, except the Pr based compounds, the ordered magnetic moment appears to lie within the basal plane and perpendicular to the propagation vector for both $GdNi_2Si_2$ and $GdCu_2Si_2$. In these compounds without noticeable magnetocrystalline anisotropy, this result should indicate the presence of an intrinsic anisotropy in the exchange interactions, similar in both series.

The last remark concerns the variation of the resistivity below T_N. These variations are quite different: while in the commensurate Cu based compound it exhibits a positive curvature with a well defined anomaly at T_N, in the incommensurate Ni based compound the variation has a negative curvature and an almost imperceptible anomaly at T_N. As previously discussed for the other compounds of the series [7], in the simple antiferromagnetic case ($GdCu_2Si_2$) the scattering of the conduction electrons by magnetic moments with a constant magnitude is smaller than in compounds with modulated structure as $GdNi_2Si_2$, for the same reduced temperature T/T_N.

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