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MAGNETIC PROPERTIES OF RARE EARTH DISILICIDES RSi_2

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Summary

The magnetic properties of the rare earth disilicides (RSi_2) have been re-investigated. We confirm the occurrence of ferromagnetism in $PrSi_2$ and antiferromagnetism in $GdSi_2$, $TbSi_2$, $DySi_2$ and $HoSi_2$. $NdSi_2$ orders at T_N = 10 K and $ErSi_2$ orders at T_C = 4.5 K. Crystal field effects are important throughout the entire series.

1. Introduction

Transition metal disilicides MSi_2 have recently been studied in some detail owing to their potential applications in semiconductor technology [1, 2]. Rare earth disilicides may also be formed as epitaxial layers on silicon [3]. Owing to their magnetism and other physical properties, they may be of particular interest for some integrated devices, such as magnetoresistive, thermoelectric or optical elements.

The crystallography of these phases is rather well known [4, 5]. There are three different but related structures in the series. Surprisingly, only a few data are available on their physical properties, with the exception of $LaSi_2$ and $CeSi_2$ (numerous papers are devoted to the intermediate-valent properties of $CeSi_2$ [6 - 8]). Matthias *et al.* [9] investigated the occurrence of supraconductivity in the RGe_2 and RSi_2 series and found that $PrSi_2$ became ferromagnetic at 11 K. Sekizawa and Yazukochi [10] studied the magnetic properties of heavy rare earth disilicides and found antiferromagnetism in $GdSi_2$, $TbSi_2$, $DySi_2$ and $HoSi_2$. The Néel temperature changes very little between $GdSi_2$ (T_N = 27 K) and $HoSi_2$ (T_N = 18 K). However, some anomalies on their susceptibility curves seem to reveal the occurrence of parasitic phases in the samples.

We have undertaken a systematic study of the magnetic and transport properties of these compounds. In this paper, we report new magnetic measurements on polycrystalline samples and describe briefly the results of some resistivity measurements.

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2. Preparation and crystallography

The samples were prepared by melting stoichiometric proportions of the elements in a cooled copper crucible under purified argon in an induction furnace. Purified argon was used to avoid any contamination. The samples were checked by X-ray diffraction. There is some controversy in the literature concerning the stoichiometry of the compounds [4, 5]; it is well known that silicon-deficient phases RSi_{2-x} are stable, and the stoichiometry of heavy rare earth compounds is generally reported as $RSi_{1.7}$. However, even for the $ErSi_2$ compound, we found a very small amount of free silicon in our 1:2 samples. The measured lattice parameters were in good agreement with those reported previously, and are listed in Table 1.

The samples produced using the above procedure suffer from the presence of microcracks, and are generally not suitable for the measurement of conductivity. Some samples of $LaSi_2$ and $CeSi_2$ were also obtained using the Czochralski method. These samples were single crystals and were generally silicon deficient.

TABLE 1

Crystallographic data for our samples

Compound	*Structure*	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)
$LaSi_2$	Tetragonal	$I4_1/amd$	4.300(5)	—	13.84(2)
$CeSi_2$	Tetragonal	$I4_1/amd$	4.190	—	13.92
$PrSi_2$	Tetragonal	$I4_1/amd$	4.184	—	13.73
$NdSi_2$	Orthorhombic	*Imma*	4.174(5)	4.154(5)	13.61(2)
$GdSi_2$	Orthorhombic	*Imma*	4.090	4.010	13.44
$TbSi_2$	Orthorhombic	*Imma*	4.050	3.965	13.36
$DySi_2$	Orthorhombic	*Imma*	4.038	3.937	13.31
$HoSi_2$	Orthorhombic	*Imma*	4.015	3.906	13.22
$ErSi_2$	Hexagonal	$P6/mmm$	3.792(5)	—	4.083(2)

3. Magnetic measurements

We investigated the magnetic properties of the silicides of cerium [8], praseodymium, neodymium, gadolinium, terbium, dysprosium, holmium and erbium. The magnetic properties were measured down to 1.5 K in fields up to 8 T. A systematic investigation of the magnetization curves allows us to deduce the initial susceptibilities.

The main magnetic properties are summarized in Table 2. For all the samples investigated, the susceptibility has a Curie–Weiss behaviour at high temperatures, with an effective moment close to the value of the trivalent ion (Table 2). Deviations are sometimes observed at low temperatures, for

TABLE 2

Summary of magnetic properties

Compound	θ_p (K)	μ_{eff} (μ_B)	T_{order} (K)	*Structure*[a]
$CeSi_2$	−285	2.87	—	
$PrSi_2$	+ 11	3.54	11	F
$NdSi_2$	−12	3.61	10	AF
$GdSi_2$	−75	8.13	26	AF
$TbSi_2$	−33	9.62	16	AF
$DySi_2$	−21	10.48	10.5	AF
$HoSi_2$	−12	10.52	14	AF
$ErSi_2$	−9.5	9.48	4.5	F

[a]F, ferromagnetic; AF, antiferromagnetic.

instance in $TbSi_2$, which may be ascribed to crystal field effects. All ordering points are below 26 K.

3.1. $CeSi_2$

$CeSi_2$ is known to be an intermediate-valent compound [6 - 8]. We have re-investigated its magnetic properties and electrical resistivity (see Fig. 1).

3.2. $PrSi_2$

The onset of ferromagnetic order at 11 K is confirmed by susceptibility and resistivity measurements (see Figs. 1 and 2). The measured spontaneous magnetization (Fig. 3) is about 1.7 μ_B at 1.5 K. Owing to the magnetocrystalline anisotropy, this value is an underestimate of the saturation moment.

The resistivity has a peculiar temperature dependence (Fig. 1) with a kink at about 200 K. This kink is too sudden to be attributed to crystal field effects. Dijkman [6] has observed a peculiar behaviour of crystalline parameters in this temperature range, with a transformation from the tetragonal $ThSi_2$ phase at room temperature to another tetragonal phase at low temperatures. We thus attribute the resistivity anomaly to a transformation of this type, which however, has little effect on the magnetic susceptibility.

3.3. $NdSi_2$

In contrast with $PrSi_2$, the Curie–Weiss temperature of $NdSi_2$ is negative (−12 K) (Fig. 2). A slight deviation from the high temperature Curie–Weiss law appears below 70 K and must be related to a noticeable crystal field splitting. The Néel point is 10 K, and some discontinuity of the initial susceptibility appears near 6.5 K, probably due to the increase in magnetocrystalline anisotropy. The magnetization curves below 3 K show two steps near 3.5 and 5 T (Fig. 4) and are attributed to the reorientation of the moments.

Neutron diffraction will be undertaken in order to determine the magnetic structure.

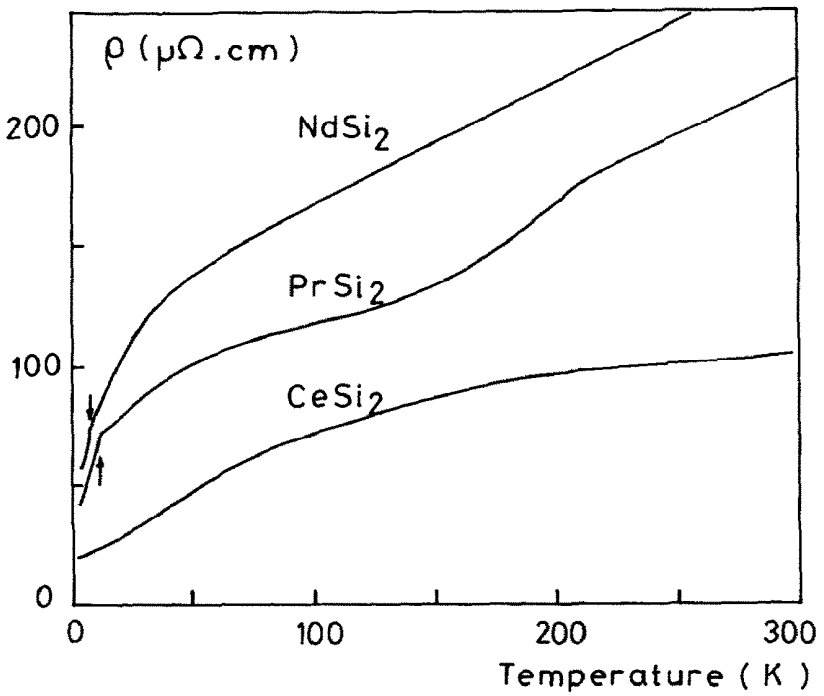

Fig. 1. Electrical resistivities of $CeSi_2$, $PrSi_2$ and $NdSi_2$ compounds. Arrows point to the ordering temperatures.

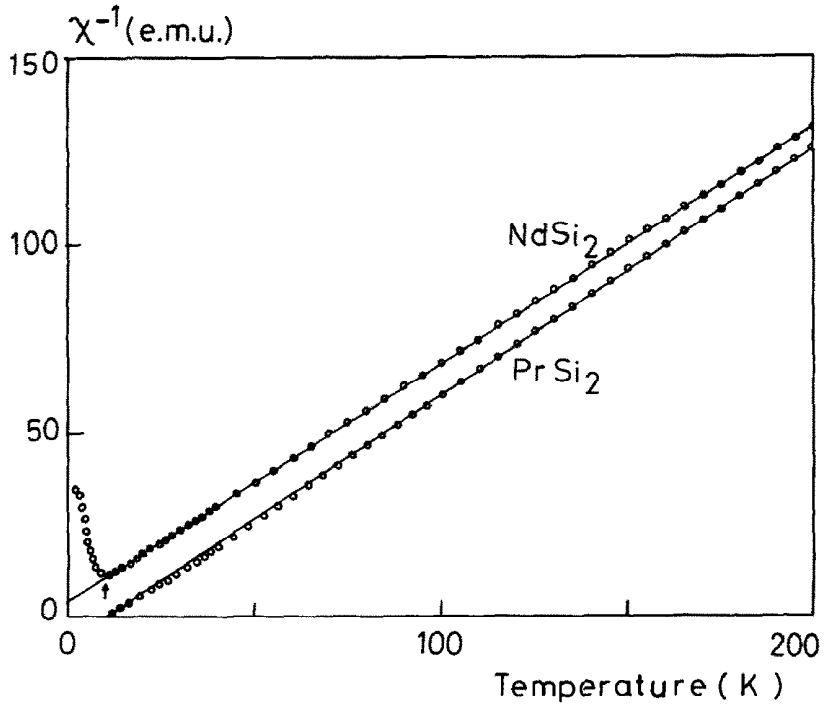

Fig. 2. Reciprocal susceptibilities of $PrSi_2$ and $NdSi_2$ compounds.

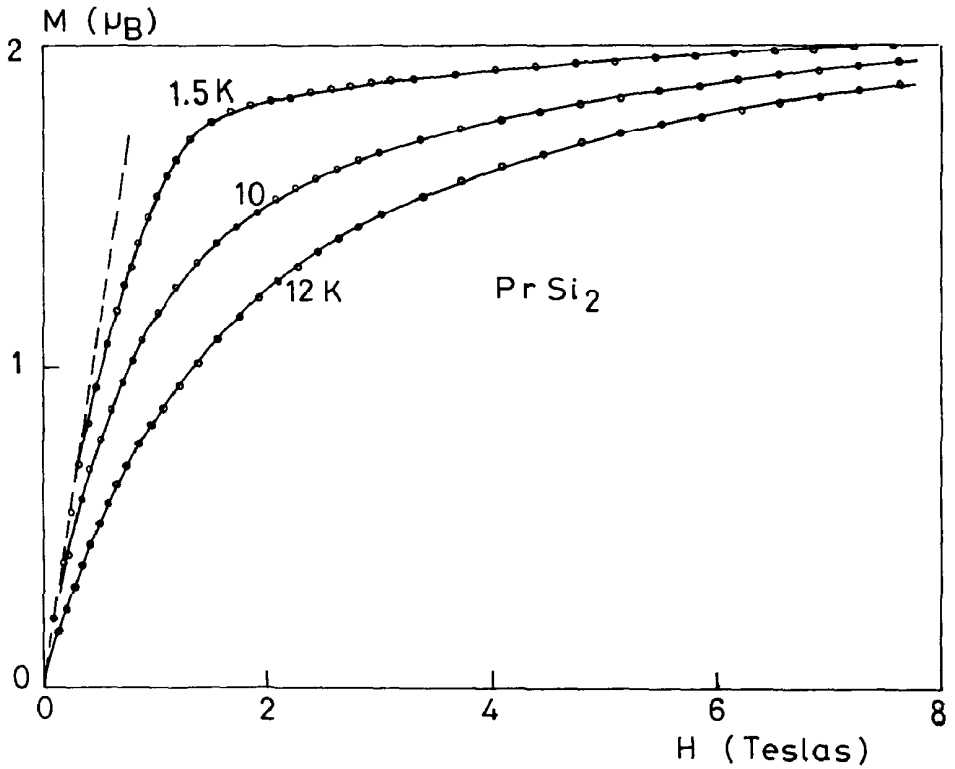

Fig. 3. Magnetization curves of $PrSi_2$. The broken line is the demagnetization field slope.

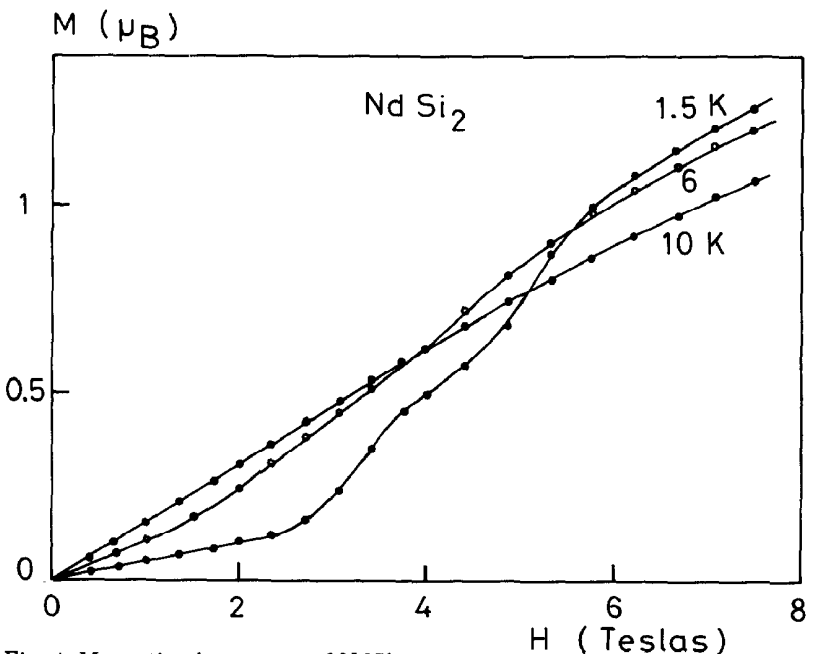

Fig. 4. Magnetization curves of $NdSi_2$.

3.4. $GdSi_2$, $TbSi_2$, $DySi_2$ and $HoSi_2$

These compounds are classical antiferromagnets. The ordering points are 26 K, 16 K, 10.5 K and 14 K for $GdSi_2$, $TbSi_2$, $DySi_2$ and $HoSi_2$ respectively (Figs. 5 and 6). These values are slightly lower than the values of Sekizawa and Yasukochi [10]; however, we agree with them that the Néel temperatures do not follow the so-called De Gennes law in the series. In the ordered range, all compounds exhibit spin-flopping phenomena (Fig. 7).

3.5. $ErSi_2$

The reciprocal susceptibility of $ErSi_2$ (Fig. 5) exhibits a strong negative curvature below 20 K. Thus, despite a negative Curie–Weiss temperature of −9 K extrapolated from the high temperature range, the susceptibility diverges at about 4.5 K, which is the Curie point of this compound. Resistivity measurements confirm this value.

The spontaneous magnetization at 1.5 K is found to be about 1.3 μ_B for the polycrystalline sample (Fig. 8). The magnetization increases linearly up to 2 T (rotation of moments towards the field) and tends to saturate above 4 T; an extrapolation of the high field range down to $H = 0$ gives an estimate

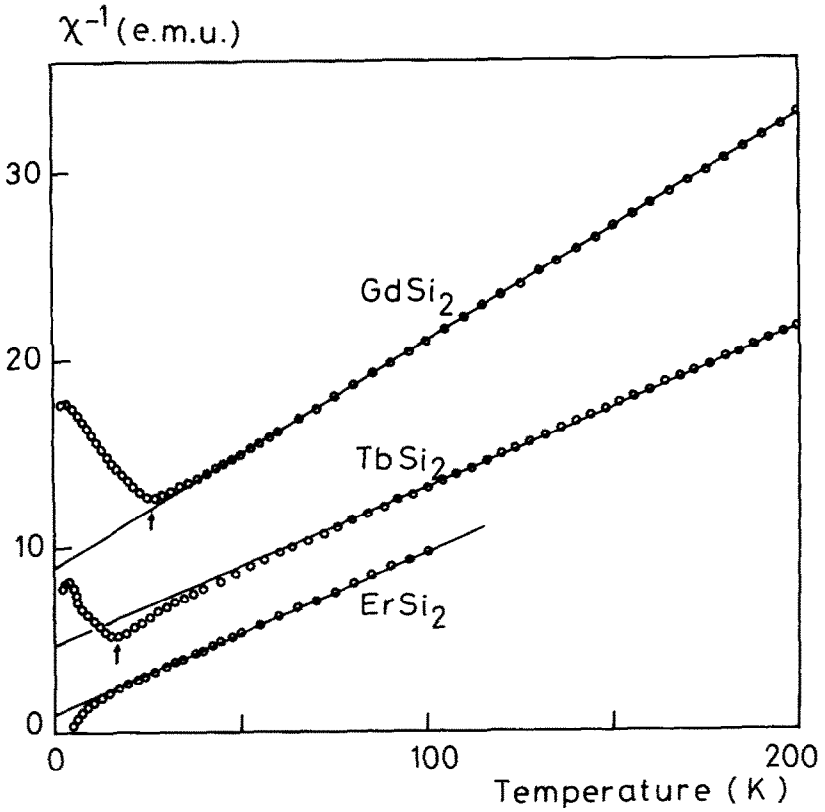

Fig. 5. Reciprocal susceptibility of $GdSi_2$, $TbSi_2$ and $ErSi_2$.

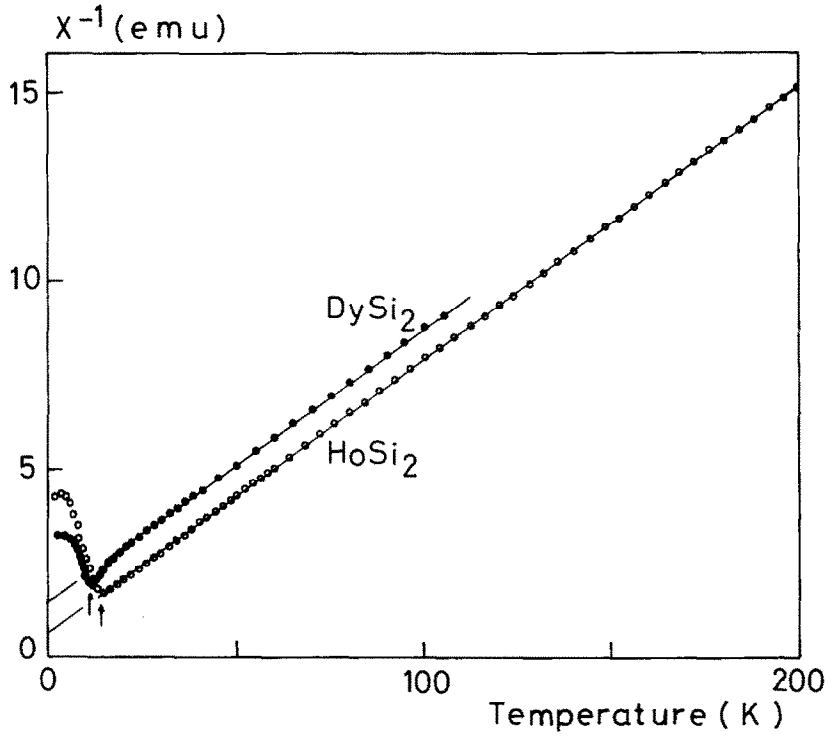

Fig. 6. Reciprocal susceptibility of $DySi_2$ and $HoSi_2$.

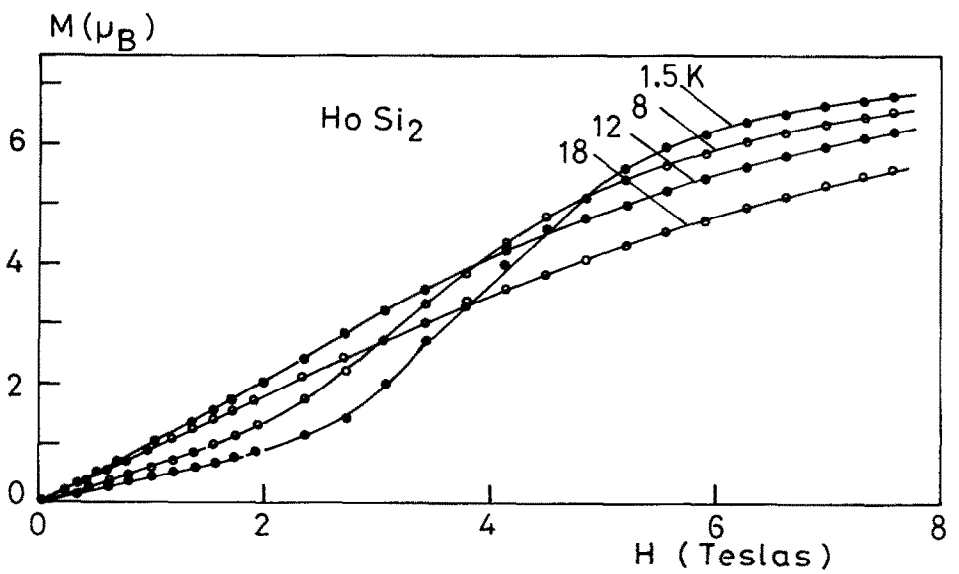

Fig. 7. Magnetization curves of $HoSi_2$.

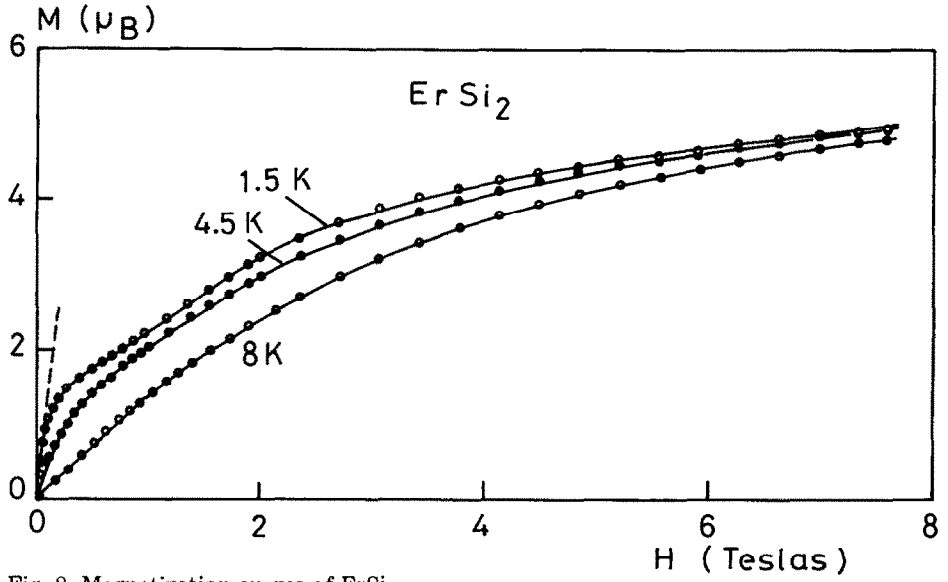

Fig. 8. Magnetization curves of $ErSi_2$.

of the spontaneous magnetization, which is about 3.5 μ_B for this compound. At the present time, we cannot decide whether or not $ErSi_2$ is a simple ferromagnet.

4. Discussion

The magnetic properties of RSi_2 compounds exhibit a large variety of ordering, *i.e.* no order in $CeSi_2$, ferromagnetism in $PrSi_2$ and possibly $ErSi_2$ and antiferromagnetism in $NdSi_2$, $GdSi_2$, $TbSi_2$, $DySi_2$ and $HoSi_2$.

Such varying behaviours may be explained by the occurrence of a large magnetocrystalline anisotropy, which is governed by the three different crystallographic structures in the series, and by the different signs of the Stevens coefficients. For instance, the magnetic structure is antiferromagnetic in $HoSi_2$, which has a negative second-order Stevens coefficient α, and has a ferromagnetic component in the case of $ErSi_2$, which has a positive α value.

A complete understanding of the properties must rely on the determination of the crystal field level scheme, which has been undertaken using inelastic neutron scattering measurements, measurement of the susceptibility on single crystals, and determination of the magnetic structure by neutron diffraction.

Looking at the resistivity behaviour, for instance in the light rare earth compounds (Fig. 1), we observe that the high temperature phonon slope increases from cerium to neodymium, which probably indicates a change in

the free area of the Fermi surface. Indeed, these materials, are expected to be semi-metals, and resistivity should be very sensitive to the band overlap.

In particular, the resistivity of $CeSi_2$ is smaller than those of $PrSi_2$ and $NdSi_2$, whereas the opposite would be expected as a result of the intermediate-valent character of cerium.

$PrSi_2$ is the only compound with a positive Curie–Weiss temperature. We note that silicon-deficient cerium disilicides $CeSi_{2-x}$ also show ferromagnetic behaviour [7]. In addition, the preliminary inelastic neutron scattering experiments for $PrSi_2$ show a rapid relaxation of crystal field excitations. Therefore the hybridization of f electrons with the conduction band may occur in this compound.

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