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Magnetic properties of rare earth–manganese compounds of the type $RMnSi_2$

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Abstract

We have studied the temperature dependence of the intrinsic coercivity of the compounds $RMnSi_2$ (R≡La, Ce, Pr, Nd) from 4.2 to 300 K. The differences in coercivity behaviour observed for these compounds were correlated with the corresponding temperature behaviour of the magnetic structures and with the valence instability of Ce in $CeMnSi_2$.

Magnetic isotherms of $LaMnSi_2$ and $CeMnSi_2$ at 4.2 K were studied in field strengths up to 35 T.

Neutron diffraction measurements were performed on $CeMnSi_2$ at 8 and 408 K. From the results of neutron diffraction and high field measurements it was concluded that Ce loses its magnetic moment at low temperatures. This is the first example of a strongly ferromagnetic compound in which Ce has an unstable valence.

1. Introduction

This paper serves a dual purpose. In the first place it is intended to show that Mn atoms in ternary intermetallic compounds are not only able to carry a moment and give rise to magnetic ordering above room temperature, but that they are also able to generate substantial magnetic hardness. The latter property is a prerequisite for the use of Mn-based materials in permanent magnets.

In the second place this paper is intended to show that an unstable Ce valence may also be found in a strongly ferromagnetic material in which the ferromagnetism is due to a second magnetic component. Here the prerequisite is that the coupling between the ferromagnetic sublattice and the Ce lattice be sufficiently weak, as is the case in the $RMnSi_2$ compounds.

2. Experimental procedures and results

2.1. Preparation

The $RMnSi_2$ samples (R≡La, Ce, Pr, Nd) were prepared by arc melting from starting materials of at least 99.9% purity. Vacuum annealing (2 weeks at 800 °C) was performed by wrapping the samples in Ta foil and sealing then in an evacuated quartz tube. The samples were checked for single-phase condition by X-ray diffraction. In all cases we confirmed the orthorhombic $TbFeSi_2$ type of structure reported earlier [1, 2].

2.2. Magnetic measurements

Measurements of the magnetic isotherms at 4.2 K were performed on $LaMnSi_2$ and $CeMnSi_2$ in fields up to 35 T. In both cases fine powders were used for the measurements, the powder particles being allowed to rotate freely into their equilibrium position. The results are displayed in Fig. 1. It can be seen that saturation is reached in $LaMnSi_2$ in fields higher than 10 T. The saturation moment, obtained by extrapolating the high field part to zero field, equals 1.70 μ_B/f.u. (Bohr magneton per formula unit).

The situation is different for $CeMnSi_2$, since here the magnetization does not saturate even in the highest field strengths applied. Extrapolation of the almost linear high field part of the isotherm to zero field would lead to the value 1.6 μ_B/f.u.

Hysteresis loops were measured at various temperatures on a superconducting quantum interference de-

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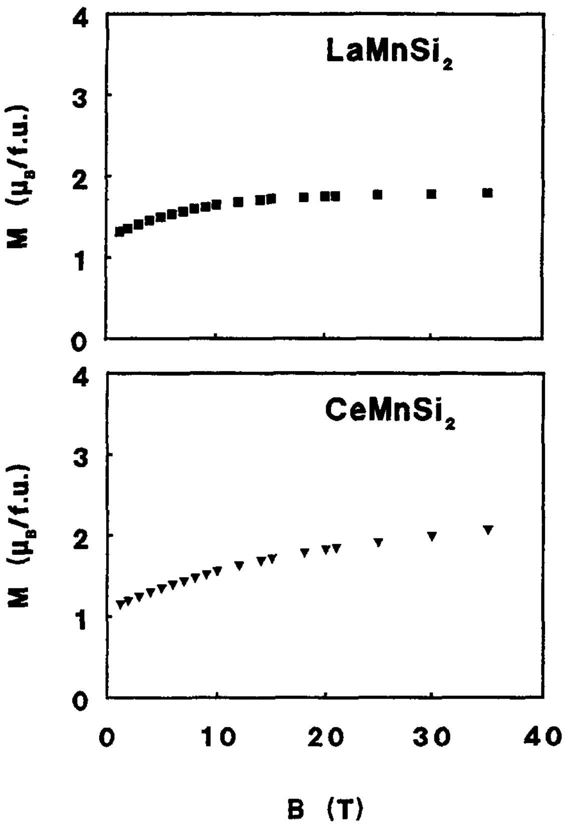

Fig. 1. Magnetic isotherms at 4.2 K for LaMnSi$_2$ and CeMnSi$_2$.

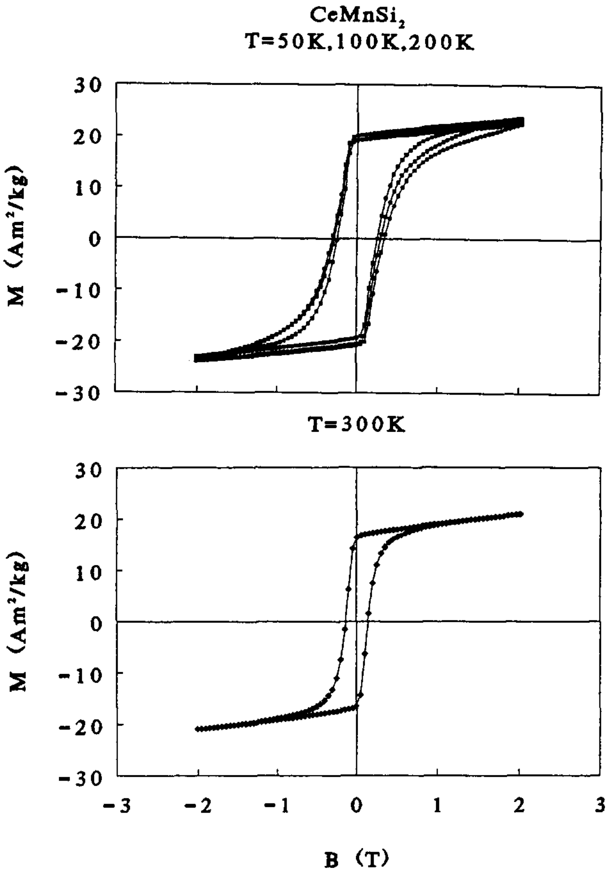

Fig. 2. Hysteresis loops at various temperatures for CeMnSi$_2$. For the three loops shown in the top part the width of the loops increases in the sequence 200, 100, 50 K.

vice (SQUID) magnetometer on polycrystalline samples of all compounds considered. Representative examples are shown in Fig. 2 for CeMnSi$_2$ and in Fig. 3 for NdMnSi$_2$. It can be seen from these figures that the coercivity varies considerably with the temperature. In the case of CeMnSi$_2$ the coercivity increases with decreasing temperature, whereas in the case of NdMnSi$_2$ it decreases with decreasing temperature.

Measurements of the room temperature coercivity of NdMnSi$_2$ were also conducted by means of Kerr effect measurements using a polished surface of a sample piece of about 5 g. From the hysteresis loop measured via the Kerr effect, about the same value of H_c was found as obtained from the SQUID measurements.

A survey of the temperature dependence of the coercivity of the four RMnSi$_2$ compounds considered is given in Fig. 4. The results shown for LaMnSi$_2$ are the only ones that can be taken as exclusively representing the contribution of the Mn sublattice. In order to be able to compare the coercivity with the anisotropy field associated with the Mn sublattice magnetization, we performed magnetic measurements in two mutually perpendicular directions on a powder sample of LaMnSi$_2$ after aligning the powder particles in a magnetic field and fixing the oriented powder particles with epoxy resin. The results obtained at 4.2 K are shown in Fig. 5. It follows from these results that the alignment of the powder particles in the sample may not be quite perfect. The intersection of the $M_{\parallel}$ and $M_{\perp}$ curves shown leads to an anisotropy field of $\mu_0 H_A \approx 12$ T. The intersection point at room temperature is at about $\mu_0 H_A = 6$ T. X-Ray diffraction performed on the aligned powders suggests that the easy magnetization direction at room temperature is along the *b* direction.

Cerium is the least expensive of all rare earth metals. For this reason any ferromagnetic Ce-based material in which coercivity can be generated fairly easily deserves proper attention. From a comparison of the lattice constants of the RMnSi$_2$ compounds and from magnetic measurements carried out in the paramagnetic regime of CeMnSi$_2$, it can be deduced that Ce behaves trivalently [2]. The situation is less clear in the magnetically ordered state, where CeMnSi$_2$, like LaMnSi$_2$, behaves ferromagnetically. However, the saturation moment at 4.2 K of CeMnSi$_2$ is not significantly higher than that of LaMnSi$_2$, the main difference being the presence of a sizable high field susceptibility in the former compound compared with the latter (see Fig. 1).

Previous neutron diffraction studies of CeMnSi$_2$ have not led to entirely conclusive results either, because

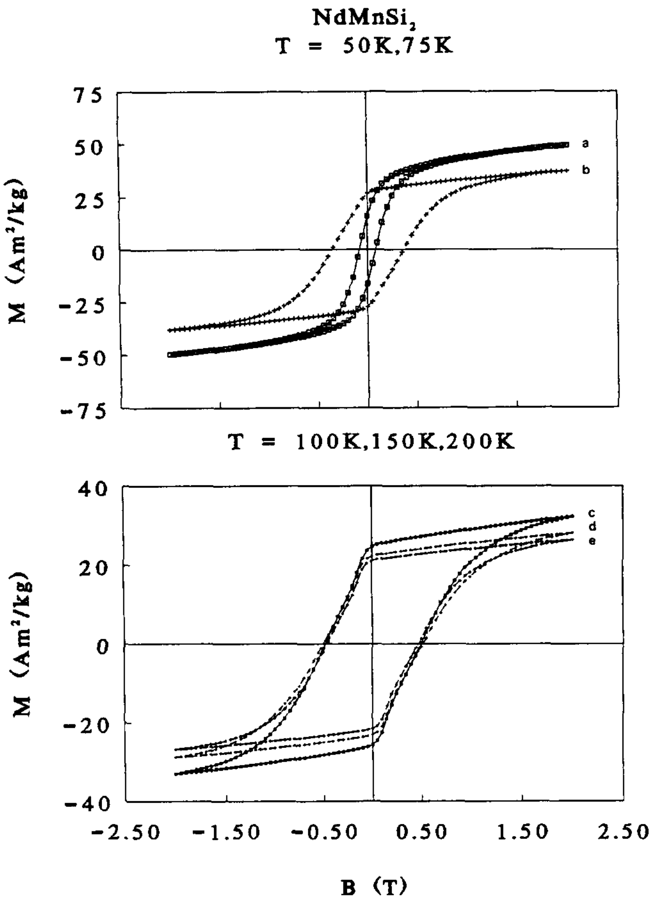

Fig. 3. Hysteresis loops at various temperatures for NdMnSi$_2$: a, 50 K; b, 75 K; c, 100 K; d, 150 K; e, 200 K.

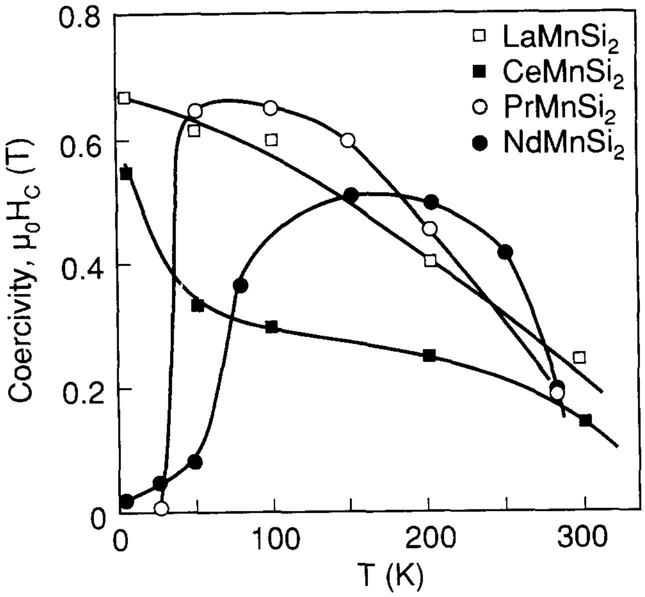

Fig. 4. Temperature dependence of the coercivity in various RMnSi$_2$ compounds.

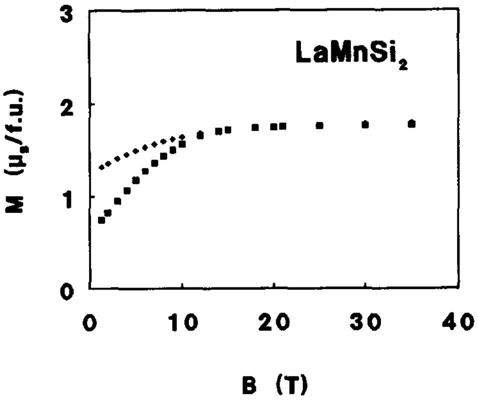

Fig. 5. Field dependence of the magnetization measured at 4.2 K on aligned LaMnSi$_2$ powders with the measuring field parallel (top curve) and perpendicular (bottom curve) to the alignment direction.

satisfactory fits to the neutron data could be obtained both with and without a moment on the Ce atoms [3].

In order to clarify this situation, we have performed neutron diffraction measurements on CeMnSi$_2$ using a more extended 2θ range than in the previous investigation and including measurements above the magnetic ordering temperature.

2.3. Neutron diffraction

Neutron diffraction powder data on CeMnSi$_2$ powder in the paramagnetic state at 408 K (Fig. 6, top part) confirm the TbFeSi$_2$ type of structure [1]. This type is adopted by all ternary rare earth intermetallic disilicides of the chemical formula RMSi$_2$ where M≡ Mn, Fe. A small amount of the tetragonal phase CeSi$_{1.86}$ (a = 0.4181 nm, c = 1.3885 nm, of α-ThSi$_2$ type) and a second unidentified impurity phase were present in the sample. The former phase was included in the refinement, while one non-overlapping reflection of the second phase was excluded from the refinement. The rather high χ^2 = 15 value is attributed to the presence of the impurity. Refined parameters are given in Table 1. The refinement was carried out using the FULLPROF computer program [4]. A possible deviation from stoichiometry for the Mn or Si sites did not improve the R factors.

The low temperature neutron diffraction pattern (T = 8 K) is shown in the bottom part of Fig. 6. The appearance of the magnetic reflections at reciprocal lattice positions of the chemical cell is not easily detectable by visual inspection, while no other reflections are seen to be present. This already indicates a rather reduced moment value. A direct comparison of the two spectra is not feasible owing to the different experimental environment. The intensity ratios I_{obs}(8 K)/I_{obs}(408 K)

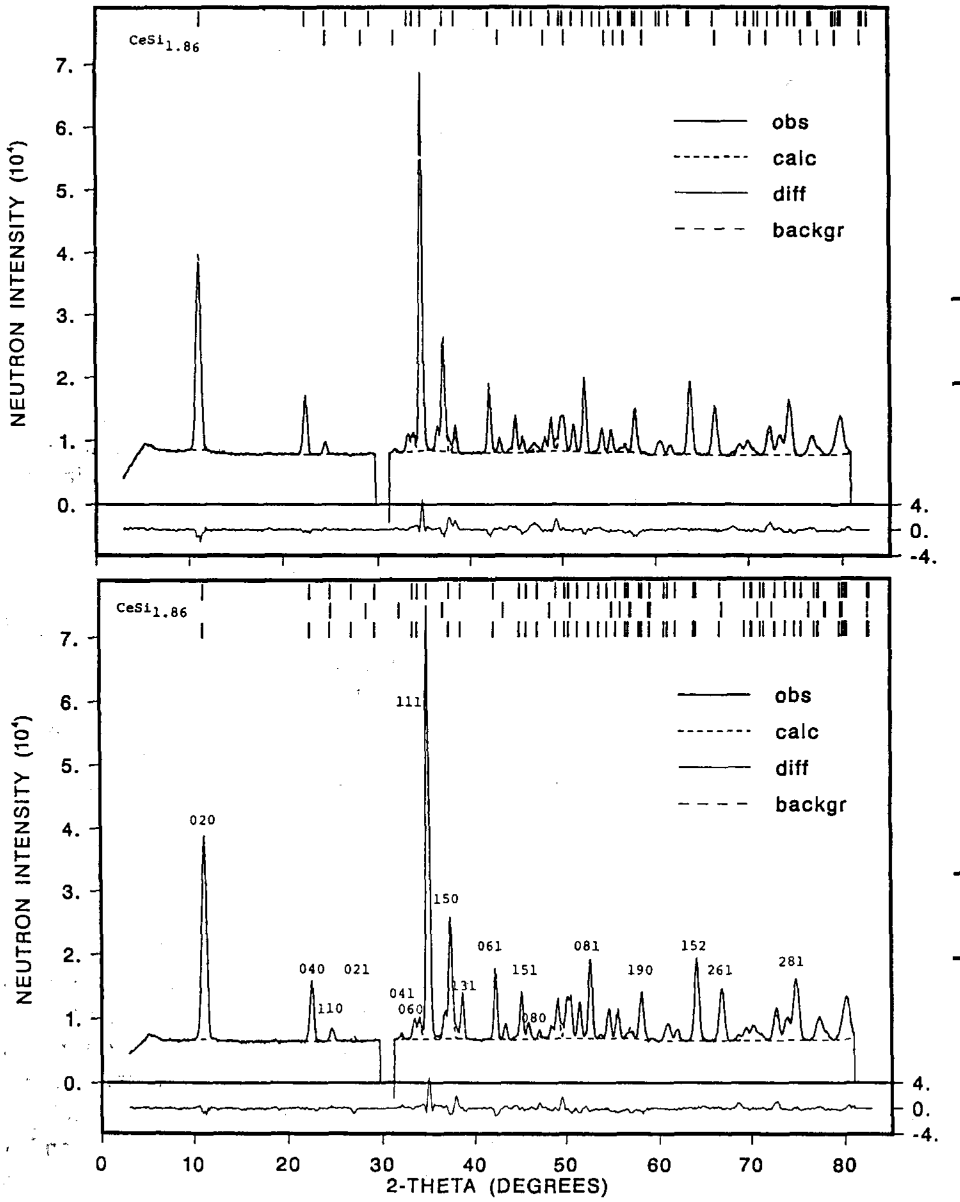

Fig. 6. Neutron diffraction diagrams of CeMnSi$_2$ at 408 K (top) and 8 K (bottom).

of the first few observable magnetic reflections (020), (040), (110), (021), (111) and (131) (see Table 2) that would have major Mn or Ce contributions to the structure factor suggest the following: the magnetic moments cannot be confined to the (*a*,*c*) plane. This would result in a large magnetic contribution to the (020) and (040) reflections, which is not observed (the former would correspond to a dominant Mn and the latter to a Ce contribution). A structural model with antiparallel coupling of the Mn and Ce moments strongly affects the (040) intensity. In a logarithmic plot of the measured data the (021) line that would have had the strongest Ce contribution was found to be absent. This shows that the ferromagnetically ordered moment value, if any, lies below 0.2 μ_B.

The refinement converges for a magnetic moment direction along the *b* axis. The corresponding magnetic space group is $Cm'cm'Sh_{63}^{464}$, which only allows an F_y ferromagnetic contribution for the 4*c* symmetry position. The ordered moment value for Mn of 2.7(2) μ_B is higher than the value of 2.0 μ_B found in the magnetic measurements at 4.2 K in an applied field of 35 T (see Fig. 1). The refined moment value is also higher than the value of 2.24 μ_B/Mn found in a previous neutron diffraction investigation [3].

3. Discussion

In a previous investigation Venturini *et al.* [2] found that the RMnSi$_2$ compounds show Curie–Weiss be-

TABLE 1. Refined structural parameters (neutron diffraction) of the CeMnSi$_2$ compound in the paramagnetic state at 408 K and in the magnetically ordered state at 8 K. Space group *Cmcm* (No. 63), all atoms at 4*c* (0, *y*, $\frac{1}{4}$). B_{of} = overall temperature factor

Parameter	Value	
	408 K	8 K
y_{Ce}, B_{Ce} (nm^2)	0.1015(3), 0.007(1)	0.1013(3)
y_{Mn}, B_{Mn} (nm^2)	0.7505(3), 0.007(1)	0.7510(3)
y_{Si1}, B_{Si1} (nm^2)	0.4642(3), 0.009(2)	0.4650(3)
y_{Si2}, B_{Si2} (nm^2)	0.3247(3), 0.005(2)	0.3246(3)
μ_y (μ_B), Mn^{2+}	–	2.7(2)
μ_y (μ_B), Ce^{3+}	–	−0.10(5)
a (nm)	0.41268(5)	0.41034(5)
b (nm)	1.75550(2)	1.7489(16)
c (nm)	0.40456(5)	0.40267(4)
B_{of} (nm^2)	–	0.0039(6)
R_n (%), R_{wp} (%)	6.8, 11.4	4.8, 10.5
R_m (%), R_{exp} (%)	–, 2.9	11.3, 2.7

haviour above the corresponding magnetic ordering temperatures. The effective moment $\mu_{eff} = 2.6$ μ_b/f.u. found for LaMnSi$_2$ is due to the Mn moments and should be compared with $2[S(S+1)]^{1/2}\mu_B$, where S is the Mn spin quantum number. The corresponding ordered moment is then obtained as $2S\mu_B = 1.79$ μ_B. This value is in good agreement with the value of 1.70 μ_B obtained from the extrapolation of the high field data in Section 2.2. The good agreement between these two values shows that the Mn moments are fairly constant and do not change much when subjected to molecular fields upon magnetic ordering. It is therefore likely that the Mn moment will not change much in compounds where La is replaced by a magnetic rare earth moment. This means that the value of $\mu_{eff} = 2.39$ μ_B/Ce obtained for CeMnSi$_2$ under the assumption that $\mu_{eff} = 2.6$ μ_B/Mn in the same compound has to be regarded as a reliable means for characterizing the properties of Ce. This value, $\mu_{eff} = 2.39$ μ_B/Ce, is close to the free-ion value for Ce^{3+} (2.54 μ_B/Ce). Together with the lattice constants of CeMnSi$_2$ (when compared with the other members of the RMnSi$_2$ series), these results show that Ce in CeMnSi$_2$ has to be regarded as trivalent or very close to trivalent at room temperature and higher temperatures [2].

In the present paper we will not discuss further the modest discrepancy in ordered Mn moment between results of the high field measurements (Fig. 1) and the neutron diffraction data obtained in this investigation and in a previous investigation [3]. Both neutron investigations have shown, however, that the ordered moment on the Ce atoms is either absent or only very small at low temperatures. These results suggest that Ce in CeMnSi$_2$ is not strictly trivalent but rather ambivalent, losing its moment when the temperature decreases. In this connection it is interesting to note that an ambivalent valence of Ce was also reported [2, 5, 6] for other compounds of the same type CeTiSi$_2$ (T ≡ Fe, Cu, Rh). It is well known from many earlier high field studies of Ce compounds with an unstable valence [7] that these materials give rise to an almost linear increase in the magnetic low temperature isotherm, showing no tendency to saturation even in the highest fields applied. This may explain the results shown for CeMnSi$_2$.

The assumption of an unstable valence of Ce in CeMnSi$_2$ may also be used to explain the data shown in Fig. 4. The temperature dependence of H_c shown for LaMnSi$_2$ reflects the effect of the Mn sublattice anisotropy on the coercivity. The sudden drop in H_c for PrMnSi$_2$ is due to the change from ferromagnetism to antiferromagnetism when the temperature decreases [3].

In the case of NdMnSi$_2$ the drop at low temperatures is due to the Nd sublattice anisotropy. The latter anisotropy becomes dominant at low temperatures and leads to an easy magnetization direction for the Nd moments parallel to the *c* axis. Owing to the comparatively weak coupling between the Nd and Mn sublattices, the latter easy magnetization direction is only partly followed by the Mn sublattice, leading to an Mn sublattice magnetization deviating by 45° from the *c* axis [3]. This magnetic structure will hamper the development of large coercivities, which explains the drop in coercivity mentioned.

Inspection of Fig. 4 shows that the coercivity of CeMnSi$_2$ is the only one that increases with decreasing

TABLE 2. Observed integrated neutron intensities of selected reflections with major possible ferromagnetic contributions to structure factor $(F_c)^2 = F^2_{calc} \times M \times LP$ of the Mn and/or Ce sites of the CeMnSi$_2$ compound in the paramagnetic state at 408 K and in the magnetically ordered state at 8 K. (M = multiplicity of the reflection, LP = Lozenz Polarisation factor)

hkl	2θ (deg)	I_o(408 K)	I_o(8 K)	I_o(8 K)/I_o(408 K)	$(F_c)^2$ for Ce	$(F_c)^2$ for Mn
020	11.13	19211(146)	19991(175)	1.040	180	1000
040	22.46	4527(77)	4696(155)	1.030	583	253
110	24.63	904	978	1.08	791	0.1
021	26.88	–	–	0	1000	0.3
111	34.9	25559(112)	29661(145)	1.16	492	439
131	38.58	1933(135)	2722(124)	1.40	916	366

temperature. In the low temperature range in particular there is a strong increase. At 4.2 K almost the same value is reached as in $LaMnSi_2$. Since the latter value is only representative of the Mn sublattice contribution, these results again point to a loss of moment on the Ce atoms at low temperatures.

4. Concluding remarks

The $RMnSi_2$ compounds ($R \equiv La$, Ce, Pr, Nd) are ferromagnetic at room temperature, which is attributed to magnetic ordering of the Mn sublattice. In all compounds an intrinsic coercivity of about 0.2 T is found at room temperature, increasing with decreasing temperature. The compounds $PrMnSi_2$ and $NdMnSi_2$ lose their coercivity in the lowest temperature range, which is attributed to the loss of the collinear ferromagnetic structures present at room temperature.

Although heavily obscured by the presence of the Mn sublattice magnetization, our data obtained for $CeMnSi_2$ indicate an unstable valence for Ce in $CeMnSi_2$. Whereas at high temperatures the Ce ions have a magnetic moment, the low temperature data obtained by neutron diffraction, high field magnetization and coercivity measurements all indicate the absence of a moment on the Ce atoms.

The results obtained in the course of the present investigation show that the hard magnetic properties of the $RMnSi_2$ compounds are exclusively due to the Mn sublattice. Although the hard magnetic properties are still insufficient for practical applications in permanent magnets, the capability of the Mn sublattice to generate substantial magnetic hardness can be regarded as hopeful for future exploitation of ternary compounds based on Mn.

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