Magnetic and structural relationship of RFe₂Si₂ and $R(Fe_{1-x}M_x)₂Si₂ (x = 0 − 1)$ systems ($R = La, Y$ and Lu, $M = Ni$, Mn and Cu)

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Received 19 June 2014, revised 17 September 2014
Accepted for publication 30 September 2014
Published 27 October 2014

Abstract

Due to the similarity between AFe₂As₂ ($A = Ba$, Sr) and RFe₂Si₂ ($R = La$, Y and Lu), the RFe₂Si₂ system has been proposed as a potential candidate for a new high $T_C$ superconducting family containing Fe–Si (instead of Fe–As) layers as a structural unit. Various $R(Fe_{1-x}M_x)₂Si₂ (M = Ni$ and Cu) materials were synthesized and measured for their magnetic properties. None of these materials is superconducting down to 1.8 K. A pronounced peak at 232 K was observed in the magnetization curve of YFe₂Si₂. $^{57}$Fe Mössbauer studies confirm the absence of any long-range magnetic ordering below 232 K. Similar peaks at various temperatures also appear in $R(Fe_{1-x}M_x)₂Si₂$ samples. For Y $(Fe_{1-x}Mn_x)₂Si₂$ the peak position is dramatically affected by the magnetic Mn dopants. Four independent factors affect the peak position and shift it to lower temperatures: (i) the lattice parameters, (ii) the concentration of $x$ (iii) the applied magnetic field and (iv) the magnetic nature of $M$. It is proposed that the magnetic peaks observed in RFe₂Si₂ and in $R(Fe_{1-x}M_x)₂Si₂$ represent a nearly ferromagnetic Fermi liquid system, its nature is yet to be determined.

Keywords: magnetic properties, rare-earth silicides, nearly ferromagnetic Fermi liquid, superconductivity

(Some figures may appear in colour only in the online journal)

1. Introduction

Over the last four decades the ternary intermetallic compounds, which crystallize in the body-centered tetragonal (bct) ThCr₂Si₂ (space group 14/mnm), have been of great interest due to the variety of physical phenomena observed in these compounds. As early as 1974, both magnetic and $^{57}$Fe Mössbauer effect spectroscopy (MS) studies suggest that in bct RFe₂M₂ ($R = La$, Y and Lu and any other rare-earth element, $M = Si$ or Ge), the Fe ions are not magnetically ordered [1]. Indeed, neutron powder diffraction measurements on NdFe₂Si₂ confirmed the absence of any magnetic moment on the Fe sites [2, 3].

The recent discovery of superconductivity (SC) at relatively high temperatures in F doped SmFeAsO (1 1 1 1), up to $T_C = 55$ K [4], as well as in the doped AFe₂As₂ ($A = Ba$, Sr) (1 2 2) systems, has stimulated a large number of experimental and theoretical studies and intensified the search for high temperature superconductors (HTSC) in materials containing Fe–As layers as a structural unit. The pristine bct BaFe₂As₂ sample, has a spin-density-wave (SDW) ground state at $T_N = 136(1)$ K. The suppression of the SDW state by doping, in most cases, induces SC in the system. Notably, SC is generated by both electron and hole doping and even by iso-valent atomic substitution, e.g. P for As. Subsequently, partial substitution of Ni or Co for Fe in BaFe₂As₂, induces
SC in the Ba(Fe1−xNi1−y)2As2 and the Ba(Fe1−xCoy)2As2 systems [5–12]. A higher value for $T_C = 38$ K, was observed by optimal doping in the Ba1−xKxFe2As2 system [5] and in pristine BaFe2As2 by application of high pressure [9]. Also associated with or preceding the magnetic transition is a tetragonal to orthorhombic structural transition, which is suppressed in the SC state. Perhaps, even more remarkable than the large $T_C$, is the large tunability these systems possess. It should be noted, that in the layered AFe2As2 systems (for non-magnetic A atoms such as Ba or Sr) suppression of the long-range magnetic ordering of the Fe sublattice is necessary for the appearance of SC, similar to the behavior of the HTSC cuprates. On the other hand, the problem of these systems is the toxicity of As which limited their fabrication.

The above discoveries motivated a search for new superconductors at elevated temperatures of other systems having the same ThCr2Si2-type structure. In the tetragonal RFe2Si2 (as well as in BaFe2As2 at elevated systems) (figure 1) the $R$(Ba), Fe and Si(As) ions reside in the 2a, 4d and 4e crystallographic positions, respectively. The close relation between the Fe–As and Fe–Si(Ge) systems, strongly suggests similar major role of Fe in the occurrence of SC. Therefore an extensive search for HTSC at elevated temperatures in the two similar RFe2Si2 and RFe2Ge2 systems is appealing. In both systems the Fe ions are not magnetic, thus no suppression of the SDW state mentioned above is needed. In addition both Si and Ge are cheap, non-toxic and very convenient materials. Indeed, very recently YFe2Ge2 was found to be SC at $T_C \sim 1.8$ K in [13]. That strengthens our intuition and prediction for extensive searching for new superconductors in these two systems.

Up to date, little information is available on the electronic structure of RFe2Si2 and RFe2Ge2. The electronic structures of LaFe2Si2 and LaFe2Ge2 were calculated from first principles [14]. Despite of the almost two-dimensionality of the crystal structure, the Fermi surface is three-dimensional. The density of states (DOS) at the Fermi level strongly depend on the distortion of the FeX4 ($X = $ Si and/or Ge) tetrahedra and/or the height of the Si (Ge) atom from the two-dimensional Fe plane. A steep increase of the DOS of Fe is observed below the Fermi energy. It is claimed that this condition, creates excellent chances that doping in the Fe site will shift the DOS to the Fermi level, condition which is essential for HTSC [14].

The desire to dramatically change or tune the properties of any compound, preferably through small changes in stoichiometry or composition, motivated us to search for new HTSC in doped $R$Fe2Si2($R = $ La, Y and Lu) systems in which $R$ is a non-magnetic rare-earth element. Similar to SC induced in doped BaFe2As2 system, it was expected that partial substitutions of $R$, Fe or Si in RFe2Si2 will induce SC at elevated temperatures. Therefore, substitution was made in all three elements which all crystallize in the tetragonal ThCr2Si2 type structure.

Here, we present only the magnetic properties of $R$Fe1−xMx2Si2, in which doping was done in the Fe site. All other systems such as: Ce3+ substituted for La3+, or magnetic Ho substituted for Y, will be described elsewhere. For all $R = $ (La, Y and Lu), Ni was substituted for Fe, whereas in YFe2Si2 the Fe atoms were also partially replaced by Cu and Mn. In this tetragonal structure both Ni and Cu atoms are non-magnetic [15] and our magnetic measurements show that none of these compounds exhibits SC traces down to 1.8 K, although SC in Fe or Ni-containing 122 compounds was observed at low temperatures, e.g. YFe2−xSi2($T_C = 3.0$ K) [16], BaNi2P2($T_C = 3.0$ K) [17] and LaNi2P2 ($T_C = 1.8$ K) [18]. Unexpectedly, pronounced magnetic peaks appear at various temperatures, which are affected by the applied magnetic field ($H$) and/or by the dopant concentrations. For example: (i) the peak observed in YFe2Si2 at 232 K (measured at $H = 15$ G), is shifted to 220 K when measured at $H = 1$ kOe. (ii) In Y(Fe1−xNi1−x)2Si2, the peak shifts with $x$ to lower temperatures and for YNi2Si2 ($x = 1$) no noticeable peak is observed. Its magnetic behavior is reported here for the first time. On the other hand, in Y(Fe1−xCu1−y)2Si2, the peak at $T > 300$ K (for $x = 0.1$), is shifted back to lower temperatures for higher $x$ values. Since both R and Si are non-magnetic elements, the magnetic peaks are definitely related to the Fe sites. Our 57Fe Mössbauer spectroscopy (MS) studies on various materials indicate clearly the absence of any permanent long-range ordering of Fe, below the peaks position. We propose that the peaks observed in RFe2Si2 and in their derivatives represent a new nearly ferromagnetic (FM) Fermi liquid (NFFL) systems, their nature will be discussed.

2. Experimental details

Polycrystalline samples with nominal composition La(Fe1−x

Ni1−y)2Si2 ($x = 0, 0.05$ and $0.15$), Y(Fe1−x

Ni1−y)2Si2 ($x = 0, 0.05, 0.15, 0.50, 0.75$ and $1$), Y(Fe1−x

Mnx)2Si2 ($x = 0.10, 0.20, 0.30, 0.5, 0.7$ and $1$), Y(Fe1−x

Co)xSi2 ($x = 0.10, 0.25$ and $0.5$) and Lu(Fe1−x

Ni1−y)2Si2 ($x = 0, 0.1, 0.2, 0.3$), were prepared by melting stoichiometric amounts of $R$, Fe and Si with Ni, Mn or Cu (all of at least 99.9% purity) in an arc furnace under high-purity Ar atmosphere. The arc-melted buttons were...
flipped and re-melted several times to ensure homogeneity. The samples were structurally and chemically characterized by a Panalytical X’pert powder x-ray diffraction (XRD) diffractometer and energy dispersive spectroscopy (EDS) using EDS-JOEL JSM-7700 scanning electron microscopy (SEM). The EDS instrumental error is ∼2–3%. The XRD patterns of all samples could be well indexed on the basis of bct $I4/mmm$ type structure. Magnetization measurements at various applied magnetic fields in the temperature interval $1.8 \text{ K} < T < 350 \text{ K}$ have been performed using the commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer, with samples mounted in gel-caps. Prior to recording the zero-field-cooled (ZFC) curves, the SQUID magnetometer was always adjusted to be in a ‘true’ $H = 0$ state. The temperature dependence of the field-cooled (FC) and the ZFC branches were taken via warming the samples. The sharp peaks were assigned as the temperatures in which the maximum magnetic moments were observed. For the broad peaks, we used the full-width at half-maximum (FWHM) method. The real ($\chi'$) and imaginary ($\chi''$) ac susceptibilities were measured with a home-made pickup coil method at a field amplitude of $h_0 = 0.05 \text{ Oe}$ at frequencies of $\omega/2\pi = 56$ and $1465 \text{ Hz}$. Resistivity measurements down to $1.8 \text{ K}$ have been performed by conventional four probe methods. $^{57}$Fe MS studies at 90 and 295 K (RT) were performed using a conventional constant acceleration drive, with a 50 mC $^{57}$Co: Rh source. The spectra were analyzed in terms of least-squares fit procedures to theoretical expected spectra. The velocity calibration was performed with $\alpha$-Fe foil at RT and the reported isomer shift (IS) values are relative to this foil at RT.

### 3. Experimental results

#### 3.1. Structural and chemical characterization of $R(\text{Fe}_{1-x}\text{Ni}_x)_2\text{Si}_2$ and $Y(\text{Fe}_{1-x}\text{Cu}_x)_2\text{Si}_2$ samples

All XRD patterns obtained were indexed on the basis of a bct structure with the lattice constants given in table 1.

A typical XRD pattern obtained for YFe$_2$Si$_2$ is shown in figure 2. Rietveld refinement on a long term XRD run yields $z = 0.371(1)$ for the free parameter of Si in the $4(e)$ site. The lattice parameters for YFe$_2$Si$_2$ are in fair agreement with $a = 3.910$ and $c = 9.92 \text{ Å}$ published in [19]. EDS chemical analysis of YFe$_2$Si$_2$ shows that the $Y:Fe:Si$ ratio is exactly $1:2:2$.

The R ($\text{Fe}_{1-x}\text{Ni}_x)_2\text{Si}_2$ system was extensively investigated and the XRD patterns indicate single-phase materials which crystallize in the tetragonal ThCr$_2$Si$_2$ structure. For small $x$ values the $a$ lattice is practically constant, whereas the regular decrease in the $c$ lattice constant can be attributed to the smaller atomic radii of Ni ($1.49 \text{ Å}$) as compared to that of Fe ($1.56 \text{ Å}$) [20]. That leads to the decrease of unit cell volume with $x$ (table 1) and to the decrease of $c/a$ ratio in $Y(\text{Fe}_{1-x}\text{Ni}_x)_2\text{Si}_2$ as shown in figure 2 (inset).

EDS studies of $Y(\text{Fe}_{1-x}\text{Ni}_x)_2\text{Si}_2$ confirm the nominal compositions of the Ni-doped samples; e.g. for $x = 0.05$, and 0.15 the measured Ni concentrations are: 0.06 and 0.17 respectively. On the other hand, table 1 shows that the unit cell volume for $Y(\text{Fe}_{1-x}\text{Mn}_x)_2\text{Si}_2$ and $Y(\text{Fe}_{1-x}\text{Cu}_x)_2\text{Si}_2$ increases with $x$. For Mn (atomic radius 1.61 Å) this increase is quite obvious, whereas for Cu (atomic radius 1.45 Å) [20] this increase needs more consideration and will be discussed later. In YFeCuSi$_2$ ($x = 0.5$), additional extra lines in the XRD pattern which account to 5–7% of the spectral area, were observed. These lines can be indexed on a basis of a hexagonal structure (AlB$_2$ type) which belong to the non-magnetic YCuSi with $a = 4.031$ and $c = 4.008 \text{ Å}$ [21]. Extra lines which account to 15% of the spectral area were observed in YFeMnSi$_2$ ($x = 0.5$). They belong to an orthorhombic unit cell (SG $Cmcm$) with $a = 4.047$, $b = 15.83$ and $c = 3.924 \text{ Å}$, similar to the structure of YFe$_{0.33}$Si$_2$.

### 3.2. Magnetic studies of $R\text{Fe}_2\text{Si}_2$ ($R = Y, \text{La and Lu}$)

Comprehensive magnetic measurements have been performed on the parent YFe$_2$Si$_2$ materials and on all Ni and Cu doped samples listed above. No traces for SC were detected down to 1.8 K. A typical resistivity study (at ambient pressure) for YFe$_2$Si$_2$ also indicates the absence of SC down to 1.8 K (figure 3, lower panel). On the other hand, the parent YFe$_2$Si$_2$ and LuFe$_2$Si$_2$ compounds exhibit pronounced magnetic peaks at various temperatures in the magnetization $M(T)$ curves. Generally speaking, the magnetic features of the Ni and Cu doped materials are very similar to that of their parent compounds. For the sake of clarity, we start with the data measured for YFe$_2$Si$_2$.

(i) $Y\text{Fe}_2\text{Si}_2$.

Figure 3 shows the ZFC magnetization curve ($M(T)$) of YFe$_2$Si$_2$ measured at $H = 250 \text{ Oe}$, in which the peak at 226 K is readily observed. The peak position (which is defined as the maximum of $M$) depends strongly on $H$. Figure 3 (inset) shows (a) that for $H = 1 \text{ kOe}$ the peak shifts to 220 K and (b) that the same position is obtained regardless of whether the $M(T)$ was measured via ZFC or FC processes. The bifurcation observed at low temperatures is probably due to a tiny FM phase discussed hereafter. The field dependence
of the peak position for YFe$_2$Si$_2$ is shown in figure 4. The peak obtained at 232 K for $H = 15$ Oe, shifts to 118 K for $H = 10$ kOe (main panel) and further to 209 K, 197 K and 186 K for $H = 20$ kOe, 30 kOe and 45 kOe (inset) respectively. The almost linear field dependent of the peak position yields a slope of 1.2 K kOe$^{-1}$. It should be noted, that no observable FM impurity probably corresponds to an extra FM phase. This clearly indicates that for the FM impurity the magnetic temperature ordering ($T_C$) is well above RT and that its presence does not affect the peak positions. This impurity probably corresponds to ~0.14% unreacted pure Fe (422 emu g$^{-1}$, $T_C = 1040$ K), or alternatively, to the binaries: Fe$_x$Si (Fe$_2$Si, $T_C = 808$ K) [24] and/or YFe$_2$ or YFe$_3$ ($T_C = 542$ and 525 K) [25]. The tiny amount of this FM impurity phase is below the detection limit of XRD and MS techniques. The hysteresis loop at 5 K (shown in figure 6 (inset)) with a coercive field ($H_C$) of 245 Oe reflects this FM phase. The $M(T)$ curve at 250 Oe (figure 3), is the net moment values after subtracting the FM contribution. The isothermal magnetization $M(H)$ curves of YFe$_2$Si$_2$ measured at 5 and 295 K are shown in figure 6. These curves can be fitted as $M(H) = M_S + \chi_p H$, where $M_S$ is the spontaneous FM magnetization and $\chi_p H$ is the linear paramagnetic (PM) intrinsic susceptibility. For both temperatures, $M_S = 0.31(2)$ emu g$^{-1}$ (table 1) is attributed to a tiny FM extra phase. This clearly indicates that for the FM impurity the magnetic temperature ordering ($T_C$) is well above RT and that its presence does not affect the peak positions. This impurity probably corresponds to ~0.14% unreacted pure Fe (422 emu g$^{-1}$, $T_C = 1040$ K), or alternatively, to the binaries: Fe$_x$Si (Fe$_2$Si, $T_C = 808$ K) [24] and/or YFe$_2$ or YFe$_3$ ($T_C = 542$ and 525 K) [25]. The tiny amount of this FM impurity phase is below the detection limit of XRD and MS techniques. The hysteresis loop at 5 K (shown in figure 6 (inset)) with a coercive field ($H_C$) of 245 Oe reflects this FM phase. The $M(T)$ curve at 250 Oe (figure 3), is the net moment values after subtracting the FM contribution. The isothermal magnetization $M(H)$ curves of YFe$_2$Si$_2$ measured at 5 and 295 K are shown in figure 6. These curves can be fitted as $M(H) = M_S + \chi_p H$, where $M_S$ is the spontaneous FM magnetization and $\chi_p H$ is the linear paramagnetic (PM) intrinsic susceptibility. For both temperatures, $M_S = 0.31(2)$ emu g$^{-1}$ (table 1) is attributed to a tiny FM extra phase. This clearly indicates that for the FM impurity the magnetic temperature ordering ($T_C$) is well above RT and that its presence does not affect the peak positions. This impurity probably corresponds to ~0.14% unreacted pure Fe (422 emu g$^{-1}$, $T_C = 1040$ K), or alternatively, to the binaries: Fe$_x$Si (Fe$_2$Si, $T_C = 808$ K) [24] and/or YFe$_2$ or YFe$_3$ ($T_C = 542$ and 525 K) [25]. The tiny amount of this FM impurity phase is below the detection limit of XRD and MS techniques. The hysteresis loop at 5 K (shown in figure 6 (inset)) with a coercive field ($H_C$) of 245 Oe reflects this FM phase. The $M(T)$ curve at 250 Oe (figure 3), is the net moment values after subtracting the FM contribution.

Well above the peak position the $M(T)$ curves exhibit a typical PM shape and adhere closely to the Curie–Weiss (CW) law: $\chi(T) = \chi_0 + C/(T-\theta)$, where $\chi (= M/H)$, $\chi_0$ is the temperature-independent part C is the Curie constant, and $\theta$ is the CW temperature. The PM parameters extracted from $M(T)$ measured at 1 kOe (at 260–350 K) are: $\chi_0 = 5.5 \times 10^{-3}$ emu mol$^{-1}$ Oe$^{-1}$, $C = 2.34(1)$ emu K mol$^{-1}$ Oe$^{-1}$ and $\theta = 191(3)$ K. The $\chi_0$ infers to the temperature independence FM impurity as discussed. This C value corresponds to a PM

| Compound | $a$(Å) | $c$(Å) | $V$(Å$^3$) | Peak at 250 Oe ± 2 K | $M_S$ (5 K) (emu g$^{-1}$)$^a$ |
|----------|--------|--------|------------|---------------------|-----------------------------|
| $Y (Fe_{1-x}Ni_x)_2 Si_2$ | | | | | |
| $x = 0$ | 3.923 | 9.951 | 153.1 | 226 | 0.31(2) |
| $x = 0.05$ | 3.920 | 9.912 | 152.3 | 211 | 0.42 |
| $x = 0.15$ | 3.923 | 9.874 | 151.9 | 192 | 0.13 |
| $x = 0.50$ | 3.930 | 9.76(1) | 150.7 | 54$^b$ | 1.82 |
| $x = 0.75$ | 3.943 | 9.73(3) | 151.2 | 49$^b$ | 2.21 |
| $x = 1.0$ | 3.963 | 9.544 | 149.8 | — | |
| $Y (Fe_{1-x}Cu_x)_2 Si_2$ | | | | | |
| $x = 0.10$ | 3.924 | 9.94(1) | 153.0 | >350 | 0.008 |
| $x = 0.50^c$ | 3.949 | 9.90(2) | 154.4 | 170 | 0.014 |
| $Y (Fe_{1-x}Mn_x)_2 Si_2$ | | | | | |
| $x = 0.10$ | 3.923 | 9.963 | 153.3 | 61 | — |
| $x = 0.20$ | 3.925 | 9.759 | 153.6 | 16 | — |
| $x = 0.30$ | 3.921 | 10.013 | 153.9 | — | |
| $x = 0.50$ | 3.921 | 10.129 | 155.7 | — | |
| $Lu (Fe_{1-x}Ni_x)_2 Si_2$ | | | | | |
| $x = 0$ | 3.875 | 9.869 | 148.2 | 70 | 0.001 |
| $x = 0.10$ | 3.876 | 9.824 | 147.6 | 46 | — |
| $x = 0.20$ | 3.878 | 9.790 | 147.2 | 31 | — |
| $x = 0.30$ | 3.881 | 9.761 | 147.0 | 23 | 0.002 |
| $Lu (Fe_{1-x}Cu_x)_2 Si_2$ | | | | | |
| $x = 0$ | 4.059 | 10.163 | 167.4 | >350 | 0.96(1) |
| $x = 0.05$ | 4.054 | 10.130 | 166.5 | >350 | 1.63 |
| $x = 0.15$ | 4.054 | 10.10 | 166.0 | >385 | 2.34 |

$^a$ $M_S$ are remnant values due to FM impurity phases.

$^b$ Determined by FWHM.

$^c$ Contain extra lines.
effective moment of $P_{eff} = 3.06(2)\mu_B/\text{Fe}$, a value which is very similar to $2.9\mu_B/\text{Fe}$ obtained for LuFe$_2$Ge$_2$ [26]. $\chi(T)$ obtained fits well with $X_p$ deduced at 5 K. It appears that the Fe in YFe$_2$Si$_2$ carries a net PM moment. That is in stark contrast to virtually temperature-independent magnetic susceptibility (Pauli PM) claimed in the past [1]. Note, that the measured peak size magnitude for YFe$_2$Si$_2$ at 250 Oe is $\sim 10^{-2}$ emu, which is below the sensitivity of the old magnetometer used in [1].

(ii) LaFe$_2$Si$_2$ and LuFe$_2$Si$_2$. The ZFC magnetic behavior of LaFe$_2$Si$_2$ is a bit different. In contrast to YFe$_2$Si$_2$ (figure 3), the magnetization measured at $H = 250$ Oe increases up to 350 K but no definite peak is observed (figure 7). Presumably, higher temperatures are needed to reveal this peak as observed for the iso-structural LaNi$_2$Ge$_2$ material [27]. A small bump around 225 K is observed, its nature is yet not known. On the other hand, for LuFe$_2$Si$_2$ the peak at 70 K under $H = 250$ Oe is clearly observed. The isothermal magnetization curves at 5 K of LaFe$_2$Si$_2$ and LuFe$_2$Si$_2$(figure 7 lower inset) can be fitted in the same manner as the $M(H)$ plots of YFe$_2$Si$_2$ (figure 6). The deduced FM $M_S$ values are: 0.96 and 0.001 emu g$^{-1}$ respectively (table 1). The almost straight line at 5 K for LuFe$_2$Si$_2$ excludes the existence of the SC Lu$_3$Fe$_2$Si$_5$ phase.
Figure 7. ZFC magnetization curve of LaFe$_2$Si$_2$ and LuFe$_2$Si$_2$ (upper inset) measured at 250 Oe. The lower inset shows the isothermal $M(H)$ plots of LaFe$_2$Si$_2$ and LuFe$_2$Si$_2$ measured at 5 K. Note the almost linear curve of LuFe$_2$Si$_2$.

Figure 8. ZFC magnetization curve of Y(Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ ($x = 0, 0.05, 0.15$) measured at 250 Oe. The inset shows the $M(T)$ curve measured at 20 Oe.

Figure 9. $M(T)$ plot of Y(Fe$_{0.25}$Ni$_{0.75}$)$_2$Si$_2$ measured at 250 Oe. The inset shows the $M(T)$ curve measured at 20 Oe.

Figure 10. Temperature dependence of the magnetization of Y(Fe$_{0.25}$Ni$_{0.75}$)$_2$Si$_2$ measured at 250 Oe. The inset shows the peak position of all Y(Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ samples measured at 20–30 Oe.

3.3. Magnetic studies of R(Fe$_{1-x}$Ni$_x$)$_2$Si$_2$

The magnetic behaviors of all R(Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ samples studied resemble the features observed in their parent compounds and the relevant data obtained are listed in table 1. For each $x$ value, the $M(T)$ curves show distinct peaks at elevated temperatures which decrease with $H$. All $M(H)$ plots contain an extra FM phase similar to that shown in figure 6. The differences among the samples are (i) the peak position which is strongly depends on $x$, (ii) the spread $M_S$ values as listed in table 1.

$Y(Fe_{1-x}Ni_x)_{2}Si_2$. (i) Figures 8–10 show representative $M(T)$ plots of Y(Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ samples. Figure 8 shows the $M(T)$ curve for $x = 0, 0.05$ and 0.15 all measured at 250 Oe. The peak at 226 K for YFe$_2$Si$_2$ ($x = 0$) shifts to 211 and to 193 K (inset) for $x = 0.05$ and 0.15 respectively. Broad peaks (determined by the FWHM methods) are observed for higher Ni concentrations: $x = 0.5$ and 0.75 at 54 and 49 K respectively (table 1). (ii) For each Y(Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ material, the peak is also field depended. For example: (a) for $x = 0.05$, the peak at 220 K under 15 Oe shifts to 211 K (figure 8) and to 193 K when measured at 250 Oe and 1 kOe respectively. (b) For $x = 0.15$, the peak at 193 K, measured at 250 Oe (figure 8 inset), shifts to 180 K when measured at 1 kOe. (c) For $x = 0.5$ the relatively broad peak at 86 K measured at 20 Oe (figure 9 inset), shifts at 250 Oe to a broad peak its maximum is at 54 K (table 1). The peak position of Y(Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ samples measured at 15–25 Oe is shown in figure 10 (inset). (iii) All $M(H)$ plots measured below and above the peak position are...
similar to these obtained for YFe$_2$Si$_2$ (figure 6) and can be fitted by the same manner. The spread $M_S$ (at 5 K) values deduced are listed in table 1. Note that the highest $M_S = 2.21$ emu g$^{-1}$ obtained (for $x = 0.75$), is equivalent to the saturation moment of $\sim$1% unreacted Fe, a level which is undetectable neither by XRD nor by MS.

An additional point of interest is the magnetic behavior of YNi$_2$Si$_2$ (figure 11) which is presented here for the first time. The lattice parameters obtained for YNi$_2$Si$_2$ (table 1) are in fair agreement with data published in [19]. The $M(T)$ curve depends on the temperature (not a Pauli behavior), but all attempts to fit it to the CW law were unsuccessful. Both $M(H)$ curve measured at 5 K and at 250 K are linear and the calculated slope $\chi(=M/H)$ value at 5 K and 246 K are $3.76 \times 10^{-4}$ emu mol$^{-1}$ K$^{-1}$ and $1.96 \times 10^{-4}$ emu mol$^{-1}$ K$^{-1}$ respectively. This linear behavior strengthens our suggestion that the undetermined extra FM phase is due to pure Fe or to any other Fe intermetallic compound.

La$(Fe_{1-x}Ni_x)_2Si_2$ and Lu$(Fe_{1-x}Ni_x)_2Si_2$. In these two systems only materials with low Ni concentration have been synthesized. Their $M(T)$ and $M(H)$ plots are very similar to their parent compounds and the relevant data obtained are listed in table 1. Although the peak position strongly depends on $x$, no peak is observed in La$(Fe_{0.85}Ni_{0.15})_2Si_2$ up to 385 K. Here again a bump in the $M(T)$ is observed around 260 K (figure 12). Table 1 shows that for La$(Fe_{1-x}Ni_x)_2Si_2$ the deduced $M_S$ values (at 5 K) increases with $x$. The $^{57}$Fe MS measured at 90 K (figure 12 inset) exhibits a narrow singlet with almost the same parameters obtained for YFe$_2$Si$_2$. This proves once again the absence of sizable permanent local magnetic moments in the Fe sites.

In Lu$(Fe_{1-x}Ni_x)_2Si_2$ (similar to Y$(Fe_{1-x}Ni_x)_2Si_2$) the peak position shifts with $x$ to lower temperatures (figure 13). At 250 Oe, the peak for $x = 0.1$ and 0.2 are at 46, 31 K respectively (table 1). For $x = 0.2$, the peak is shifted to 43 K when measured at 25 Oe. For both materials, an additional broad peak is observed at 205 K (not shown) its origin is yet to be determined. For $x = 0.3$, at 100 Oe the peak location is at 31 K (figure 13) and it is shifted to 18 K when measured at 1 kOe. At higher temperatures the $M(T)$ curve for $x = 0.3$ also exhibit a typical PM shape and can be fitted by the CW law. The extracted PM parameters (at 1 kOe) are: $\chi_0 = -4.2 \times 10^{-3}$ emu mol$^{-1}$ K$^{-1}$, $C = 2.60(2)$ emu K mol$^{-1}$ Oe$^{-1}$ and $\theta = -70(1)$ K. This C value corresponds to $P_{eff} = 3.71\mu_B$/Fe and proves once more the FM nature of Fe in the RFe$_2$Si$_2$ systems. The $M(H)$ curves of Lu$(Fe_{1-x}Ni_x)_2Si_2$ are almost linear and the deduced $M_S$ values are small and negligible (table 1).

3.4. Magnetic studies of Y$(Fe_{1-x}Cu_x)_2Si_2$

The change in lattice parameters Y$(Fe_{1-x}Cu_x)_2Si_2$ is a bit different than that of R$(Fe_{1-x}Ni_x)_2Si_2$ systems. Table 1 shows that for Cu the $a$ lattice parameter increases with $x$ whereas the $c$ constant practically remains unchanged. This
agrees well with the higher \( a \) lattice constant of \( \text{YC}_{2}\text{Si}_{2} \) \((a = 4.153 \text{ and } c = 9.92 \text{ Å})\) as compared to that of \( \text{YFe}_{2}\text{Si}_{2} \) \[19\]. In the \( \text{ThCr}_{2}\text{Si}_{2} \) type structure the shortest 3d–3d distance is given by \( 2^{-1/2}a \), which means that the Cu size is larger than that of Fe. That is due to the well accepted determination that in many intermetallic compounds Cu is formally monovalent, in contrast to a formal divalent Fe (and also Ni) deduced from MS spectra (figure 5). Thus, the Fe–Cu bonds are larger than Fe–Fe and/or Fe–Ni bonds. That probably affects the peak position of \( \text{Y(Fe}_{1-x}\text{Cu}_x)_{2}\text{Si}_2 \). Indeed, figure 14 shows that for \( x = 0.1 \), the \( M(T) \) measured at 250 Oe, increases up to 300 K but no definite peak is observed. At 5 K, a shallow peak is obtained at 302(2) K. In addition, a sharp peak is observed at 24 K (not shown) its nature is not yet known.

As expected, increase of Cu concentration shifts the peak position to lower temperatures, as shown in figure 15 for \( \text{YFeCu}_{2}\text{Si}_2 \). The peak at 182 K \((H = 30 \text{ Oe})\) shifts to 170 K and to 166 K \((H = 250 \text{ Oe})\) respectively.

Thus, the applied magnetic field affects the \( \text{Y(Fe}_{1-x}\text{Cu}_x)_{2}\text{Si}_2 \) system in the same manner. All \( M(H) \) curves are almost linear (figures 14 and 15 (insets)) and the FM impurities are negligible. This indicates once again that the peaks observed are intrinsic and not from FM impurity phases. The extra hexagonal YCuSi phase in \( \text{YFeCu}_{2}\text{Si}_2 \) (detected by XRD) is not magnetic and cannot account for peaks observed in figure 15 \[29\].

**Magnetic studies of \( \text{Y(Fe}_{1-x}\text{Mn}_x)_{2}\text{Si}_2 \)**

The \( \text{RMn}_{2}\text{Si}_2 \) system was extensively studied in the past. All compounds are magnetically ordered at high temperatures and the interactions within the layers between the Mn–Mn moments are always FM. The nature of the interlayer exchange interaction is FM or AFM, depending on the lattice constants size. e.g. \( \text{LaMn}_{2}\text{Si}_2 \) is FM with \( T_C = 310 \text{ K} \) and becomes AFM ordered up to 470 K whereas \( \text{YMn}_{2}\text{Si}_2 \) is AFM with \( T_N = 510 \text{ K} \) \[30, 31\]. Using the \( ^{57}\text{Fe} \) MS we have shown that (i) in the doped materials Fe has no magnetic moment of its own and reveals the magnetic order of the Mn sublattice through transferred hyperfine field. (ii) In contrast to the systems described above, Mn in \( \text{Y(Fe}_{1-x}\text{Mn}_x)_{2}\text{Si}_2 \) carries a local magnetic moment \[31\]. The major goal here is study the effect of magnetic Mn on peak positions in \( \text{YFe}_{2}\text{Si}_2 \).

XRD studies on \( \text{Y(Fe}_{1-x}\text{Mn}_x)_{2}\text{Si}_2 \) \((x = 0.1, 0.2, 0.3, 0.5, 0.7 \text{ and } 1)\) show that single-phase materials could be obtained for low Mn compositions only. In \( \text{YFeMn}_{2}\text{Si}_2 \) \((x = 0.5)\) a few extra lines which belong to the orthorhombic \( \text{YFe}_{0.33}\text{Si}_{2} \) type structure have been observed. In addition, for \( x = 0.7 \) and \( \text{YMn}_{2}\text{Si}_2 \) \((x = 1)\) extra lines which belong to the AFM \( \text{Y}_2\text{Mn}_{3}\text{Si}_5 \) \((T_N = 96 \text{ K})\) phase were detected \[32\]. Therefore, their magnetic properties will not be discussed here.

The effect of Mn substitution on the peak position is more dramatic. Figure 16 (inset) exhibits the \( M(T) \) curve for \( \text{Y(Fe}_{0.8}\text{Mn}_{0.2})_{2}\text{Si}_2 \) measured at 250 Oe in which the peak at 63 K is well observed. Although, the lattice parameters of this material and pure \( \text{YFe}_{2}\text{Si}_2 \) are very similar (table 1), the
shift in the peak location is ~160 K as compared to ~40 K in Y(Fe$_{0.85}$Ni$_{0.15}$)Si$_2$. Further increase of x to 0.2, shifts the peak to 16 K at 250 Oe (figure 16) and to 13 K at 1 kOe. No peak is observed for the x = 0.3 sample. Figure 16 also shows for x = 0.2, a decrease in the $M(T)$ curve around 160 K which reminiscences a FM like behavior with a transition ($T_M$) ~ 220 K. $^{57}$Fe MS spectra taken at 90 K and RT indicate clearly, that the 90 K spectrum is much broader than the RT one (figure 18). Least-squares fits of the two spectra yield the hyperfine parameters as follows: the line width in both spectra is 0.33(3) mm s$^{-1}$. At RT the small quadrupole splitting = 0.12 ± 0.02 mm s$^{-1}$ and the IS = 0.205 ± 0.002 mm s$^{-1}$ obtained, agree well with those obtained for YFe$_2$Si$_2$ presented above. The broader line at 90 K (IS = 0.30 mm s$^{-1}$) was fitted by adding a magnetic hyperfine field parameter $H_{\text{eff}} = 30.3(3)$ kOe, a value which is an order of magnitude small than $H_{\text{eff}} = 330$ kOe for pure Fe. That indicates that at 90 K, Fe in YFeMnSi$_2$ senses transferred magnetic fields produced by the magnetic Mn ions. The sharp increase of the bulk magnetization below 29 K, is probably attributed to reorientation of the Mn magnetic sublattice a phenomenon which is very common to the $R$Mn$_2$Si$_2$ system [34]. A supporting evidence for this reorientation is given by the $M(H)$ plots shown in figure 17 (inset). Above the magnetic transition (at 290 K) a linear $M(H)$ curve is obtained. On the other hand, the two nonlinear $M(H)$ plots at 5 and 90 K, overlap at $H > 25$ kOe, but exhibit a quite different shape at low $H$ values. At 5 K only, a small hysteresis loop is developed with a coercive field of 235 Oe. (For Y(Fe$_{0.3}$Mn$_{0.7}$)Si$_2$ (x = 0.7) the $^{57}$Fe MS spectrum at RT is also broad and is fitted with $H_{\text{eff}} = 39.2$ kOe, indicating $T_M > RT$, indicating the increase of $H_{\text{eff}}$ with x).

Using the same token, we may analyze the magnetic curve for Y(Fe$_{0.3}$Mn$_{0.7}$)$_2$Si$_2$ (figure 16) as composed of two magnetic contributions: the peak at 16 K arises from the Fe ions and the FM like behavior stems from the Mn ions. Due to the huge shift in the peak position caused by the magnetic Mn ions, we tend to believe that these two components coexist. If that is the case, the produced transferred hyperfine field is very small and is below the sensitivity of the Mössbauer technique. On the other hand, a phase separation case cannot be excluded. For this scenario, the absence of $H_{\text{eff}}$ on the Fe nuclei is obvious.

We are turning now to the small deduced $H_{\text{eff}} = 30.3$ kOe in YFeMnSi$_2$ at 90 K. If the Fe had its own magnetic moment, then $H_{\text{eff}}$ should not be so sensitive to x and rather will be in full saturation with an order of magnitude higher $H_{\text{eff}}$. But if the $H_{\text{eff}}$ is transferred from neighboring magnetic Mn ions, then each Fe which has different Mn ions as first neighbors will experience strongly reduced hyperfine fields. Assuming random distribution of Mn in the 3d layers, 94% of the Fe nuclei (given by (1 − (1 − x$^3$)$^3$) should experience reduced fields which lead to the broadening of the spectrum at 90 K. Further calculations of $H_{\text{eff}}$ for other x values, is beyond the scope of this paper. However the $H_{\text{eff}} = 30.3$ kOe obtained, fits well with the calculated $H_{\text{eff}}$ values for the Y (Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ system and to measured values on similar systems [32, 33, 35].

4. Discussion and conclusions

Single or nearly single-phase polycrystalline samples of $R$ (Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ ($R = $ La, Y and Lu), Y (Fe$_{1-x}$Cu$_x$)$_2$Si$_2$ and Y (Fe$_{1-x}$Mn$_x$)$_2$Si$_2$ were synthesized and their magnetic properties have been measured. XRD patterns showed that all samples crystallize in the bct ThCr$_2$Si$_2$ type structure. Because of the smaller ionic radius of Ni, the unit cell volume in all $R$ (Fe$_{1-x}$Ni$_x$)$_2$Si$_2$ systems, decrease with x. On the other hand, for Y (Fe$_{1-x}$Mn$_x$)$_2$Si$_2$ and Y (Fe$_{1-x}$Cu$_x$)$_2$Si$_2$ the unit cell volume increases with x. This is caused by the larger Mn radius and by the formal monovalent state of Cu in intermetallic compounds.
In both HTSC cuprates and Fe–As based materials the SC phase evolves from an AFM (or SDW) parent compound and it was proposed that the magnetic state is essential to mediate SC ([4, 36]). As stated above, the similarity between the two BaFe2As2 and RFe2Si2 systems motivated us to look for SC at elevated temperature in various doped RFe2Si2 materials, although Fe is not magnetic. The recent observation of bulk SC in YFe2Ge2 at TC~1.8 K in [13], strengthens this intuition. None of the R (Fe1−xMx)2Si2 (M = Cu and Ni) samples listed above is SC above 1.8 K. This piece of evidence may shed some light on the SC mechanism, by proving the necessity of magnetic interactions in the parent compounds in order to induce SC. However, this assumption is not conclusive, because the full phase diagram of the R–Fe–Si is yet not known. One may argue that magnetic ordering might exist in compositions other than 1:2:2, therefore the absence of magnetic ordering in the stoichiometric 1:2:2 materials is just accidental.

Two characteristic features in the dc magnetization studies are observed. (a) Pronounced peaks in the M(T) plots for all systems (except for R = La). Four independent factors affect the peak position from which the first and the last factors are more drastic than the rest. (i) The peak is very sensitive to the lattice parameters. In RFe2Si2 for R = La the peak is well above RT, but for R = Y and Lu (all measured at 250 Oe) the peak is at 226 K and 70 K respectively. In the doped R (Fe1−xMx)2Si2 samples, either (ii) increasing of x, (iii) applying magnetic fields or (iv) magnetic ions (such as Mn) all shift the peak to lower temperatures. The peak at 226 K for YFe2Si2 is lowered by ~40 in Y(Fe0.85Ni0.15)2Si2 but ~160 K in Y(Fe0.8Mn0.1)2Si2, and not observed down to 5 K in Y(Fe0.7Mn0.3)2Si2. No peak is observed in YNi2Si2 its magnetic features are first reported here. Therefore, we attribute all peaks observed to the Fe sublattice in this structure. The peak position depends strongly of the Fe content. The absence of magnetic hyperfine field on the Fe nuclei (figure 5) in YFe2Si2 (and in other compounds) confirms that Fe has no sizable long-range magnetic moment by its own. In Y (Fe1−xMn)x2Si2 the small transferred hyperfine field observed on Fe is induced by the magnetic Mn sublattice. (b) A tiny extra FM phase at TC higher than RT, is obtained in all Y (Fe1−xNi)x2Si2 samples whereas in the rest: Lu (Fe1−xNi)x2Si2, Y (Fe1−xM)x2Si2 (M = Cu or Mn) materials the impurity phase is negligible (figures 7, 14 and 15 and table 1). The absence of FM impurities in these systems excludes the possibility that the peaks observed are due to FM extra phase. The impurity phase probably due to tiny amount of unreacted Fe (or from YFe2, YFe3 or FeSi), contributes a constant moment to the various M(T) plots and change their absolute values, but does not affect their features. Thus the main issue remains is the nature of the peaks observed in the systems studied here, which presumably all have the same origin. For the sake of simplicity we’ll discuss the magnetic behavior of YFe2Si2.

The shortest Fe–Fe distance (given by 2−1/2 a0) in YFe2Si2, is 2.77 Å. This distance is much longer than the critical value of 2.52 Å for FM interactions in Fe-based intermetallic compounds [37]. Thus no long-range magnetic order exists in this sample at any temperature, as determined by our MS studies (figure 5). YFe2Si2 was claimed to be AFM ordered at 275 K [19] or FM ordered at TC = 790 K [38]. Both determinations are shown to be wrong. The high reported TC just reflects the existing impurity phase (probably Fe3Si). In previous publications, it was proposed that for non-magnetic R in RFe2Si2, the divalent Fe ions are Pauli paramagnet with a virtually temperature-independent magnetic susceptibility [1, 39]. The present measurements using the high sensitive SQUID magnetometer reveals that Fe in YFe2Si2 and in all its derivatives are rather PM. This is supported by (1) the high temperature M(T) region which follows the CW law from which an average effective moment of μeff ~ 3.1(1)μB/Fe is deduced. A similar μeff value was obtained in LuFe2Ge2 [26]. (2) In all isothermal M(H) curves the PM component is very pronounced. Peaks in the susceptibility around 50 and 400 K were observed in the iso-structural LuFe2Ge2 [26] and LaNi2Ge2 [27] but their origin remains unclear. A shallow peak is also observed in SrCu2As2 but its appearance is ignored and not discussed [40]. Maximum in the susceptibility (around 70 K) was already observed for pure Pd metal which is considered as the classic example of NFFL, with large effect of spin fluctuations. With its high DOS at the Fermi energy and large Stoner exchange enhancement (~10), Pd is easily polarized by dilute magnetic moments and often to FM at relatively high temperatures [41]. This maximum is a common feature in other NFFL compounds such YCo2, and LuCo2 [42]. Quantitative calculation of the susceptibility is still a challenge even for the simplest case of Pd. YFe2Zn20 (with Stoner enhancement factor of Z = 0.88) is closer to FM than Pd [43, 44] and also serves as an archetypical examples of NFFL. A faint maximum in the susceptibility around 10 K was obtained when measured at low magnetic fields. This maximum is monotonically decreased with increasing H.

We tend to believe that YFe2Si2 (similar to YFe2Zn20) and its derivatives are additional examples for NFFL systems. In contrast to all examples mentioned, here the lattice parameters and/or the applied field, has a pronounced effect on the peak position. Doping of non-magnetic Ni ions also shift the peak to lower temperatures, but this shift is more dramatic when magnetic ions such as Mn are introduced. The current state of experiments does not allow us to suggest a consistent explanation to all phenomena presented here. We cannot exclude the possibility that nearly AFM or short-range AFM correlations are the origin of the peaks described here. Whatever the explanation is, the discovery of a pronounced peak in YFe2Si2 is challenging for the theory of magnetism and propitious to further theoretical and experimental investigations. The study of these systems is a topic of ongoing research and promises to be a fruitful new phase space for several years to come.

Acknowledgments

The research in Jerusalem was partially supported by the joint German–Israeli DIP project and in Houston by US AFOSR and TCSUH. We thank Professor I Nowik carrying out the Mössbauer studies.
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