Structural, thermal and magnetic properties of Y$_2$Fe$_2$Si$_2$C

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A B S T R A C T

We report detailed investigations on the structural, thermal and magnetic properties of Y$_2$Fe$_2$Si$_2$C over the temperature range 2–300 K using x-ray diffraction, specific heat. $^{57}$Fe Mössbauer spectroscopy and first-principles calculations. Low temperature measurements show no pronounced anomalies which might signal magnetic ordering of the Fe sublattice at low temperature. Analyses of the specific heat data of Y$_2$Fe$_2$Si$_2$C reveal the presence of a localised Einstein mode, suggesting the importance of an optical contribution to the phonon spectrum of Y$_2$Fe$_2$Si$_2$C. Based on electronic structure calculations, we found a low density of states of the Fe 3d bands at the Fermi level. The corresponding density of states are below the Stoner criterion, thus indicating a non-magnetic state of the Fe atoms in Y$_2$Fe$_2$Si$_2$C, in agreement with the experimental findings.

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1. Introduction

R$_2$Fe$_2$Si$_2$C (Y, La - Nd, Sm, Gd - Tm and Lu) compounds crystallise in the monoclinic Dy$_2$Fe$_2$Si$_2$C-type structure with the $C2/m$ space-group [1–3]. The R, Fe and Si atoms occupy the 4i sites ($m$ point symmetry) in the unit cell with four atomic positions: (x,0,z), (x+$\frac{1}{2}$, 0, z), (−x,0,−z), and (−x+$\frac{1}{2}$, 0,−z), while the C atom occupies the 2a site ($2/m$ point symmetry) with two atomic positions: (0,0,0) and (1,1,0). The magnetic studies of the R$_2$Fe$_2$Si$_2$C (R = Y, Pr, Nd, Gd, Tb, Dy, Ho and Er) compounds by Schmitt et al. [4] and Pöttgen et al. [2] revealed that the magnetism of the R$_2$Fe$_2$Si$_2$C (R = Nd, Gd, Tb, Dy, Ho, Er and Tm) set of compounds can be attributed solely to the R atoms, i.e. the Fe atom was reported to be non-magnetic as indicated by the similarity between the values of the experimental effective moment and the theoretical effective moment for the R$^{3+}$ ions. However, neutron diffraction studies on Nd$_2$Fe$_2$Si$_2$C and Tb$_2$Fe$_2$Si$_2$C were interpreted in terms of the magnetic ordering in both the R and Fe sublattice [5].

Recently, we used high-resolution neutron diffraction to determine the magnetic structures of R$_2$Fe$_2$Si$_2$C (R = Gd, Tb, Dy and Ho) compounds [6–9]. The magnetic structures of the Gd, Tb and Ho compounds below their antiferromagnetic ordering temperatures of 39 K, 44 K and 16 K, respectively, are characterised by the propagation vector of $k$ = [0, 0, 0] with the rare-earth magnetic moments pointing along the $b$-axis. Dy$_2$Fe$_2$Si$_2$C on the other hand is antiferromagnetic below the Néel temperature of $T_N$ ~ 26 K and undergoes a spin-reorientation transition at the lower temperature of $T_t ~ 6$ K [9]. $^{57}$Fe Mössbauer spectroscopy has been used to establish that the Fe is non-magnetic in R$_2$Fe$_2$Si$_2$C (R = Gd, Tb, Dy and Ho). The increase in linewidth observed in the $^{57}$Fe Mössbauer spectra for the set of R$_2$Fe$_2$Si$_2$C compounds below their antiferromagnetic ordering temperature $T_N$ has been used to track the temperature dependence of the antiferromagnetic order of the R sublattice, with this behaviour indicating that the line broadening is related to a transferred hyperfine field at the Fe site due to the ordering of the R sublattice [6–9].

Previous magnetic studies revealed no magnetic phase transition in Y$_2$Fe$_2$Si$_2$C down to 2 K [4], thus indicating that Y$_2$Fe$_2$Si$_2$C acts as an ideal non-magnetic reference material for investigating the magnetism of the R$_2$Fe$_2$Si$_2$C system. Accordingly, we have used Y$_2$Fe$_2$Si$_2$C as a reference material to estimate the magnetic contribution to the total specific heat of magnetic R$_2$Fe$_2$Si$_2$C compounds.

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[7–10]. Despite the significance of Y$_2$Fe$_2$Si$_2$C for enhanced understanding of the magnetism of R$_2$Fe$_2$Si$_2$C compounds, no detailed studies have so far been reported for Y$_2$Fe$_2$Si$_2$C. In this paper, we have used X-ray diffraction, $^{57}$Fe Mössbauer spectroscopy, specific heat measurements and first-principles calculations to investigate the structural, thermal and magnetic properties of Y$_2$Fe$_2$Si$_2$C. Our low temperature specific heat, X-ray diffraction and $^{57}$Fe Mössbauer spectroscopy measurements reveal no pronounced anomalies, thus excluding the presence of any magnetic ordering of the Fe sublattice. First-principles calculations also confirm a non-magnetic state of Y$_2$Fe$_2$Si$_2$C. However, we found that it is necessary to consider the Debye-Einstein model to properly describe the specific heat data, highlighting the importance of the optical contributions to the phonon spectrum of Y$_2$Fe$_2$Si$_2$C.

2. Experimental methods

The polycrystalline Y$_2$Fe$_2$Si$_2$C sample was prepared by arc melting the constituent elements of purity better than 99.9 wt% under a high purity argon atmosphere (< 1 ppm impurity), following the procedure outlined by Pöttgen et al. [2]. The appropriate quantities of Y metal, Fe powder, Si powder, and graphite flakes in a total amount of ~500 mg, were first cold-pressed together into a pellet. This pressed pellet was then melted in an argon arc furnace. To ensure homogeneity, the sample was turned together into a pellet. This pressed pellet was then melted in an argon arc furnace. All spectra were recorded using an X-ray diffractometer (Cu-K$_\alpha$ radiation) equipped with an Oxford Instruments Phenix closed-cycle refrigerator. All XRD patterns were refined by the Rietveld method using the FullProf/Winplotr software [11,12]. For specific heat measurements, the Y$_2$Fe$_2$Si$_2$C powder sample was pressed and cut into a square-shape around 3 mm x 3 mm. The specific heat data was measured using a Quantum Design Physical Property Measurement System (PPMS) from 2 K to 300 K.

$^{57}$Fe Mössbauer spectra of Y$_2$Fe$_2$Si$_2$C were collected in standard transmission mode using a $^{57}$Co-Rh source. The spectrometer was calibrated with an α-Fe foil at room temperature and the sample temperature was varied from 11 K to 293 K using a closed-cycle refrigerator. All spectra were fitted using the Recoil software [13].

Full-potential first-principles electronic structure calculations were performed with the linear augmented-plane-wave (LAPW) method with the WIEN2K package [14] within the framework of the density functional theory (DFT). The Perdew-Burke-Ernzerhof (PBE) functionals [15] under the generalized gradient approximation (GGA) were used to describe the exchange-correlation potential. Lattice parameters and atomic positions obtained from diffraction experiments were used as input parameters and no geometry optimisations were employed in the calculations.

3. Results

3.1. Crystal structure

The X-ray diffraction pattern of Y$_2$Fe$_2$Si$_2$C obtained at 295 K is shown in Fig. 1. Refinement of the X-ray diffraction pattern confirmed the formation of the monoclinic Dy$_2$Fe$_2$Si$_2$C-type structure with an impurity phase identified as YCo$_{2.13}$ (yttrium carbide) present in the amount of 2.8 wt%. The refinement parameters are presented in Table 1. We explored the possibility of off-stoichiometric samples due, for example, to weight losses on arc melting, by allowing the atomic occupations to vary in our set of refinements. In the event, such variations to the atomic occupations led to refinements with higher $R_{Bragg}$ and $R_F$ values than those obtained using ideal occupancies. The values for the ideal occupancies were therefore applied in the final refinements.

3.2. Specific heat

Previous magnetic studies show that Y$_2$Fe$_2$Si$_2$C does not order magnetically down to 2 K [4]. Similarly, our zero field specific heat study on Y$_2$Fe$_2$Si$_2$C (Fig. 2(a)) shows no anomalies down to 2 K. In the low temperature region ($T < 70$ K) the $C_p/T$ versus $T^2$ curve is linear and can be fitted with $C_p(T) = \gamma T + \beta T^3$ (inset of Fig. 2(a)), yielding the Sommerfeld coefficient, $\gamma = 16.3(5)$ mJ/molK$^2$ and the $\beta$ value of 0.133(1) mJ/molK$^4$. The Debye temperature $\theta_D$ calculated from the $\beta$ value is 468(1) K. The $C_p$ data of Y$_2$Fe$_2$Si$_2$C over the temperature range of measurement were then fitted using the Debye model i.e. $C_p = \gamma T + 9N\beta T^3 \int_0^{\theta_D^2} \frac{x^4 e^x}{(e^x-1)^2} dx$ (where $N$ is the number of atoms per formula unit). During the fitting process, $\gamma$ was kept constant at 16.3 mJ/molK as determined above. The $\theta_D$ obtained from the least-squares fitting to the $C_p(T)$ data is 490(2) K, slightly larger than the value of 468 K derived from fitting the low temperature $C_p(T)$ data. The best fit curve to the $C_p(T)$ data using the Debye model is plotted as the dashed line in Fig. 2(a).

It can be seen that fitting the $C_p(T)$ curve using the Debye model

<table>
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<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
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<tr>
<td>Y</td>
<td>0.5616(11)</td>
<td>0</td>
<td>0.294(2)</td>
</tr>
<tr>
<td>Fe</td>
<td>0.205(2)</td>
<td>0</td>
<td>0.097(3)</td>
</tr>
<tr>
<td>Si</td>
<td>0.156(3)</td>
<td>0</td>
<td>0.700(3)</td>
</tr>
<tr>
<td>a</td>
<td>-10.615(15) Å</td>
<td>0</td>
<td>0.129(27)(1)</td>
</tr>
<tr>
<td>b</td>
<td>-3.9234(6) Å</td>
<td>0</td>
<td>0.129(27)(1)</td>
</tr>
<tr>
<td>c</td>
<td>-6.7489(9) Å</td>
<td>0</td>
<td>0.129(27)(1)</td>
</tr>
<tr>
<td>$R_{Bragg}$ (%)</td>
<td>12.9</td>
<td>$R_F$ (%)</td>
<td>10.6</td>
</tr>
</tbody>
</table>

![Fig. 1. Rietveld refinements of the X-ray diffraction pattern of Y$_2$Fe$_2$Si$_2$C collected at 295 K (Cu-K$_\alpha$ radiation). The Bragg markers from top to bottom represent Y$_2$Fe$_2$Si$_2$C and the impurity phase YCo$_{2.13}$ (2.8 wt%), respectively with the differences between the experimental and calculated patterns shown by the blue line. The asterisks indicate peaks from an unknown impurity. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)
resulted in a poor fit as evident by the deviation of the fitted curve from the experimental data above ~30 K. This deviation might be due to the importance of the optical contributions (Einstein term) to the phonon spectrum of Y₂Fe₂Si₂C which is highlighted by the presence of a hump in the \( \frac{C_p}{T^3} \) versus \( T \) curve at \( T \sim 50 \) K (see Fig. 2(b)). In order to describe fully the experimental \( C_p \) data we have employed both the Debye and Einstein models which can be written as

\[
C_p = \gamma T + 9R n_D \left( \frac{T}{\theta_D} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx + 3R n_E \left( \frac{x exp(x)}{exp(x) - 1} \right)^2
\]

The first term represents the electronic contribution to the specific heat whereas the second and the third terms represent the Debye and Einstein terms, respectively, with \( x_E = \theta_E/T \) where \( \theta_E \) is the Einstein temperature. \( n_D \) and \( n_E \) are the number of the Debye and Einstein modes, respectively, whose sum should be equal to the number of atoms per formula unit.

In Table 2, we present the fitting parameters to the specific heat data of Y₂Fe₂Si₂C using the Debye-Einstein model as in Eq. (1). The data were well described with the Debye temperature of \( \theta_D = 572(12) \) K and the Einstein temperature of \( \theta_E = 184(3) \) K. The Debye temperature obtained from the Debye-Einstein model is higher than that obtained from the Debye model. This is expected since the Debye temperature derived from the Debye model represents the whole phonon spectrum (both the acoustic and optic modes), whereas the Debye temperature in the Debye-Einstein model represents the acoustic modes only. The sum of \( n_D \) and \( n_E \) is 6.7 close to that expected in the case of R₂Fe₂Si₂C where \( n_D + n_E = 7 \). As is evident from the \( C_p/T^3 \) versus \( T \) curve shown in Fig. 2(b), the hump in the specific heat data around \( T \sim 50 \) K is reproduced well by the Einstein modes represented in our fit, reflecting the importance of the optical contribution (Einstein term) to the phonon spectrum of Y₂Fe₂Si₂C.

### Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Debye model</th>
<th>Debye-Einstein model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma ) (mJ/mol K^4)</td>
<td>16.3(5)</td>
<td>16.3 (fixed)</td>
</tr>
<tr>
<td>( \beta ) (mJ/mol K^4)</td>
<td>0.133(1)</td>
<td>—</td>
</tr>
<tr>
<td>( \theta_D ) (K) (low T)</td>
<td>468(1)</td>
<td>—</td>
</tr>
<tr>
<td>( \theta_E ) (K)</td>
<td>490(2)</td>
<td>572(12)</td>
</tr>
<tr>
<td>( n_D )</td>
<td>—</td>
<td>5.1(1)</td>
</tr>
<tr>
<td>( n_E )</td>
<td>—</td>
<td>184(3)</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>1.6(2)</td>
</tr>
</tbody>
</table>

3.3. Thermal expansion

The temperature dependences of the lattice parameters and the unit cell volume of Y₂Fe₂Si₂C from 20 K to 300 K are shown in Fig. 3. The lattice parameters and the unit cell volume of Y₂Fe₂Si₂C decrease monotonically from 300 K down to 20 K. In order to describe the volume and linear thermal expansion curves, we first used the Grüneisen approximation for the zero pressure equation of state in which the effects of thermal expansion are considered as elastic strains [16]. Within the first-order Grüneisen approximation, the temperature dependence of the unit cell volume can be expressed as

\[
V(T) = V_0 + x_V U(T)
\]

where \( V_0 \) is the unit cell volume at 0 K and \( x_V = -V_0 \gamma_u \) is a Grüneisen parameter and \( B_0 \) the isothermal bulk modulus. \( U(T) \) is the internal energy of the system which can be written (within the Debye model) as

\[
U(T) = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^\infty \frac{x^3}{e^x - 1} dx
\]
takes the form

\[ l(T) = l_0 + x_l U(T) \]  

(4)

where \( l \) represents the lattice parameters \((a, b, c\) and \(\beta)\), \( l_0 \) represents the lattice parameters at \(0\ K\) (temperature independent term) and \(x_l\) is a constant of proportionality.

The solid lines in Fig. 3 represent the fits obtained to the data using Eqs. (2) and (4). The fits highlight that no deviation of the temperature dependence of the lattice parameters and the unit cell volume from the Debye model is observed down to \(20\ K\). By comparison, the temperature dependence of the lattice parameters and the unit cell volume of \(\text{Tb}_2\text{Fe}_2\text{Si}_2\text{C}\) show a strong deviation from the Debye model due to the presence of spontaneous magnetostriction related to the ordering of the Tb magnetic sublattice [8].

The least-squares fitting procedure to the temperature dependence of the unit cell volume yields the Debye temperature of \(\theta_D = 501(16)\ K\).

The fitted constant \(g_g = B_0 / C_0\) is \(0.11(2)\ \text{GPa} / \text{C}_0\) which is comparable to the value determined for \(\text{FeSi}\) i.e. \(0.14(1)\ \text{GPa} / \text{C}_0\) [17]. Since the Grüneisen parameter \(\gamma_g\) is unknown, the related Bulk modulus \(B_0\) of \(\text{Y}_2\text{Fe}_2\text{Si}_2\text{C}\) cannot be determined in this work. The fitted parameters obtained from the unit cell volume and the lattice parameters of \(\text{Y}_2\text{Fe}_2\text{Si}_2\text{C}\) using the Debye model are summarised in Table 3. Note that due to a large uncertainty in the \(\beta\) parameter, the Debye temperature determined from the unit cell volume was kept constant during the fitting of the \(\beta\) parameter.

Table 3  
Fitted parameters of the lattice and volume thermal expansion of \(\text{Y}_2\text{Fe}_2\text{Si}_2\text{C}\) obtained using Eqs. (2) and (4).

<table>
<thead>
<tr>
<th>(V_0 (\text{Å}^3))</th>
<th>(l_0 (\text{Å}))</th>
<th>(x_l \times 10^{-2} \text{ GPa}^{-1})</th>
<th>(\theta_D (\text{K}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>216.59(2)</td>
<td>11(2)</td>
<td>501(16)</td>
<td></td>
</tr>
<tr>
<td>(a(\text{Å}))</td>
<td>10.5981(5)</td>
<td>0.18(5)</td>
<td>481(25)</td>
</tr>
<tr>
<td>(b(\text{Å}))</td>
<td>3.9195(2)</td>
<td>0.04(2)</td>
<td>529(48)</td>
</tr>
<tr>
<td>(c(\text{Å}))</td>
<td>6.7347(3)</td>
<td>0.16(3)</td>
<td>481(19)</td>
</tr>
<tr>
<td>(\beta(\text{°}))</td>
<td>129.268(2)</td>
<td>0.06(5)</td>
<td>501(fixed)</td>
</tr>
</tbody>
</table>

Although the temperature dependence of the lattice parameters and the unit cell volume can be described by the Debye model, our analysis in Section 3.2 revealed that a localised Einstein mode is needed to describe the specific heat data of \(\text{Y}_2\text{Fe}_2\text{Si}_2\text{C}\). Correspondingly, we therefore expect that the thermal expansion data would also reflect the presence of an Einstein mode.

In order to investigate the presence of an Einstein mode, we re-evaluated the temperature dependence of the unit cell volume of \(\text{Y}_2\text{Fe}_2\text{Si}_2\text{C}\) using the Debye-Einstein model. Within the Debye-Einstein model, the temperature dependence of the unit cell volume should be modified by introducing an additional term as follows (e.g. Ref. [18])

\[ V(T) = V_0 + x_V U(T) + x_E E(T) \]  

(5)

where \(x_V\) and \(x_E\) are constants of proportionality. \(U(T)\) is calculated using the Debye model as in Eq. (3) whereas \(E(T)\) represents the internal energy of an Einstein oscillator which can be expressed as

\[ E(T) = \frac{3Nk_B\theta_E}{(\exp(\theta_E/T) - 1)} \]  

(6)

The parameters determined from the fits to the temperature dependence of the unit cell volume of \(\text{Y}_2\text{Fe}_2\text{Si}_2\text{C}\) using both the Debye and Debye-Einstein models are summarised in Table 4. As noted (Fig. 3), the Debye model describes the data well with the Debye-Einstein model also giving a very good representation of the experimental data. The fitted curve derived using the Debye-Einstein model is virtually indistinguishable from the Debye model, although the least-square fitting indicates that the fitting to the unit cell volume using the Debye-Einstein model as in Eq. (5) yields a smaller \(\chi^2\) value compared with the Debye model only.
thus indicating that the Debye-Einstein model is more appropriate to describe the temperature dependence of the unit cell volume of Y$_2$Fe$_2$Si$_2$C. In addition, the Debye and Einstein temperatures determined from the fit to the unit cell volume, i.e. $\theta_D$ of 578(26) K and $\theta_E = 166(79)$ K, agree with those obtained from the fit to the specific heat data ($\theta_D = 572(12)$ K and $\theta_E = 184(3)$ K; Table 2).

### 3.4. $^{57}$Fe Mössbauer spectroscopy

The $^{57}$Fe Mössbauer spectra of Y$_2$Fe$_2$Si$_2$C obtained at various temperatures from 300 K to 11.4 K show no evidence of magnetic splitting confirming that the Fe is non-magnetic in this compound. Examples of these spectra for 293 K and 11.4 K are shown in Fig. 4. All spectra can be fitted with a single doublet.

The temperature dependences of the hyperfine parameters for Y$_2$Fe$_2$Si$_2$C are shown in Fig. 5. The linewidth is essentially temperature independent as evident from the absence of systematic line broadening down to 11 K (see Fig. 5(a)). By comparison, a small degree of spectral line broadening was observed in the $^{57}$Fe Mössbauer spectra of Gd$_2$Fe$_2$Si$_2$C [7], Tb$_2$Fe$_2$Si$_2$C [8], Dy$_2$Fe$_2$Si$_2$C [9] and Ho$_2$Fe$_2$Si$_2$C [6] collected below the magnetic ordering temperatures with the line broadening associated with a small transferred hyperfine field at the Fe site due to the ordering of the surrounding R moments.

As shown in Fig. 5(b), the isomer shift of Y$_2$Fe$_2$Si$_2$C increases with decreasing temperature. The temperature dependence of the isomer shift is due to the second-order Doppler shift. The solid and dotted lines in (c) represent fits using Eq. (8) as described in the text.

$$IS(T) = IS(0) - \frac{9}{2} \frac{k_B T}{\theta_M} \left(\frac{T}{\theta_M}\right)^3 \int_0^{\theta_M} \frac{x^3}{e^x - 1} dx.$$  \hspace{1cm} (7)

where $c$ is the speed of light, $M$ is the mass of the $^{57}$Fe nucleus, $\theta_M$ is the Mössbauer Debye temperature and $IS(0)$ is the temperature-independent term of the isomer shift. The temperature dependence of the isomer shift of Y$_2$Fe$_2$Si$_2$C can be fitted with $\theta_M = 475(7)$ K, which is slightly higher than the Debye temperature evaluated from the low temperature specific heat measurements, i.e. $\theta_D = 468$ K. While these values agree within uncertainties, the difference is likely to be due to the fact that the Mössbauer Debye temperature represents the phonon spectrum due to the vibration

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Debye model</th>
<th>Debye-Einstein model</th>
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<tr>
<td>$V_0$ (Å$^3$)</td>
<td>216.59(2)</td>
<td>216.58(3)</td>
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<tr>
<td>$\theta_D$ (K)</td>
<td>501(16)</td>
<td>578(26)</td>
</tr>
<tr>
<td>$\theta_E$ (K)</td>
<td>166(79)</td>
<td>166(79)</td>
</tr>
<tr>
<td>$x_V$</td>
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<td>0.10(4)</td>
</tr>
<tr>
<td>$x_E$</td>
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<td>0.02(2)</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.97</td>
<td>0.85</td>
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</table>

(see Table 4), thus indicating that the Debye-Einstein model is more appropriate to describe the temperature dependence of the unit cell volume of Y$_2$Fe$_2$Si$_2$C.
of the Fe atom whereas the Debye temperature estimated from the specific heat measurements reflects the overall phonon spectrum in the sample.

The temperature dependence of the quadrupole splitting (QS) of Y$_2$Fe$_2$Si$_2$C also increases as the temperature is lowered. Following Verma and Rao [20], we fitted the temperature dependence of QS using

$$Q_5(T) = Q_5(0)(1 - bT^\gamma), \quad (8)$$

where $Q_5(0)$ is the quadrupole splitting at 0 K (temperature independent term) and $b$ is the constant of proportionality. The temperature dependence of the QS was fitted initially by fixing the exponent $\gamma$ to 1.5 with the resultant fitted curve plotted as a solid line in Fig. 5(c). This dependency—known as the $T^{3/2}$ law—has been observed in many metallic systems with non-cubic symmetry [21,22]. The $T^{3/2}$ law can account for the increase in QS upon lowering the temperature, however some deviation is clearly seen in the intermediate temperature region e.g. between ~100 K and ~200 K. We therefore allowed the exponent $\gamma$ to vary, yielding $\gamma = 2.5(2)$ with the fitted curve shown as a dotted line in Fig. 5(c). The fitted curve with $\gamma = 2.5$ is clearly superior to the fitted curve obtained with the $T^{3/2}$ law, although the reason for this deviation from the ‘universal’ $T^{3/2}$ law is unknown at present. However it should be noted that such deviations from the $T^{3/2}$ law were observed in several cases involving transition metals and rare-earth metals hosts [20]. This deviation was also observed in the case of filled skutterudites Eu$_{0.88}$Fe$_4$Sb$_{12}$, where the temperature dependence of QS obtained from $^{57}$Fe Mössbauer experiments can be well-fitted with $\gamma = 2.43$ [23].

3.5. Electronic density of states

The density of states (DOS) of Y$_2$Fe$_2$Si$_2$C is presented in Fig. 6. The total DOS curve is characterised by a broad valence band from $-5$ eV to 2 eV relative to the Fermi energy ($E_F$) which is dominated by the Fe 3d states. The Fe 3d states are distributed from $-5$ eV to 2 eV forming a broad maximum centred at about $-1$ eV below $E_F$ with a second maximum occurring around 1 eV above $E_F$. The Si 3p states are situated from $-3$ eV to $-1$ eV while the C 2p states are mainly distributed in the energy range $-5$ eV to $-2$ eV. The main contribution to the DOS at $E_F$ originates primarily from the Fe 3d states with some admixture of the Y 5d and C 2p states, while the unoccupied states above 2 eV have a dominant contribution from the Y 5d states and minor contributions from the Fe 3d and C 2p states.

The important feature of the DOS curve is the presence of strong hybridisation between the Fe 3d, Si 3p and C 2p states in the energy range between $-5$ eV to $-1$ eV. This $p-d$ hybridisation is also observed in the electronic structure calculations on other R-Fe$	extsubscript{2}$Si$	extsubscript{2}$C systems. We suggest that the strong hybridisation between the Fe 3d and C 2p states causes the increase of bandwidth of Fe 3d states. An example showing the effect of the strong $p-d$ hybridisation in reducing the magnetism of the 3d element is the disappearance of the Cr magnetic moment in RCrSi$_2$C [31]. First-principles calculations on YCr$_2$Si$_2$C reveal that the Cr magnetic moment in YCrSi$_2$ is gradually suppressed upon insertion of carbon [31] highlighting the importance of $p-d$ hybridisation in suppressing the magnetism of the transition metal in such compounds.

The density of states of the Fe 3d bands at $E_F$ is only 2.3 states/eV per formula unit or 1.1 states/eV per Fe atom. Using a typical Stoner factor $I$ for Fe of 0.46 eV [32], this value leads to $N(E_F)/I = 0.51$ which is far below the Stoner criterion for ferromagnetism i.e. $N(E_F)/I > 1$. This indicates that the Y$_2$Fe$_2$Si$_2$C compound is far from being magnetic. This result is supported by the spin-polarised calculations on Y$_2$Fe$_2$Si$_2$C (not shown here) which converge into a non-magnetic ground state as evidenced by the absence of the Fe band splitting.

The density of states at $E_F$ ($N(E_F)$) of 4.7 states/eV per formula unit corresponds to a Sommerfeld coefficient of $\gamma_{\text{band}} = 11.1$ mJ/mol K$^2$, which is lower than the experimental $\gamma_{\exp}$ value of 16.3 mJ/mol K$^2$ as determined from the specific heat measurement. The mass enhancement factor $\lambda$, defined as $\gamma_{\exp} = (1 + \lambda)\gamma_{\text{band}}$, can be used to estimate the strength of the electron-electron and electron-phonon couplings. Based on the values of $\gamma_{\text{band}}$ and $\gamma_{\exp}$ of 11.1 mJ/mol K$^2$ and 16.3 mJ/mol K$^2$, respectively, the enhancement factor $\lambda$ is calculated to be 0.45, corresponding to weak electron-electron and electron-phonon interactions in Y$_2$Fe$_2$Si$_2$C.

4. Discussion

Analyses of the specific heat data and volume thermal expansion of Y$_2$Fe$_2$Si$_2$C reveal the presence of a localised Einstein mode with $\theta_E = 180$ K corresponding to the energy of ~16 meV. The presence of an Einstein mode in Y$_2$Fe$_2$Si$_2$C is rather unexpected. In general, the presence of a localised Einstein mode occurs in the systems with specific structure, i.e. cage-like structure such as in clathrates (e.g. Refs. [33,34]) and skutterudites (e.g. Refs. [35,36]) in which the Einstein mode is associated with the local vibration of the atoms inside the cage structure. In the case of Y$_2$Fe$_2$Si$_2$C, the presence of a cage structure in which the atoms are weakly bound is not obvious. Clearly, additional first-principles calculations to determine the phonon density of states of Y$_2$Fe$_2$Si$_2$C would be beneficial to determine the origin of this Einstein mode. Further experimental investigations, such as inelastic neutron scattering, would also provide additional insights into the phonon spectrum of Y$_2$Fe$_2$Si$_2$C.

The first-principles calculations on Y$_2$Fe$_2$Si$_2$C shown in Fig. 6 reveal that the Fermi level is located in a low DOS region of the Fe 3d bands. As a consequence, the Stoner criterion is not fulfilled in any case, and as such, is likely to account for the absence of the Fe sublattice ordering in the R$_2$Fe$_2$Si$_2$C compounds. However, this will in fact change if the Fermi level is located at the peak of the Fe 3d bands (i.e. at $\sim -1$ eV), which will create an Fe moment instability and fulfilment of the Stoner criterion. It is known that by introducing an impurity with a different number of d-electrons into the
system, the Fermi level can be tuned to higher or lower energies. This creates the possibility of tuning the Fe 3d state to be close to magnetic, as in the case of R(Co, Ni)2 [37] or R(Co, Ti)2 [38]. Therefore, it would be interesting to study the evolution of the magnetism of the Fe sublattice in R2Fe2Si2C by decreasing the number of Fe-d electrons i.e. by partially substituting of the Fe atom with an element that has fewer d-electrons such as Re, Mn or Ti.

5. Conclusions

We have investigated the structural, thermal and magnetic properties of Y2Fe2Si2C. From the 57Fe Mössbauer spectroscopy measurements, we observed no systematic line broadening and anomalies in the quadrupole splitting in Y2Fe2Si2C down to ~11 K, thus excluding the presence of magnetic ordering of the Fe sublattice at low temperature. Similarly, specific heat and X-ray diffraction experiments show no pronounced anomalies at low temperatures which would signal magnetic ordering. In addition, we found the presence of a localised Einstein mode from the analyses of specific heat data which reflects the importance of optical contributions to the phonon spectrum of Y2Fe2Si2C. We have shown that the density of states of the Fe 3d bands at the Fermi energy are below the Stoner criterion, thus accounting for the absence of Fe magnetism in Y2Fe2Si2C.

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References