Tuning the magneto-elastic transition of \((\text{Mn,Fe,V})_2(\text{P, Si})\) alloys to low magnetic field applications

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The first-order magneto-elastic transition in the Mn–Fe–P–Si alloys can be tailored by vanadium substitution. Alloys with a suitable V substitution provide an excellent magnetocaloric effect with minor hysteresis in low magnetic fields up to 1.2 T. Mössbauer measurements show that the hyperfine field is reduced by V substitution. Neutron diffraction reveals that Fe is substituted by V on the 3f site and the magnetic moment on the 3f site is enhanced by the V substitution. The modified magnetic exchange field around the 3f and 3g positions in the lattice can be utilized to design suitable magnetocaloric materials that operate in low magnetic fields.

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1. Introduction

Based on the giant magnetocaloric effect (GMCE), novel technologies as magnetic heat pumps [1–3] and thermomagnetic motors [4,5] have been developed for caloric cooling and waste heat recovery. The GMCE is attributed to a first-order magneto-structural or magneto-elastic transition (FOMT), which has been found in e.g. Gd₅(Ge,Si)₄ [6], Heusler alloys [7], La(Fe,Si)₁₃ [8] and \((\text{Mn,Fe})₂(\text{P, Si})\) [9] alloys near room temperature.

Among these systems, the La(Fe,Si)₁₃ and \((\text{Mn,Fe})₂(\text{P, Si})\) alloys have an excellent magnetocaloric effect and show an instability in the electronic structure and magnetic moment. This effect has been termed ‘mixed magnetism’ as strong magnetism coexist with weak magnetism in a single alloy [16]. The magneto-elastic transition in \((\text{Mn,Fe})₂(\text{P, Si})\) alloys can be tuned by other 3d metals like Co, Ni, Cu [17,18], or metalloids like As, Ge [19,20], B [21], C [22], N [23]. In addition, the annealing conditions [24,25] also strongly affect the magneto-elastic transition in the Fe₂P-type alloys. Vanadium (V) substitution in the \((\text{Mn,Fe})₂(\text{P, Si})\) alloys has been investigated in detail and reveals that the magneto-elastic transition can be tuned to the critical condition where an enhanced GMCE was obtained [26]. However, the influence of V substitution on the evolution of the magnetic exchange-field between the magnetic atoms has not been investigated yet. These exchange fields are a key ingredient to understand how the magneto-elastic transition can be induced in low magnetic fields.

Neutron diffraction and Mössbauer spectroscopy were used to reveal the evolution of the magnetic moments and the hyperfine field in Mn–Fe–P–Si–V alloys. We show that V substitution shifts the FOMT towards the border to the SOMT, which results in a...
reduction in the hyperfine field of the alloy and an increase in the local $M_b$. These investigations pave the way to a better design of MCE materials for magnetic heat pumps and thermomagnetic motors that can operate in low applied magnetic fields.

1.1. Methods

Polycrystalline alloys were prepared by powder metallurgy. The starting materials, in the form of Mn (99.7%), Fe (99.7%), P (99%), Si (99.7%) and V (99.5%) powders, were mechanically ball milled in a PULVERISSETTE 5 planetary mill for 10 h in an Ar atmosphere with a constant rotation speed of 380 rpm, then pressed into small tablets (ø 13 mm, mass 3–5 g), and finally sealed in quartz ampoules under 200 mbar of Ar. These tablets were then annealed at 1343 and 1373 K for 25 h and quenched into water. The samples are listed as follows: (V0H) Mn$_{11.7}$Fe$_{70.3}$Si$_{0.5}$ alloys annealed at 1373 K, (V2H) Mn$_{11.7}$Fe$_{71.0}$Si$_{0.5}$V$_{0.0}$ alloys annealed at 1373 K and (V2L) Mn$_{11.7}$Fe$_{70.7}$P$_{0.5}$Si$_{0.5}$V$_{0.0}$ alloys annealed at 1343 K.

X-ray diffraction (XRD) patterns were collected on a PANalytical Xpert Pro diffractometer with Cu-Kα radiation (1.54056 Å) at room temperature. The neutron diffraction data at 370 and 110 K were collected at a wavelength of 1.67105 Å on the neutron powder diffraction instrument PEARL [27] at the research reactor of Delft University of Technology. The temperature dependence of the magnetization was measured by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS 5XL) in the reciprocating sample option (RSO) mode. The in-field DSC is measured in a Peltier cell based DSC using a Hallbach cylinder magnetic field (≤1.5 T) with a scanning rate of 3.0 K/min. Transmission $^{57}$Fe Mössbauer spectra were collected at 350 K with a conventional constant-analyzer acceleration spectrometer and at 110 K with a sinusoidal velocity spectrometer, using a $^{57}$Co(Rh) source. A velocity calibration was carried out using $^{57}$Fe foil at room temperature. The source and the absorbing samples were kept at the same temperature during all measurements. The Mössbauer spectra were fitted using the Mosswinn 4.0 program [28]. All spectra were fitted with a binomial distribution model, as previously described for the Mössbauer spectroscopy experiments on FeMnP$_{1-x}$As$_x$ compounds [29].

2. Results

2.1. Magnetic properties

Fig. 1 shows the temperature dependence of the magnetization for samples V0H, V2H and V2L in a magnetic field of 1 T. The heating and cooling curves depict the thermal hysteresis ($\Delta T_{hyp}$), which is 1.5, 0.7 and 0.5 K for samples V0H, V2H and V2L, respectively. The Curie temperature (T$_C$), determined by the peak value of $-dM/dT$ in the heating curves, is 311.2, 290.1 and 289.7 K for samples V0H, V2H and V2L, respectively. An increase in the value of $-dM/dT$ for sample V2H measured at 1.0 T, shown in the inset of figure (a), indicates a higher magnetic entropy change ($-\Delta S_M$) at a low magnetic field change of 1.0 T. This is consistent with the $-\Delta S_M$ results at different magnetic field changes shown in Fig. 1(b). The $-\Delta S_M$ curves are extracted from heat capacity measurements in magnetic fields of 0, 0.5, 1.0 and 1.5 T. Open circle is the $-\Delta S_M$ extracted from magnetic measurement for sample V2H by applying the Maxwell equation to the iso-field magnetization under different magnetic field [26]. The $-\Delta S_M$ values obtained from the caloric and the magnetic measurement show good consistency. Particularly, sample V2H shows a larger value of $-\Delta S_M$ than sample V0H for the low magnetic field range up to 1.2 T. The value of $-\Delta S_M$ under a magnetic field of 1.0 T is 8.7, 9.2 and 6.8 J/kgK for V0H, V2H, and V2L, respectively. However, when the applied magnetic field increases to a higher magnetic field of 1.5 T, the value of $-\Delta S_M$ for V2H becomes lower than that of V0H, which is 11.7 and 12.7 J/kgK, respectively. This unusual field response will be addressed in the discussion section. The saturation magnetization measured at a temperature of 5 K for magnetic fields up to 5 T, shown in Fig. 1(c), is 163.8, 156.7, 145.5 Am/kg for samples V0H, V2H and V2L, respectively.

3. Hyperfine interactions

The Mössbauer spectra measured at 350 and 110 K for the three samples are shown in Fig. 2. In the paramagnetic (PM) high-temperature phase, a single broad absorption line is observed. In the ferromagnetic [FM] low-temperature phase, a more complex absorption profile is observed that includes six rather broad spectral lines, which indicates a distribution in hyperfine field. Since P and Si are randomly distributed over the 2c and the 1b crystallographic positions, this leads to five inequivalent Fe nearest neighbors. In such a case the experimental Mössbauer spectra are usually fitted with a model that weighs the contribution of each Fe environment using a binomial distribution [29]. A similar model is used in this work and a summary of the derived average hyperfine parameters, together with the linewidth, and the fraction of the magnetic phase are given in Table 1.

At 110 K, most of the Fe species are ferromagnetic, with about 6% of the Fe atoms being still in the paramagnetic state. Interestingly, the hyperfine magnetic field is decreasing for V substitution from 22.3 T for sample V0L without vanadium to 21.9 and 21.7 T for vanadium containing samples V2H and V2L, respectively. The hyperfine magnetic field is only slightly decreasing for sample V2L compared to V2H, indicating that it is sensitive to the annealing temperature. The current Mössbauer data demonstrate that V is substituted into the Fe lattice and lowers the measured hyperfine field. The degree of substitution depends on the annealing temperature: the one annealed at 1343 K (V2L) has a higher degree than the one annealed at 1373K (V2H). According to the nominal sample composition, the V substitution is expected to result in a 2.1% reduction (= 0.02 (0.73) in the Fe occupancy of the 3f site. When such a reduction is applied to the hyperfine field of Fe a value of 21.7 T is estimated for the vanadium containing samples.

4. X-ray diffraction and neutron diffraction

Rietveld refinement of XRD data for V2H sample at 370 K is shown in the Fig. 3 (a). The main phase is hexagonal Fe$_2$P-type phase (space group P-6m2) and the (Mn,Fe)$_2$Si-type phase (space group Fm$ar{3}$m) is identified as impurity phase. The volume fraction of impurity phase for samples V0H, V2H and V2L is $2.37 \pm 0.51$, $3.22 \pm 0.58$, $3.42 \pm 0.95$ vol%, respectively. Neutron diffraction measurements were performed for the V0H, V2H and V2L samples at temperatures of 370 and 110 K. The refinement pattern of V2H is illustrated in Fig. 3 (b) and the results are shown in Table 3. All samples are in the paramagnetic state at 370 K and in the ferromagnetic state at 110 K.

According to the Mössbauer results, there is still 6% of paramagnetic phase present at 110 K, which is different to the extracted fraction of impurity phase (≈ 3%) from the XRD refinement results. This deviation is also observed in a previous Mössbauer study for the Mn–Fe–P–Si systems [14], which may be caused by a small fraction of amorphous phase, that is invisible to diffraction. The neutron diffraction patterns can be fitted with the Fe$_2$P-type hexagonal structure (space group P-6m2) with 4 different crystallographic sites, i.e. the 3f and 3g site for the Mn and Fe atoms and the 2c and 1b for the P and Si atoms, respectively [30]. The alignment of magnetic moment is within the $a$–$b$ plane. The quality of Rietveld refinement in the paramagnetic state, indicates that V has a slight
Fig. 1. (a) Magnetization as a function of the temperature measured in an applied magnetic field of 1 T with the $-\frac{dM}{dT}$ values shown in the inset; (b) magnetic entropy change $-\Delta S_M$ as a function of temperature for a magnetic field change up to 1.5 T (solid symbols are extracted from caloric measurement and open circles are extracted from magnetic measurement for sample V2H) and (c) Magnetization as a function of the applied magnetic field at a temperature of 5 K for samples V0H, V2H and V2L.

Fig. 2. Mössbauer spectra obtained for the magnetocaloric samples V0H, V2H and V2L at (a) 350 K and (b) 110 K.
preference to occupy the 3f site rather than a random distribution on the Fe₃P-type lattice reported in a previous investigation [26]. For the ferromagnetic state in the current case of V₂H, refinements have been conducted assuming that V is (i) all located exclusively on the 3f site, (ii) located exclusively on the 3g site or (iii) randomly distributed over the 3f and 3g sites and resulting in χ² values of 5.89, 6.89 and 6.51, respectively. Thus, the refinement results suggest that a better value of χ² is obtained when V is located on the 3f site. And the calculated total magnetic moment is 3.9 ± 0.17, 3.5 ± 0.06 and 3.4 ± 0.06 μB, respectively. For the V₂L sample, the value of χ² is 7.89, 7.64 and 6.39, respectively. And the calculated total magnetic moment is 3.9 ± 0.17, 3.9 ± 0.14 and 4.2 ± 0.15 μB, respectively. Note that the experimental spontaneous magnetic moments of Mₓf and Mₓg, the calculated magnetic moments derived in the case of V on the 3f shows a better agreement. Because a 63% reduction of Mₓf would be an overestimation when V is located on either the 3g or 3f and 3g randomly distribution. Thus, it is concluded that V has a preference to occupy the 3f site.

The total refined magnetic moments are 4.2 ± 0.1, 3.9 ± 0.2 and 3.9 ± 0.2 μB for the V₀H, V₂H and V₂L samples, respectively. These values are in agreement with the spontaneous magnetic moment (Mₓtotal) [31], calculated from the magnetization in the Fig. 1 (c), which decreases with the V content. The refined Mₓg decreases from 2.6 μB for the V₀H sample without V to 2.2 and 2.0 μB for the V containing samples V₂H and V₂L, respectively. The Mₓf increases from 1.6 μB for the V₀H sample without V to 1.7 and 1.9 μB for the V containing samples V₂H and V₂L, respectively. For the V₀H alloys, which does not contain V, the neutron diffraction results are comparable to the previous published calculation for the Mn–Fe–P–Si system [30,32,33]. It suggests that our current refinement of the experimental uncertainties: Isomer shift: IS ± 0.01 mm s⁻¹; Quadrupole splitting: QS ± 0.01 mm s⁻¹; Line width: Γ ± 0.01 mm s⁻¹; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%; P/F: ferromagnetic/paramagnetic phases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (K)</th>
<th>IS (mm s⁻¹)</th>
<th>QS (mm s⁻¹)</th>
<th>Hyperfine field*(T)</th>
<th>Γ (mm s⁻¹)</th>
<th>Phase</th>
<th>Spectral contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₀H</td>
<td>350</td>
<td>0.22</td>
<td>0.31</td>
<td>–</td>
<td>0.32</td>
<td>P</td>
<td>100</td>
</tr>
<tr>
<td>V₀H</td>
<td>110</td>
<td>0.29</td>
<td>–0.19</td>
<td>22.3</td>
<td>0.32</td>
<td>F</td>
<td>94</td>
</tr>
<tr>
<td>V₂H</td>
<td>350</td>
<td>0.14</td>
<td>0.53</td>
<td>–</td>
<td>0.32</td>
<td>P</td>
<td>100</td>
</tr>
<tr>
<td>V₂H</td>
<td>110</td>
<td>0.29</td>
<td>–0.19</td>
<td>21.9</td>
<td>0.36</td>
<td>F</td>
<td>94</td>
</tr>
<tr>
<td>V₂L</td>
<td>350</td>
<td>0.21</td>
<td>0.31</td>
<td>–</td>
<td>0.32</td>
<td>P</td>
<td>100</td>
</tr>
<tr>
<td>V₂L</td>
<td>110</td>
<td>0.29</td>
<td>–0.18</td>
<td>21.7</td>
<td>0.36</td>
<td>F</td>
<td>94</td>
</tr>
</tbody>
</table>

Table 2
Neutron diffraction refined results of magnetic moment and χ² for assuming that V is (i) all located exclusively on the 3f site, (ii) located exclusively on the 3g site or (iii) randomly distributed over the 3f and 3g sites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V position</th>
<th>Mₓf (μB)</th>
<th>ERₓf (μB)</th>
<th>Mₓg (μB)</th>
<th>ERₓg (μB)</th>
<th>Mₓtotal (μB)</th>
<th>Eₓtotal (μB)</th>
<th>Mₓmeas (μB)</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂H</td>
<td>3f</td>
<td>1.7</td>
<td>0.125</td>
<td>2.2</td>
<td>0.115</td>
<td>3.9</td>
<td>0.17</td>
<td>3.70</td>
<td>5.89</td>
</tr>
<tr>
<td></td>
<td>3f, 3g</td>
<td>0.9</td>
<td>0.046</td>
<td>2.6</td>
<td>0.032</td>
<td>3.5</td>
<td>0.04</td>
<td>6.51</td>
<td></td>
</tr>
<tr>
<td>V₂L</td>
<td>3f</td>
<td>0.9</td>
<td>0.097</td>
<td>2.0</td>
<td>0.066</td>
<td>3.9</td>
<td>0.15</td>
<td>6.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3f, 3g</td>
<td>2.3</td>
<td>0.104</td>
<td>1.6</td>
<td>0.090</td>
<td>3.9</td>
<td>0.14</td>
<td>7.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3g</td>
<td>1.8</td>
<td>0.131</td>
<td>2.4</td>
<td>0.120</td>
<td>4.3</td>
<td>0.17</td>
<td>7.89</td>
<td></td>
</tr>
</tbody>
</table>
results are acceptable. Note that the magnetic moment of Mn–Fe–P–Si system containing V has not been reported yet. The higher moment on 3f for V2H compared to the V free alloy, should be related to the introduction of V on 3f site, that probably reduces the hybridization of 3d states with Si p states. The V2L sample shows a negligible thermal hysteresis of 0.5 K, which suggest that it is very close to the SOMT. This is different from the previous reported samples with FOMT. The previous neutron data also showed an increase of $M_{3f}$ when the first order phase transition is weakened [30].

### 5. Discussion

The latent heat is generally regarded as a sign of the strength of FOMT [10]. The latent heat, extracted from the heat capacity curves in Fig. 4 (a), is 9.3, 6.3, 5.6 kJ/kg for samples V0H, V2H and V2L, respectively. These values indicate that the strength of the first-order magneto-elastic transition is weakened by the V substitution. The phenomenon that $-\Delta S_M$ of V2H is sharper and larger than that of V0H is observed at 1.0 T, which suggest a better performance for the V2H under 1.0 T. This result is consistent with the entropy change shown in the Fig. 1 (b). When comparing the $-\Delta S_M$ under a higher magnetic field of 1.5 T, the $-\Delta S_M$ value of V2H is lower than V0H. On the other hand, the latent heat of V2H is smaller than V0H. This is because the latent heat indicates the lattice contribution to $-\Delta S_M$. However, $-\Delta S_M$ includes both lattice and spin (magnetic and electronic) contribution [34]. The larger $-dM/dT$ or entropy change of V2H suggests a larger magnetic contributions is induced at a low field range than the one in V0H. As shown the Fig. 1(c), the magnetic permeability of V2H is also enhanced by V substitution. In comparison to sample V0H without V, the magnetization saturates in a lower field for sample V2H with V.

Since $\Delta T_{hys}$ correlates to both intrinsic and extrinsic properties [27] and the amount of impurity phase of the current samples is essentially at the same level, the value of $\Delta T_{hys}$ here represents the strength of the magneto-elastic coupling, i.e. how strong the FOMT is. Therefore, it is interesting to investigate the magnetic moments and the hyperfine fields as functions of $\Delta T_{hys}$. Fig. 4 (b) shows the dependence of $\Delta T_{hys}$ with the hyperfine field (diamond) and $M_{total}$ (triangle), $M_{3g}$ (Rectangle) and $M_{3f}$ (cycle) in the ferromagnetic state. The reduced hyperfine field is consistent with the weakened FOMT on substituting Fe by V as indicated by the latent heat results. However, the trend of hyperfine field differs somewhat from the trend of $M_{total}$, but is in good agreement with the trend of $M_{3g}$. This phenomenon can be explained by the mixed magnetism in the Fe54P19-type alloys. The meta-magnetic behavior of binary Fe54P19 alloys have been investigated theoretically by Yamada et al. [35] According to Landau–Ginzburg theory, the ferromagnetic state of Fe atoms on the 3f site is stabilized by the exchange field from the magnetic Fe sites on the 3g site. Therefore, the exchange field is governed by $M_{3g}$. In consequence, a small moment of 0.3 $\mu_B$ is
induced on Fe(3f) and a moment of 0.4 μB is induced on Fe(3g) in the binary Fe2P alloys. Therefore, in the current Mn–Fe–P–Si–V system, the trend of M3f determines the trend of exchange field, as shown in Fig. 4 (b).

As mentioned above, in the binary Fe2P alloy, M3f is affiliated with the change of M3g, i.e. a reduced M3g will result in a weaker M3f [35]. Astonishingly, M3f in the current Mn–Fe–V–P–Si system is raised when M3g is reduced, see Fig. 4 (b). It suggests a minor addition of V in the quaternary alloy complicates the magnetic coupling in the Fe2P-type structure. The mechanism of the enhanced magnetic moment of M3f can be explained through the competition between bond formation (3d–2p hybridization) and moment formation since this is the intrinsic basis of the FOMT in the Fe2P type structure [15]. A strong FOMT will show a strong bond formation and a weak moment formation on the 3f site. The decrease of the hyperfine field and latent heat suggests that bond formation is weakened by V substitution. As a result, the moment formation is strengthened. Thus, the preference of moment formation instead of bond formation on the 3f site should be the intrinsic origin of high M3f. In the current experimental method, we directly observed that the increase is caused by adding the V on the 3f site. To better understand the mechanism of it, more experimental probes like x-ray magnetic circular dichroism (XMCD) [36], which can clarify the role of each Mn, Fe and V atoms on the 3f site, and theoretical calculations are necessary to reveal the mechanism behind it. The enhancement of M3f makes it possible to lower the magnetic field inducing the FOMT. As a result, sample V2H shows a larger value of -ΔSt than the sample V0H for the low magnetic field range up to 1.2 T. The current mechanism suggests that enhancing M3f can bring a better low-field MCE, which enables the design of suitable MCE materials that operate in low magnetic fields. Further decreasing the exchange field in sample V2L will approach the critical region. The character of FOMT for V2L becomes insufficient and a nearly second-order magnetic phase transition is found, as indicated by the heat capacity in Fig. 4 (a).

6. Conclusions

V substitution in the Mn–Fe–P–Si alloys makes it feasible to tune the magneto-elastic transition towards the critical point between FOMT and SOMT. A decreasing hyperfine field proves that the magnetic exchange field between the magnetic 3f and 3g sites in the Fe2P-type structure is decreased, which lowers the total magnetic moment. V is found to occupy the 3f site and results in the development of an enhanced M3f. The mechanism of the enhanced M3f is the reduction of 3d–2p hybridization or bonding on the 3f site when introducing V. In consequence, the magnetic contribution of the entropy change is increased and an enhanced MCE below 1.2 T is achieved in the sample V2H.

Author contribution

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Bowei Huang., Investigation; Methodology;
Jiu Liu., Investigation; Methodology;
Michael Maschek., Investigation; Methodology;
Lambert van Eijk, Neutron diffraction Resources; Software;
Supervision; Validation;
Niels van Dijk, Conceptualization; Supervision; Writing - review & editing.

Elkes Brück Funding acquisition, Conceptualization; Supervision; Writing - review & editing.

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