Magnetization and magnetic phase diagram of Heusler compounds Fe$_{3-y}$(Mn$_{1-x}$V$_x$)$_y$Si ($y = 1$ and 1.5)

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Abstract. Fe$_2$MnSi exhibits a ferromagnetic transition at $T_C$ and another transition to a phase with antiferromagnetic components at a low temperature of $T_A$. By substituting V for Mn, so as to obtain Fe$_2$Mn$_{1-x}$V$_x$Si, $T_A$ decreases with $x$ and then vanishes around $x = 0.2$. In this study, the magnetic transitions are investigated by magnetization measurements for Fe$_2$Mn$_{1-x}$V$_x$Si ($y = 1$, $0 \leq x \leq 0.2$) in high magnetic fields up to $\sim 70$ T and for Fe$_{1.5}$(Mn$_{1-x}$V$_x$)$_{1.5}$Si ($y = 1.5$, $0 \leq x \leq 0.1$) up to 5 T. For $y = 1.5$, with increasing $x$, $T_C$ increases and $T_A$ decreases as for $y = 1$, and the rate of the decrease in $T_A$ with $x$ is slightly smaller than for $y = 1.0$. In the low magnetic field region, $T_A$ for $y = 1$ does not significantly change due to the magnetic field but a distinct decrease is observed in high fields. The critical field at 0 K of this transition in Fe$_2$MnSi is found to be larger than 70 T, and with increasing $x$, the critical field decreases corresponding to the decrease of $T_A$ at zero field.

1. Introduction

Half-metallic materials in Heusler compounds have attracted considerable attention because of their potential applications in spintronics [1-3]. Half-metals are ferromagnetic metals wherein at the Fermi energy, the density of states (DOS) exists only in one spin band and there is a gap in the other spin band; this implies that there are 100% spin-polarized conduction electrons. Half-metals are thus promising materials for magneto-resistive and spin-injection devices. The possibility of some Heusler compounds being half-metals was suggested some time ago. Co$_2$MnSi and Fe$_2$MnSi were predicted to be half-metals based on first-principles band structure calculations [4-8]. Co$_2$MnSi has since been revealed to exhibit half-metallicity. On the other hand, Fe$_2$MnSi shows a ferromagnetic transition at a temperature $T_C$ (Curie temperature) of $\sim 230$ K, and a transition occurs to a phase with antiferromagnetic components at a lower temperature of $\sim 60$ K, defined as $T_A$; this phase, however, has a large ferromagnetic component. In this paper, we refer to this phase as the AF phase and to the ferromagnetic phase between $T_A$ and $T_C$ as the F phase. The transition and properties of the AF phase have
been studied previously [6, 9–14], and neutron scattering experiments have revealed a complex magnetic structure with the magnetic moment carried by Mn [10, 15].

The presence of an antiferromagnetic order in Fe$_2$MnSi shows that the ground state is not half-metallic ferromagnetism as has been predicted theoretically. Although the half-metallic ground state is not realized in Fe$_2$MnSi, the saturation magnetization of alloy systems containing Fe$_2$MnSi was re-interpreted in terms of the Slater-Pauling (SP) rule in Heusler compounds, which holds when a substance is a half-metal [16–19]. For V-substituted Fe$_{1-x}$Mn$_x$Si, as $x$ increases, $T_C$ increases and $T_A$ decreases, whereas $T_A$ vanishes around $x \approx 0.2$ [16, 20, 21]. Its saturation magnetization for $x > 0.2$ appears to obey the SP rule, but for $x \approx 0.2$ it deviates because of the appearance of the AF phase [22].

We investigated the magnetization of Fe$_{2}$Mn$_{1-x}$V$_x$Si ($0 \leq x \leq 0.2$) at 4.2 K up to ~70 T with pulsed magnetic fields [23], and we observed that in the high field limit, where the F phase is supposed to be realized, the magnetization approaches the value indicated by the SP rule. This result suggests that the electronic structure of the high field F phase is intimately related to the half-metallic state, although the fact that magnetization does not agree completely with the SP rule implies that the half-metallic state is not completely realized in the high field F phase.

In this study the transition between the AF phase and the F phase is investigated by magnetization measurements for Fe$_{2}$Mn$_{1-x}$V$_x$Si including high field regions with pulsed fields. Moreover, Fe$_{1.5}$(Mn$_{1-x}$V$_x$)$_{1.5}$Si is studied in order to compare the effect of V. Although the $T_A$ of Fe$_2$MnSi and Fe$_{1.5}$Mn$_{1.5}$Si is almost the same, their $T_C$s are different. This difference may affect the properties of the AF phase. Because the increase of V content decreases $T_A$ at zero magnetic field and accordingly the critical magnetic field of the transition, this may allow us to study the entire phase boundary of the transition. Therefore, V substitution is expected to be a useful tool to study the AF transition and phase. Some of the results for Fe$_{2}$Mn$_{1-x}$V$_x$Si have already been published [21, 23].

2. Experimental
Polycrystalline samples of Fe$_{2}$Mn$_{1-x}$V$_x$Si ($0 \leq x \leq 0.2$) and Fe$_{1.5}$(Mn$_{1-x}$V$_x$)$_{1.5}$Si ($0 \leq x \leq 0.1$) were prepared by arc-melting high-purity constituent elements in a high-purity argon atmosphere. Crystal structures were examined using X-ray powder diffraction measurements with Cu Kα radiation. X-ray diffraction measurements showed that the prepared samples were single phase, and the crystal structure was $L2_1$. The profiles of the X-ray diffraction patterns were practically the same for all the samples. These results showed, at least in view of X-ray diffraction, the same sample quality of these samples. Magnetization was measured using SQUID magnetometers (MPMS: Quantum Design). Pulsed magnetic fields of up to 72 T were generated using non-destructive magnets with a duration of several milliseconds. Magnetization was measured by the induction method using a standard pick up coil in the magnetic fields. The absolute values of the data obtained by the pulsed magnets were calibrated by comparing the raw data obtained by the pulsed magnets with the absolute values of the magnetization below 7 T, which were measured by SQUID magnetometers.

3. Results
Figures 1 and 2 show the temperature dependence of magnetization $M(T)$ for Fe$_{2}$Mn$_{1-x}$V$_x$Si ($x = 0, 0.1$, and 0.18) and Fe$_{1.5}$(Mn$_{1-x}$V$_x$)$_{1.5}$Si ($x = 0, 0.05$, and 0.1) at a magnetic field $B$ of 1 T, respectively. These results exhibited the same behavior as that of Fe$_2$MnSi. With decreasing temperature $M$ increased rather rapidly. The increase shows the ferromagnetic transition to the F phase, and the transition temperature is $T_C$. And $M$ exhibits a peak or kink (the AF transition becomes less sharp and the peak collapses with increasing $x$). This anomaly shows the transition to the AF phase and we refer to this transition temperature as $T_A$. 


Figure 1. Temperature dependence of magnetization of Fe$_2$Mn$_{1-x}$V$_x$Si ($x = 0$, 0.1, and 0.18) at $B = 1$ T.

Figure 2. Temperature dependence of magnetization of Fe$_{1.5}$(Mn$_{1-x}$V$_x$)$_{1.5}$Si ($x = 0$, 0.05, and 0.1) at $B = 1$ T.

In Fig. 3, reduced $T_C$ and $T_A$ as a function of $x$ are shown for $y = 1$ and 1.5. Reduced $T_C$ and $T_A$ are $T_A(x)/T_A(x=0)$ and $T_C(x)/T_C(x=0)$, respectively. $T_A(x=0) = 65$ K for both $y$: $T_C(x=0) = 220$ K for $y = 0$ and $T_C(x=0) = 142$ K for $y = 1.5$. In addition, on the right axis, the scale of $T_A$ is also shown. With increasing V content, $x$, $T_C$ increases and $T_A$ decreases. $T_C$ for $y = 1$ is higher than for $y = 1.5$. The rate of the increase of reduced $T_C$ and that of the decrease of (reduced) $T_A$ against $x$ are not so largely different between the two series. Nevertheless, the rate of the decrease of $T_A$ for $y = 1.5$ appears slightly smaller than that for $y = 1$; $T_A$ for $y = 1$ vanishes around $x = 0.2$ [21].

Figure 4 (a) and (b) show $M(T)$ for Fe$_{1.5}$Mn$_{1.5}$Si and Fe$_{1.5}$(Mn$_{0.9}$V$_{0.1}$)$_{1.5}$Si for magnetic fields $0 < B \leq 5$ T, respectively. In Fig.4 (a), at a low field, 0.01 T, hysteresis of $M(T)$ in a zero-field cooling and a field cooling process is observed. However, the hysteresis becomes much smaller when the magnetic field reaches 1 T. As seen in the figure, $T_A$ slightly changes with magnetic field. The sharpness of the anomaly at the transition at $T_A$ is also not considerably affected by the magnetic field, as exhibited remarkably in the derivatives $dM/dT$ shown in the insets. Compared with the case of $y = 0$, the AF transition in the case of $y = 1.5$ appears to be less affected by the magnetic field.

In order to determine the influence of the magnetic field on the transition, high field magnetization was measured for Fe$_2$Mn$_{1-x}$V$_x$Si up to 70 T with pulsed magnetic fields. Figure 5 (a) shows, in an expanded scale, magnetization as a function of the magnetic field $M(B)$ at several temperatures between 4.2 K and 70 K for Fe$_2$MnSi ($T_A^0 = 65$ K, where $T_A^0$ is the transition temperature at zero field.). In the inset of Fig. 5 (a), $M(B)$ is shown over the
Figure 4. (a) Temperature dependence of magnetization $M(T)$ of Fe$_{1.5}$Mn$_{1.5}$Si for different values of the magnetic field. For $B = 0.01$ T and 1 T, data for zero-field cooling (solid line and solid circles) and field cooling (broken line and open circles) are shown. The inset shows the derivative $dM/dT$.  (b) Temperature dependence of magnetization $M(T)$ of Fe$_{1.5}$(Mn$_{0.9}$V$_{0.1}$)$_{1.5}$Si for different values of the magnetic field. The inset shows the derivative $dM/dT$.

Figure 5. (a) Magnetization versus magnetic field $M(B)$ for Fe$_2$MnSi ($T_A^0 = 65$ K) up to 70 T in an expanded scale. In the inset, $M(B)$ over the entire magnetic field range is shown. (b) Values of the derivative $dM/dB$. The arrows show the transitions.

Figure 6. (a) Magnetization versus magnetic field $M(B)$ for Fe$_2$Mn$_{0.9}$V$_{0.1}$Si ($T_A^0 = 30$ K) up to 63 T in an expanded scale. In the inset, $M(B)$ over the entire magnetic field range is shown. (b) Values of the derivative $dM/dB$. The arrows show the transitions.

entire field range. With increasing $B$, at low fields $M$ initially increases rapidly, reflecting its ferromagnetism, and slows down at higher fields. Although no anomaly appears to indicate a transition in the $M(B)$ curves at first glance, the derivative $dM/dB$, as shown in Fig. 5 (b), reveals that there is, in fact, a transition. The $dM/dB$ curves at $T < T_A^0$ similarly decrease at low fields, but at a field that depends on the temperature of measurement, they bend downward and then coincide with the $dM/dB$ curve at 70 K ($> T_A^0$), the point at which the F phase is considered to exist all over the field range and no transition occurs. From these results, we can
recognize that this anomaly shows the transition from the AF to the F phase. In addition, the transition is actually discernible when the $M(B)$ curves are compared at different temperatures. As shown in Figure 5 (a), in the lower field range, the $M(B)$ curves at 40 K and 50 K, for example, almost coincide with that at 4.2 K, before starting to shift downward at around 25 T and 11 T, respectively. Although the transition around 47 T for 30 K can be identified, the transition becomes difficult to recognize at lower temperatures because the difference between $M(B)$ curves become even smaller and $M(B)$ and $dM/dB$ curves appear to almost coincide besides the inevitable enhancement of noise around the upper limit of the pulsed field.

Figure 6 shows $M(B)$ and $dM/dB$ for Fe$_2$Mn$_{0.9}V_{0.1}$Si ($T_A^0 = 30$ K). As seen in the figures, the transition becomes smeared as $x$ increases and becomes more difficult to distinguish in $M(B)$. Nevertheless, as for Fe$_2$Mn$_2$Si the $M(B)$ and $dM/dB$ curves allow us to spot the transition, as shown by the arrow in the figure. The magnetic field at the transition becomes smaller according to the decrease of $T_A^0$ with $x$.

Figure 7 shows the $B$-$T$ magnetic phase diagram of Fe$_{3-y}(Mn_{1-x}V_x)_y$Si. ($y=1$ and 1.5, 0 $\leq x \leq 0.18$). In the magnetic field range of up to $\sim$ 70 T, the dependence of the AF transition on the magnetic field is clearly demonstrated. The phase boundaries between the AF and the F phases of Fe$_2$Mn$_{1-x}V_x$Si almost look like straight lines up to the high field region, which is different from usual curved phase boundaries. However, at lower temperatures, the phase transition cannot be recognized mainly because the $M(B)$ curves are almost the same. This is because in the high field region, the magnetic states of the F phase and the AF phase are likely to be similar. Although a part of the data suggest that the straight phase boundaries bend down at lower temperatures toward 0 K, we could not draw reliable phase boundaries near 0 K due to the technical difficulty of measurements in the high field limits of pulsed magnetic fields.

Nevertheless, we can estimate the order of the critical field of this transition at 0 K, $B_{CA}$, reliably. $B_{CA}$ is found to be $\sim k_BT_A^0/\mu_B$, which is expected of usual local moment antiferromagnets. The transition temperature $T_A$ in magnetic fields for Fe$_{1.5}(Mn_{1-x}V_x)_{1.5}$Si exhibits similar behavior, whereas it appears to be less affected by a magnetic field below 5 T for the V-substituted samples. This may demonstrate more robustness to the magnetic field for $y = 1.5$ compared with the case for $y = 1$. However, data are limited to below 5 T for Fe$_{1.5}(Mn_{1-x}V_x)_{1.5}$Si. In this field range, notable magnetic field dependence was not recognized in Fe$_2$Mn$_{1-x}V_x$Si. In order to obtain definite conclusions, measurements in a higher field are desired.

4. Conclusions
The transition between the ferromagnetic phase (F phase) and the antiferromagnetic phase with large ferromagnetic component (AF phase) in Fe$_{1.5}(Mn_{1-x}V_x)_{1.5}$Si ($y = 1$ and 1.5) was investigated in magnetic fields, including in a high field region of up to $\sim$70 T with pulsed

![Figure 7. Magnetic phase diagram](image-url)
fields, and a magnetic phase diagram is constructed. Although the phase boundaries of Fe$_2$Mn$_{1-x}$V$_x$Si at low temperatures near the 0 K axis in the $B$-$T$ magnetic phase diagram were not clearly determined, the whole phase boundaries in the $B$-$T$ plane were obtained. Furthermore, magnetic transition in Fe$_{1.5}$(Mn$_{1-x}$V$_x$)$_{1.5}$Si was investigated. The same type of transition as in Fe$_2$Mn$_{1-x}$V$_x$Si, i.e., the AF transition at $T_A$ and the ferromagnetic transition at $T_C$, were found. On the other hand, in Fe$_{1.5}$(Mn$_{1-x}$V$_x$)$_{1.5}$Si, although the measurements is limited to the magnetic field range below 5 T, $T_A$ appeared to be less affected by the magnetic field compared with the case for $y = 1$.

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