High-field magnetization of Heusler compound $Fe_2Mn_{1-x}V_xSi$

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Fe_2MnSi exhibits a ferromagnetic transition at $T_C \sim 230$ K and another transition to a phase with antiferromagnetic components at $T_A \sim 60$ K. By substituting V for Mn, so as to obtain $Fe_2Mn_{1-x}V_xSi$, T_A is revealed to decrease with x and then vanish around $x \sim 0.2$. In this study, the phase boundary of the transition at T_A in the high-field range is found for $0 \leqslant x \leqslant 0.15$ with pulsed fields up to ~70 T. The magnetization of $Fe_2Mn_{1-x}V_xSi$ slowly increases even at the highest field of ~70 T, though it occurs more gradually as x increases. We compare the magnetization for $0 \leqslant x \leqslant 0.20$ at 62 T with the Slater-Pauling rule, which holds when a Heusler compound is a half-metal, and find fairly good agreement. This suggests an intimate relation between the high-field phase and the half-metallic electronic structure, and that at the high-field limit the phase approaches the half-metallic state, which has been predicted by band-structure calculations.

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Half-metallic materials in Heusler compounds have attracted great attention because of their potential applications in *spintronics* [1–3]. Half-metals are ferromagnetic metals in which, at the Fermi energy, E_F, the density of states 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 promising materials for magnetoresistive and spin-injection devices. The possibility of some Heusler compounds being half-metals was suggested some time ago. Heusler compounds have the formula X_2YZ, where X and Y are transition elements, Z is an sp element, and the structure is $L2_1$ [1]. Among such compounds, Co_2MnSi and Fe_2MnSi were predicted to be half-metals based on the first-principles band-structure calculations [4,5]. Co_2MnSi has since been revealed to exhibit half-metallicity [6]. Although Fe_2MnSi shows a ferromagnetic transition, at a temperature T_C (Curie temperature) of ~230 K, at a lower temperature of ~60 K, defined as T_A, there is a transition to a phase with antiferromagnetic (AFM) components; 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 AFM order have been studied in many magnetic and thermodynamic measurements [7–13], and neutron-scattering experiments have revealed a complex magnetic structure with the magnetic moment carried by Mn [8,14]. According to a theoretical calculation, some AFM states are more energetically favorable than the ferromagnetic states [5]. The AFM order in Fe_2MnSi shows that the ground state is not half-metallic ferromagnetism as has been predicted theoretically. Nevertheless, Fe_2MnSi has recently attracted renewed interest, and new theoretical studies have predicted that it is indeed a half-metal [13,15,16].

Even though the half-metallic ground state is not realized in Fe_2MnSi, the saturation magnetization of alloy systems containing Fe_2MnSi was reinterpreted in terms of the Slater-Pauling (SP) rule in Heusler compounds, which holds when a substance is a half-metal. The SP rule states that $M_s = N_v - 24$ (μ_B per formula unit), where M_s and N_v are the saturation magnetization and number of valence electrons, respectively [2]. For $Fe_2Mn_{1-x}V_xSi$, as x increases, T_C increases and T_A decreases, while T_A vanishes around $x \sim 0.2$ [17–19]. Its saturation magnetization for $x > 0.2$ appears to obey the SP rule (Fig. 5) [20]. From a similar viewpoint, the saturation magnetization of $Fe_{2-x}Co_xMnSi$ has been studied experimentally and theoretically [18,21–23]. These studies show that the saturation magnetization in these alloy systems agrees quite well with the SP rule, although experimentally the magnetization has been lesser than that indicated by the SP rule around $x \sim 0$ where the AF phase exists. This suggests that there are half-metals in these compounds, except in the vicinity of Fe_2MnSi [20]. Even though the half-metallic ferromagnetic state appears to reside in Fe_2MnSi, there are competing possible AFM states, and consequently an AFM state that is energetically favorable is realized. Note that the F phase between T_A and T_C does not show a behavior that is expected of a half-metal. This is because the assumed saturation magnetization of the F phase—which is estimated by extrapolating the temperature dependence of magnetization, $M(T)$, at a magnetic field, B, of 1 T above T_A to 0 K—is smaller than 3 μ_B/f.u.; this value is indicated by the SP rule for identifying half-metals. The actual M at 0 K in the AF phase is even smaller. It should be noted that in Heusler compounds disorder in crystal lattice is inevitable and may affect the magnetization values. It was reported that in Fe_2MnSi there is a 12–15% ratio of swap of Fe (X site)-Mn

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(Y site) [7,9]. The Fe-Mn swap is likely to lead to the reduction of the magnetization. However, a band-structure calculation showed that the magnetization and the half-metallicity are retained even when there is the swap [16]. So it is not evident that in Fe_2MnSi disorder affects the magnetization and degrades the half-metallicity. Meanwhile, there is a suggestion that the Mn-Fe swap may be the cause of the emergence of the AF phase [13]. Even though the Mn-Fe swap may play some role, we think it unreasonable to ascribe it mainly to the swap, because the transition at T_A is definite.

For $Fe_2Mn_{1-x}V_xSi$ ($x = 0$ and 0.2), magnetization measurements were carried out up to $B = 27$ T at 4.2 K [20]. For $Fe_2Mn_{0.8}V_{0.2}Si$, with increasing B magnetization $M(B)$ initially increases rapidly and almost saturates at higher fields, reflecting its ferromagnetism. For Fe_2MnSi, $M(B)$ initially increases rapidly as well, but continues to increase gradually even around 27 T and does not exhibit any sign of saturation. Considering that Fe_2MnSi exhibits an AFM transition at $T_A =$ 60 K under 0 T, at 4.2 K, the AF phase appears to be present under a field of 27 T and continues to be present in the higher field range. These results indicate that the transition to the high-field phase, which should be the F phase, occurs around 70 T since this is where M is expected to reach 3 μ_B/f.u. The measurement of higher field magnetization of Fe_2MnSi is, therefore, desirable, as it helps elucidate the phase boundary in the high-field region as well as the magnetization of the F phase. However, the expected critical field of the transition to the F phase, B_c, for Fe_2MnSi, is still difficult to detect even with a pulsed magnet. As mentioned above, the substitution of V decreases T_A and is accordingly expected to decrease B_c, i.e., to reduce the AF phase in the B-T phase diagram. In this study, therefore, we investigate the whole phase boundary of the transition between the AF and F phases and the relation of its magnetization to the half-metallicity in $Fe_2Mn_{1-x}V_xSi$ ($0 \leqslant x \leqslant 0.2$).

Polycrystalline samples of $Fe_2Mn_{1-x}V_xSi$ ($0 \leqslant x \leqslant 0.2$) were prepared by arc melting high-purity constituent elements under 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 lattice constant of Fe_2MnSi was found to be 0.567 nm. The lattice constant of $Fe_2Mn_{1-x}V_xSi$, meanwhile, ranged between 0.565 and 0.567 nm, and it did not change much with changes in x. This is consistent with previous findings [17]. The profiles of the x-ray-diffraction patterns were practically the same for $0 \leqslant x \leqslant 0.2$. These results showed, at least in view of x-ray diffraction, the same sample quality for $0 \leqslant x \leqslant 0.2$. T_A and T_C of these samples were confirmed to agree with the results of previous studies by magnetic measurements using superconducting quantum interference device (SQUID) magnetometers (MPMS: Quantum Design). It is noted, furthermore, that in previous studies the magnetization and electrical resistivity were revealed to change systematically with x; this is another support for proper preparation of these compounds [17,19]. Pulsed magnetic fields of up to 72 T were generated using nondestructive magnets with a duration of several milliseconds. Magnetization was measured by the induction method using a standard pickup 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.

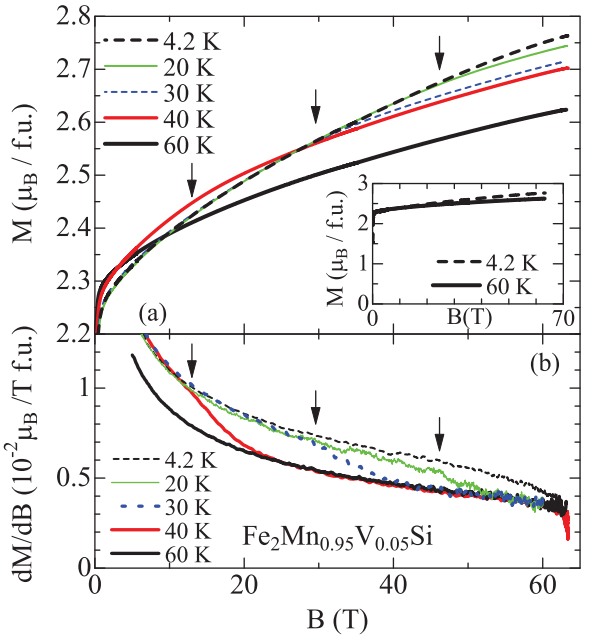

FIG. 1. (a) Magnetization versus magnetic field $M(B)$ for $Fe_2Mn_{0.95}V_{0.05}Si$ at up to 63 T in an expanded scale. In the inset, $M(B)$ over the entire magnetic field range is shown. (b) Values from the derivative dM/dB. The arrows show the transitions.

Figure 1(a) shows, in an expanded scale, magnetization as a function of the magnetic field $M(B)$ at several temperatures between 4.2 and 60 K for $Fe_2Mn_{0.95}V_{0.05}Si$ ($T_A = 52$ K, see Fig. 3). In the inset of Fig. 1, $M(B)$ is shown over the entire field range. With increasing B, at low fields M initially increases rapidly, reflecting its ferromagnetism, and slows down at higher fields. Even though no anomaly indicates a transition in the $M(B)$ curves, the derivative dM/dB, as shown in Fig. 1(b), reveals that there is, in fact, a transition. The dM/dB curves at $T < T_A$ similarly decrease at low fields, but at a field that depends on the measurement temperature they bend downward and then coincide with the dM/dB curve at 60 K ($>T_A$), 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. Additionally, the transition is discernible when the $M(B)$ curves are compared at different temperatures. As shown in Fig. 1(a), in the lower field range, the $M(B)$ curves at 20 and 30 K almost coincide with that at 4.2 K, before starting to shift downward at around 46 and 30 T, respectively. For $T \leqslant 15$ K, the $M(B)$ and dM/dB curves appear to almost coincide, and the dM/dB curves appears to exhibit a bend at ~55 T (not shown for 15 K in Fig. 1). We cannot conclude that this is due to the transition, since around the upper limit of the pulsed field, the enhancement of noise is inevitable.

Figure 2 shows $M(B)$ and dM/dB for $Fe_2Mn_{0.85}V_{0.15}Si$. As seen in the figures, the transition becomes smeared as x increases and is barely discernible in $M(B)$. Nevertheless, the dM/dB curves allow us to spot the transition, as shown by

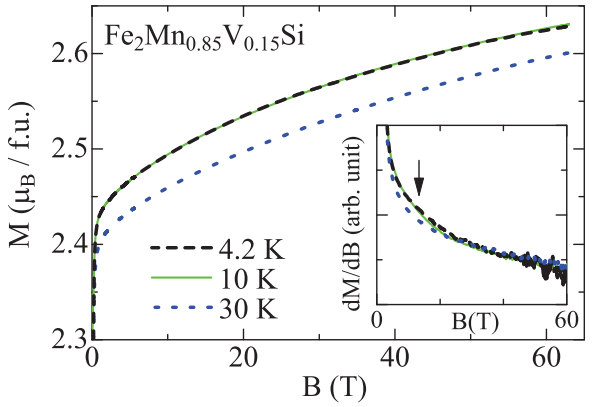

FIG. 2. Magnetization versus magnetic field $M(B)$ for $Fe_2Mn_{0.85}V_{0.15}Si$ at up to 63 T in an expanded scale. In the inset, the derivative dM/dB is shown. The arrow shows the transition.

the arrow in the figure. However, the dM/dB curves at 10 and 4.2 K almost coincide; they bend downward at ∼10 T, and merge with the curve at 30 K ($>T_A$) around 30 T. It seems, then, that the transition occurs at almost the same field. Nevertheless, it is difficult to consider that the transition occurs at the same field for different temperatures, and so one may doubt that this bend can be attributed to the transition. At present we consider the following: distinguishing where the transition occurs is more difficult at lower temperatures, because the change at the transition is subtle even in dM/dB. It is not just a technical problem either, because the difference between the F and AF phases becomes smaller at lower temperatures. Nevertheless, it is plausible that for $x = 0.15$, the transition at 4.2 K occurs at less than 30 T, where the dM/dB curve merges with that for $T = 30$ K ($>T_A$). This presumption may also apply for $x = 0.05$ and the transition at 4.2 K is supposed to occur at $B \lesssim 70$ T.

Figure 3 shows the B-T magnetic phase diagram for $0 \leqslant x \leqslant 0.15$ where the transition between the AF and F phases is plotted. From this figure, the phase boundaries are found to be almost straight lines at least down to ∼20 K. Even though, at lower temperatures, the transition is very difficult to detect from the $M(B)$ and dM/dB curves, the straight phase

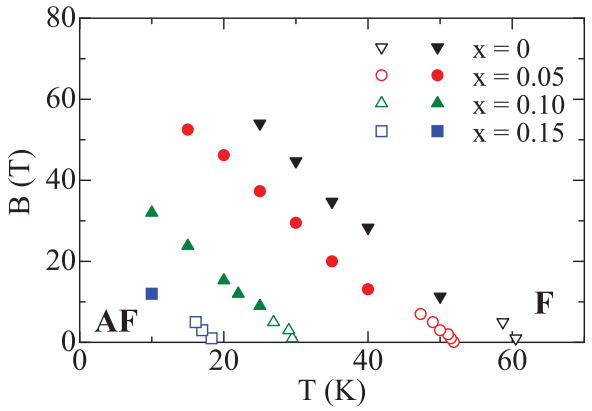

FIG. 3. Transitions between the AF and F phases. Open symbols show the transitions determined from the measurements using SQUID and solid symbols show those obtained using pulsed magnets.

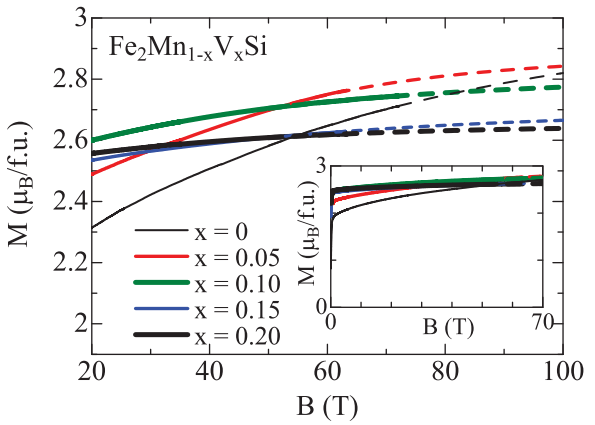

FIG. 4. Magnetization versus magnetic field $M(B)$ for $Fe_2Mn_{1-x}V_xSi$ (x =0, 0.05, 0.1, 0.15, and 0.2) up to 72 T (63 T) at 4.2 K. The broken lines show examples of extrapolations.

boundary is likely to bend downward at lower temperatures, as discussed above. Therefore, B_c of Fe_2MnSi is supposed to be ∼75 T, as expected.

Figure 4 shows $M(B)$ for $0 \leqslant x \leqslant 0.2$ at 4.2 K up to 72 or 63 T. We do not find any anomaly indicating the transition in the $M(B)$ and dM/dB curves at 4.2 K for $x = 0.2$, though the transition from the AF to the F phase is almost indiscernible at 4.2 K for all values of x. Probably for $x = 0$ the AF phase persists all over the field range, while for $0.05 \leqslant x \leqslant 0.15$ the transition exists in this field range, and for $x = 0.2$ the F phase exists all over the field range. Figure 5 shows the magnetizations of $Fe_2Mn_{1-x}V_xSi$ ($0 \leqslant x \leqslant 0.2$) at $T = 4.2$ K as a function of x at $B = 62$ T obtained in the present experiments (open circles), and at $B = 1$ T that had been obtained in a previous study (crosses) [17], and can be seen as saturation magnetization for $x \geqslant 0.2$. The solid straight line follows the SP rule, which suggests half-metallicity in Heusler

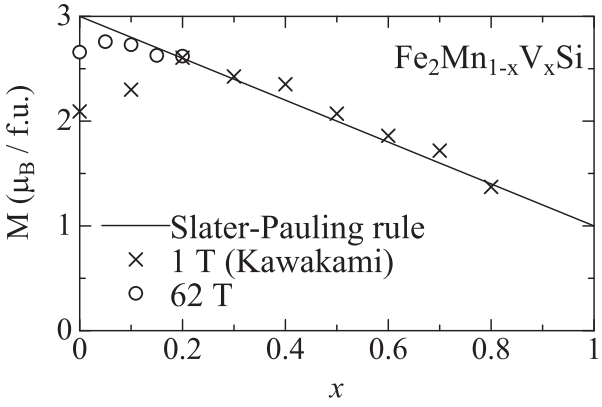

FIG. 5. Plot of the magnetizations at $T = 4.2$ K under $B = 1$ T as a function of x for $Fe_2Mn_{1-x}V_xSi$ (crosses) from Kawakami [17]. In this case, the measured magnetization can be seen as the saturation magnetization for the ferromagnetic state, while the magnetizations at $T = 4.2$ K under $B = 62$ T are the present measurements (open circles). The solid line follows the Slater-Pauling rule, which holds when Heusler compounds are half-metals.

compounds. Magnetization of a half-metal should be robust to external perturbations because there is a gap at E_F in one of the spin states [24]. If the F phase were a half-metal, increasing B would result in $M(B)$ maintaining the constant value, which is indicated by the SP rule. However, as shown in Figs. 1, 2, and 4, M continues to increase gradually at low temperatures, even in the high-field F phase. This is consistent with the fact that the F phase at low fields is not a half-metal. In Fig. 5, the broken line shows examples of extrapolations of the $M(B)$ curves. If these extrapolations are valid, the assumed saturated values agree with the SP rule quite well. Because of the continuous increase in the magnetization even at the highest field, it is difficult to simulate higher field behavior and to estimate the saturated values correctly, particularly for $x = 0$, because it is still in the AF phase. Nevertheless, experimentally, we can stress that the magnetization measured at 62 T, as shown in Fig. 5, already almost agrees with the values indicated by the SP rule, and any extrapolation to a higher field would not significantly surpass the value indicated by the rule. Meanwhile, even for $x = 0.2$ gradual increase in M was observed at the highest field. This might originate from electronic spin contribution [25,26] or from even more extrinsic causes such as the paramagnetism of the grain boundaries. As shown in Fig. 5, the magnitude of the increase for $B > 1$ T is small, and this does not affect our discussion. Therefore we can expect that, in high fields, magnetization may asymptotically approach the value indicated by the SP rule.

This result implies an intimate connection between the F phase and a half-metallic state. Based on the x dependence of the high-field magnetization, one hypothesis based on a rigid band picture is presented in the following. The F phase has the same band structure as that of the assumed half-metallic Fe_2MnSi, in that it has an energy gap at E_F in the down-spin states, whereas E_F is located above the band gap of the down-spin states. In other words, E_F is at an energy level in the bands just above the gap. In this case, it is not a half-metal and the magnetization is smaller than that indicated by the SP rule. This is because the SP rule is derived from the energy gap of the down-spin states at E_F [2]. By increasing x from zero, N_v decreases by a value of $2x$, and accordingly, E_F drops and just about reaches the top of the gap in the down-spin states at $x \sim 0.2$. As x increases further, E_F continues to fall, and as a result, becomes situated in the gap. At this point, it becomes a half-metal and obeys the SP rule for a larger value of x. In the case of $Fe_{2-x}Co_xMnSi$, where N_v increases with x, the ferromagnetic interaction seems larger than that in the case of $Fe_2Mn_{1-x}V_xSi$. It, therefore, yields a large exchange splitting and elevates the down-spin band and the energy gap, thereby leading to the half-metallic state. In this model, the high-field magnetization increases asymptotically toward the value indicated by the SP rule and has a high-field susceptibility due to electrons at E_F, which exists all the way up to extremely high fields. This is consistent with our present results. Such high-field magnetic susceptibility was studied experimentally and theoretically in well-known ferromagnetic alloys [25,26]. The assumed band structure of Fe_2MnSi, however, disagrees with the band-structure calculations which showed that E_F is situated in the middle of the energy gap in the down-spin states. The rigid band picture is obviously not accurate, and as a result, this model is only appropriate for use in qualitative discussions. Progress in understanding the antiferromagnetic interactions in Fe_2MnSi is consequently desired.

In conclusion, the phase boundaries between the ferromagnetic and antiferromagnetic phases of $Fe_2Mn_{1-x}V_xSi$ ($0 \leqslant x \leqslant 0.15$) were determined in the high-field range through pulsed magnetic fields. In addition, we clarified that saturated values of magnetization at the high-field limit are likely to agree with those indicated by the Slater-Pauling rule. These results, along with the saturation magnetization of substituted Fe_2MnSi, can be explained by a rigid band model where a half-metallic band structure resides in Fe_2MnSi. This provides a realistic implication for the half-metallic band structure of Fe_2MnSi, which has been predicted by band-structure calculations.

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