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Thermodynamic Study of the Magnetic Ordering of $Fe_{3-x}Mn_xSi$ Alloys[1]

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The compounds $Fe_{3-x}Mn_xSi$ exhibit a complex magnetic behavior for $0.6 \leqslant x \leqslant 1.75$ involving ferromagnetic ordering followed by a reordering at lower temperature. Measurements of the thermal expansion α and the specific heat C_p show only a weak anomaly at the Curie temperature, T_C, whereas a large, relatively sharp peak occurs at the magnetic reordering temperature, T_R. Thermal expansion measurements for the $Fe_{2.2}Mn_{0.8}Si$ compound made about T_R are indicative of long-range ordering that can be suppressed in an applied field of ~ 0.4 T. Magnetization measurements show that low fields, 1–2 mT, strongly influence the bulk magnetization. Irreversible magnetization behavior, similar to that in spin-glass systems, is displayed.

KEY WORDS: domain configuration; irreversible magnetization; spin-glass; thermal expansion.

1. INTRODUCTION

The series of solid solutions, $Fe_{3-x}Mn_xSi$, is one of a number of 3d transition metal ternary systems based upon Fe_3Si that have been the subject of extensive examination [1]. The present study is concerned with the thermodynamics associated with the magnetic ordering in these compounds.

Fe_3Si orders ferromagnetically at 850 K, whereas Mn_3Si becomes antiferromagnetic below 22 K. The magnetic ordering among the alloys across the pseudobinary system is complex. For $x < 0.6$ the compounds are ferromagnetic with a Curie temperature T_C that decreases with Mn content

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[2, 3]. For $x > 0.6$ a magnetic reordering occurs below a temperature T_R, which increases to 60 K at $x = 1.0$ and then is approximately constant up to $x < 1.8$ [2, 4, 5]. The reordering results in a drop in the zero-field saturation moment that has been interpreted in terms of a canting of the atomic magnetic moments from the ferromagnetic [111] axis [2]. This magnetic reordering is dependent upon applied magnetic field [2].

Thermophysical studies of the system [3–7] reveal that the sharp anomalies associated with the magnetic ordering in Fe_3Si and Mn_3Si are rapidly suppressed in the pseudobinary alloys. For $Fe_{3-x}Mn_xSi$ compounds with $0.8 \leqslant x \leqslant 1.6$ Smith *et al.* [6] concluded that in terms of the ground-state magnetic order, the reordering at T_R played a more significant role than the initial ordering at T_C. This view has been supported by thermal expansion measurements for Fe_2MnSi that show a large cusp-shaped peak at T_R and a much broader anomaly at T_C [5]. It was concluded that the transition at T_R has a stronger long-range order than the transition at T_C.

The magnetic Grüneisen parameters derived from the specific heat and the thermal expansion data for Fe_2MnSi indicate strong pressure dependencies for T_C and T_R [5]. Furthermore, it was concluded that the magnetic entropy has the form $S(E_M/T)$, where E_M is the appropriate magnetic interaction energy corresponding to the ordering and reordering.

Here we report further thermophysical studies of the magnetic ordering for an alloy in the $Fe_{3-x}Mn_xSi$ system; specifically the influence of an applied magnetic field on the thermal expansion and magnetization at the reordering transition in $Fe_{2.2}Mn_{0.8}Si$.

2. EXPERIMENTAL DETAILS

The thermal expansion sample of $Fe_{2.2}Mn_{0.8}Si$ was cut from the ingot for which the earlier specific heat capacity measurements had been made [6]. The sample was approximately cylindrical, with a diameter of 8 mm and a length of 26.2 mm. The end faces of the sample were lapped flat to within 0.25 μm and parallel to within 5 min of arc.

An electron microprobe analysis on a polished section of the sample confirmed the composition and the single-phase $L2_1$ structure was confirmed by X-ray diffraction on powder produced by crushing pieces remaining after cutting the ingot. The lattice parameter was determined to be 5.662 ± 0.001 Å, in excellent agreement with the values reported by Yoon and Booth [2].

The thermal expansion measurements were made in a three-terminal, capacitance dilatometer [8] following the same procedure described for Fe_2MnSi [5]. The present study also includes thermal expansion

measurements in magnetic fields up to 0.5 T. A superconducting magnet, designed to fit closely around the outer stainless-steel vacuum jacket of the expansion cell, was used for these measurements. The magnet was wound in a three-coil configuration designed to provide a uniform field to within $\pm 1.5\%$ over the length of the sample. Current was supplied throughout the high-field measurements from a conventional stabilized high-current magnet power supply.

The procedure followed for the expansion measurements in a magnetic field was to cool the sample to 4.2 K in zero field. The magnet current was then switched on, resulting in a change in cell capacitance owing to the magnetostriction of both the cell and the sample. The cell was then thermally cycled to ~ 30 K and back to 4.2 K to relieve any mechanical stress caused by the application of the magnetic field. The expansion measurements were then made following the standard zero-field procedure [5].

The magnetic state of the sample was monitored during the expansion measurements by placing a pair of coils about the sample, exciting the primary coil with a 350-Hz signal, and detecting the secondary coil output. Magnetization measurements were also made on a bar of approximate dimensions $10 \times 3 \times 2\ \text{mm}^3$, cut from the expansion sample, using a vibrating sample magnetometer (VSM). The VSM, described in detail by Nethercott [9], was designed to operate in magnetic fields up to 1.8 T over a temperature range of 4.2 to 300 K. Temperature control and measurement to ± 0.1 K were achieved using a conventional temperature controller and an Au–0.07 at % Fe thermocouple attached to the detection coils. A lock-in amplifier was used to measure the AC signal from the pickup coils.

3. RESULTS

3.1. Thermal Expansion Measurements

The linear expansion coefficient for the $Fe_{2.2}Mn_{0.8}Si$ compound over the full temperature range of the measurements (2–300 K) is shown in Fig. 1. However, most of the measurements were confined to temperatures below 45 K, with applied magnetic fields up to 0.5 T. These cover the reordering temperature at $T_R \sim 35$ K. The ferromagnetic ordering temperature, $T_C = 320$ K, was beyond the temperature range of the dilatometer.

The history of the expansion behavior for the $Fe_{2.2}Mn_{0.8}Si$ sample is complex. The data shown in Fig. 1 and, in more detail, in the vicinity of T_R in Fig. 2, were made in April 1986 after the sample had been stored at room temperature for over 6 years following the heat capacity

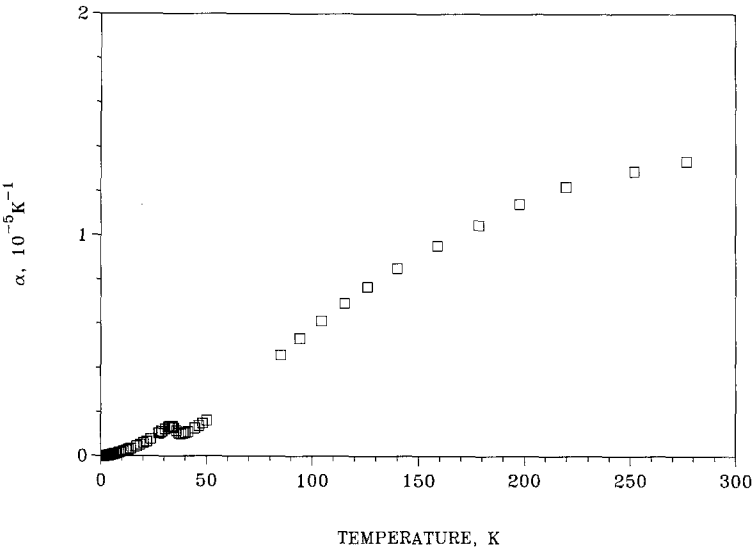

Fig. 1. Variation of the linear thermal expansion coefficient for $Fe_{2.2}Mn_{0.8}Si$ as a function of temperature.

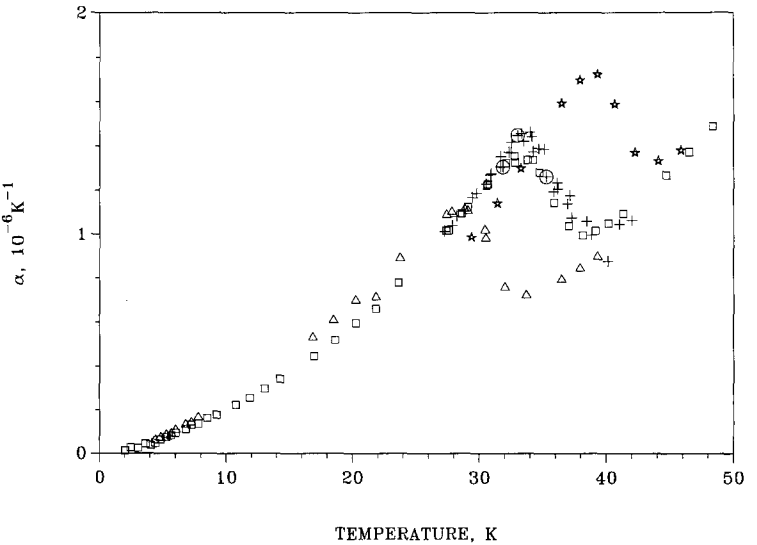

Fig. 2. Variation of the linear thermal expansion coefficient for $Fe_{2.2}Mn_{0.8}Si$ as a function of temperature about the magnetic reordering temperature. The symbols distinguish the sequence of the measurements as follows: □, April 1986; ☆, May 1988 (after 0.4 T); △, June 1988 (after heat treatment); +, July 1988 (remounted); ○, July 1988 (after 0.5 T).

measurements [6]. Approximately 2 years after these zero-field thermal expansion measurements were taken, the sample was remounted for measurements in a magnetic field. Prior to the application of the magnetic field, a zero-field value ~ 39 K for T_R was obtained from an AC coil measurement. Expansion data were then taken in the sequence of applied fields 0.344, 0.413, 0.103, 0.052, and 0.0 T over a period of 3 weeks (Fig. 3). During this period the temperature of the sample did not rise above 90 K. These measurements and simultaneous AC coil measurements confirmed the increased value of 39 K for T_R, compared with the value of 35 K determined 2 years before. The application of the magnetic field rapidly suppressed the peak in the expansion coefficient but did not change T_R.

The sample was warmed to room temperature and then recooled to 4.2 K and T_R $(= 39 \pm 1$ K) redetermined in zero field by AC coil measurements. The sample was then removed from the cell and heat treated at 300°C in flowing nitrogen gas for 1 h, followed by furnace cooling to room temperature over ~ 30 min. The sample was remounted in the cell and the zero-field expansion redetermined. The peak in α was now found at ~ 28 K (Fig. 2).

The sample was again removed from the cell and kept at room temperature for 6 weeks, after which time it was replaced in the cell and a further set of zero-field expansion data was taken. These measurements

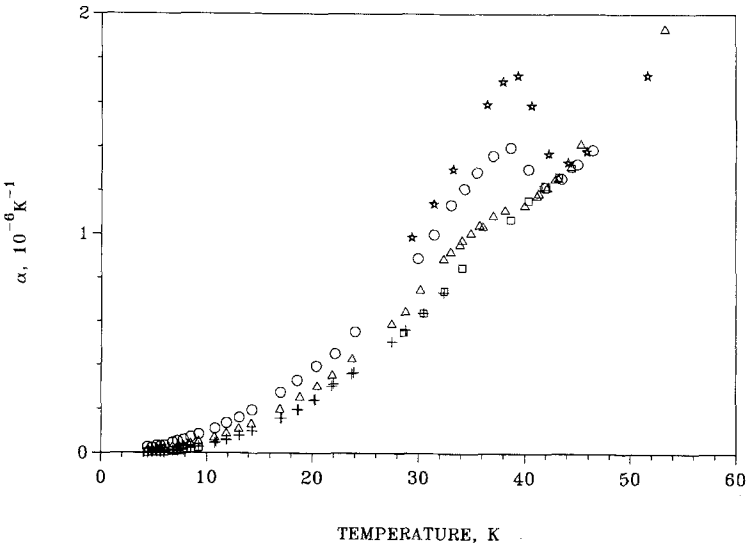

Fig. 3. Variation of the linear thermal expansion coefficient for $Fe_{2.2}Mn_{0.8}Si$ as a function of temperature. The symbols distinguish various applied magnetic fields (in T) as follows: ☆, 0; ○, 0.05; △, 0.1; +, 0.34; □, 0.42.

indicated that T_C had returned to ~ 34 K, a value that was unaffected by subjecting the sample to a field of 0.5 T (Fig. 2). The heat treatment at 300°C was repeated and a final set of zero-field expansion data taken for which T_R was ~ 35 K. (These measurements are not shown in Fig. 2.)

From these series of measurements and treatments it is clear that the zero-field T_R was sensitive to some feature of the sample condition. We believe that we have eliminated the application of magnetic fields as a possible cause. Another source of change in the state of the sample considered was the force applied to the sample by the mounting springs in the expansion cell. However, this force has been measured to be of the order of 0.3 N, which is many orders of magnitude smaller than the $\sim 2.5 \times 10^4$ N which would be required to displace T_R by 5 K. (This assumes the value of $dT_R/dP = 1$ K GPa^{-1} estimated from the discontinuities in α and C_p [6] at T_R, using Ehrenfest's equation [5].) There is some evidence that aging and heat treatment influence T_R, possibly via changes to the microstructure or to the chemical ordering. Further measurements involving a series of carefully controlled heat treatments are required to clarify the position. We have no immediate explanation for the variations in T_R other than to suggest that the reordering mechanism is inherently sensitive to the condition of the sample.

The peak in α with $T_R \sim 15$ K for $Fe_{2.4}Mn_{0.6}Si$ was also suppressed in a magnetic field of 0.1 T, whereas no significant change occurred in the peak in α associated with the reordering at $T_R = 60$ K for $Fe_{1.86}Mn_{1.14}Si$ in fields up to 0.5 T.

3.2. Magnetization Measurements

Magnetization measurements were made over the same temperature range as that for the thermal expansion on a $5 \times 3 \times 2$-mm^3 block spark cut from the side of the expansion sample. Initially the results obtained were confusing until it was established that the magnetization depended upon whether the sample was cooled through T_R in an applied magnetic field or not. This is illustrated in Fig. 4 in which the following sequence of measurements is shown. The sample was first cooled to 4 K in zero applied magnetic field. A field of 10 mT was then applied and measurements were taken with increasing temperature up to 45 K (ZFC). The sample was then cooled back to 4 K in the 10-mT field and the magnetization was again measured on warming to 45 K (FC). Finally, the sample was field-cooled to 4 K, the field was removed, and the thermal remanent magnetization (TRM) was monitored in zero applied field as the temperature was increased to 45 K.

Above T_R ($= 34 \pm 1$ K) the FC and ZFC magnetizations are

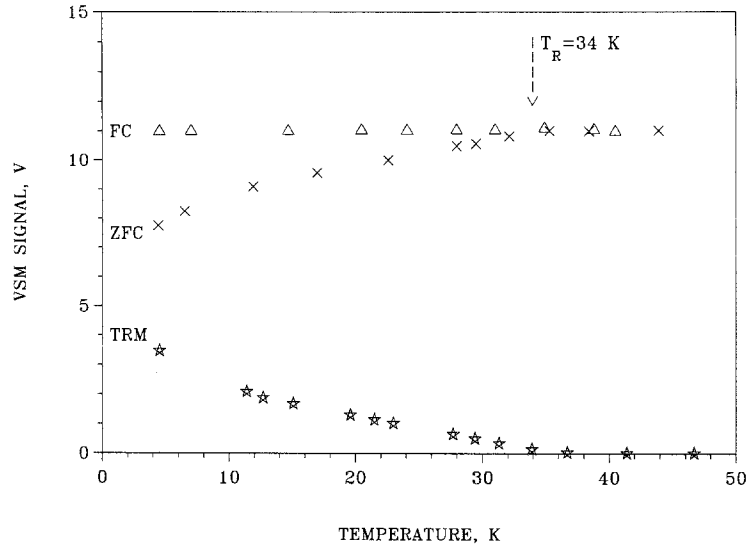

Fig. 4. Magnetization (vibrating sample magnetometer (VSM) signal) as a function of temperature for $Fe_{2.2}Mn_{0.8}Si$ showing the variations for the sequence of zero-field coding (ZFC), followed by warming in a field of 10 mT, field cooling (FC) in 10 mT, and thermal remanence after field-cooling in 10 mT (TRM).

indistinguishable. However, below T_R, the ZFC values decrease with decreasing temperature, whereas the FC values are relatively constant. The TRM curve corresponds closely to the difference between the ZFC and the FC measurements. A set of measurements carried out with a 1.5-mT field showed identical behavior.

The influence of higher magnetic fields was investigated at 5 K. Following cooling in zero applied field, a saturation field of approximately 0.2 T was observed, which agrees well with the value reported by Yoon and Booth [2] for $Fe_{2.25}Mn_{0.75}Si$. The ZFC magnetization in 0.2 T was found to be almost temperature independent between 4 and 45 K, although a small increase up to T_R was evident. This is again in accord with the observation by Yoon and Booth [2] of small decreases below T_R in the magnetization measured in fixed fields up to 1 T.

4. DISCUSSION

Although the peaks in the specific heat capacity and in the thermal expansion coefficient at T_R for $Fe_{2.2}Mn_{0.8}Si$ are much weaker and broader than those in Fe_2MnSi, they are nevertheless indicative of the onset of long-range ordering. The expansion measurements in a magnetic

field confirm the field suppression of the magnetic reordering [2] and establish that it is associated with the *bulk* magnetization.

The low-field magnetization measurements reveal a previously unknown irreversible behavior associated with the reordering transition, reminiscent of a mictomagnet or a spin-glass [10].

A model is required that explains a transition to a ferromagnetic state that

(i) has a high degree of disorder;

(ii) transforms in zero field to a more ordered configuration with a long-range antiferromagnetic component [2] which can be suppressed in an applied magnetic field; and

(iii) has a magnetization that is spin-glass-like below the reordering temperature.

We suggest that (i) and (ii) may be accommodated by an extension of the model proposed by Yoon and Booth [2, 11] to describe their neutron scattering data. Rather than having the magnetic spins colinear with the [111] magnetic axis in the ferromagnetic state ($T_R < T < T_C$), we propose that the spins are canted at an angle to [111] and randomly distributed in direction such that the average moment perpendicular to the ferromagnetic axis is zero. Thus, there would be a net ferromagnetic component along [111] but a high degree of spin disorder. At T_R the spins lock into specific directions to give a net antiferromagnetic component perpendicular to the ferromagnetic axis.

This model requires that the canting angle increase slightly as the spins lock in, leading to the observed reduction in zero-field saturation magnetization. The model also has the advantage that the changes observed in the C-site moment [2] as the temperature or manganese concentration is varied may now be attributed to changes in the canting angle rather than to direct changes in a collinear moment. The application of a strong enough magnetic field inhibits the locking-in of the magnetic spins and the disordered state is retained.

It is significant that low magnetic fields (10 mT) influence the magnetization behavior at T_R but *not* the thermal expansion anomaly. This indicates that the low fields are not affecting the microscopic reordering process, leading us to conclude that an explanation for the low-field magnetization behavior will involve magnetic clusters or domains. However, the divergence of the FC and ZFC branches below T_R indicates that the reordering process and the low-field irreversible behavior are linked.

The following model is proposed to explain the low-field magnetization

behavior. On cooling through T_R in zero applied field the onset of the antiferromagnetic order induces a rearrangement of the equilibrium domain configuration from that in the ferromagnetic state. The application of a low field at 4 K results in the growth of favorably oriented domains, producing an increase in magnetization in the normal manner. Increasing the temperature increases the intrinsic domain magnetization, owing to the destruction of the reordered state and the reestablishment of the ferromagnetic state domain configuration corresponding to the applied field. At T_R the reordered state is completely destroyed, the intrinsic magnetization stops increasing, and the domain growth ceases. The result is a low field magnetization that increases with temperature below T_R but remains constant above T_R. This is the ZFC branch in Fig. 4.

Field-cooling the sample to 4 K inhibits the rearrangement of the ferromagnetic state domain configuration, resulting in a relatively constant magnetization for increasing temperature because of the irreversible "locking-in" of the domain structure. Removing the field at 4 K allows the reversible components of the domain structure to rearrange in such a way that the magnetization is reduced in the normal manner. However, the domain structure, which had been locked in the FC branch, is now meta-stable with respect to the zero-field configuration for the reordered state. Domain wall pinning prevents rearrangement to a more perfect domain closure and hence lower sample magnetization. This results in the TRM at 4 K in zero field. Increasing the temperature again increases the intrinsic magnetization and allows the meta-stable domains to overcome the intervening potential barriers. The resulting improvement in domain closure leads to a reduction of the sample magnetization. The sample magnetization (TEM) will continue to decrease until the temperature reaches T_R, at which point the intrinsic magnetization ceases to increase and there are no more meta-stable domains, leading to zero TRM above T_R.

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