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Thermal Expansion of Fe_2MnSi

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Abstract

Measurements of the thermal expansion of Fe_2MnSi in the temperature range 200–300 K are reported. A large, relatively narrow peak is found at the magnetic re-ordering temperature in contrast to a broad, weak anomaly at the Curie temperature. Values for the magnetic Grüneisen parameter γ_m are derived from the thermal expansion data and previously reported specific heat data following the subtraction of a non-magnetic background.

1. Introduction

The Heusler alloy Fe_2MnSi is a member of the $Fe_{3-x}Mn_xSi$ system which forms as a continuous pseudo-binary solid solution between Fe_3Si and Mn_3Si (Gladysevskij *et al.* 1956). The crystal structure of this system ($L2_1$) may be described as a body-centred cubic lattice with a face-centred cubic superlattice or, equivalently, as four interpenetrating face-centred cubic sublattices, labelled A, B, C and D. In Fe_2MnSi the B and D sites are occupied by iron atoms, the C sites by manganese atoms and the A sites by silicon (Yoon and Booth 1974, 1977).

Fe_2MnSi has two magnetic phase transitions below 300 K. The high temperature transition, at T_c, corresponds to a change from a paramagnetic state to a ferromagnetically ordered state. The low temperature transition, at the reordering temperature T_R, has been interpreted as a rearrangement of the atomic moments on the C sites to a rhombohedral anti-ferromagnetic arrangement (Yoon and Booth 1974).

Smith *et al.* (1980) measured the specific heat of $Fe_{3-x}Mn_xSi$ compounds with $x = 0{\cdot}6$, $0{\cdot}8$, $1{\cdot}0$, $1{\cdot}2$ and $1{\cdot}6$ over the temperature range 4–460 K. Distinct cusp-shaped peaks were found at T_R, whereas no gross features were evident at T_c. By using the data for the $x = 0{\cdot}6$ and $1{\cdot}6$ compounds as a composite background, small 'step-like' anomalies were resolved in the specific heat close to T_c for $x = 1{\cdot}0$, $1{\cdot}2$ and $1{\cdot}6$ compounds.

To complement these specific heat measurements, the thermal expansion of Fe_2MnSi has been measured over the temperature range 2–300 K, with special attention being paid to the behaviour of the expansion coefficient α in the vicinity of T_c.

2. Experimental Details

Two Fe_2MnSi samples were measured, one of which was the same as that used in the earlier specific heat measurements. The second sample was prepared using the

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procedure described in Smith *et al.* (1980), except that the heat treatment was followed by slow cooling rather than quenching. Both samples were roughly cylindrical, with lengths of approximately 20 mm and diameters of 8 mm. The end-faces of each sample were lapped flat to within 0·25 μm and parallel to within 5 minutes of arc.

Electron microprobe analyses on a polished section of each sample were used to verify the compositions. X-ray diffraction measurements, performed on a Scintag PADV diffractometer, using both polished sections and powders produced by crushing alloy pieces, showed that the samples were all single phase and had the $L2_1$ structure. The lattice parameters, derived by extrapolating $\cos^2\theta$ plots, were both 5·663±0·001 Å, which is in excellent agreement with the lattice parameter obtained by interpolating the values reported by Yoon and Booth (1977).

The thermal expansion measurements were made in a three terminal, capacitance dilatometer, identical to that described by White and Collins (1972). The samples were built up to a length of 5·07 cm using spring-loaded copper spacers. Measurements were made with liquid helium as a coolant for temperatures up to 80 K, and with liquid nitrogen from 80 to 300 K.

The same measuring procedure as that described by White and Collins (1972) was followed. For temperatures greater than 50 K, times of the order of one hour were required for the cell to reach thermal equilibrium.

The temperature of the capacitance cell was monitored using two thermometers, a germanium cryo-resistor for temperatures between 1·5 and 25 K, and a four-wire platinum resistor for temperatures between 13 and 300 K. Both thermometers had calibrations directly traceable to the CSIRO Division of Applied Physics, giving a precision of better than ±10 mK for T and an accuracy better than 1% for ΔT. The capacitance of the cell was measured using a ratio-transformer capacitance bridge with a resolution better than $\pm 10^{-6}$ pF, giving a sensitivity of approximately ±0·1 Å in the measurement of the change in length of the sample, relative to the cell.

Across the full temperature range, the thermal expansion coefficient could be determined with a precision of $\pm 1\times 10^{-8}$ K^{-1}. The thermal expansion of a rod of 5 N copper, measured using this apparatus, agreed with published data (Kroeger and Swenson 1977) to better than 1% from 10 to 300 K.

The magnetic state of the sample was monitored during the thermal expansion measurements using an a.c. transformer method. A pair of coils was placed around the sample within the expansion cell. The primary coil was excited by an a.c. signal of constant amplitude and frequency (2 V, 350 Hz). The current induced in the secondary coil was measured using a phase-locked amplifier. This enabled detailed measurement of the thermal expansion in the vicinity of both transition temperatures to be made.

3. Results

The linear thermal expansion coefficients of both samples of Fe_2MnSi as functions of temperature are shown in Fig. 1. Slow cooling the sample rather than quenching had no discernible effect on the thermal expansion over the temperature range 80 to 300 K. The significant anomaly in the vicinity of T_R and the relatively small kink at T_c are similar to the specific heat anomalies near the transition temperatures (Smith *et al.* 1980; Kalishevich *et al.* 1977). There were no apparent discontinuities in the sample length at the transition temperatures.

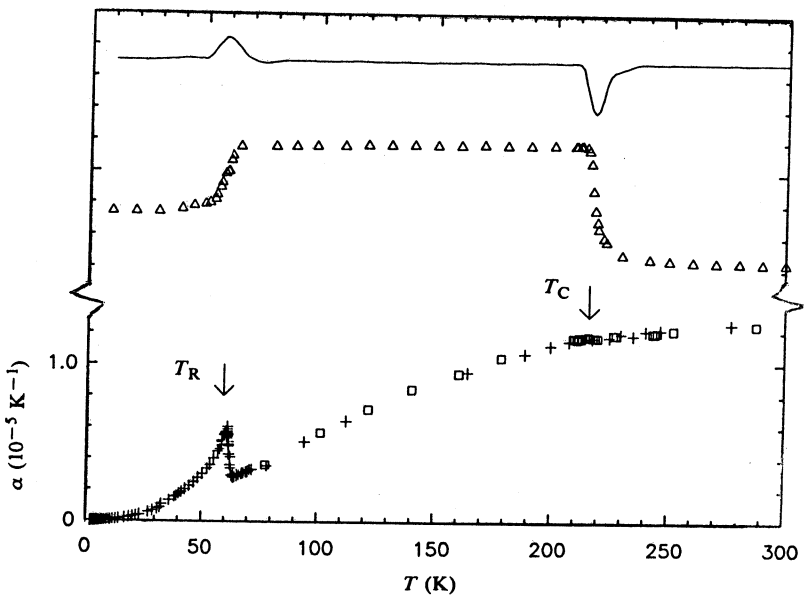

Fig. 1. Linear thermal expansion for Fe_2MnSi as a function of temperature: Pluses, quenched sample; squares, slow-cooled sample; triangles, secondary coil signal (arbitrary units); and solid curve, derivative of the interpolated coil signal.

Fig. 1 shows the secondary coil signal as a function of temperature (triangles). Low field a.c. susceptibility in the vicinity of a magnetic transition is a complex function of magnetic domain and demagnetisation effects. The assignment of values to transition temperatures on the basis of the secondary coil signal is relatively arbitrary (Simpson and Smith 1982; Maartense and Williams 1976; Ododo 1979). A similar situation exists in the measurement of other thermophysical and magnetic properties, as evidenced by the range of values for T_R (59–69 K) and T_c (214–24 K) reported in the literature (Yoon and Booth 1974, 1977; Ziebeck and Webster 1976; Lutskaya *et al.* 1976; Smith *et al.* 1980; Lutskaya 1985). We have chosen T_R and T_c to be the temperatures given by the inflection points in the change of coil signal with temperature at the magnetic transitions. The inflection points were determined by interpolating the coil signal measurements and taking the first derivative with respect to temperature. Fig. 1 shows the derivative as a function of temperature (solid curve). The transition temperatures correspond to the position of the peaks. This gives $T_R = 60$ K in excellent agreement with Lutskaya (1985) ($T_R = 59{\cdot}5$ K) and with the position of the maximum in the low temperature expansion coefficient anomaly. Similarly we obtain $T_c = 216$ K, in agreement with Ziebeck and Webster (1976) ($T_c = 214$ K).

The extraction of the magnetic contribution to the thermal expansion requires an estimate of the lattice and electronic contributions which are subtracted from the experimental values. The same approach is used to extract the magnetic contribution to the specific heat. Smith *et al.* (1980) used a background curve consisting of data for the specific heat of $Fe_{2{\cdot}4}Mn_{0{\cdot}6}Si$ below 134 K and $Fe_{1{\cdot}4}Mn_{1{\cdot}6}Si$ above 134 K. The assumptions were that the magnetic contribution to the specific heat (C_m) associated with T_c at 450 K for the $x = 0{\cdot}6$ compound is negligible below 134 K and that C_m associated with T_c at 134 K for the $x = 1{\cdot}6$ compound is negligible above 134 K.

This approach has the drawback that, whereas molecular field theory predicts a sharp cutoff in the magnetic specific heat at T_c, measurements on many ferromagnetic materials, including iron, nickel and gadolinium (Hofmann *et al.* 1956), show that C_m generally persists well above T_c, reflecting the presence of short range order. This effect could significantly affect the background used by Smith *et al.*, making it too large above 134 K.

Alternatively, the specific heat of Fe_3Si may be used as a background. This assumes that the magnetic contribution to the specific heat of ferromagnetic Fe_3Si ($T_c \sim 850$ K) is negligible in the range 0–300 K and that the lattice and electronic contributions are the same for Fe_3Si and Fe_2MnSi. Support for the latter assumption is based, firstly, on the fact that Fe_2MnSi is isostructural with Fe_3Si and that iron and manganese have almost identical atomic weights, indicating a similarity of the lattice contribution for each compound. Secondly, the closeness of the total specific heats of Fe_3Si and antiferromagnetic Mn_3Si ($T_N \sim 22$ K) over the range 100–300 K indicates a closeness of both the lattice and electronic contributions to the specific heat of each compound (Kalishevich *et al.* 1977). It must be emphasised, however, that a similarity in the lattice and electronic contributions for the end members of the pseudo-binary alloy system $Fe_{3-x}Mn_xSi$ does not guarantee that these contributions remain the same throughout the compositional range.

Measurements of the elastic constants of $Fe_{3-x}Mn_xSi$ compounds (Lutskaya 1985) showed that the bulk modulus of Fe_2MnSi ($B_T \sim 315$ GPa) is considerably higher than the bulk modulus of Fe_3Si ($B_T \sim 180$ GPa) (Rausch and Kayser 1977). This implies a lower lattice contribution to the specific heat for Fe_2MnSi compared with that for Fe_3Si. However, in the absence of a more reliable method for separating the various contributions to the specific heat in a magnetic system, the use of Fe_3Si as a non-magnetic background over the temperature range investigated is taken to be a reasonable choice even though it probably underestimates the magnetic contribution.

Data for the specific heat of Fe_3Si were taken from several sources (Gel'd and Krentsis 1963; Touloukian and Buyco 1970; Kalishevich *et al.* 1977). The specific heat measurements of Fe_2MnSi by Smith *et al.* (1980) were combined with the measurements of Kalishevich *et al.* (1977) and with low temperature (1·8–40 K) specific heat measurements of the slow-cooled Fe_2MnSi sample (to be published), conducted at the CSIRO Division of Applied Physics. The Smith *et al.* results required a 7–8% shift in the temperature scale to bring them into agreement with the other measurements. The probable origin of this discrepancy is thermometry errors in their continuous calorimeter measurements.

Measured values for C_p were converted to C_v by the relationship

$$C_p - C_v = V T \beta^2 B_T, \tag{1}$$

where V is the molar volume, $\beta = 3\alpha$ and B_T is the isothermal bulk modulus.

The Fe_2MnSi specific heat data are shown in Fig. 2, along with the Fe_3Si background. The magnetic contribution to the specific heat of Fe_2MnSi, obtained by subtracting the Fe_3Si background, is shown in Fig. 3. It is apparent that there is a relatively flat region between T_R and T_c, possibly the result of combining a high temperature tail in the magnetic specific heat associated with the transition at T_R with the rising magnetic specific heat associated with the transition at T_c.

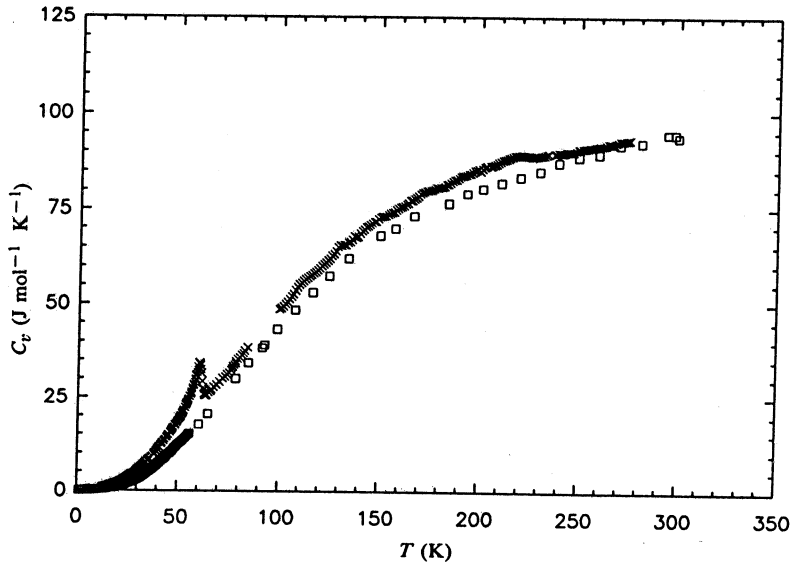

Fig. 2. Specific heat data: Crosses, Fe_2MnSi; squares, Fe_3Si.

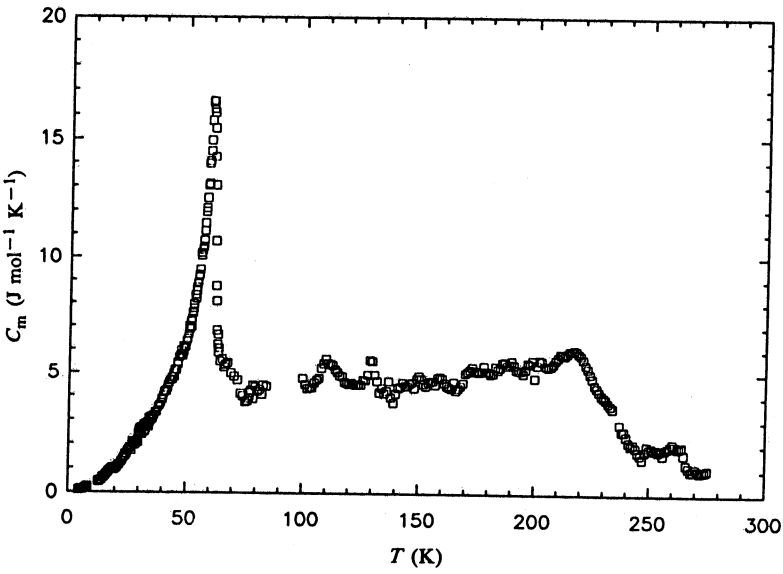

Fig. 3. Magnetic contribution to the specific heat for Fe_2MnSi.

The total magnetic entropy was derived from numerical integration of C_m/T as a function of temperature. The value of $S_m = 11\,\mathrm{J\,mol^{-1}\,K^{-1}}$ has a 10–20% uncertainty due to the uncertainty involved in estimating the non-magnetic background. It is apparent, however, that the total magnetic entropy is considerably smaller than the $3R\ln 2 = 17{\cdot}3\,\mathrm{J\,mol^{-1}\,K^{-1}}$ associated with the ordering of $3N$ magnetic spins, each with $s = \frac{1}{2}$.

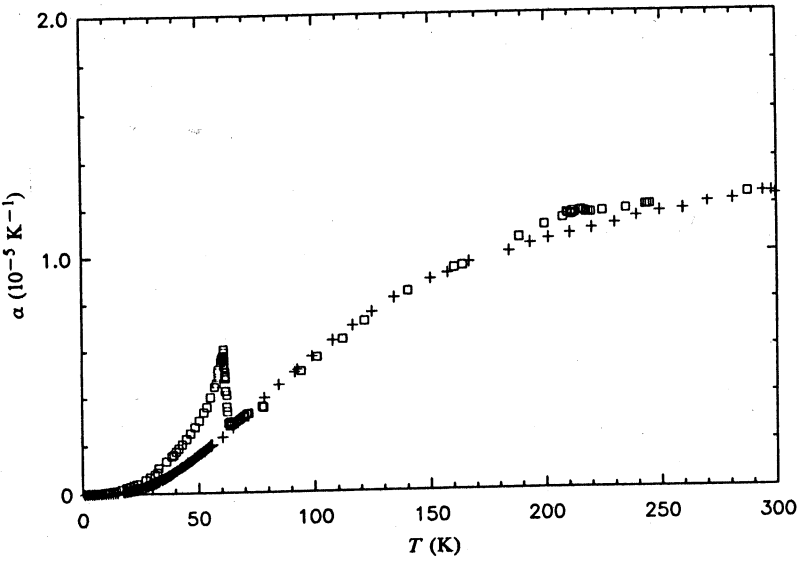

Fig. 4. Squares: linear thermal expansion coefficient data; crosses: non-magnetic background for Fe_2MnSi as a function of temperature.

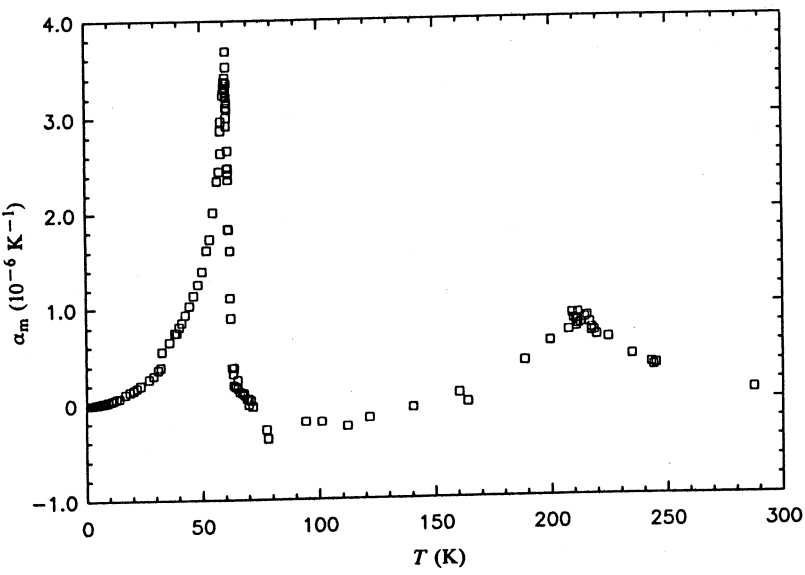

Fig. 5. Magnetic contribution to the linear thermal expansion coefficient of Fe_2MnSi as a function of temperature.

In the case of the thermal expansion it is to be expected that the greater stiffness of the Fe_2MnSi lattice will result in a lower lattice contribution compared with Fe_3Si, and thus an overestimate of the non-magnetic contribution if the approach adopted for the heat capacity is extended to the thermal expansion. In fact, the thermal

expansion of Mn_3Si (Barmin *et al.* 1984) is greater than the expansion of Fe_2MnSi over the temperature range 100–300 K (i.e. above the Néel temperature for Mn_3Si).

An approximate estimate of the non-magnetic background may be obtained by assuming that the total non-magnetic electronic and lattice Grüneisen parameter for Fe_2MnSi, given by

$$\gamma_{e,l} = \frac{3VB_T\alpha_{e,l}}{C_{e,l}}, \tag{2}$$

is not strongly temperature dependent. This assumption was supported by determining the temperature dependence of the total Grüneisen parameter for Mn_3Si over the range 100–300 K. Using specific heat and thermal expansion measurements of Mn_3Si (Letun *et al.* 1965; Barmin *et al.* 1984) and the bulk modulus of Fe_3Si, a total Grüneisen parameter of 2·2, varying by less than 1% from 100–300 K, was obtained.

A value for $\gamma_{e,l}$ for Fe_2MnSi may be obtained by assuming that for temperatures above 250 K the magnetic contribution to the specific heat and thermal expansion is negligible. This procedure gives $\gamma_{e,l} = 3{\cdot}4\pm1$ and since B_T varies by less than 3% from 0–300 K (Lutskaya 1985), equation (2) may be used to calculate the non-magnetic thermal expansion background from the specific heat data for Fe_3Si. The results are shown in Fig. 4 and the magnetic contribution to the thermal expansion of Fe_2MnSi, obtained by subtracting the non-magnetic background, is shown in Fig. 5.

The (α_m, T) curve is similar to the (C_m, T) curve, with two peaks centred at $T_R = 60\pm1$ K and $T_c = 214\pm2$ K, in excellent agreement with Lutskaya (1985) and Ziebeck and Webster (1976). The negative values for α_m between T_R and T_c demonstrate the shortcoming in the choice of background. However, it is not possible to obtain a better estimate for the non-magnetic thermal expansion background on the basis of current information.

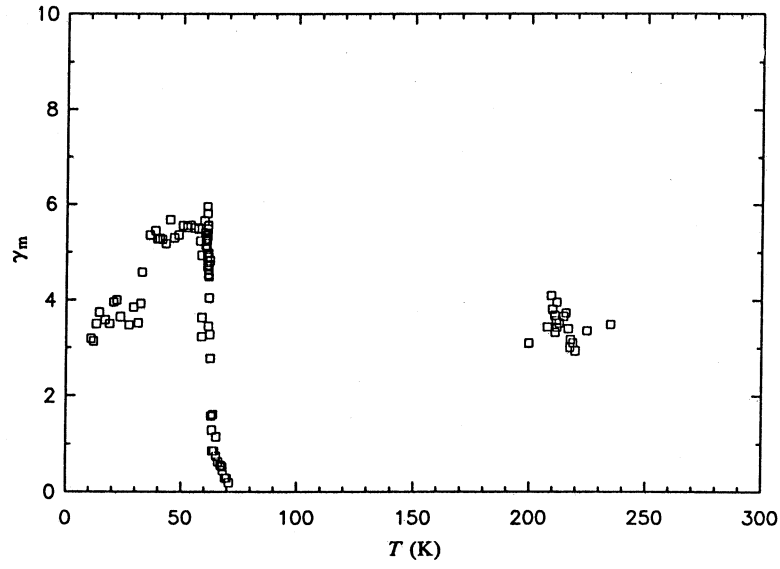

Fig. 6. Magnetic Grüneisen parameter for Fe_2MnSi as a function of temperature.

The magnetic Grüneisen parameter γ_m, calculated from the magnetic specific heat and thermal expansion data in Figs 3 and 5, is shown in Fig. 6; γ_m is not shown in the temperature ranges where the uncertainties due to the uncertainty in background are considered to dominate.

4. Discussion

A significant feature of both the thermal expansion and the specific heat measurements is the relatively small and broad anomaly at T_c compared with the large, narrow, cusp-shaped anomaly at T_R. The persistence of C_m and α_m above the Curie temperature is usually ascribed to the presence of short-range order above T_c. This leads to the conclusion that the transition at T_R has a stronger long-range character than the transition at T_c.

The narrowness of the peak at T_R for the thermal expansion measurements and the sharpness of the change in the a.c. coil signal at T_c indicate that the broadening of the peak at T_c is not due to chemical clustering or to the influence of local strains on the exchange parameters.

The observation that the total magnetic entropy is much smaller than the $3R\ln 2$ associated with the ordering of $3N$ magnetic spins each with $S = \frac{1}{2}$ is contrary to a model based on strictly local moments. Recent neutron diffuse scattering and saturation magnetisation measurements on $Fe_{3-x}Mn_xSi$ alloys for $x < 0{\cdot}6$ (Kepa *et al.* 1988) showed that the magnetic moment on the Mn atom, substituted on the C sites, is strongly temperature dependent. The magnetic moment at low temperature was reported to be $2{\cdot}2\mu_B$ (Yoon and Booth 1974), whereas Kepa *et al.* proposed a value of $0{\cdot}6\mu_B$ at room temperature. A reduction of the Mn magnetic moment with increase of temperature could be a significant factor in explaining the differences at T_R and T_c in the shape of the thermal expansion and specific heat anomalies and would account for the low magnetic entropy.

The high values of γ_m at T_R and T_c indicate a strong volume dependence of the magnetic entropy, with the volume dependence at the reordering temperature being slightly greater than that at the Curie temperature. The absence of discontinuities in the sample length temperature dependence indicates that both magnetic transitions are second order. The pressure dependence of the transition temperatures may therefore be obtained using Ehrenfest's equation (Krishnan *et al.* 1979):

$$\frac{dT_m}{dP} = \frac{T_m \Delta\beta V}{\Delta C_p} = \frac{\Delta\chi_T}{\Delta\beta}, \tag{3,4}$$

where $\Delta\beta = 3\Delta\alpha$ and $\Delta\chi_T$ is the change in the isothermal compressibility at the transition temperature.

Using equation (3) we obtain $dT_R/dP = 1{\cdot}1\pm0{\cdot}2\ \mathrm{K\,GPa^{-1}}$ at the reordering temperature, while $dT_c/dP = 4{\cdot}0\pm2\ \mathrm{K\,GPa^{-1}}$ at the Curie temperature. Here $\Delta\chi_T$ was derived from the changes in Poisson's ratio and Young's modulus reported by Lutskaya (1985). This was only possible at T_R as the elastic constant measurements at T_c did not have sufficient resolution to obtain a reliable value for $\Delta\chi_T$. The value for $\Delta\chi_T$ at T_R was $(1{\cdot}5\pm2)\times10^{-5}\ \mathrm{GPa^{-1}}$, giving $dT_R/dP = 1{\cdot}3\pm1\ \mathrm{K\,GPa^{-1}}$ using equation (4), in agreement with the value obtained using (3).

The quantity dT_m/dP and the thermodynamic magnetic Grüneisen parameter are related subject to the condition that the magnetic entropy can be represented by

$S_m = S(E_m/T)$, where the magnetic interaction energy E_m alone determines the magnetic transition temperature (Barron *et al.* 1980). It follows that

$$\gamma_m = \left(-\frac{\partial \ln T_m}{\partial \ln V}\right)_T, \tag{5}$$

and hence that

$$\frac{dT_m}{dP} = \frac{\gamma_m T_m}{B_T}. \tag{6}$$

Using the values for γ_m derived above, we obtain $dT_R/dP = 1{\cdot}1_4 \pm 0{\cdot}2$ K GPa^{-1} and $dT_c/dP = 3{\cdot}4_0 \pm 0{\cdot}4$ K GPa^{-1}, in good agreement with the values calculated using Ehrenfest's equation. It follows that E_m alone determines the transition temperatures T_R and T_c.

Agreement between direct measurements of dT_m/dP and values calculated from magnetic Grüneisen parameters has been demonstrated for several alloy systems, specifically spin glass alloys (Simpson *et al.* 1981; Smith 1981) and iron–nickel alloys (Barron *et al.* 1980). One exception is the behaviour of nickel–chromium alloys close to the critical composition for ferromagnetism (Simpson and Smith 1982). Direct measurements of dT_m/dP for Fe_2MnSi are currently being conducted to verify the values obtained from the thermal measurements.

5. Conclusions

Measurements of the thermal expansion of Fe_2MnSi confirm the general features of the specific heat measurements, namely a large cusp-shaped peak at T_R in contrast to a weaker and broader anomaly at T_c. The anomaly at T_c has a more conventional shape in the thermal expansion, rising to a maximum and then slowly falling above T_c. The persistence above T_c is indicative of short-range order.

Values for the magnetic Grüneisen parameters indicate a strong volume dependence of the magnetic entropy at T_R and T_c. Agreement between dT_m/dP values calculated from Ehrenfest's equation and those obtained from the magnetic Grüneisen parameters indicates that the magnetic entropy has the form $S_m = S(E_m/T)$, i.e. E_m is the major factor determining T_R and T_c.

We are extending our thermal expansion measurements to more alloys in the $Fe_{3-x}Mn_xSi$ series. This should enable us to determine the composition dependence of the magnetic Grüneisen parameters.

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