

Negative magnetocaloric effect from highly sensitive metamagnetism in $\text{CoMnSi}_{1-x}\text{Ge}_x$ K. G. Sandeman,¹ R. Daou,² S. Özcan,² J. H. Durrell,¹ N. D. Mathur,¹ and D. J. Fray¹¹*Department of Materials Science and Metallurgy, University of Cambridge, New Museums Site, Pembroke Street, Cambridge, CB2 3QZ, United Kingdom*²*Cavendish Laboratory, University of Cambridge, JJ Thompson Avenue, Cambridge, CB3 0HE, United Kingdom*

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We report a negative magnetocaloric effect in $\text{CoMnSi}_{1-x}\text{Ge}_x$ arising from a metamagnetic magnetoelastic transition. The effect is of relevance to magnetic refrigeration over a wide range of temperature, including room temperature. In addition we report a very high shift in the metamagnetic transition temperature with applied magnetic field. This is driven by competition between antiferromagnetic and ferromagnetic order which can be readily tuned by applied pressure and compositional changes.

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I. INTRODUCTION

While the magnetocaloric effect (MCE) has been known since 1881,¹ it has only recently been thought of as providing a potential alternative to conventional gas compression refrigeration in the room temperature range. The conventional, positive, MCE—where a material heats when a magnetic field is applied adiabatically—has historically been used to achieve milliKelvin temperatures for scientific research by demagnetization of paramagnetic salts. However, the effect is largest around sharp magnetic transitions, and recent work has demonstrated giant MCEs near first-order magnetic transitions that, by varying material composition and/or applied magnetic field, occur over a wide range of temperatures extending above room temperature.^{2,3}

There has already been significant progress in the design of prototype magnetic refrigerators,⁴ fuelled by the prediction that such devices could impact on carbon emissions as they are potentially 40% more efficient than a conventional refrigerator.⁵ However, initial excitement arising from such developments has been tempered by two factors: the size of the magnetic fields required and the cost of the magnetocaloric refrigerants. Ideally, permanent magnets (of strength below 2 T) should be used. In contrast, many prototype refrigerators have used high fields generated by superconducting coils. On the second point, high purity gadolinium, on which several proposed magnetocaloric alloys are based, has a cost of the order of \$500/kg. Less expensive alternative refrigerants suffer from other problems: martensitic Heusler alloys such as $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ and $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Sn}$ have a large magnetic hysteresis,^{6,7} $\text{MnFeP}_{1-x}\text{As}_x$ (Ref. 3) and MnAs-based materials⁸ contain toxic As. $\text{Fe}_{0.49}\text{Rh}_{0.51}$ is both expensive and loses its negative MCE upon multiple cycling of the applied field.⁹

Almost all room temperature magnetocalorics exhibit a positive MCE associated with a Curie transition. Only the metamagnets FeRh and $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Sn}$ have exhibited a significant negative magnetocaloric effect, where the material cools when a field is applied. The lack of study of metamagnetic transitions by the magnetocaloric community is perhaps surprising given that they are more likely to be first order than their ferromagnetic cousins. In this article we study the pseudoternary metamagnet $\text{CoMnSi}_{1-x}\text{Ge}_x$, a room temperature negative magnetocaloric material system which addresses the issues of cost, hysteresis, and toxicity outlined

above. In particular we draw attention to the rapid variation of its metamagnetic transition temperature, T_t with magnetic field (large $|\partial T_t / \partial H|$). This highly desirable property usually brings about a large adiabatic temperature change in a magnetocaloric material when it is exposed to a rapid change in applied magnetic field over a wide range of working temperatures. We will show in particular that CoMnSi exhibits an MCE over a wide range of temperatures, but this MCE is limited by such a high $|\partial T_t / \partial H|$. We will point to ways in which CoMnSi might be optimized from this point of view.

II. PREVIOUS WORK ON $\text{CoMnSi}_{1-x}\text{Ge}_x$

The various magnetic phases of the $\text{CoMnSi}_{1-x}\text{Ge}_x$ material system were examined by Nizioł and co-workers in the 1970s and 1980s.^{10,11} This paper will focus on the range $x < 0.1$. CoMnSi is orthorhombic, with space group $Pnma$ and exhibits competition between helical noncollinear antiferromagnetic order and ferromagnetic order. It is antiferromagnetic at low temperatures and shows a sample-dependent first-order metamagnetic transition to a ferromagnetic state at a transition temperature T_t of between 207 K and 360 K.¹² The ferromagnetic state has a second-order T_c which in much of the literature is at about 390 K.¹¹ A schematic phase diagram of the orthorhombic phase of $\text{CoMnSi}_{1-x}\text{Ge}_x$ for $x < 0.3$ is summarized in Fig. 1.

We concentrate here on the first-order metamagnetic transition at T_t in $\text{CoMnSi}_{1-x}\text{Ge}_x$. We note that other authors have found a wide variation in the zero-field value of T_t . Medvedeva quotes a value of 260 K in a 1 T field¹³ from samples made by melting elemental Co, Mn, and a 1% excess of Si together in a high frequency furnace under an argon atmosphere. Early work by Bińczycka *et al.* found values as low as 207 K in samples grown by melting elemental Co, Mn, and Si, followed by annealing at 1273 K and rapid quenching.¹⁴ The latter results were later attributed to a lack of sample homogeneity, and a higher T_t was obtained by a change in growth method.¹² Specifically, the change involved melting binary CoSi and elemental Mn, followed by annealing at temperatures between 1000 K and 1200 K. We note here that the choice of annealing routine (hold temperature and rate of cooling) was also observed to have an effect on the magnetic properties of CoMnSi as early as 1973 in the work of Johnson and Frederick,¹⁵ and was

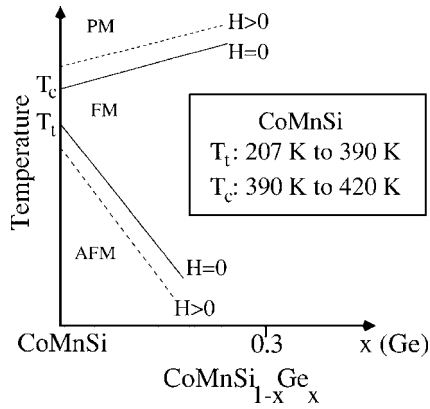


FIG. 1. Schematic magnetic phase diagram of $\text{CoMnSi}_{1-x}\text{Ge}_x$, after Nizioł *et al.* (Ref. 11). Both the temperature of the transition between paramagnetic (PM) and ferromagnetic (FM) states, T_c and that between the FM and antiferromagnetic (AFM) states, T_t , shift with Ge content and applied magnetic field, H as shown. Exact temperatures are not shown due to the variability in literature data (see inset). Hydrostatic pressure also reduces T_t (see text).

cited as the main cause for the sample-dependent magnetic behavior in the work of Medvedeva.¹³

Thus, the precise magnetism of CoMnSi has been found to be extremely sample dependent. We suggest that this may be because the magnetism of this material is highly sensitive to the separation of manganese atoms, on which most of the magnetic moment is to be found.¹² Both small amounts of Ge substitution on the Si site and the application of hydrostatic pressure have been shown to cause a rapid decrease in T_t . The rate of change of T_t with pressure is very high: dT_t/dp is between -60 K/GPa¹³ and -100 K/GPa.¹⁶ Previous crystallographic work shows that there is a volume contraction associated with the transition from the low-temperature antiferromagnetic state to the high-temperature ferromagnetic state.¹² This would explain why the application of hydrostatic pressure stabilizes the ferromagnetic phase, reducing T_t .^{13,16} Although Ge substitution expands the lattice relative to stoichiometric CoMnSi , perhaps the reduction of T_t in that instance is driven by a change in the thermal expansion properties of the material. (For example, if the critical atomic separation for a change in the exchange interaction is reached at a lower temperature—see later.) There is also the possibility of the observed variability in sample behavior being controlled by atomic disorder, as yet unquantified.

In small fields, the metamagnetic transition at T_t is probably to a fan spin state of small net moment. Previous literature indicates that fields of around 2 T are required to observe a transition at T_t in CoMnSi at 280 K (Ref. 10) to a state approaching a large magnetization of 100 Am²/kg. Here, we seek to obtain a unified picture of the effects of substitution, pressure and magnetic field on the tunability of the metamagnetic transition in a set of samples of $\text{CoMnSi}_{1-x}\text{Ge}_x$. The variability and possible tunability of T_t in CoMnSi makes this material an interesting candidate magnetic refrigerant if we can readily alter the region of temperature where the isothermal entropy change, ΔS is maximal and where the largest magnetocaloric effect is found.

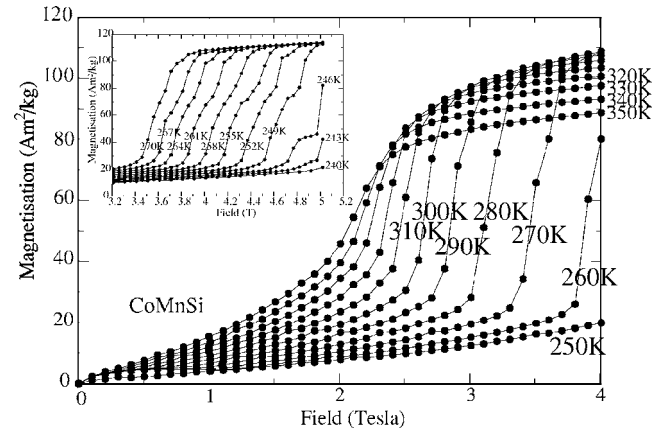


FIG. 2. Magnetization vs field for CoMnSi (slowly cooled after annealing), at 10 K intervals in temperature, between 250 K and 350 K. The inset shows the same measurement between 240 K and 270 K in 3 K intervals. In this temperature range, the metamagnetic field is in the range 3.4 T to 5 T and the metamagnetic transition appears to split in two.

III. SAMPLE PREPARATION AND EXPERIMENT

Samples of $\text{CoMnSi}_{1-x}\text{Ge}_x$ with $x=0, 0.05$ and 0.08 were prepared by induction melting pieces of elemental Mn (99.99%, chemically etched according to the method used by Fenstad¹⁷), Co (99.95%, electropolished to the correct mass), Si and Ge (both 99.9999%) in 1 bar of argon. Weight losses were 0.3% to 0.5%. All samples were annealed in evacuated silica ampoules at 1223 K for 60 h, and all but one were slowly cooled to room temperature at a rate of 0.2 K per minute. One duplicate sample of CoMnSi was quenched to room temperature for comparison of its magnetic properties. X-ray diffraction of powdered samples at room temperature showed only an orthorhombic ($Pnma$) phase. Scanning electron microscopy images of the materials showed a lack of significant contrast, which, if present, would be indicative of compositional variations. These two observations suggest the absence of a second phase. Rietveld refinement of lattice parameters and atomic coordinates was also performed. Measurements of magnetization were performed in a vibrating sample magnetometer (maximum field 1.8 T) and a Quantum Design superconducting quantum interference device (SQUID) magnetometer (maximum field 5 T). We also measured the adiabatic change of temperature of one sample in a field change of zero to 5 T over a temperature range of 230 K to 290 K. This was achieved using a K -type thermocouple attached to a sample much larger than the dimensions of the thermocouple, all encased in teflon. Fields were generated in an 8 T Oxford Instruments cryostat.

IV. EXPERIMENTAL RESULTS

A. Crystallographic structure

The results of Rietveld refinement of room temperature x-ray diffraction data on the samples synthesised are shown in Table I. We observe a gradual increase in the volume of the lattice as the Ge content is increased. We also find that

TABLE I. Structural parameters for samples of $\text{CoMnSi}_{1-x}\text{Ge}_x$ with values of $x=0$ (slow cooled and quenched), 0.05, and 0.08, obtained as a result of Rietveld refinement of data from x-ray diffraction of powdered samples at room temperature. The space group used is $Pnma$, Wyckoff position $4c(x, 1/4, z)$.

	CoMnSi (this work)	CoMnSi _{0.95} Ge _{0.05}	CoMnSi _{0.92} Ge _{0.08}	CoMnSi (quenched)
$a(\text{\AA})$	5.8683	5.8683	5.8716	5.8472
$b(\text{\AA})$	3.6855	3.6947	3.6980	3.6889
$c(\text{\AA})$	6.8520	6.8698	6.8709	6.8556
$V(\text{\AA}^3)$	148.2	148.9	149.2	147.8
x_{Mn}	0.0157(8)	0.0192(5)	0.0249(6)	0.0192(6)
z_{Mn}	0.1781(5)	0.1797(4)	0.1791(4)	0.1823(3)
x_{Co}	0.1549(6)	0.1578(5)	0.1554(5)	0.1566(4)
z_{Co}	0.5571(6)	0.5640(4)	0.5521(5)	0.5626(4)
$x_{\text{Si/Ge}}$	0.762(1)	0.7649(9)	0.7707(9)	0.7729(9)
$z_{\text{Si/Ge}}$	0.626(1)	0.6228(7)	0.6266(7)	0.6225(7)

quenching the material from 1223 K produces a crystal structure with smaller volume (147.8 \AA^3), as found by Bińczycka *et al.*,¹⁴ although the volume of our quenched material is not as low as in their case (147.2 \AA^3). The main source of the volume change in this latter case is a change in the a lattice parameter.

B. Magnetic properties

From low-field magnetization measurements, we found a peak in magnetization at $T_t \sim 390 \text{ K}$ and a Curie temperature, $T_c \sim 420 \text{ K}$ for the sample of CoMnSi which was slowly cooled after annealing. These are the highest values of T_t and T_c yet recorded for this material. We note, however, that differential scanning calorimetry yields an anomaly at a temperature of 379 K, lower than T_t and closer to the temperature of the specific heat anomaly (381 K) observed by Johnson and Frederick.¹⁵ Ge doping has the effect of steadily shifting the low-field peak in $M(T)$ to lower temperatures; to 380 K for CoMnSi_{0.95}Ge_{0.05} and to 375 K in the case of CoMnSi_{0.92}Ge_{0.08}.

On applying a magnetic field to CoMnSi-based materials we expect to stabilize the ferromagnetic state, resulting in an upward shift of T_c and a downward shift of T_t , as shown in Fig. 1. We now examine the effect of magnetic field on the metamagnetic transition associated with T_t . In Fig. 2 we show the isothermal magnetization vs applied field for CoMnSi at temperatures between 250 K and 350 K. Data at each temperature were taken in increasing fields directly after zero-field cooling from 350 K. The first-order metamagnetic transition is very sensitive to applied field: it shifts by 100 K in the range 2 T to 4 T. Just as T_t is higher than previously measured, so the metamagnetic transition fields at a given temperature are larger than previously found. Corresponding magnetization curves were obtained for CoMnSi_{1-x}Ge_x with $x=0.05$ or 0.08 (see Figs. 3 and 4). These lead to the magnetic phase diagram shown in Fig. 5. In all cases, the metamagnetic field was taken as the point(s) of inflexion in the $M(H)$ curve. In all three compounds the transition seems to split in two in the highest applied fields. This is illustrated for CoMnSi in the inset to Fig. 2, and the splitting becomes more pronounced as the level of Ge substitu-

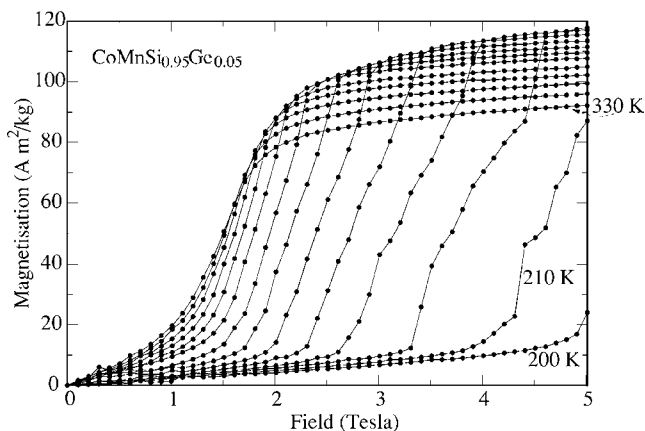


FIG. 3. Magnetization vs field for CoMnSi_{0.95}Ge_{0.05}, at 10 K intervals in temperature, between 200 K and 330 K. At the highest fields, the metamagnetic transition appears to split in two.

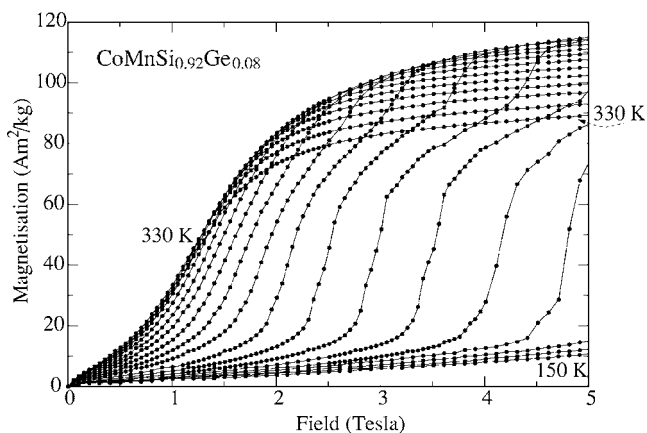


FIG. 4. Magnetization vs field for CoMnSi_{0.92}Ge_{0.08}, at 10 K intervals in temperature, between 150 K and 330 K. At the highest fields, the metamagnetic transition appears to split in two, even more markedly than in the case of CoMnSi or CoMnSi_{0.95}Ge_{0.05}.

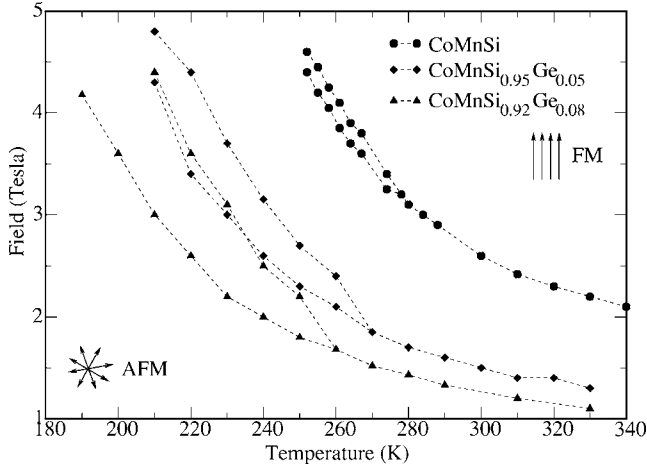


FIG. 5. Variation of the metamagnetic transition temperature T_t with applied field, for $\text{CoMnSi}_{1-x}\text{Ge}_x$ ($x=0, 0.05$, and 0.08). In each case, the metamagnetic transition splits into two transitions at the highest fields.

tion is increased. At this stage we cannot establish whether the splitting of the metamagnetic transition is due to a lack of homogeneity or is a consequence of a high field transition to an intermediate, canted ferromagnetic state, similar to that predicted for helical antiferromagnets by Nagamiya.¹⁸ We note that previous authors associated a canted state with a much smaller magnetic crossover feature at lower fields.¹⁰

The magnetocaloric effect has not previously been measured in CoMnSi -based materials, either directly or indirectly. For our indirect measurements of the effect, we use a Maxwell relation to obtain the isothermal change in total entropy from the isothermal $M(H)$ curves:

$$\Delta S_{\text{total}}(T, \Delta H) = \int_0^{H_{\text{final}}} \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

This still holds true in the first-order scenario if we choose to ignore magnetic and thermal hysteresis for the moment. It is a fair approximation as the measured thermal hysteresis in CoMnSi is only 3 K at 3 T, corresponding to a small shift in the metamagnetic transition field of around 0.1 T. From Eq. (1), and the $M(H, T)$ data, entropy change curves for each of the three compounds were obtained and are shown in Fig. 6. In a field change of 5 T, all three compounds display a large, broad, positive isothermal entropy change associated with T_t and the onset of a negative change associated with T_c . For a large entropy change associated with the metamagnetic transition to be observed, T_t must be far removed from the Curie temperature. This necessitates fields in excess of ~ 2 T. Ge substitution reduces the fields and temperatures required for the metamagnetic transition relative to those in CoMnSi , as expected. However, the transition is made less first order by substitution, so there is not a great increase in the size of ΔS for a given applied field. We also measured the magnetocaloric effect directly, in a field change of 0 to 5 T, in the case of the slowly cooled CoMnSi sample. As can be seen from the data in Fig. 6, the resulting $\Delta T(T)$ curve peaks at nearly 2 K at ~ 250 K, following the trend in the relevant 0 to 5 T

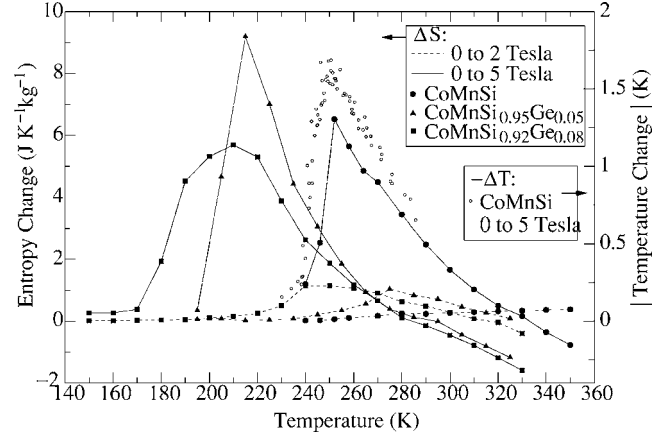


FIG. 6. The isothermal entropy change of $\text{CoMnSi}_{1-x}\text{Ge}_x$ ($x=0, 0.05$, and 0.08), on changing the applied field from zero to either 2 T or 5 T. Also shown is the magnitude of the negative adiabatic temperature change, ΔT , of CoMnSi when the applied field is raised from zero to 5 T, together with an estimate of ΔT using our ΔS data and Eq. (3).

isothermal entropy change curve as one would expect.

V. DISCUSSION

A. Thermodynamics of magnetocaloric effect

We henceforth focus on CoMnSi , for which there exists the greatest amount of literature data with which to draw comparisons. The isothermal entropy change at the metamagnetic transition in CoMnSi is smaller than that in other metamagnets previously investigated (FeRh , Mn_3GaC) and this is consistent with another observation. The rate at which the metamagnetic transition temperature changes with applied field is very large—as high as -50 K/T in low fields (right-hand side of Fig. 3), compared to -8 K/T for FeRh ¹⁹ and -5 K/T for Mn_3GaC .²⁰ Such a large magnitude of $\partial T_t / \partial H$ (or, equivalently, small $\partial H_c / \partial T$) may enable a wide range of working temperatures to be covered by a single material in a practical device, but it also reduces the isothermal ΔS , as given by the Clausius Clapeyron equation for first-order magnetic phase transitions:

$$\Delta S_{\text{total}}(T, \Delta H) = -\Delta M \left(\frac{\partial H_c}{\partial T} \right) = -\Delta M \left(\frac{\partial T_t}{\partial H} \right)^{-1}. \quad (2)$$

Here ΔM is the change in magnetization at the transition, assumed to be independent of the strength of the applied field. The extraordinarily large $\partial T_t / \partial H$ of CoMnSi in fields below 2 T has a profound effect on the adiabatic temperature change, ΔT :

$$\Delta T(T, \Delta H \equiv H) \sim -\frac{T}{C_H} \Delta S_{\text{total}}(T, \Delta H \equiv H) \quad (3)$$

where C_H is the field-dependent heat capacity in the region of the magnetic transition. We then see, by connection to Eq. (2), that a very large $\partial T_t / \partial H$, as in the case of CoMnSi , severely reduces ΔS_{total} and hence the adiabatic ΔT .

B. Tuning crystalline and magnetic structure

As stated earlier, this study is the first examination of CoMnSi or related materials in the context of the magnetocaloric effect. Clearly the current value of ΔT , approaching 2 K in a 5 T field means that CoMnSi is beyond the realms of straightforward use in a permanent magnet-based refrigerator. However, our data, when compared with that from previous studies on CoMnSi, opens up the possibility of tuning the behavior of the metamagnetic transition in this material, through substitution and perhaps through heat treatment. First we make some comments regarding magnetic structure.

In CoMnSi, noncollinear antiferromagnetism and ferromagnetism are in close competition, as shown by the fact that the metamagnetic and Curie transition temperatures are very close. The appearance at the metamagnetic transition of a large isothermal entropy change only in fields above 2 T is ultimately due to the magnetic structures that are apparent in high fields either side of the transition. The magnetic structure of CoMnSi was studied using neutron diffraction by Nizioł *et al.*¹² They found a noncollinear antiferromagnetic cycloidal arrangement of Mn moments ($\mu_{\text{Mn}} \sim 2.2\mu_B$) and a small cobalt moment ($\mu_{\text{Co}} \sim 0.3\mu_B$). The ordering vector of the Mn moments was close to $[0\ 0\ 0.37]$ at 4 K in a sample which was slowly cooled after annealing. Furthermore, the magnitude of the propagation vector decreased with increasing temperature as the magnetic structure tended towards ferromagnetism. The isovalent and isostructural compounds, RhMnSi¹⁵ and IrMnSi²¹ are both antiferromagnets, and, as the unit cell volume increases from CoMnSi to RhMnSi to IrMnSi, ferromagnetic order in a window of finite temperature disappears. In the case of IrMnSi, there is only one (Néel) transition at 460 K and the antiferromagnetic structure now has a propagation vector of $[0\ 0\ 0.45]$ at 4 K.

From the above, two conclusions can be drawn. First, in fields above 2 T the metamagnetic transition temperature in CoMnSi is presumably low enough for paramagnetic fluctuations associated with T_c to be irrelevant. Then the metamagnetic transition can be between an antiferromagnetic state with a reasonably high ordering vector and a ferromagnetic state of high moment. For fields below 2 T, there is a rapid release of the competition between antiferromagnetic and ferromagnetic order, and so $\partial T_i/\partial H$ is very large. Second, it is clear that unit cell volume has a strong role to play in XMnSi materials, with antiferromagnetism being stabilized by high unit cell volumes (in the absence of Si/Ge substitution, which has the opposite effect). We suggest here that the fact that our slowly cooled CoMnSi sample has the highest recorded zero-field T_i and the highest H_c at a given temperature may be related to the observation that it has the largest measured lattice a parameter (5.868 Å) at room temperature. It is known that there is a reduction in the a parameter as the temperature is increased towards the metamagnetic transition.¹² Therefore, a high room temperature value of a might yield the observed high zero-field value of T_i if the metamagnetic transition occurs at a favored lattice spacing, as suggested in the phenomenology of Kittel.²² This is shown graphically in Fig. 7 where extrapolations of measured lattice a parameter to the metamagnetic transition temperature yield approximately the same critical value of a . We include in this

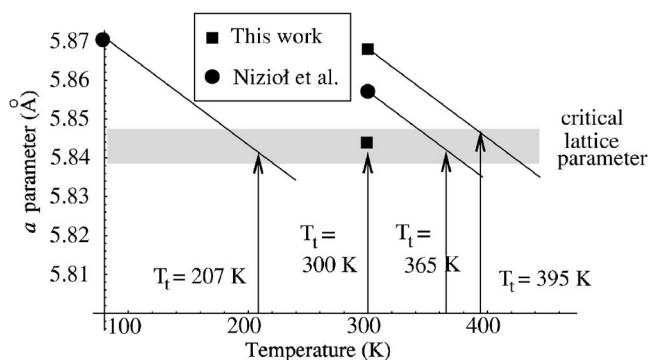


FIG. 7. The points show the measured a -axis parameter for samples of CoMnSi annealed in different ways (Refs. 10, 12, and 14). Extrapolations of a to higher temperature, based on a fixed value of $da/dT = -2.3 \times 10^{-4} \text{ \AA K}^{-1}$ [extracted from Nizioł *et al.* (Ref. 12)] are also shown. The experimentally observed metamagnetic transition temperatures (arrows) correspond approximately to the same critical value of a of about 5.84 Å.

plot both of our CoMnSi samples; one slowly cooled after annealing (our usual heat treatment), and a second sample which was quenched instead of slowly cooled, which had a broad metamagnetic transition at around 300 K and a reduced room temperature lattice a parameter of 5.846 Å (see Table I).

The parameter leading to the differences between samples in the literature and in this study may be the annealing method. Annealing is made necessary in this material because of a structural phase transition from a hexagonal phase at around 1100 K encountered on cooling from the molten state during synthesis.¹¹ Documented annealing temperatures vary considerably, and there is incomplete information in the literature about the rates of cooling used. It may be possible that different hold temperatures and cooling rates freeze in different lattice strains, altering the separation of Mn atoms, and thereby the sensitive metamagnetic properties of CoMnSi.

We conclude that CoMnSi_{1-x}Ge_x exhibits a significant magnetocaloric effect in large fields (5 T) with the size of the effect at lower fields being inhibited by the proximity of the metamagnetic transition to the Curie transition of this material. We have demonstrated a relation between unit cell size and the temperature scale of metamagnetism in CoMnSi, with annealing being a tuning parameter. Knowledge and suitable systematic control of the magnetic exchange interactions, density of states at the Fermi level and/or atomic order could adjust H_c , T_i , and $|\partial T_i/\partial H|$, and thereby make CoMnSi a useful negative magnetocaloric in relatively low magnetic fields. In this regard, neutron diffraction studies of differently annealed materials and an evaluation of the electronic component of the specific heat across the metamagnetic transition when tuned to zero temperature would be of interest. We have demonstrated that a very sensitive metamagnetic transition—unlike many of those previously studied by the magnetocaloric community—enables a broad range of magnetocaloric working temperatures around room temperature to be covered by a single material, while harnessing the first-order nature of the transition.

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