Negative magnetocaloric effect from highly sensitive metamagnetism in CoMnSi$_{1-x}$Ge$_x$

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We report a novel negative magnetocaloric effect in CoMnSi$_{1-x}$Ge$_x$ arising from a metamagnetic magnetocaloric 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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Whilst the magnetocaloric effect (MCE) has been known since 1881, 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 mK temperatures for scientific research by demagnetisation 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.

There has already been significant progress in the design of prototype magnetic refrigerators, fuelled by the prediction that such devices could impact on carbon emissions as they are potentially 40% more efficient than a conventional refrigerator. 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 Tesla) 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 Ni$_2$+xMn$_1$−xGa and Ni$_2$+xMn$_1$−xSn have a large magnetic hysteresis; MnFeP$_{1−x}$As$_x$ and MnAs-based materials contain toxic As. Fe$_{0.49}$Rh$_{0.51}$ is both expensive and loses its negative MCE upon multiple cycling of the applied field.

Almost all room temperature magnetocalorics exhibit a positive MCE associated with a Curie transition. Only the metamagnets FeRh and Ni$_2$+xMn$_1$−xSn 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 surprising given that they are more likely to be first order than their ferromagnetic cousins. In this Letter we study the pseudoternary metamagnet CoMnSi$_{1-x}$Ge$_x$, a novel 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 optimised from this point of view.

The various magnetic phases of the CoMnSi$_{1-x}$Ge$_x$ material system were examined by Nizioł and coworkers...
ers in the 1970s and 1980s. This paper will focus on the range \( x < 0.1 \). CoMnSi is orthorhombic, with space group \( Pnma \) and exhibits competition between helical non-collinear 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. The ferromagnetic state has a second order \( T_p \) which in much of the literature is at about 390 K. A schematic phase diagram of the orthorhombic phase of CoMnSi\(_{1-x}\) Ge\(_x\) for \( x < 0.3 \) is summarised in Figure 1.

We concentrate here on the first order metamagnetic transition at \( T_t \) in CoMnSi\(_{1-x}\) 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 Tesla field 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. 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. 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, and was cited as the main cause for the sample dependent magnetic behaviour in the work of Medvedeva.

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. 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/GPa and −100 K/GPa. 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. This would explain why the application of hydrostatic pressure stabilises the ferromagnetic phase, reducing \( T_t \). 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 behaviour 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 Tesla are required to observe a transition at \( T_t \) in CoMnSi at 280 K to a state approaching a large magnetisation of 100 emu/g. 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 identically fabricated samples of CoMnSi\(_{1-x}\) 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, \( \Delta S \), is maximal and where the largest magnetocaloric effect is found.

Samples were prepared by induction melting pieces of elemental Mn (99.99%), Co (99.95%), 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 hours, and slowly cooled to room temperature at a rate of 0.2 K per minute. X-ray diffraction of powdered samples 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. Magnetic measurements were performed in a vibrating sample magnetometer (maximum field 1.8 T) and a SQUID (maximum field 5 T).

From low field magnetisation measurements, we found \( T_t \sim 390 \) K and \( T_c \sim 420 \) K for CoMnSi; the highest values yet recorded for this material. In Figure 2, we show...
the isothermal magnetisation vs applied field for CoMnSi at temperatures between 250 K and 350 K. Data at each temperature was 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 hitherto measured, so the metamagnetic transition fields at a given temperature are larger than previously found. Corresponding magnetisation curves were obtained for CoMnSi$_{1-x}$Ge$_x$ with $x=0.05$ or 0.08. These lead to the magnetic phase diagram shown in Fig. 3. 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 Figure 2, and the splitting becomes more pronounced as the level of Ge substitution 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, as predicted for helical antiferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller ferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller the isothermal magnetisation vs applied field for CoMnSi at temperatures between 250 K and 350 K. Data at each temperature was 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 hitherto measured, so the metamagnetic transition fields at a given temperature are larger than previously found. Corresponding magnetisation curves were obtained for CoMnSi$_{1-x}$Ge$_x$ with $x=0.05$ or 0.08. These lead to the magnetic phase diagram shown in Fig. 3. 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 Figure 2, and the splitting becomes more pronounced as the level of Ge substitution 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, as predicted for helical antiferromagnets by Nagamiya 17. We note that previous authors associated a canted state with a much smaller magnetic crossover feature at lower fields 10.

We use a Maxwell relation to obtain the isothermal change in total entropy from the isothermal $M(H)$ curves:

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

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 Tesla, corresponding to a small shift in the metamagnetic transition field of around 0.1 Tesla. From Equation 1, and the $M(H,T)$ data, entropy change curves for each of the three compounds were obtained and are shown in Figure 4. In a field change of 5 Tesla, 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 $\sim$2 Tesla. 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 $\Delta S$ for a given applied field. We henceforth focus on CoMnSi, for which there exists the greatest amount of literature data with which to make comparisons. The entropy change in CoMnSi is smaller than that in other metamagnets previously investigated (FeRh, Mn$_3$GaC) and this is consistent with another observation. The rate at which the metamagnetic transition temperature changes with applied field is given by the Clausius Clapeyron equation for first order magnetic phase transitions:

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

Here $\Delta M$ is the change in magnetisation at the transi-
tion, assumed to be independent of the strength of the applied field. Once fields in excess of 2 Tesla are applied to CoMnSi–Ge, the metamagnetic transition becomes more first order and $\partial T_i/\partial H$ decreases in magnitude, both factors leading to a much enhanced isothermal entropy change. Nevertheless, the extraordinarily large $\partial T_i/\partial H$ of CoMnSi in fields below 2 Tesla has a profound effect on the adiabatic temperature change, $\Delta T$:

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

(3)

where $C_H$ is the field-dependent heat capacity in the region of the magnetic transition. We then see, by connection to Equation 2, that a very large $\partial T_i/\partial H$, as in the case of CoMnSi, severely reduces the adiabatic $\Delta T$. We have also measured this adiabatic $\Delta T$ in a field change of zero to 5 Tesla over a temperature range of 230 K to 290 K, 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 Tesla Oxford Instruments cryostat. As can be seen from the data in Figure 4, the resulting $\Delta T(T)$ curve peaks at nearly 2 K at $\sim 250$ K and is consistent with a crude estimate which may be obtained by using the 5 Tesla $\Delta S(T)$ curve and Eq. 8 with a fixed value of heat capacity, taken here to be 700 J/kg, the value we obtain at $T_i$ in zero field measurements using a TA Instruments Q1000 DSC.

Our data, when compared with that from previous studies on CoMnSi, opens up the possibility of tuning the behaviour of the metamagnetic transition in this material, perhaps through heat treatment. We suggest here that the fact that our material 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 favoured lattice spacing, as suggested in the phenomenology of Kittel [20]. This is shown graphically in Figure 5 where extrapolations of measured lattice $a$ parameter to the metamagnetic transition temperature yield approximately the same critical value of $a$. We include in this plot two of our CoMnSi samples; one slowly cooled after annealing (our usual heat treatment), and a second sample 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. 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 suitable systematic control of the magnetic exchange interactions and/or atomic order could adjust $H_c$, $T_i$ and $|\partial T_i/\partial H|$ and thereby make CoMnSi a useful new negative magnetocaloric in relatively low magnetic fields. 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, whilst harnessing the first order nature of the transition.

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[1] E. Warburg, Ann. Phys. 13 141 (1881).
[2] V.K. Pecharsky and K.A. Gschneidner, Jr., Phys. Rev. Lett. 78 4494 (1997).
[3] O. Tegus et al., Nature 415 150 (2002).
[4] American Physical Society March Meeting Session K7: Magnetocaloric Effect, Austin, Texas (2003).
[5] C. Zimm et al., Adv Cryog Eng 43 1759 (1998).
[6] L. Paret et al., Eur. Phys. J. B 32 303 (2003).
[7] T. Krenke et al., Nature Materials 4 450 (2005).
[8] H. Wada and Y. Tanabe, Appl. Phys. Lett. 79 3302 (2001).
[9] M.P. Annaorazov et al., Cryogenics 32 866 (1992).
[10] S. Nizioł et al., Phys. Stat. Sol. 51 K23 (1979).
[11] S. Nizioł et al., J Magn Magn Mater 79 333 (1989).
[12] S. Nizioł et al., Phys. Stat. Sol. 45 591 (1978).
[13] L.I. Medvedeva, Ukr. Fiz. Zh. 24 1752 (1979).
[14] H. Bińczycka et al., Phys. Stat. Sol. 35 K69 (1976).
[15] V. Johnson and C.G. Frederick, Phys. Stat. Sol. (a) 20 331 (1973).
[16] R. Zach et al., Acta Physica Polonica A68 143 (1985).
[17] T. Nagamiya, Solid State Phys. 20 305 (1967).
[18] M.P. Annaorazov et al., J. Appl. Phys. 79 1689 (1996).
[19] T. Tohei et al., J. Appl. Phys. 94 1800 (2003).
[20] C. Kittel, Phys. Rev. 120 335 (1960).