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Pressure-tuned magnetocaloric effect in $\mathbf{Mn_{0.93}Cr_{0.07}CoGe}$

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Effects of physical and chemical pressures in the $Mn_{1-x}Cr_xCoGe$ series of compounds are studied. Cr substitution and hydrostatic pressure play similar roles in displacing T_C to lower temperatures and coupling or decoupling magnetic and crystallographic transitions. In this work the similarities and differences between the effects of chemical and physical pressures are explored, helping unveil the nature of the first-order phase transition presented by MnCoGe-based compounds.

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Since the discovery of the giant magnetocaloric effect on FeRh[1] and the subsequent observation of a tunable giant entropy change (ΔS_M) on $Gd_5Ge_2Si_2$,[2] magnetic refrigeration based on the magnetocaloric effect has gained increasing attention. It is regarded as a promising, more efficient, and environmentally friendly alternative to gas-compression-based refrigeration due to its potential applications in a wide range of temperatures.

Materials presenting first-order magnetic phase transitions are of special interest since they intrinsically present high ΔS_M originating from the discontinuous character of the transition. These transitions can be observed in a series of low-cost 3*d* metal-based compounds such as MnAs,[3] $MnAs_{1-x}Sb_x$,[4] $Ni_{0.5}Mn_{0.5}Sn$,[5] and $(Mn,Fe)_2(P,As)_1$.[6] Such transitions are always accompanied by a discontinuous change in the lattice parameters and often in volume, but do not always result in a crystal symmetry change. Materials presenting only lattice parameters and/or volume change around the phase transition are said to undergo a magnetoelastic phase transition, e.g., all Fe_2P-based compounds as well as $La(Fe,Si)_{13}$,[7] while those which also show a change in crystal structure undergo a magnetostructural phase transition, e.g., FeRh, $Gd_5Ge_2Si_2$, MnAs, and $Ni_{0.5}Mn_{0.5}Sn$.

Since magnetic interactions are sensitive to interatomic distances, chemical pressure—substitutions, dopings, and interstitial elements—has been largely used to tune magnetic properties. Both magnetic and crystallographic phase-transition temperatures can be tuned using chemical pressure. This allows for first-order phase-transition temperatures to be easily tuned. But, more importantly, it allows for chemical pressure to be used to simultaneously tune separate magnetic and crystallographic transitions to coincide, giving rise to coupled first-order transitions. Thus, chemical pressure is an invaluable tool not only to tune but also to create magnetoelastic and magnetostructural couplings. A good example of both the creation and tuning of a magnetostructural coupling comes from the MnCoGe system.

MnCoGe is a 3*d* metal-based ferromagnet with a Curie temperature (T_C) of ∼345 K and a diffusionless crystallographic phase transition from the low-temperature orthorhombic TiNiSi type to the high-temperature hexagonal Ni_2In type of structure at ∼650 K.[8,9] In both orthorhombic and hexagonal structures it behaves as a typical ferromagnet with second-order phase transitions (and saturation magnetizations) at 345 K ($M_S = 4.13\mu_B$) and 283 K ($M_S = 2.76\mu_B$), respectively.[10,11]

The magnetic and crystallographic transitions can be coupled in many ways. We have recently reported that the addition of B as an interstitial and the substitution of Cr on the MnCoGe lattice can be used to make the magnetic and structural phase transitions coincide, giving rise to a giant magnetocaloric effect.[12,13] Moreover, by controlling the amount of B addition or Cr substitution, the temperature of the first-order phase transition can be tuned in a similar fashion as that of the Fe_2P-based compounds.[6]

We found that for the $Mn_{1-x}Cr_xCoGe$ series of compounds, 4 at. % Cr substitution is enough to couple magnetic and structural phase transitions into one first-order magnetostructural phase transition. For $0.04 \leqslant x < 0.27$, T_C decreases with increasing Cr content until the transitions are decoupled for 27 at. % Cr substitution[15] (see the inset of Fig. 1). The appearance of a low-temperature antiferromagnetic ordering accompanies the decrease in T_C. The transition temperature from the antiferromagnetic to the ferromagnetic state increases as T_C decreases, such that the transitions occur simultaneously for 25 at. % Cr.

All $Mn_{1-x}Cr_xCoGe$ samples presenting the magnetostructural coupling show sharp discontinuities in both the temperature-dependent magnetization and the lattice parameters. Large thermal hysteresis and giant changes in ΔS_M are also observed, which are signs of a large energy barrier and of a first-order phase transition, respectively. However, no discontinuity on dM/dB arises from the phase transition, i.e., no metamagnetic transition is observed. While ΔS_M is well within giant values, the observed change in critical temperature dT_C/dB is usually well below its Fe_2P counterpart (≈4 K/T). Such mixed first- and second-order characteristics point to a rather different magnetocrystalline coupling.

Another way to change interatomic distances and influence magnetocrystalline couplings is the use of physical pressure. Unlike its chemical counterpart, physical pressure does not suffer from parasitic effects originating in the substitution itself, since it retains the composition, purity, and shape of the sample. Thus the use of physical pressure provides a clean way of probing the spin-lattice coupling and moreover can shed light on the effects of chemical pressure.[16–18] Earlier studies using hydrostatic pressure in the related $Co_xNi_{1-x}MnGe$ system show that both chemical and physical pressures can be

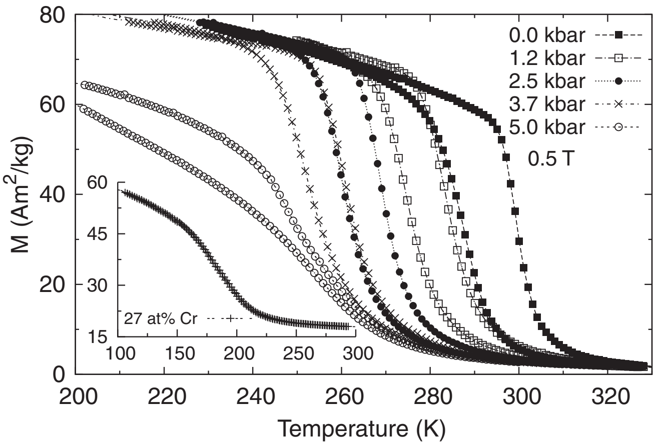

FIG. 1. Magnetization as a function of temperature under 0.5-T magnetic field for $Mn_{0.93}Cr_{0.07}CoGe$ at different applied hydrostatic pressures. Inset: Magnetization as a function of temperature for $Mn_{0.73}Cr_{0.27}CoGe$.

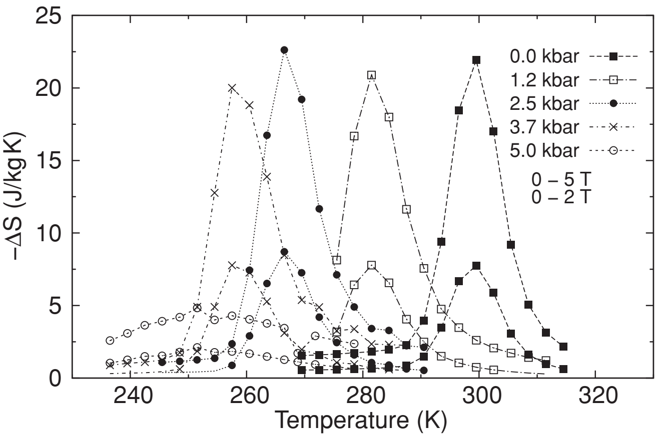

FIG. 2. Magnetic entropy change for 0–5 and 0–2 T (upper and lower curves, respectively) field change at different applied hydrostatic pressures.

used to tune the MnCoGe system. In their work Niziol *et al.*[19] show that separate magnetic and crystallographic transitions can be made to coincide in a given temperature and pressure interval, after which both transitions continue to be observed separately.

In this context, the nature of the magnetocrystalline coupling is probed using hydrostatic pressure. For such a study a sample from the $Mn_{1-x}Cr_xCoGe$ series with T_C close to room temperature was chosen: $Mn_{0.93}Cr_{0.07}CoGe$. The effects of chemical and physical pressure are studied and compared and a final analysis of the nature of the first-order phase transition is drawn.

The samples used in this experiment were prepared as described by Trung *et al.*[12] The magnetic measurements were performed in a Quantum Design MPMS5S magnetometer with SQUID sensors. ΔS_M is calculated from isothermal magnetization data using the Maxwell relations. Isothermal measurements were performed using the so-called loop process as described by Caron *et al.*,[20] which accounts for the magnetic history of the sample. Magnetic measurements under hydrostatic pressure were performed in a homemade clamp-type CuBe pressure cell. The design of the cell is similar to that used by Koyama *et al.*[21] with the proper change in dimensions so that the cell fits the MPMS sample chamber. The pressure cell works at pressures up to 8 kbar and mineral oil is used as the pressure transmitting medium. The pressure inside the cell is calibrated in two ways. The first is that the pressure can be directly calculated from the force applied on the pistons when the cell is loaded at room temperature. This calculation was double checked against the T_N of MnAs[22] and found to be in good agreement with the latter. Because MnAs has a high magnetic moment and presents a first-order magnetic phase transition at ~318 K, Sn is used as a reference manometer in routine measurements. Sn shows a superconducting transition at ~3.8 K (at ambient pressure) for which the pressure dependence is known.[23] For that, a small piece of Sn is loaded together with the sample. We found a 2-kbar difference in pressure from room-temperature MnAs to superconducting Sn measurements, which is consistently linear throughout the pressure range employed.

The first-order magnetostructural phase transition was further characterized through temperature-dependent x-ray diffraction (XRD) using Cu $K\alpha$ radiation. All temperature-dependent XRD data was collected during a heating cycle and analyzed using FULLPROF's implementation of the Rietveld refinement method.[24,25]

$Mn_{0.93}Cr_{0.07}CoGe$ has a T_C of ~300 K on heating under 0.5 T and a thermal hysteresis of ~12 K. T_C is strongly affected by pressure, showing a linear shift to lower temperatures at a rate of $dT_C/dP = 10$ K/kbar (see Fig. 1). Surprisingly, characteristics of the transition such as width and thermal hysteresis remain unaffected for $P < 5$ kbar. For $P \geqslant 5$ kbar the transition is broadened while retaining thermal hysteresis, mixing first- and second-order characteristics. It is, however, clear from the calculated ΔS_M that magnetic and crystallographic transitions are no longer simultaneous (see Fig. 2).

XRD measurements at ambient pressure around the phase transition show the normal expansion of the lattice plus the characteristic discontinuity at the phase transition. The volume change due to the transition is ~4%, a value in agreement with literature for similar compounds.[9] The upper graph of Fig. 3 represents the orthorhombic and hexagonal volumes together with the phase fractions. Note that the width of the phase transition is marked in gray for all graphs. The two lower graphs show the lattice parameters as a function of temperature.[9,26]

In the $Mn_{1-x}Cr_xCoGe$ compounds, the role of chemical and physical pressures present many parallels. From earlier results of Trung and collaborators[12] the role of Cr is known. It decreases both the temperature of the crystallographic transition and T_C—at a lower rate—until the transitions are coupled at ~322 K for the sample with 4 at. % Cr substitution. Once coupled, increasing Cr content decreases T_C at a rate of −4.6 K/Cr at. %. Since Cr has a smaller atomic radius than Mn, the volume of the hexagonal high-temperature phase decreases with increasing Cr content, destabilizing the ferromagnetic ordering and pushing T_C to lower temperatures. Pressure does the same for the 7 at. % Cr compound. It decreases volume stabilizing the hexagonal phase, bringing T_C down.

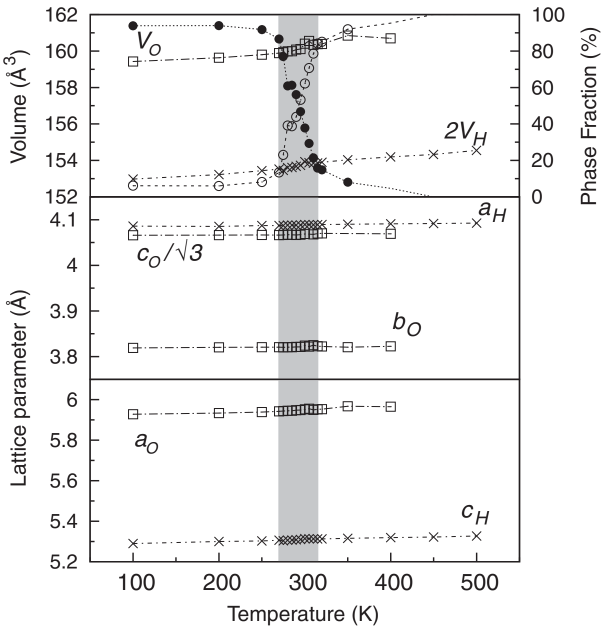

FIG. 3. Volume and lattice parameters as a function of temperature. Orthorhombic lattice parameters and volume are represented by open squares while hexagonal by the x. In addition, overlaid to the volume is also represented the evolution of the phase fractions as a function of temperature, corresponding to the right y-axis. The orthorhombic phase fraction is represented by closed circles and the hexagonal by open circles.

However, the chemical and physical decouplings are rather distinct. While chemical decoupling is observed for 27 at. % Cr content with a T_C of ~190 K, pressure-induced decoupling occurs ~5 kbar with a T_C of ~255 K. The magnetocaloric properties observed are also markedly different. For the 27 at. % Cr compound, ΔS_M drops as low as 1.8 J/kg K (0–5 T), and the transition is clearly second order. For the pressure-induced decoupling ΔS_M drops to ~5 J/kg K, also a value corresponding to a second-order phase transition. However, this value is still larger than that observed for hexagonal 27 at. % Cr compounds. This is evidence that the crystallographic phase transition, although decoupled, is likely to be at a slightly lower temperature than the magnetic transition: enough to decouple the transitions, but close enough to enhance ΔS_M. Thus, at $P \geqslant 5$ kbar, $Mn_{0.93}Cr_{0.07}CoGe$ behaves as MnCoGe with a lower T_C due to the different lattice parameters brought about by the Cr substitution. This is confirmed by simply inspecting the M_S (230 K, 5 T)—directly below T_C at 5 kbar. M_S decreases ~30% from the coupled to the decoupled state, which is also the difference observed from orthorhombic to hexagonal MnCoGe[11]. Such results suggest that the crystallographic transition is now at a lower temperature than the magnetic one, as is observed for $Co_{0.5}Ni_{0.5}MnGe$[19] under hydrostatic pressure for $P \geqslant 8$ kbar.

We observe that both the variation of composition and hydrostatic pressure—which primarily affect the structural transition—are capable of driving the first-order phase transition. Pressure experiments rule out any possible parasitic effects of chemical pressure, confirming that the crystallographic transition per se is able to effectively trigger the magnetostructural phase transition. The absence of metamagnetic transitions for this compound, plus the rather low $dT_C/dB \approx 1.5$ K/T, point out that the magnetic field is not as effective in triggering the magnetostructural transition. In fact, the observation of metamagnetic transitions above 4 T for B-substituted compounds confirms this assumption.[15] Thus, the energy barrier in between the paramagnetic-hexagonal and the ferromagnetic-orthorhombic phases is more easily overcome by the crystallographic change than by field-induced spin-lattice coupling.

Usually in magnetocaloric materials presenting first-order phase transitions of the order-disorder type, it is found that both the crystallographic change—be it by chemical or physical pressure, or temperature—and magnetic field are equally effective in driving the first-order transition. This behavior is observed in most Fe_2P-based compounds, for example. But there are extremes where the phase transition is insensitive or excessively sensitive to magnetic field. In this case we observe a phase transition which is poorly driven by the magnetic field, where a large entropy jump is observed but shifted very little by the magnetic field, resulting in a narrow and high entropy change peak. The other extreme would be a first-order phase transition which is overly sensitive to the magnetic field, resulting in a lower entropy change smeared out over a much larger temperature range.[27]

This is a clear example of the cooperative-type transition described by Anzai and Ozawa.[28] Such a transition is defined considering the interaction between two order parameters which have different physical origins. As such, the transition occurs for both order parameters simultaneously, but its driving force is contained in only one of them. The other one can only change with the former in a cooperative sense.

In our case the driving force is the crystallographic transition, and the magnetic transition occurs cooperatively. However, one must bear in mind that Anzai and Ozawa's classification does not account for the more common behavior of the magnetocrystalline coupling observed in magnetocaloric materials. Namely, most magnetostructural and magnetoelastic transitions are of the cooperative type, except that in most magnetocaloric materials it is hardly possible to tell which of the order parameters, crystallographic or field changes, is actually driving the first-order phase transition. In fact, the most desirable properties for applications, i.e., large ΔS_M and ΔT_{ad}, span from the balance between the coupled order parameters. This means that for applications one should look for the exception of Anzai and Ozawa's cooperative type of transition, where it is not possible to tell which parameter drives the transition.

Pressure experiments on $Mn_{0.93}Cr_{0.07}CoGe$ reveal that pressure is able to tune the temperature at which the magnetostructural phase transition occurs in a way not unlike that of chemical pressure. The decoupling of structural and magnetic phase transitions occurs at a pressure of ~5 kbar, when the magnetic properties of $Mn_{0.93}Cr_{0.07}CoGe$ become similar to that of pure MnCoGe.

By comparing magnetic and crystallographic data obtained using chemical and physical pressures, we conclude that the magnetocrystalline coupling present in these compounds is more easily driven by crystallographic than by magnetic field changes. In fact, this also explains why the effect of pressure in pure MnCoGe and on Cr-substituted MnCoGe are opposite. In response to pressure, the T_C of MnCoGe increases[19] while for $Mn_{0.93}Cr_{0.07}CoGe$ it sharply decreases. Note that pure MnCoGe presents a second-order ferromagnetic-to-paramagnetic phase transition, thus pressure influences the exchange interaction in a system where the driving force for the transition is solely the change in magnetic states. The response of the second-order magnetic phase transition in pure MnCoGe is to increase T_C. As we have verified, in the case of Cr-substituted MnCoGe, the coupling and thus the exchange interaction is ruled by the crystallographic change. The response of the crystallographic change to pressure is to occur at lower temperatures, be it coupled or not to a magnetic phase transition. Therefore, considering that the magnetostructural transition in $Mn_{0.93}Cr_{0.07}CoGe$ has a dominant component on the crystallographic change, a decrease in T_C is to be expected.

In summary, the interaction has a dominant component in the crystallographic transition, which drives the magnetostructural coupling triggering the magnetic phase transition in a cooperative sense. In this sense the $Mn_{1-x}Cr_xCoGe$ compounds are an exception among magnetocaloric materials presenting magnetoelastic or magnetostructural coupling, where it is usually impossible to tell which order parameter is the transition's driving force. Such a description successfully explains why large entropy changes but rather weak field dependence of the transition dT_C/dB are observed in $Mn_{1-x}Cr_xCoGe$. It may also shed light on the nature of the magnetostructural transition of compounds with similar properties, such as NiMnSn.[5] It also points to a rather unique and desirable characteristic of first-order magnetocaloric materials: Good properties for applications arise from the fact that there is no dominant parameter, i.e., both crystallographic and magnetic field changes are equally effective in driving the transition.

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