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Pressure induced magneto-structural phase transitions in layered RMn₂X₂ compounds (invited)

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Abstract

We have studied a range of pseudo-ternaries derived from the parent compound PrMn₂Ge₂, substituting for each constituent element with a smaller one to contract the lattice. This enables us to observe the magneto-elastic transitions that occur as the Mn-Mn nearest neighbour distance is reduced and to assess the role of Pr on the magnetism. Here, we report on the PrMn₂Ge_{2-x}Si_x, Pr_{1-x}Y_xMn₂Ge₂, and PrMn_{2-x}Fe_xGe₂ systems. The pressure produced by chemical substitution in these pseudo-ternaries is inherently non-uniform, with local pressure variations dependent on the local atomic distribution. We find that concentrated chemical substitution on the R or X site (e.g., in Pr_{0.5}Y_{0.5}Mn₂Ge₂ and PrMn₂Ge_{0.8}Si_{1.2}) can produce a separation into two distinct magnetic phases, canted ferromagnetic and canted antiferromagnetic, with a commensurate phase gap in the crystalline lattice. This phase gap is a consequence of the combination of phase separation and spontaneous magnetostriction, which is positive on transition to the canted ferromagnetic phase and negative on transition to the canted antiferromagnetic phase. Our results show that co-existence of canted ferromagnetic and antiferromagnetic phases depends on chemical pressure from the rare earth and metalloid sites, on local lattice strain distributions and on applied magnetic field. We demonstrate that the effects of chemical pressure bear close resemblance to those of mechanical pressure on the parent compound.

Keywords

compounds, rmn₂x₂, layered, transitions, invited, phase, pressure, structural, magneto, induced

Disciplines

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Pressure induced magneto-structural phase transitions in layered RMn_2X_2 compounds (invited)

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We have studied a range of pseudo-ternaries derived from the parent compound $PrMn_2Ge_2$, substituting for each constituent element with a smaller one to contract the lattice. This enables us to observe the magneto-elastic transitions that occur as the Mn-Mn nearest neighbour distance is reduced and to assess the role of Pr on the magnetism. Here, we report on the $PrMn_2Ge_{2-x}Si_x$, $Pr_{1-x}Y_xMn_2Ge_2$, and $PrMn_{2-x}Fe_xGe_2$ systems. The pressure produced by chemical substitution in these pseudo-ternaries is inherently non-uniform, with local pressure variations dependent on the local atomic distribution. We find that concentrated chemical substitution on the R or X site (e.g., in $Pr_{0.5}Y_{0.5}Mn_2Ge_2$ and $PrMn_2Ge_{0.8}Si_{1.2}$) can produce a separation into two distinct magnetic phases, canted ferromagnetic and canted antiferromagnetic, with a commensurate phase gap in the crystalline lattice. This phase gap is a consequence of the combination of phase separation and spontaneous magnetostriction, which is positive on transition to the canted ferromagnetic phase and negative on transition to the canted antiferromagnetic phase. Our results show that co-existence of canted ferromagnetic and antiferromagnetic phases depends on chemical pressure from the rare earth and metalloid sites, on local lattice strain distributions and on applied magnetic field. We demonstrate that the effects of chemical pressure bear close resemblance to those of mechanical pressure on the parent compound. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

The RMn_2X_2 series (where R is a rare earth and X is Si or Ge) are layered intermetallic compounds in which the R and Mn atoms lie in alternate layers, separated by layers of X atoms. These compounds display a fascinating array of magnetic phases, due to the strong dependence of the Mn-Mn magnetic exchange interaction on the intralayer near neighbour distance, and the interplay between the magnetism of the 3d and 4f layers.¹ Magnetic phase transitions in these compounds are often accompanied by isostructural changes (strictions) due to the strong magnetoelastic coupling of both R and Mn sites. Up to eight different magnetic structures are observed for Mn-Mn near neighbour distances in the range from ~ 2.84 Å to ~ 2.92 Å, and it is possible to vary that distance by changing chemical composition or temperature and by applying mechanical pressure or a magnetic field. By systematic investigation of the influence of these variables on magnetic and atomic structure, we learn a great deal about the nature of these compounds and about their potential for technological applications.

Here, we report our findings on the pseudo-ternaries, $PrMn_2Ge_{2-x}Si_x$ (Ref. 2), $Pr_{1-x}Y_xMn_2Ge_2$ (Ref. 3), and $PrMn_{2-x}Fe_xGe_2$ (Ref. 4), derived from the parent compound $PrMn_2Ge_2$, (in which the Mn-Mn nearest neighbour distance is 2.915 Å at room temperature), substituting for each constituent element with a smaller one to contract the lattice so as to observe the magneto-elastic transitions that occur as the Mn-Mn nearest neighbour distance is reduced and to assess the role of Pr on the magnetism.

II. EXPERIMENTAL DETAILS

The synthesis of the compounds discussed here, $PrMn_2Ge_{2-x}Si_x$, $Pr_{1-x}Y_xMn_2Ge_2$, and $PrMn_{2-x}Fe_xGe_2$, have been described in Refs. 4–6.

It suffices to note here that all samples studied had been subjected to long annealing at high temperatures (typically above 900 °C for at least 7 days) and were of high phase purity (98% or above).

Magnetization measurement, differential scanning calorimetry (DSC) measurements were performed at the Institute of Superconducting and Electronic Materials, University of Wollongong, in order to identify the magnetic phases and phase transition temperatures in these compounds.

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Neutron diffraction measurements variously evaluated here have been obtained at ANSTO on Wombat, Echidna, and Medium Resolution Powder Diffractometer (MRPD), at HZ-Berlin on E6, at ISIS on GEM, and at FRM-II on Spodi. Synchrotron X-ray diffraction experiments were performed at the powder diffraction beamline (PD) at the Australian Synchrotron.

III. RESULTS AND DISCUSSION

A. Magnetic phases of PrMn_2Ge_2

The magnetic properties of PrMn_2Ge_2 have been well reported^{7–9} and will not be covered in detail here. Suffice to note that four magnetic phases have been observed, as depicted in Fig. 1, with transition temperatures of 105 K, 286 K, 330 K, and 420 K for $Fmi + FPr$, Fmi , Fmc , and AFI phases, respectively.

Primarily the magnetism is located in the planes of Mn atoms, which display planar antiferromagnetic order at all temperatures below T_N (~ 420 K) and an additional axial ferromagnetic component below the transition between AFI and Fmc phases ($T \sim 330$ K). Pr orders ferromagnetically (with moments parallel to the ferromagnetic component of the Mn moments) at $T_{C(\text{Pr})} \sim 105$ K.

Identification of these magnetic structures is made with neutron powder diffraction, as illustrated in Fig. 2, where we see a selected region of the diffraction pattern from PrMn_2Ge_2 between 4 K and 450 K. For convenience, the magnetic phase transitions are marked on the plot. Most of the transitions are clear from changes in the diffraction pattern, and we note, in particular, the change in the position of the magnetic satellites of the incommensurate Fmi phase, around the (101) and (103) reflections, signifying a decrease in the period of rotation of the magnetic moments about the c-axis with increasing temperature.

B. Pseudo-ternaries of PrMn_2Ge_2

Mixing of any of the three constituent atoms of PrMn_2Ge_2 with a smaller atom invariably reduces the interatomic spacings, leading to modification of the magnetic structure. Typically, at a critical interatomic spacing ($d_{\text{Mn-Mn}} = 2.86$ Å) where the axial component of the Mn-Mn magnetic exchange interaction changes sign, we observe a transition from Fmc to one in which the axial component of the

Mn moment couples antiferromagnetically between planes (denoted by $AFmc$). This change is independent of the nature of the substitution, being an essential feature of the electronic interactions between Mn atoms. We illustrate this point with the magnetic phase diagrams for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ (Fig. 3), and $\text{PrMn}_{2-x}\text{Fe}_x\text{Ge}_2$ (Fig. 4), where the magnetic phase boundaries are drawn as a function of a lattice parameter to highlight the importance of interatomic spacing between nearest neighbour Mn atoms. Here, the lines of thermal expansion for specific values of substituent are kinked near the boundary between $AFmc$ and Fmc and in the region where Pr orders ferromagnetically.

The electronic origin of the boundary between Fmc and $AFmc$ magnetic states has been established by first principles calculations of the electronic structure of the two magnetic states³ using a spin polarized localized density approximation. Due to the anisotropic nature of the response of the lattice to changes in temperature and pressure, corresponding changes in the magnetic exchange energy of the two magnetic states (Fmc and $AFmc$) have different dependencies. Specifically, the calculations indicate that in $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ the Fmc state is favoured at ambient pressure below ~ 50 K and above ~ 150 K, whereas the $AFmc$ state is favoured between those temperatures, in agreement with our experimentally determined phase diagram (Fig. 3).

Experimentally, we observe that the boundary between Fmc and $AFmc$ is associated with a region of co-existence of both states.² In neutron diffraction studies of the $\text{PrMn}_2\text{Ge}_{2-x}\text{Si}_x$ series, we find that the transition from AFI to either Fmc or $AFmc$ is also accompanied by spontaneous magnetostriction, which is positive on transition to Fmc , and negative on transition to the $AFmc$ phase.² Because of this magneto-elastic coupling co-existence of these two magnetic states is accompanied by a structural separation, such that a large “gap” ($\partial a/\partial \sim 0.5\%$) appears in the phase diagram of $\text{PrMn}_2\text{Ge}_{2-x}\text{Si}_x$. This gap, as shown in Fig. 3 of Ref. 2, appears to be temperature independent, extending all the way from 2 K to the transition to the AFI state.

Identification of a phase gap in $\text{PrMn}_2\text{Ge}_{2-x}\text{Si}_x$ prompts us to suggest that there will also be one in the shaded regions of Figs. 3 and 4 as well. Confirmation of this will require more detailed structural studies.

The appearance of a region of magnetic phase co-existence raises the question, as to why some crystallites

FIG. 1. Schematic of the magnetic structures found in PrMn_2Ge_2 . Pr atoms are green, Mn atoms are maroon, and Ge atoms are grey.

FIG. 2. Selected region of neutron powder diffraction patterns from PrMn_2Ge_2 , showing four magnetic phase transitions between 4 K and 450 K. (Data collected on the Wombat diffractometer at ANSTO.) The magnetic phases $Fmi + FPr$, Fmi , Fmc , AFf , and PM are depicted in Fig. 1.

adopt the Fmc state whereas others adopt the $AFmc$ state. It is pertinent to add here that, to our knowledge, co-existence is only found in pseudo-ternary compounds and ternary compounds where the rare earth ion is suspected to be in a mixed valence state (as shown in Fig. 5 of Ref. 2).

We know from diffraction studies that there is no hint of long range chemical ordering on the mixed lattice site. Whether the chemical distribution is random or non-random is unclear from neutron diffraction. Certainly, considerable local lattice strain fields could be expected.¹⁰ Short range chemical order may also be present, and even the possibility of a miscibility gap is not excluded. Indeed strain can be seen in the neutron diffraction from $\text{PrMn}_2\text{Ge}_{2-x}\text{Si}_x$, even though instrumental factors dominate the measured peak widths.^{2,5} Concentration dependent lattice and magneto-elastic strain components can be identified in the (110) and (002) reflections. The lattice component, which is largely independent of temperature, is seen in both (110) and (002) reflections while the magneto-elastic component is

FIG. 3. Magnetic phase diagram of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ as a function of a lattice parameter. Values of x are indicated above the line for Neel temperature (T_N). Thermal expansion for selected concentrations of Y is indicated by fine black lines. The dashed line shows the extrapolated boundary between Fmc and Fmi .

FIG. 4. Magnetic phase diagram of $\text{PrMn}_{2-x}\text{Fe}_x\text{Ge}_2$ as a function of a lattice parameter. Values of x are indicated above the line for Neel temperature (T_N). Thermal expansion for selected concentrations of Fe is indicated by fine black lines.

evident only in the (110) reflection at Ge/Si concentrations where Fmc and $AFmc$ co-exist.

C. Magneto-structural anomalies

High resolution scattering studies are needed to accurately determine strain distributions, domain sizes and the potential role of atomic short range order.

Our high resolution X-ray powder diffraction study of the $\text{PrMn}_2\text{Ge}_{2-x}\text{Si}_x$ series of compounds¹¹ reveals many details of the structural features of these pseudo-ternaries. Most notably, we clearly see that chemical order is present in the Ge/Si planes of all the pseudo-ternaries of this series, and that the lattice strain broadening is highly anisotropic. We illustrate this point in Fig. 5, which shows the (220) and (008) Bragg reflections from a pseudo-ternary ($\text{PrMn}_2\text{Ge}_{0.8}\text{Si}_{1.2}$) in which the two phase region is clearly seen. As in the neutron diffraction pattern of Fig. 2, the magnetic phase transitions are marked on the plot. Several features of note are; spontaneous magnetostriction can be seen at both the $AFf \leftrightarrow PM$ and $Fmc/AFmc \leftrightarrow AFf$ phase boundaries, the magnetostriction at

FIG. 5. Thermal dependence of the [220] (left) and [008] (right) X-ray Bragg peaks from $\text{PrMn}_2\text{Ge}_{0.8}\text{Si}_{1.2}$, showing spontaneous magnetostriction at the magnetic phase transitions, and phase separation in the $Fmc/AFmc$ region. Magnetic labels as above in Fig. 1, except $AFmc = AFf$ plus axial antiferromagnetic order. (Data collected on the PD beamline at the Australian Synchrotron.)

the $AFmc \leftrightarrow AFl$ is of opposite sign to that of the $Fmc \leftrightarrow AFl$ phase boundary, the (220) reflection is substantially broader than the (008) reflection, and whereas the (220) reflection is completely resolved into two peaks in the mixed $Fmc/AFmc$ phase, the (008) reflection barely broadens. Thus, we see that one signature of the $AFmc$ phase is an increase in c/a ratio. The variation in intensity of Fmc and $AFmc$ components of the (220) reflection indicate the changing concentration of the two phases, with Fmc dominating near 310 K and $AFmc$ dominating at 80 K.

The anisotropic nature of the elastic response to the magnetic phase transitions is illustrated in the schematic (Fig. 6) of the crystal planes involved in the two reflections shown in Fig. 5. The substantial increase of the (220) peak angle in the $AFmc$ phase indicates drastic, uniform contraction of the a - b plane, coupled with a mild contraction along the c -axis. Equally the broadness of the (220) reflection indicates large local atomic displacements in the a - b plane, just as the relative narrowness of the (008) reflection indicates rather minor local atomic displacements in the direction of the c axis.

Close examination of the high resolution X-ray diffraction patterns of the $PrMn_2Ge_{2-x}Si_x$ series collected at 450 K reveals a separation into two distinct phases in all of the pseudo-ternaries. Since this is seen in the paramagnetic phase it cannot be related to the magnetic order and must therefore be chemical in nature. Rietveld analysis of these diffraction patterns provides further insights. These are summarized in Figs. 7(a)–7(c), where the two phases are denoted as Si rich (with blue symbols) and Ge rich (with orange symbols).

Both a and c lattice parameters and the Si/Ge concentration were fitted in the Rietveld refinement process. The concentration dependence of the lattice parameters (Fig. 7(a)) shows a displacement to the left for the Ge rich phase and to the right for the Si rich phase. Although the slope of the concentration dependence of lattice parameters for the two phases is not identical they are quite close to each other, and to the value predicted by Vegard's law (indicated by full and

FIG. 6. Schematic of selected crystal planes (a) (220) and (b) (002) planes. In each case, only the planes containing Mn atoms (maroon colour) are indicated.

FIG. 7. (a) Lattice parameters in paramagnetic phase of $PrMn_2Ge_{2-x}Si_x$, ($T=450$ K) (the full and dashed lines show concentration dependence expected due to Vegard's Law), (b) percentages of Si/Ge rich phases shown in (a), and (c) lattice strain in each phase. In each plot, the blue/orange symbols denote Si/Ge rich phases, respectively.

dashed lines in Fig. 7(a)). The relative concentration of the two phases (shown in Fig. 7(b)) changes sharply for $x \leq 0.8$, but then appears to be relatively constant at $\sim 75\%$ of the Ge rich phase and $\sim 25\%$ of the Si rich phase for all higher concentrations of Si. This rather surprising result indicates that the difference between Si/Ge concentration of the two phases remains relatively constant across the series. Finally, the lattice strain (shown in Fig. 7(c)) is high even in the end compounds ($PrMn_2Ge_2$ and $PrMn_2Si_2$) and is greater in the Ge rich phase than the Si rich phase, increasing to quite large values around $x = 1$.

D. Effect of mechanical pressure

Thus, far we have considered the effect of chemical distributions on the magnetic and structural properties. We now consider the effect of mechanical pressure.

Fig. 8 shows the measured pressure dependence of lattice volume (Fig. 8(a)) and c/a ratio (Fig. 8(b)) for three compounds in this series. The data were obtained by X-ray diffraction on the PD beamline at the Australian Synchrotron, using a diamond anvil pressure cell.¹² The compressibility of $PrMn_2Ge_2$ is noticeably greater than $Pr_{0.5}Y_{0.5}Mn_2Ge_2$ and $PrMn_2Si_2$, particularly at lower pressures. We note that both $PrMn_2Ge_2$ and $Pr_{0.5}Y_{0.5}Mn_2Ge_2$ adopt the Fmc state at

FIG. 8. Plot of (a) change in lattice volume and (b) change in c/a ratio in response to applied “mechanical” pressure for PrMn_2Ge_2 , $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$, and PrMn_2Si_2 (at room temperature). The grey dashed line in Fig. 8(a) indicates the critical volume where the $Fmc \leftrightarrow AFmc$ transition may be expected.

ambient temperature and pressure, whereas PrMn_2Si_2 is in the $AFmc$ state.

We also note from the report of pressure dependence of magnetization in $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ (Ref. 3) that the critical pressure for the $Fmc \leftrightarrow AFmc$ transition occurs at $P \sim 6.7$ kilobars, as indicated by the grey cross in Fig. 8(a). Taking this as a general indication of critical volume for the $Fmc \leftrightarrow AFmc$ transition, we deduce that the critical pressure for the transition in PrMn_2Ge_2 lies at $P \sim 38$ kilobars.

This interpretation is well supported by the trends in c/a ratios (Fig. 8(b)), where we see a pronounced increase in the c/a ratio of $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ from very low pressure and an increase in slope of the c/a ratio for PrMn_2Ge_2 at $P = 38$ kilobars. In contrast, the c/a ratio of PrMn_2Si_2 , which is in the $AFmc$ state under ambient conditions, does not increase with pressure.

E. Comparison of chemical and mechanical pressure

In order to compare the effects of mechanical pressure with those of chemical distributions, we describe the lattice response to pressure with the equation of state whereby, the bulk modulus (B) describes the change in volume (V) of a solid in response to pressure (P)

$$B = -V \left(\frac{\delta P}{\delta V} \right)_T. \quad (1)$$

Defining (B') to describe the pressure dependence of the bulk modulus, such that

$$B' = \left(\frac{\delta B}{\delta P} \right)_T. \quad (2)$$

In practice B' is generally constant and can be reduced to B'_o , so we can write

$$B = B_o + B'_o P, \quad (3)$$

where B_o is B at ambient pressure, and we can integrate Eq. (1) to give

$$P(V) = \frac{B_o}{B'_o} \left(\left(\frac{V_o}{V} \right)^{B'_o} - 1 \right), \quad (4a)$$

or equivalently

$$V(P) = V_o \left(1 + B'_o \frac{P}{B_o} \right)^{-1/B'_o}, \quad (4b)$$

where V_o is the volume of the solid at ambient pressure.

We have applied Eq. (4a) to our room temperature diffraction data with values of B_o and B'_o from a closely related compound (UGe_2Mn_2) (Ref. 13) to derive the equivalent “chemical pressure” from our three series of pseudo-ternary compounds.

The results are summarized in Fig. 9, where we plot chemical pressure against substituent concentration (x). The dashed lines in Fig. 9 broadly indicate the slope of chemical pressure for each compound, and highlight the transition at $x = 0.5$, which marks the boundary between Fmc and $AFmc$ magnetic state in $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ (Ref. 3) and $\text{PrMn}_2(\text{Ge}_{1-x}\text{Si}_x)_2$ (Ref. 2).

For those compounds, we see a marked increase in compressibility in the $AFmc$ phase. In contrast, $\text{Pr}(\text{Mn}_{1-x}\text{Fe}_x)_2\text{Ge}_2$

FIG. 9. Plot of “chemical pressure” against substituent concentration (x) for Y, Fe, and Si substitution in PrMn_2Ge_2 .

undergoes a magnetic transition from *Fmc* to *AFI* near $x = 0.1$ and another to *PM* near $x = 0.7$. Clearly, neither magnetic transition affects the compressibility of the $\text{Pr}(\text{Mn}_{1-x}\text{Fe}_x)_2\text{Ge}_2$ compound.

The initial slope of the change in chemical pressure with concentration reflects the magnitude of response to the mismatch between atom sizes in the mixed lattice plane, in the absence of any magnetic transition. For $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ and $\text{PrMn}_2(\text{Ge}_{1-x}\text{Si}_x)_2$, the initial slope is roughly in proportion to the relative sizes of the ions in the mixed plane (i.e., Y^{3+} is $\sim 10\%$ smaller than Pr^{3+} and Si^{4+} is $\sim 25\%$ smaller than Ge^{4+}). It is perhaps surprising that substitution of Fe for Mn, where the electron density distribution is only slightly more compact, applies by far the strongest chemical pressure. It may be that dilution of the Mn-Mn exchange interaction with increasing Fe concentration produces an effective increase in compressibility.

Finally, we compare the relative efficiencies of mechanical and chemical pressure on PrMn_2Ge_2 . Although Fig. 9 indicates that the magnetic *Fmc* $\leftrightarrow$ *AFmc* transition in $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ and $\text{PrMn}_2(\text{Ge}_{1-x}\text{Si}_x)_2$ occurs around $x = 0.5$, we note that both $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ and PrMn_2GeSi actually display mixed *Fmc/AFmc* character at room temperature, and the boundary is not sharp. The chemical boundary for complete conversion to the *AFmc* magnetic state at room temperature is closer to $\text{Pr}_{0.4}\text{Y}_{0.6}\text{Mn}_2\text{Ge}_2$ (see Fig. 3) and $\text{PrMn}_2\text{Ge}_{0.6}\text{Si}_{1.4}$ (Ref. 2), corresponding to chemical pressure of $P \sim 27$ kilobars (for Y substitution) and 55 kilobars (for Si substitution). These pressures are comparable to our critical value of $P \sim 38$ kilobars for applied mechanical pressure. Given the coarseness of our experimental data (in terms of chemical substitution), this result is in good agreement with our comparison of the rate of change of Pr ordering temperature (T_C^{Pr}),³ which indicates that mechanical pressure is a more efficient driver of the *Fmc* to *AFmc* magnetic transition than chemical pressure. If indeed chemical pressure is less effective, it may derive from the enhanced local strain distribution and phase separation which accompanies chemical substitution.

IV. CONCLUSIONS

We have shown that the two phase region in the $\text{PrMn}_2\text{Ge}_{2-x}\text{Si}_x$, $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$, and $\text{PrMn}_{2-x}\text{Fe}_x\text{Ge}_2$ series of compounds is associated with chemical phase

separation due to chemical distributions at the mixed site. We have also shown that chemical substitution produces large local strain distributions, mainly in the *a-b* planes. Finally, we have shown that these compounds all share a common magnetic character, dependent mainly on the Mn-Mn interatomic distance, regardless of which site bears the substituent atoms, and that this character is broadly consistent with the effect of mechanical pressure.

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