Experimental report

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Proposal: 5-31-2499 **Council:** 4/2016

Title: Pressure-induced Quantum Critical Points in Mn_{1-x}Rh_{x}Ge Chiral Magnet

Research area: Physics

This proposal is a new proposal

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Samples: Mn0.8Rh0.2Ge

Instrument	Requested days	Allocated days	From	To
D20	5	5	16/11/2016	21/11/2016

Abstract:

MnGe belongs to the topical class of so-called B20 chiral magnets, studied for decades in view of their unique magnetic properties. Under ambient conditions, it possesses the largest ordered moment and shortest helical pitch of its family and displays giant topological Hall effect. Recently, a pressure-induced two-step suppression of long-range magnetic order has been evidenced in MnGe. This is clearly at odds with the other members of the B20 family, for which magnetic collapse proceeds from a monotonous decrease of the ordered magnetic moment. It could be shown that this peculiar scenario survives outside of the helimagnetic phase and proves being an essential characteristic of the system in a large parameter range. In order to get a deeper insight into the mechanisms driving such pressure-induced spin transitions, we propose to study the behavior of weakly Rh-doped MnGe (Mn0.8Rh0.2Ge) by neutron powder diffraction under applied pressure. The obtained results will complement our previous studies of pure and Co-doped MnGe and allow building a quantitative model for the pressure-induced spin transitions in MnGe, with relevance to other systems such as invar alloys.

Rapid Communications

Suppression of the bulk high spin–low spin transition by doping the chiral magnet MnGe

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In the MnGe chiral magnet, the helimagnetic order and local moment collapse in two steps, showing the succession of high spin (HS) and low spin (LS) states as pressure increases. Here, we use high-pressure neutron diffraction to study the doped compounds $Mn_{0.86}Co_{0.14}Ge$ and $Mn_{0.9}Rh_{0.1}Ge$, and show that the evolution of their microscopic magnetic properties is instead continuous. It means that the bulk HS-LS transition is a unique feature of pure MnGe, very sensitive to small changes of the band structure and easily suppressed by chemical substitution. On the other hand, the helimagnetic correlations appear to be strengthened by doping and survive up to larger pressures (≈19 GPa, to be compared with ≈13 GPa). We discuss these results in the light of other disordered systems with remarkable properties, the so-called Invar alloys.

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In itinerant magnets, the strong sensitivity of the magnetic moment to fine details of the band structure may result in magnetic states which become energetically equivalent for certain values of the lattice constant. This can, for instance, lead to electronic transitions, between a high spin (HS) state (with a large specific volume) toward a low spin (LS) state (with smaller volume), that can be observed by varying either temperature or pressure. One of the most spectacular consequences of such phenomenon is believed to be the Invar effect [1,2], discovered by Guillaume in Fe-Ni alloys [3], with numerous industrial applications. Other examples of HS-LS transitions can be found in molecular compounds containing transition metals atoms [4] (Co, Fe, Mn), such as the Prussian blues analogs [5], due to the strong sensitivity of the crystal field to external parameters (pressure, temperature, or light).

Helical magnets with a noncentrosymmetric space group, such as MnSi or FeGe, are textbook examples of itinerant magnetism, hosting skyrmion lattices and being highly sensitive to pressure and chemical substitution. Their helimagnetic ground states are built upon a hierarchical energy scheme involving ferromagnetic (FM) exchange, Dzyaloshinskii-Moriya (DM) interaction, and crystalline anisotropy energies [6]. It collapses under pressure, yielding non-Fermi liquid behavior and partial ordering of fluctuating magnetic moments [7,8].

In this family, MnGe stands as an exception. Its short helical period of ≈30 Å [9,10] cannot be explained by a bare competition between a FM exchange and DM interactions, since it would require an unphysically large spin-orbit coupling. Recent experiments suggest the presence of a *3d* soliton lattice without need of a magnetic field [11], possibly triggered by topological chiral interactions [12]. Strikingly, when applying pressure, the magnetic order and local moment of MnGe collapse in two steps, through HS and LS states [13], followed by a zero spin (ZS) state [14]. This peculiar behavior was predicted by *ab initio* calculations [15], showing rigid shifts of the spin-split bands upon compression. The HS-LS transition is associated with irreversibilities of the lattice constant [14], strongly recalling Invar anomalies [16,17].

Under chemical substitution of Mn for *3d*-Co or *4d*-Rh atoms, helical order in MnGe strongly changes, showing the onset of very long period structures above a certain doping level ($x > 0.3$ and 0.5 for Rh and Co, respectively), with characteristics similar to certain cholesteric liquid crystals [18]. These substitutions yield either a compression (Co) or a dilatation (Rh) of the cubic lattice constant a. At lower doping, when MnGe helical order is preserved, one could then expect that the chemical pressure resulting from the substitution would either enhance (Co) or counteract (Rh) the effect of the applied pressure. This should yield a shift of the HS-LS transition (situated at $p_{C1} \approx 6$ GPa in pure MnGe) toward lower (Co) or higher (Rh) pressures, depending on the nature of the substituting ion.

In order to check the above scenario, we have used high-pressure neutron diffraction to study two samples with low doping level, namely, $Mn_{0.86}Co_{0.14}Ge$ and $Mn_{0.9}Rh_{0.1}Ge$. From the lattice constants at ambient pressure and at $T = 1.5$ K ($a = 4.767$ Å for $Mn_{0.86}Co_{0.14}Ge$ and 4.794 Å for $Mn_{0.9}Rh_{0.1}Ge$ [18]), one should expect pressure shifts of −1.8 GPa for Co doping and +0.9 GPa for Rh doping with respect to MnGe ($a = 4.785$ Å). Strikingly, instead of a rigid shift of the critical pressure, we observe a *complete smearing* of the transitions in both cases. The helical period and ground state magnetic moment gradually decrease without showing any critical behavior in the studied pressure range (i.e., up to 9 GPa). Moreover, the magnetic moments of the two compounds vary in very similar ways and do not universally

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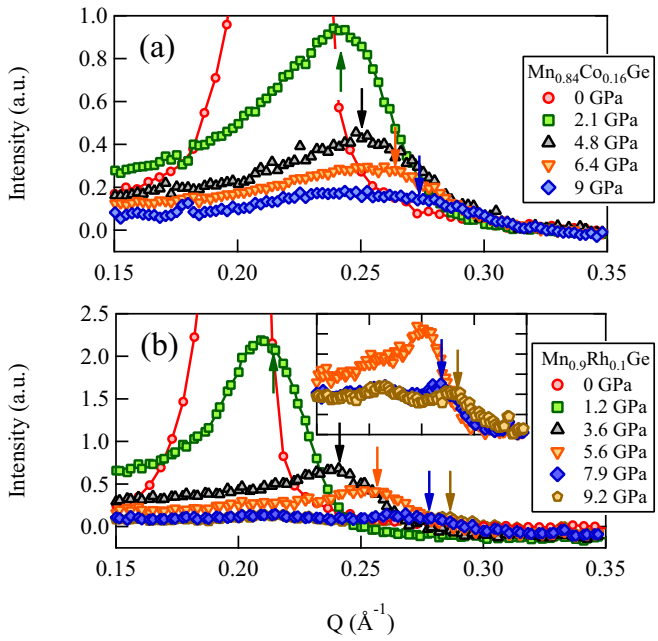

FIG. 1. Small-angle part of the NPD patterns of $Mn_{0.86}Co_{0.14}Ge$ (a) and $Mn_{0.9}Rh_{0.1}Ge$ (b), measured with a neutron wavelength $\lambda = 2.41$ Å at low temperature ($T < 10$ K) and for different applied pressures. The patterns are here corrected from a constant background and scaled to the intensity of the nuclear (110) peak in order to ease comparison. The strong helimagnetic peak asymmetry arises from the horizontal incoming beam divergence. Arrows show its position, as deduced from the Rietveld refinements [19]. The inset of (b) shows the magnetic signals recorded at the highest pressures in $Mn_{0.9}Rh_{0.1}Ge$. The Q range is the same as in the main panels.

scale with the unit cell volume. These results show that the HS-LS transition is very fragile and easily destroyed by chemical disorder, yielding a progressive breakdown of the Mn magnetism under pressure.

We have studied powder samples, synthesized under high pressure and high temperature [20], on the high-intensity diffractometer D20 of the Institut Laue Langevin [21]. The samples were inserted in a Paris-Edimburgh press, using a (4:1) deuterated methanol-ethanol mixture as transmitting pressure medium. A Pb chip was inserted in the cell to calibrate the applied pressure *in situ*, by monitoring the evolution of the Pb lattice constant [22]. The temperature was varied between ≈6 and 300 K. Pressure changes were systematically performed above the solid-liquid transition of the transmitting medium, to ensure quasihydrostatic pressure. Neutron powder diffraction (NPD) patterns, corrected from background and detector efficiency, were refined using the FULLPROF suite [23].

Patterns focusing on the main helical peak (i.e., the satellite of the $Q = 0$ Bragg peak), measured at the lowest temperatures ($T < 10$ K) are shown in Fig. 1. To be easily compared, data obtained at different pressures are corrected from a constant background then scaled to the integrated intensity of the nuclear Bragg peak (110). Figure 1 shows that in both samples, the intensity of the $Q = 0$ satellite strongly decreases under pressure, whereas its positions moves toward high angles. This gradual evolution takes place up to the highest measured pressure, without saturation of the peak intensity or blocking of the peak position. It shows that both magnetic moment and helical wavelength, respectively related to the peak intensity and peak position, continuously vary in the studied pressure range. This behavior strongly contrasts with observations in pure MnGe, where the peak intensity and position become independent of the applied pressure above $p_{C1} \approx 6$ GPa, marking the HS-LS transition (see Fig. 3 of Ref. [13]). Thus, data displayed in Fig. 1 are already a clear indication of the smearing of this transition in the substituted samples.

For each pressure, a series of patterns was measured versus temperature. Typical examples are shown in the Supplemental Material [19], together with joint Rietveld refinements of the crystal and magnetic structures. The $Q = 0$ satellite coexists with the Bragg peaks from the crystal structure at higher Q values. As in MnGe, satellites of the other Bragg reflections are much less intense and cannot be detected under pressure, since the signal-to-noise ratio is degraded by the background contribution from the pressure cell and small sample volume. Good refinements are obtained by assuming that the same type of helical order persists in the whole studied temperature and pressure (0–9 GPa) range. Taking the calculated resolution of the spectrometer into account, the helical peaks shows a small broadening with respect to the nuclear peaks, which increases with increasing pressure. From this broadening, one can extract the helimagnetic correlation lengths. They always remain much larger than the helical periodicities, suggesting well-preserved medium-to-long range magnetic ordering up to the highest pressure in both samples [19].

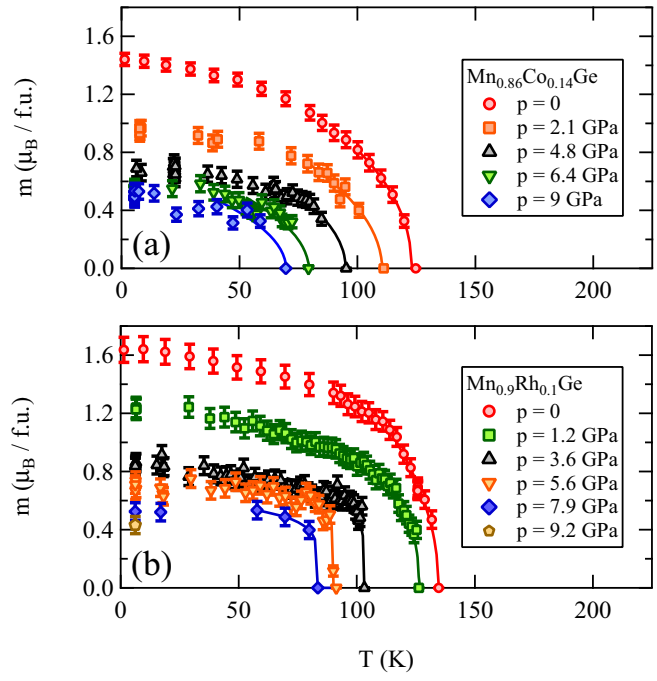

FIG. 2. Temperature dependence of the ordered magnetic moments per formula unit (f.u.) in $Mn_{0.86}Co_{0.14}Ge$ (a) and $Mn_{0.9}Rh_{0.1}Ge$ (b) for different applied pressures. The solid lines are fits of Eq. (1) to the data, performed in a temperature range limited to the vicinity of T_N (see text).

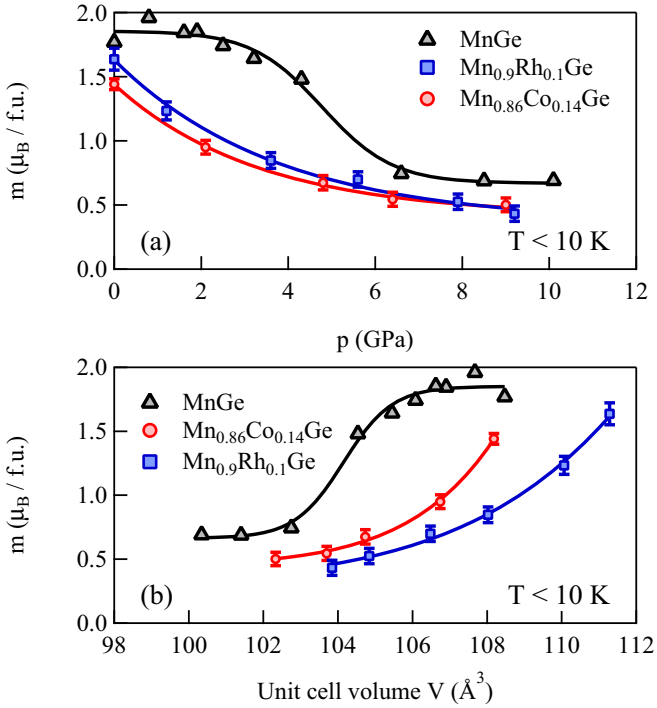

FIG. 3. Ordered magnetic moment per formula unit (f.u.) in $Mn_{0.86}Co_{0.14}Ge$, $Mn_{0.9}Rh_{0.1}Ge$, and MnGe, as a function of pressure p (a) and unit cell volume V in (b). Data for pure MnGe are taken from Ref. [13].

Thanks to the refinements, the intensity of the helical peak can be properly scaled to the intensity of the nuclear peaks, yielding a determination of the ordered moment m in absolute units. Its temperature dependence is plotted for each measured pressure in Fig. 2. In the vicinity of the ordering (Néel) temperature T_N, data are tentatively described by a power law

$$m(T) = \begin{cases} a & (1 - T/T_N)^{\beta} \quad \text{for } T \leqslant T_N \\ 0 & \text{otherwise,} \end{cases} \tag{1}$$

where a is a scaling factor and β a critical exponent. m decreases continuously with increasing temperature in both cases. Its variation is rather smooth in the Co sample ($\beta = 0.5$ as in pure MnGe), whereas it is much more abrupt in the Rh sample ($\beta \approx 0.2$), recalling a first-order transition.

The pressure dependence of the ordered magnetic moment at the lowest temperature ($T < 10$ K $\ll T_N$) is shown in Fig. 3(a) for the two samples, in comparison with previous results in pure MnGe [24]. At ambient pressure, the magnetic moments are slightly decreased in the doped samples, as expected from magnetic dilution. But as a main result, we find that their pressure dependence strongly differs from that of MnGe. In MnGe, the moment retains its HS value of $\approx 1.9\mu_B$ from ambient pressure up to $p_{C1} \approx 6$ GPa, then shows a steplike decrease toward its LS value of $\approx 0.6\mu_B$, which remains constant up to the maximum pressure of 10.1 GPa. For the two substituted samples, the moment starts to decrease *from the lowest applied pressure* which amounts to 1.2 and 2.1 GPa for Co and Rh samples, respectively. In other words, the critical pressure p_{C1} which separates the HS from the LS state in MnGe vanishes under doping.

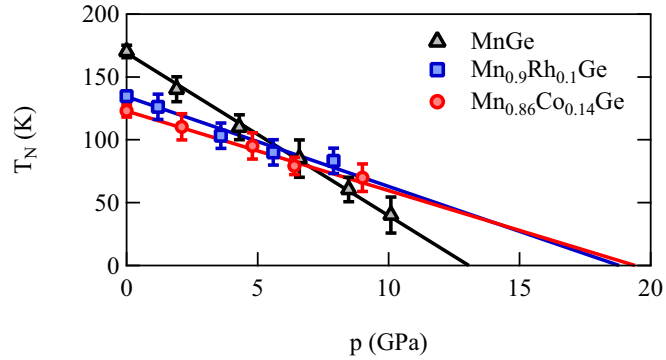

FIG. 4. Néel temperature T_N versus pressure as measured in $Mn_{0.86}Co_{0.14}Ge$ and $Mn_{0.9}Rh_{0.1}Ge$. The values of T_N in MnGe from Ref. [13] are plotted for comparison.

From the (p, V) equations of state, determined in MnGe from neutron and x-ray synchrotron data [13,25], and from neutrons in the doped samples [19], one can also plot the variation of the moment versus the unit cell volume [Fig. 3(b)]. As another important result, the pressure dependence of the moments are very similar in the Co and Rh samples with similar amount of doping, and they do not fall on a universal curve, scaling with the unit cell volumes. It means that the parameter which governs the suppression of the HS-LS transition is not the chemical pressure but most likely the magnetic disorder induced by Co and Rh ions which bear weak magnetic moments, either intrinsic [18] or induced [26]. We note that a rather smooth evolution of the saturated moment was recently reported in $MnSi_{1-x}Ge_x$, in relation to an ≈5% change of lattice constant [27]. There also, one should account for the effective magnetic contribution of Ge [26] and for the influence of disorder on the band structure to capture the nature of the observed transition.

For each pressure, fits of Eq. (1) to the temperature dependence of the magnetic moment (Fig. 2) in the hig-temperature range determine the Néel temperature T_N from the helical to the paramagnetic state where the ordered moment vanishes. In all samples, T_N decreases linearly with the applied pressure (Fig. 4) but the slope for MnGe (-12.9 ± 1.0 K GPa^{-1}) is about twice higher than for the doped samples, namely, -6.3 ± 1.0 K GPa^{-1} for Co and -7.2 ± 1.1 K GPa^{-1} for Rh. Extrapolation of these linear variations to $T_N = 0$ yields a quantum critical point (QCP) at p_0, where the ordered moment vanishes. In MnGe, $p_0 = 13.1(7)$ GPa is situated in the medium pressure range between two QCPs, namely, $p_{C1} \approx 6$ GPa which marks the HS-LS transition and $p_{C2} \approx 23$ GPa which corresponds to the Mn moment collapse [25]. On the contrary, in the doped samples where $p_{C1} \approx 0$, p_0 extrapolates toward very high values, of 19.4 ± 2.0 GPa for Co and 18.8 ± 1.6 GPa for Rh, in the pressure range of p_{C2}. This is another sign of the smearing of the HS-LS transition by doping.

We finally turn to the helical wavelength λ_h, deduced from the wave vector Q_h of the helical pitch ($\lambda_h = 2\pi/Q_h$). It exhibits a smooth dependence with pressure in the doped samples, and gradually decreases with unit cell volume without any anomaly (Fig. 5). This is not the case for MnGe [13], where λ_h saturates at a constant value of ≈20 Å above