Absence of magnetic phase separation in MnSi under pressure

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We report muon spin spectroscopy data (μSR) obtained under hydrostatic pressure on a large single crystal of the itinerant helimagnet MnSi and recorded down to 0.235 K and up to 15.1 kbar. Up to the critical pressure $p_c = 14.9(2)$ kbar, where the magnetic order is suppressed, the μSR data unambiguously demonstrate that the ground state of the system is magnetic with no indication of any phase separation.

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The strongly correlated intermetallic cubic compound MnSi has been known for a long time to order magnetically below $T_c \simeq 29$ K in a long period helical structure.[1,2] The first-order nature of the transition has only been demonstrated quite recently.[3,4] The study of the effect of pressure on the magnetic phase has shown that the transition temperature decreases with pressure, remaining first order, and tending to zero at $p_c \simeq 14$ kbar.[5,6]

It is well known that phase separation might occur near the temperature of a first-order-phase transition. Previous muon spin rotation and relaxation (μSR) experiments by Uemura *et al.* indicated a magnetic phase separation (MPS) in MnSi.[7] Prior to the μSR work, a nuclear magnetic resonance (NMR) study suggested MPS in the same pressure range $\Delta p \simeq 3$ kbar just below p_c.[8] However, since the NMR sample had to be powderized, strains problems could induce extrinsic MPS. Hence, probing a single crystal, as it has been done in Ref. 7, is certainly an advantage. However, the validity of the conclusions drawn from these measurements can be questioned since, according to Fig. 2c of Ref. 7, solely one spontaneous frequency was detected below T_c rather than two, as expected from previous ambient pressure measurements.[9] In addition, the measurements were performed only down to 2.5 K, which might be an issue when studying the behavior of the system near p_c where T_c goes to 0.

To clarify such issues, we have carried out a series of accurate μSR experiments under pressure down to 0.235 K on a large MnSi single crystal. The main result of our study is that, up to p_c and at low temperatures, the full sample volume becomes magnetic. Therefore, despite the first-order nature of the phase transition that is clearly confirmed by our data, no phase separation is detected in MnSi.

Due to its unique sensitivity to slow spin fluctuations and its local probe character providing the possibility to distinguish paramagnetic and magnetically ordered volume fractions,[10–13] no matter the compound chemical composition, the μSR spectroscopy is well suited to probe whether MPS is effectively an intrinsic property of MnSi. Since our main interest was on the existence of MPS, most of the μSR measurements were performed with the so-called weak-transverse-field (WTF) method, which is well adapted to determine the magnetic volume fraction. A small field, $B_{ext} = 5$ mT in our case, is applied perpendicular to the muon polarization $\mathbf{S}_\mu$. The depolarization function for the muons

stopping in the sample is then the sum of two precessing components. While the one which arises from the paramagnetic volume precesses at a frequency associated to the applied field and is weakly damped, the other one related to muons stopped in the magnetically ordered phase, precesses at a frequency corresponding to the spontaneous field, and exhibits a strong depolarization. This latter damping stems from the relatively large magnetic field distribution at the muon site inherent to an ordered magnetic state. By carefully determining the amplitude of these components, the volume ratio between the magnetic and paramagnetic phases can be accurately determined as a function of temperature and pressure. Measurements in zero applied magnetic field were also performed at different pressures.

The μSR measurements were carried out at the general purpose decay-channel (GPD) spectrometer of the Swiss Muon Source (SμS, Paul Scherrer Institute, Villigen, Switzerland). A detailed description of the pressure cell used for the μSR measurements is given elsewhere.[14,15] Relative to previous works, some improvements were made. The pressure cell was mounted either on the sample stick of a Janis ⁴He-flow cryostat or on the cold finger of an Oxford Instrument ³He cryostat. The temperature range from 40 down to 0.235 K could hence be covered. The extension to low temperature by more than an order of magnitude relative to previous μSR work[7] is a key ingredient to unravel the features reported in the present study. For each pressure in this study, the exact pressure applied on the sample was measured *in situ* at low temperature using the pressure dependence of the superconducting transition temperatures of small pieces of either In or Pb placed inside the pressure cell. It is worth mentioning that the pressure determination was performed at similar temperatures as the μSR measurements themselves. The pressure transmitting medium was a 1:1 mixture of n-pentane and isoamyl alcohol which is known for the excellent hydrostaticity conditions it provides in our pressure range of interest and for the absence of hysteresis effects.[16]

The MnSi sample was a cylinder of 7 mm diameter and 19 mm length cut from a single crystal prepared similarly as the one used in previously published ambient pressure μSR measurements,[17] elastic neutron-scattering investigation under pressure[18] and thermal-expansion studies[19] under pressure. The single crystal was grown by the Czochralski pulling technique from a stoichiometric melt of high-purity
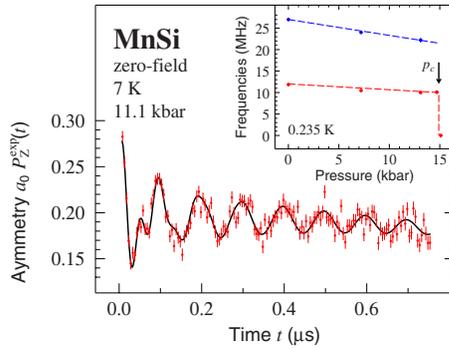
FIG. 1. (Color online) An example of a zero-field μSR spectrum recorded on a single crystal of MnSi at 7 K. The pressure as determined by the superconducting temperature of indium is 11.1 kbar. The solid line is the result of the fit consisting of two spontaneously precessing components plus an exponential spin-lattice relaxation one. The oscillations are described by exponentially damped cosine functions with frequencies $\nu_1 = 9.99(3)$ MHz and $\nu_2 = 22.9(5)$ MHz and an amplitude ratio similar to the one reported at ambient pressure value (Ref. [9]). The amplitude of the spin-lattice relaxation channel is found to account for one third of the total MnSi signal, a ratio expected for a weakly anisotropic cubic magnet like MnSi irrespective of the orientation of the muon initial polarization relative to the crystal axes. The relaxation rate is $\lambda_Z = 0.11(5)$ μs^{-1}. The signal from the pressure cell is characterized and described in Refs. [14] and [15]. Nearly half of the measured signal originates from the sample, a much larger proportion than the $\sim 30\%$ of the published work (Ref. [7]). The insert displays the pressure dependence of the two spontaneous precession frequencies measured at 0.235 K. At 14.7 kbar, the upper one is too heavily damped to be reliably extracted from the spectrum. The dashed lines are guides to the eyes.

elements ($>99.995\%$) using radio-frequency heating and a cold copper crucible. The residual resistivity ratio of such prepared crystals is about 40. Scanning electron microscope microanalysis and backscattered electron images reveal neither any deviation from the known crystal structure nor any presence of foreign phase. The possibility for off-stoichiometry was carefully investigated by examining the polycrystalline ingot remaining after a pulling especially designed to consume 99% of the initial load, instead of $\simeq 25\%$ for normal growth. No sizeable fraction of any foreign phase was found in the remaining ingot, confirming a stoichiometry in the ratio 1:1 in our MnSi single crystal.

In Fig. 1 a zero-field μSR spectrum recorded at 7 K under 11.1 kbar is reported. It serves to display the sample and pressure quality. The beating of the expected two oscillating components is clearly seen. Had the field distribution in the sample been large, due, for example, to a large pressure gradient or sample inhomogeneity, the higher frequency would not have been detected. Note that this higher-frequency precession was not observed in the previous μSR work under pressure.[7] The pressure dependence of the two low-temperature spontaneously precessing frequencies, which reflect the pressure dependence of the order parameter, is displayed in the insert of Fig. 1. An abrupt change is observed between 14.7 and 15.1 kbar, confirming the first-order nature of the phase transition. Belitz *et al.* predicted this type of transition to occur in weak ferromagnets.[20]
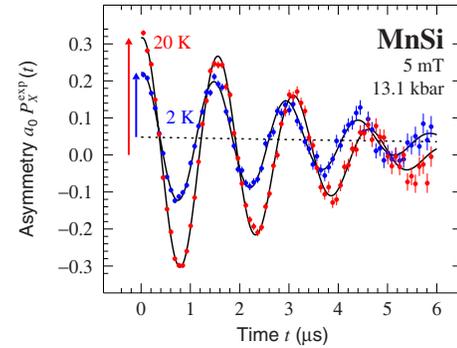
FIG. 2. (Color online) Spectra recorded in a weak transverse field of 5 mT in MnSi under a pressure of 13.1 kbar. Note that the time scale differs completely with the one of Fig. 1. The binning of the data which is adopted here averages out the oscillations of the muon spin in the MnSi spontaneous field. The initial amplitude of the 20 K spectrum which is marked by the longer arrow has the expected value in our experimental conditions. At 2 K, the precessing component observed in the plot corresponds to muons which are stopped in the pressure cell: its amplitude is indicated by the shorter arrow. The spin-lattice relaxation signature of the muons which are implanted in MnSi is seen as a shift in the mean value of the precessing signal. The solid lines are fits to a product of a cosine function and a Gaussian damping, with an additional exponential spin-lattice relaxation function (shown as a dotted line) for the 2 K spectrum. The Gaussian damping corresponds to a dominating inhomogeneous broadening.

Examples of WTF spectra are shown in Fig. 2. Muons stopped both in the pressure cell and in the MnSi crystal contribute to them. The muons implanted in paramagnetic MnSi and in the (non magnetic) pressure cell precess at a frequency which differs from $\gamma_\mu B_{ext}/(2\pi)$ only by a small Knight shift; $\gamma_\mu = 851.6$ Mrad.s^{-1}.T^{-1} is the muon gyromagnetic ratio. Muons stopped in magnetically ordered MnSi precess at a much higher frequency (see Fig. 1 and note the time scale). Since at low temperature and room pressure it is known that the whole volume of MnSi is magnetically ordered, it is simple matter to derive the pressure cell contribution to the signal. It is then possible to determine the MnSi magnetic volume fraction. The results are shown in Fig. 3 as a function of temperature and pressure. The most obvious feature is that the whole sample volume is magnetically ordered at low temperature for all the applied pressures. The magnetic volume fraction is fitted to the phenomenological law $\{1 + \exp[(T - T_c)/w]\}^{-1}$. With this formula, for a given pressure, T_c is the temperature at which half of the sample volume is magnetic. The pressure dependence of T_c will be shown and compared to the literature results in Fig. 6. Up to 13 kbar, the width of the transition observed in Fig. 3 is relatively narrow, pressure independent and about two times narrower than previously reported.[7] The data taken at 14.7 kbar single out themselves: the transition width is more pronounced. This trend if confirmed in Fig. 4 by the plot of the fit parameter w which is proportional to the width of the magnetic transition.

We present in Fig. 5 two zero-field spectra recorded at 14.7 and 15.1 kbar, respectively. The pressure at which the spontaneous μSR frequencies disappear from the μSR spec-
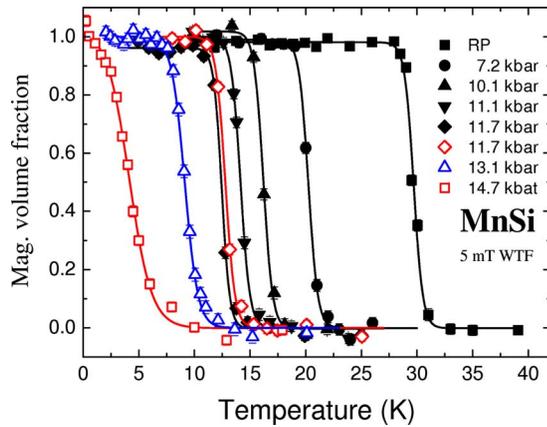
FIG. 3. (Color online) Temperature dependence of the magnetic volume fraction for a crystal of MnSi at different applied pressures. The data were obtained from 5 mT transverse-field measurements. The solid lines are fits to the phenomenological law given in the main text. RP stands for room pressure.

tra at low temperatures is taken as the critical pressure p_c, where the magnetic ground state is suppressed.

The pressure dependence of the low-temperature magnetic volume fraction derived from our measurements as well as of the critical temperature are plotted in Fig. 6. The pressure dependence of the critical temperature is consistent with recently published results obtained by various techniques (thermal expansion, specific heat and ac susceptibility) up to about 13 kbar. The possible discrepancy at higher pressure (although the experimental points are somewhat distributed) may be due to the effect of different pressure media.[19]

It may be that the sample and pressure quality plays a role in the appearance of MPS. A very clear example is given by the research on URu$_2$Si$_2$; see Ref. [24] and references therein. Better sample and pressure quality results in a sharper transition in URu$_2$Si$_2$; i.e., no MPS is observed. Finally we interpret the data recorded in the vicinity of p_c.

We first estimate a bound on the characteristic fluctuation time for the spin dynamics under 14.7 kbar at 0.235 K. Since we clearly observe oscillations up to ~ 0.2 μs, see Fig. 5, the two spontaneous fields do not flip in this time range.[25]
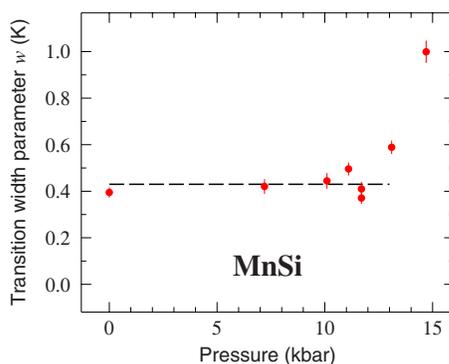
FIG. 4. (Color online) Pressure dependence of the w parameter determined from the fit of the data in Fig. 3. As shown by the dashed line, w is merely unchanged up to about 13 kbar.
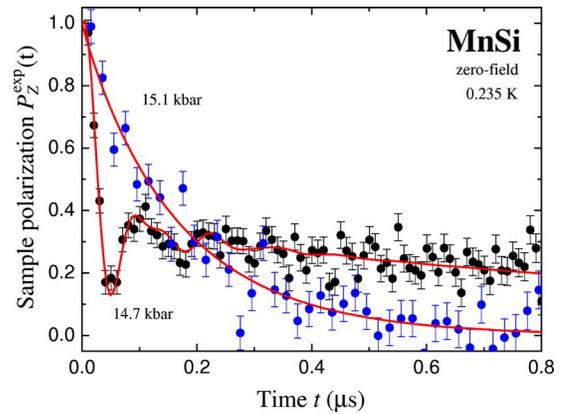
FIG. 5. (Color online) Time dependence of the zero-field muon polarization for MnSi recorded at 0.235 K on each side of the critical pressure, after subtraction of the μSR signal arising from the pressure cell. The solid lines represent the best fits to the spectra. The sample depolarization function has an exponential character at 15.1 kbar. At 14.7 kbar it is the sum of a relaxing and of two damped oscillating signals.

Therefore the time characterizing the fluctuations of the two spontaneous fields is at least as long as 0.2 μs.

We now discuss the pressure inhomogeneity in our measurements. It seems that a pressure distribution of 0.5 kbar is a reasonable value.[19,26] Because the depolarization function measured at 0.235 K under 15.1 kbar is fully characteristic of a paramagnetic state and the one recorded under 14.7 kbar at the same temperature reflects a magnetic state, we infer $p_c = 14.9(2)$ kbar. Since we now have some insight on the quality of the applied pressure, we can interpret the anomalous large width of the temperature dependence of the magnetic volume fraction observed at 14.7 kbar; see Fig. 3. We expect the μSR spectra to depend strongly on the pressure near p_c. In fact, we note that the width at 14.7 kbar in our
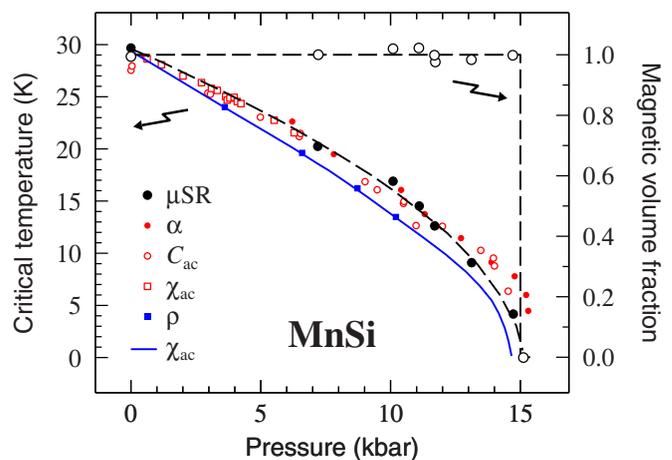
FIG. 6. (Color online) Low-temperature magnetic volume fraction and magnetic critical temperature as a function of the applied pressure determined from our μSR study. The dashed lines are guide to the eyes. The data of the pressure dependence of the critical temperature are from thermal expansion (α) (Ref. [19]), ac specific heat (C_{ac}) (Ref. [19]), ac susceptibility (χ_{ac}) (Refs. [21] and [22]), and resistivity (ρ) (Ref. [23]).

case has about the value found by Uemura *et al.*[7] at low pressure for which they did not observe MPS.

In conclusion, our work shows the importance of pressure homogeneity and access to low temperatures for getting reliable information on the phase-separation problem. We have shown that no MPS is present in MnSi at low temperature. Our data are consistent with the existence at low temperature of a sharp transition at the critical pressure $p_c = 14.9(2)$ kbar. Pfleiderer *et al.* (see also Ref. [18]) recently argued for a partial magnetic order above p_c.[27] We expect that μSR should be able to study its dynamics.

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