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Nature of the high-pressure tricritical point in MnSi

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The location of a tricritical point in the (p,T) phase diagram of MnSi and the nature of the phase transition at both sides of this point are under discussion. While the tricritical point was traditionally placed at $p_{tc}=12$ kbar and $T_{tc}=12$ K, with the first-order transition at $p>p_{tc}$, recent studies [Stishov *et al.*, Phys. Rev. B **76**, 052405 (2007)] suggested that it should be located at $p_{tc}=3.5$ kbar and $T_{tc}=25$ K with the transition being second order for $p>p_{tc}$. Based on a direct analysis of the magnetic phase transition under pressure, we demonstrate that the coordinates of the tricritical point are indeed $p_{tc}=3.5(3)$ kbar and $T_{tc}=24$ K but with the magnetic phase transition changing from second to first order as pressure increases. We also discuss the effect of spin fluctuations in the transport and magnetic properties of MnSi.

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Understanding the properties of itinerant weak ferromagnets is essential to construct a unified theory of magnetism, from paramagnetic metals to local-moment systems. The first attempts to fill this gap[1,2] resulted in a successful description of many of the properties of metallic magnets in the weak-moderate correlation limit, although many of their peculiarities remain unexplained. Among the most studied systems of this type is MnSi, a helical ferromagnet with a continuous magnetic phase transition at $T_C=30$ K.[3] In this material T_C can be reduced with pressure down to 0 K in an accessible pressure range ($\sim$14.6 kbar),[4] opening a unique opportunity to study how the spin order develops across the magnetic quantum phase transition.

On the other hand, as T_C is suppressed with pressure the system goes through a tricritical point (normally reported at $p_{tc}=12$ kbar and $T_{tc}=12$ K) beyond which the magnetic transition becomes first order.[5–7] However, based on an analysis of the pressure and field dependences of the resistivity, susceptibility, and specific heat, Petrova *et al.*[8] suggested that the tricritical-point coordinates should be relocated at $p_{tc}=3.5$ kbar and $T_{tc}=25$ K. What is more surprising, Stishov *et al.*[9] proposed that the phase transition changes from weakly first order at ambient pressure to second order across the tricritical point, changing completely the common description and understanding of the phase diagram of MnSi.

However, all these conclusions about the order of the phase transition are based on indirect qualitative proofs (disappearance of the resistivity or susceptibility peak, etc.), which could be dependent on the sample, field used, etc. In order to solve this controversy we report here a specific study aimed to elucidate the pressure dependence of the nature of the magnetic phase transition of MnSi.

The order of a magnetic phase transition can be determined directly from the analysis of the quartic term of the expansion of the free energy as a function of the even terms of the magnetization. This is a result of Landau's classical treatment of second-order magnetic phase transitions,[10] which is independent of the peculiarities of the system, provided we retain only the lower-order terms in the expansion around the critical point. In an expansion of this kind the sign of the M^4 term can be derived from the representation of the H/M vs M^2 plot (the inverted Arrot plots in mean field).[11] Here we report such a study to demonstrate that the tricritical point in MnSi is located at $p_{tc}=3.5(3)$ kbar and $T_{tc}=25$ K and, more important, the transition changes from second to first order as pressure increases. This puts an end to the controversy about the nature of the magnetic phase transition and its evolution with pressure in MnSi.

The single-crystal samples were grown by rf induction of high-purity Mn and Si in an ultrahigh-vacuum environment. High-pressure magnetization was measured in a Be-Cu cell from EasyLab using Sn as an internal manometer. We used Daphne 7373 paraffin industrial oil commonly used in high-pressure experiments in clamp cells due to its good properties at low temperature. The results of $\mu_{eff}/\mu_s \approx 5$ and $R_{300\ K}/R_{2\ K} \approx 55$ are similar to previous reports[4] and ensure a good quality of the samples.

In Fig. 1 we show the temperature dependence of the magnetization at different pressures under $H=100$ Oe and zero-field cooling conditions. T_C decreases with pressure (at a rate $d \ln T_c/dp=-5.3\times10^{-2}$ kbar^{-1} assuming a linear dependence up to 10 kbar), in accordance with previous reports,[4] at the time when the characteristic peak of the susceptibility disappears for $p>3.5(3)$ kbar. This is the pressure where Stishov *et al.*[9] placed the tricritical point in this material, although this is only indirect evidence that could be influenced by extrinsic factors such as the magnitude of the applied field or the quality of the sample. It should be noted also that we did not use He as a transmitting medium, ruling out any possibility that the effect observed at 3.5(3) kbar could be due to nonhydrostatic stress due to He crystallization.

We have carried out a detailed study of the pressure dependence of the $M(H)$ isotherms slightly above T_C. The main results are shown in Fig. 2. All the curves are measured at the same equivalent temperature, that is, at 1.03 of the corresponding T_C at each pressure. Increasing pressure changes the low-field slope of the H/M vs M^2 curves from positive at low pressure to negative at high pressure. Fitting the points to the equation

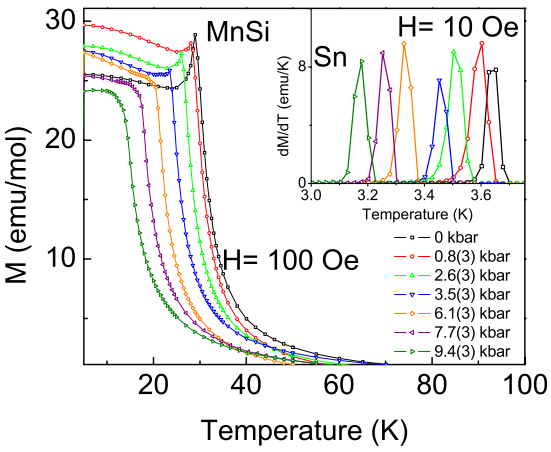

FIG. 1. (Color online) Temperature dependence of the magnetization as a function of pressure. Inset: derivative of the $M(T)$ curves of Sn under zero-field cooling (ZFC) conditions at different pressures across its superconducting transition. A small piece of Sn is placed with the sample within the pressure medium. Due to the variation of pressure with temperature (typically 1 kbar between 2 and 300 K) the pressure listed corresponds to that inside the clamp cell at ≈ 4 K.

$$H/M = a + bM^2 + cM^4 + \cdots \tag{1}$$

results in a negative b for $p \geq 3.5(3)$ kbar. Note that b in Eq. (1) corresponds to the M^4 term in the original expansion of the free energy, and hence a negative value above T_C results in a local minimum at $M \neq 0$ slightly above T_C. This is precisely the signature of a first-order phase transition. So we can conclude, unambiguously, that the tricritical point in MnSi is located at $p_{tc}=3.5(3)$ kbar and $T_{tc}=24$ K and, more important, that it corresponds to a second-to-first-order phase transition as pressure increases. We have obtained similar results from the isotherms measured at $1.02T_C$ and $1.04T_C$.

Although pressure varies about ≈ 1 kbar inside the pressure cell during a temperature run between 2 and 300 K, it remains practically constant at each temperature below the solidification temperature of the pressure medium (≈ 200 K). Because the data of Fig. 2 are taken over $M(H)$ obtained at constant temperature well below 200 K, the results cannot be affected by the small variations of the pressure with temperature inside the clamp cell.

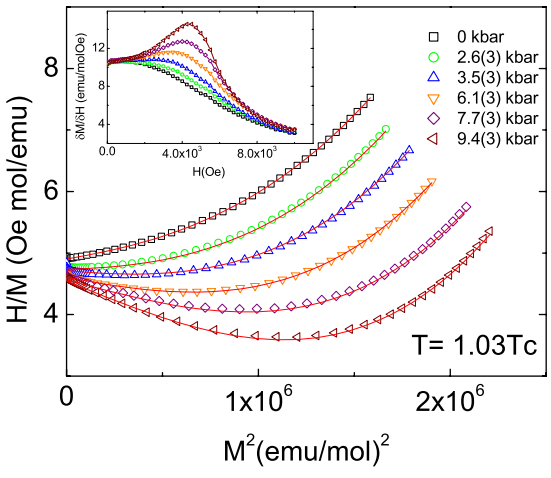

FIG. 2. (Color online) H/M vs M^2 isotherms at $1.03T_C$. The line is a fitting to Eq. (1) (see text). Inset: derivative of the $M(H)$ isotherms at $1.03T_C$.

The origin of the negative curvature in the H/M vs M^2 isotherms comes from a rapid increase in the $M(H)$ curves at around 4 kOe. In the inset to Fig. 2 we show the first derivative of the $M(H)$ curves at $1.03T_C$. The peak is reminiscent of a metamagnetic transition, although the change in magnetization is not so abrupt. The precise origin of this effect is difficult to identify from the present data. One possibility would be a change in the propagation of the spiral state that occurs above $H \approx 0.1$ T.[12] Note that, although the effect of the Dzyaloshinski-Moriya interaction should not change the functional form of Eq. (1) and the validity of our analysis, it could have a profound effect on the nature of the coefficients of M.[13] On the other hand, it was found that a magnetic field in the range of 200 mT induces a new paramagnetic phase slightly below T_C, the so-called A phase.[14] The anomaly in the susceptibility associated to the A phase disappears as the order of the phase transition changes,[12] and hence its relation to this effect at the new coordinates of the tricritical point should be investigated. Also, the existence of short-range local magnetic order slightly above T_C in the high-pressure region above the p_{tc} at 12 kbar has been documented.[6]

Belitz *et al.*[15] went beyond the phenomenological treatment exposed here and obtained a functional form of the free energy of an itinerant ferromagnet in the presence of quenched disorder. From their analysis it follows that long-wavelength correlation effects lead to a negative M^4 term in the free energy, which is generic to all these weak ferromagnets at sufficient low temperature. From this work it also follows that disorder could place the tricritical point at higher pressure and lower temperature, being a possible source of the discrepancy between the data in the literature. So, in principle the results presented here are consistent with the expectations for an itinerant weak ferromagnet in which the thermodynamic properties are governed by long-wavelength spin fluctuations.

In Fig. 3 we show the inverse susceptibility in the paramagnetic phase according to the predictions of spin-fluctuation theory. At ambient and low pressures, the inverse susceptibility follows the expected $T^{4/3}$ dependence. However, on increasing pressure the inverse susceptibility deviates from this behavior and increases faster. This can be understood by considering the effect of a random exchange field in the equation of state of a ferromagnet [the integral of Eq. (1)], as shown by Lonzarich,[2]

$$H = (a + 3b\bar{m}^2)M + bM^3 + \cdots, \tag{2}$$

where $\bar{m}^2$ refers to the variance of the fluctuations. A derivation of the temperature dependence of $\bar{m}^2$ results in $\Delta\chi^{-1} \sim T^{4/3}$, as observed in Fig. 3 at low pressures. From Eq. (2) also follows that it is the existence of an anharmonic term ($b \neq 0$) that introduces the temperature dependence. If $b \to 0$ or if it goes negative, then higher-order terms must be retained in the expansion ($\cdots + cM^5$) and

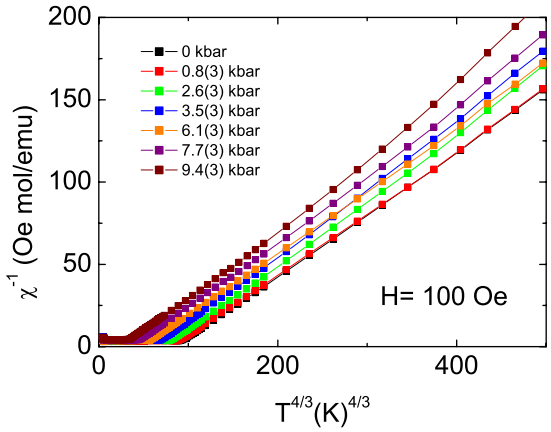

FIG. 3. (Color online) Inverse susceptibility as a function of pressure according to spin-fluctuation theory.

$$A = a + 3b\ \bar{m}^2 + 5c(\bar{m}^2)^2,\ \ \Delta b = b + 10c\bar{m}^2 \qquad (3)$$

leading to a more rapidly varying susceptibility $\Delta\chi^{-1} \sim (T^{4/3})^2$. Then, as the system goes through a tricritical point there should be a change in the rate of variation of $\Delta\chi^{-1}(T)$, as observed. However, the possibility that a variation of pressure with temperature could be affecting the rate of variation of the inverse susceptibility with temperature cannot be discarded completely and must be further investigated.

The main results of the transport properties are summarized in Fig. 4. The thermoelectric power is positive, indicating a negative curvature of the $N(E_F)$ with energy. On the other hand the value of the thermopower is too high for a metal with such a low resistivity ($\rho_{2\ \mathrm{K}} \approx 5\ \mu\Omega$ cm and $R_{300\ \mathrm{K}}/R_{2\ \mathrm{K}} \approx 55$). This could be due to a large curvature of $N(E_F)$, although the thermopower varies slower than linear with temperature and reaches an almost constant value around room temperature. These results are inconsistent with a classical analysis of the thermopower in a metal[16] and could be due to the contribution of spin fluctuations. Measurements of the thermopower under magnetic field should confirm this point.

On the other hand, although the resistivity follows a $\Delta\rho = AT^2$ dependence at low temperature, consistent with a Fermi-liquid (FL) description, the value of A [$\approx 9(2) \times 10^{-3}\ \mu\Omega$ cm K^{-2}] is larger than expected and strongly field dependent, decreasing about 50% in 9 T (see the inset to Fig. 4). Consistent with that an $m^*/m \sim 4-5$ enhancement was reported, as well as a departure of the optical conductivity from the Drude Fermi-liquid behavior.[17] So, although the transport properties could be in qualitative agreement with FL theory, the value of the A coefficient and the thermopower are much higher than expected and reveal a dominant role of spin fluctuations in the enhanced scattering rate of the quasiparticles.

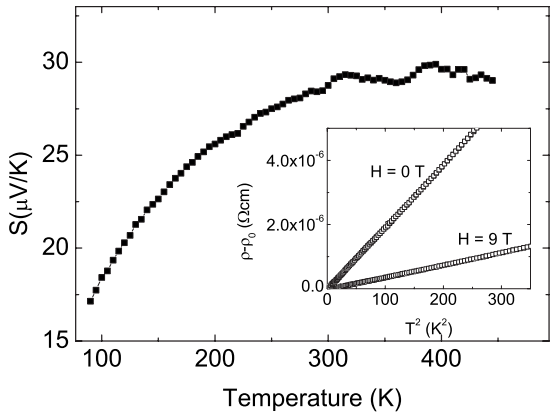

FIG. 4. Temperature dependence of the thermoelectric power. The linear behavior characteristic of a metal, expected *a priori*, is never observed, reaching an almost constant value above 300 K. Inset: Quadratic temperature dependence of the resistivity at $H=0$ and 9 T.

In summary, we have provided direct evidence of the existence of a tricritical point in the phase diagram of MnSi at $p_{tc}=3.5(3)$ kbar and $T_{tc}=24$ K, with the first-order transition line being located at $p > p_{tc}$. This should end the controversy about the nature of the magnetic phase transition at high pressure in MnSi. The tricritical point in the (p,T) phase diagram is generic to this class of materials. On the other hand, we have demonstrated that the magnetic and transport properties of this system are completely determined by long-wavelength spin fluctuations.

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