Magnetic phase transition in the itinerant helimagnet MnSi: Thermodynamic and transport properties

S. M. Stishov,[1,*] A. E. Petrova,[1] S. Khasanov,[2] G. Kh. Panova,[3] A. A. Shikov,[3] J. C. Lashley,[4] D. Wu,[5] and T. A. Lograsso[5]
[1]*Institute for High Pressure Physics, Troitsk, Moscow Region, Russia*
[2]*Institute of Solid State Physics, Chernogolovka, Moscow Region, Russia*
[3]*Russian Research Center Kurchatov Institute, Moscow, Russia*
[4]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[5]*Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA*
(Received 8 June 2007; revised manuscript received 3 July 2007; published 16 August 2007)

A careful study of thermodynamic and transport properties of a high-quality single crystal of MnSi at ambient pressure suggests that its transition to a helical magnetic state near 29 K is weakly first order. The heat capacity, temperature derivative of resistivity, thermal expansion, and magnetic susceptibility exhibit a specific structure around the phase transition point, interpreted as a combination of first- and second-order features. Striking mirror symmetry between the temperature derivative of resistivity and the thermal expansion coefficient is observed. Conclusions drawn from these experiments question prevailing views on the phase diagram of MnSi.

DOI: 10.1103/PhysRevB.76.052405 PACS number(s): 75.30.Kz, 75.40.Cx, 77.80.Bh

Physical properties of the cubic intermetallic compound MnSi, a weak itinerant helimagnet with Dzyaloshinski-Moria interaction,[1,2] have been studied extensively more than 40 years, since discovery of its spin-ordered phase at a temperature slightly below 30 K.[3] Neutron-diffraction measurements showed that MnSi had a helical spin structure with a propagation vector in the [111] direction.[4] Interest in studying MnSi was greatly enhanced by the finding that the temperature of the magnetic phase transition decreased with increasing pressure and tended to zero at about 1.4 GPa, with expectations of quantum critical behavior.[5]

Despite theoretical conclusions that the phase transition in MnSi can be fluctuation-induced first order,[6–8] all the physical properties of MnSi studied up to now seem to be continuous across the phase transition line at ambient pressure. Consequently, when a significant change in the temperature dependence of ac susceptibility at the phase transition under high pressure was observed[9,10] (see also Refs. 11 and 12), it was accepted as a manifestation of the existence of a tricritical point and first-order nature of the phase transition in MnSi at low temperatures and high pressures. Nevertheless, some remarkable properties of the phase transition in MnSi are not understood. In particular, some quantities, like the thermal expansion coefficient,[13] heat capacity,[14] and temperature coefficient of resistivity[12] display well-defined shoulders on the high-temperature side of their corresponding peaks at the phase transition, and the nature of these shoulders remains a puzzle.[15] With these unresolved issues, it is appropriate to carry out a systematic investigation of the physical properties of MnSi with the same well-characterized sample.

To this end, heat capacity, electrical resistivity, thermal expansion in magnetic fields, and dc and ac magnetic susceptibility were measured at ambient pressure on a high-quality MnSi single crystal. As will be discussed, the heat capacity, temperature derivative of resistivity, thermal expansion, and magnetic susceptibility behave as if they diverge at the Curie point. Some of these quantities (heat capacity, thermal expansion coefficient, and temperature coefficient of resistivity) display a doublet structure, with sharp and broad components at the phase transition point. We argue that the sharp component is a slightly broadened δ function, corresponding to a first-order phase transition. These results suggest that the magnetic phase transition in MnSi is weakly first order at ambient and low pressure, with a small volume change $\Delta V/V$ of order 10^{-6}, an interpretation that may reverse the prevailing view about the nature of the phase transition in MnSi and that offers a different look at the physics of MnSi at temperatures close to zero and high pressure. Specifically, these conclusions propose that the asymptotic crossing point of the phase transition line and the pressure axis at $T=0$ in MnSi may be a real, continuous quantum critical point.

For these studies, a large single crystal of MnSi was grown by the Bridgman technique from a stoichiometric melt of appropriate quantities of distilled manganese[17] and silicon with purities of 99.99% and 99.999%, respectively. Samples of necessary size and orientation for various experiments were cut by low-power spark erosion. X-ray studies give a lattice parameter $a=4.5598(2)$ Å at 298 K [compare with 4.5603(2) Å (Ref. 18) and 4.559(1) Å (Ref. 19)] and overall mosaicity less than 0.1°. A further indication of crystal quality is reflected in a resistivity ratio $R_{300}/R_{T\to 0}$ equal to 230. From the saturated magnetization at high field at $T=5$ K, the magnetic moment per atom Mn is $0.4\mu_B$, whereas fitting low-field (10 mT) inverse susceptibility data in the range 120–300 K to a Curie-Weiss form gives an effective moment of $2.27\mu_B$ per Mn in the paramagnetic phase. These values agree well with previous reports (see, for instance, Refs. 3 and 20). According to results from the current experiments, the temperature of the phase transition in our sample of MnSi is confined to the limits 28.8–29 K.

Resistivity measurements were carried out by a standard four-probe technique. Heat capacity was measured by an adiabatic calorimeter with an accuracy about of 1% in the temperature interval 4–40 K. dc magnetic susceptibility

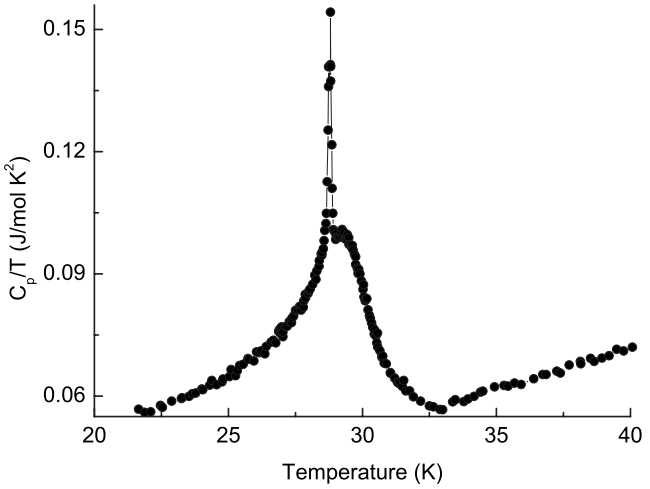

FIG. 1. Temperature dependence of heat capacity divided by temperature near the phase transition in MnSi.

measurements were made in a Quantum Design magnetic properties measurement system; whereas ac susceptibility was measured with a two-coil setup (drive and pickup coils) by a standard modulation technique at a modulation frequency 19 Hz. Linear thermal expansion measurements were performed in a capacitance dilatometer with resolution about 0.05 Å.[21] In all these experiments, temperature was measured by calibrated Cernox thermometers with potential overall resolution and accuracy not worse than 0.05 K.

As seen in Fig. 1, the heat capacity of this crystal of MnSi shows a distinct shoulder on the high-temperature side of the peak that defines the phase transition. This is similar to previous reports.[14] An additional and quite significant feature observed in the current heat capacity data, even given the accuracy and temperature resolution (~0.1 K) of the experiments, is the sharp form of the prominent peak. dc and ac magnetic susceptibility data are plotted in Fig. 2. The unusual shape of $\chi(T)$ in the vicinity of the phase transition is seen in the inset. This form can be considered as the result of a sudden jumplike increase in the magnetic susceptibility at

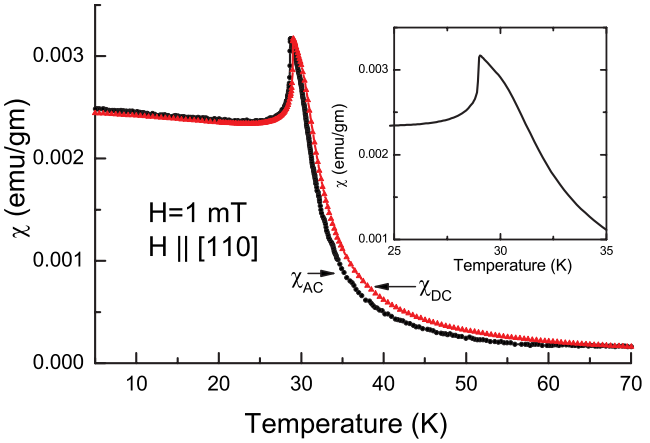

FIG. 2. (Color online) Magnetic susceptibility χ=M/H of MnSi as a function of temperature. Measurements were made in a field of 1 mT. The ac susceptibility data were scaled by simple multiplication.

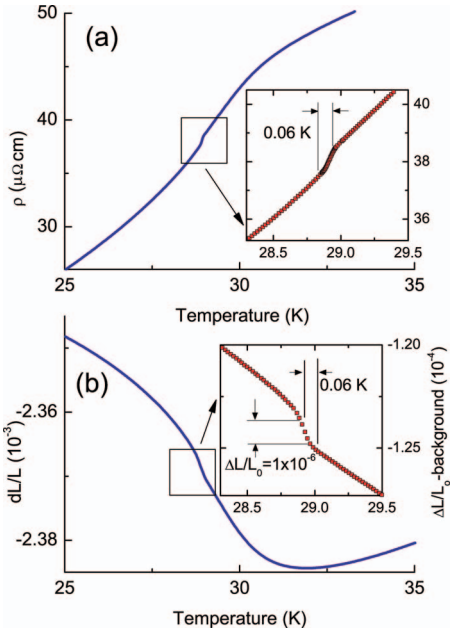

FIG. 3. (Color online) Variations of resistivity (a) and the relative length (b) of the sample of MnSi with temperature. Quasidiscontinuities at the transition point are shown in the insets. For better view a background contribution was subtracted from the original data in the inset of (b). The width of the transition is compatible with the temperature resolution of the experiment. The linear thermal expansion is calculated by integrating the thermal expansion coefficient [Fig. 4(b)].

the transition point. Without this jump, the magnetic susceptibility curve would look like one typical of an antiferromagnetic phase transition.

These nontrivial features of the phase transition in MnSi are reinforced by the high-resolution resistivity and thermal expansion data (Figs. 3 and 4). At first glance, the overall dependence of resistivity of our sample of MnSi does not differ from the numerous previous results; however, a small quasidiscontinuity can be clearly seen at ~28.9 K. The corresponding temperature derivatives of resistivity $d\rho/dT$ can be interpreted as a slightly broadened δ function developing within the continuous anomaly. The same conclusion is valid for the heat capacity and the thermal expansion coefficient $\alpha=(1/L_0)dL/dT$ of MnSi. Surprisingly the last one looks like a mirror image of $d\rho/dT$ (Fig. 4). That obviously indicates spin fluctuations as a dominant factor defining the thermodynamic and transport properties of MnSi the vicinity of the phase transition. So all the mentioned features in the behavior of heat capacity, magnetic susceptibility resistivity, and thermal expansion clearly hint at the first-order nature of the phase transition in MnSi at ambient pressure. Integration of the curve $\alpha(T)$ [Fig. 3(b)] permits one to estimate the relative volume change at the first-order phase transition in MnSi as $\sim 3\times 10^{-6}$. Using the Clausius-Clapeyron equation and taking the slope of the transition line from Ref. 11, we get for the corresponding entropy change $5\times 10^{-4}R$ (R is the gas constant).[22] This value agrees with the direct estimate from the entropy variation through the phase transition, calculated by integration of the heat capacity.

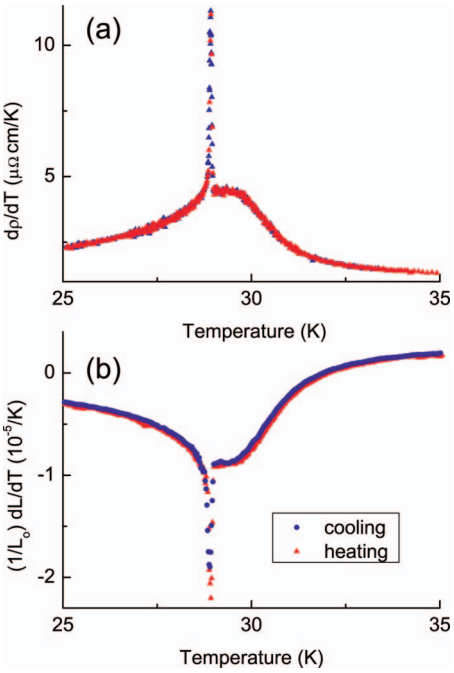

FIG. 4. (Color online) Dependence of temperature coefficient of resistivity $d\rho/dT$ (a) and linear thermal expansion coefficient of MnSi (b) on temperature in the vicinity of the phase transition.

Now we turn to Fig. 5, which illustrates the influence of magnetic field on the thermal expansion coefficient of MnSi. In the case of helical spin ordering, the magnetic field is not directly coupled with the order parameter, and hence no significant effect of magnetic field on the phase transition is expected until the field-induced ferromagnetic state appears at about 0.35 T.[24] But, as seen in Fig. 5, moderate magnetic fields, though they do not change the nature of the phase transition, strongly influence thermal expansion of the paramagnetic phase. At the same time, thermal expansion of the helical phase does not experience even slight change at least up to 0.4 T. That means significant stiffness of the helical spin structure or, in other words, lack of extensive paramagnetic fluctuations in MnSi even at the transition point. This situation most probably signifies a finite value of the order parameter at the phase transition point, therefore indicating a first-order phase transition. Then the fast degradation of the phase transition features between 0.4 and 0.5 T clearly designates formation of the ferromagnetic spin structure.

So the all experimental data obtained lead to the conclusion that the doublet structure of the peaks of the heat capacity, temperature coefficient of resistivity, and thermal expansion coefficient, the jump in the magnetic susceptibility, and

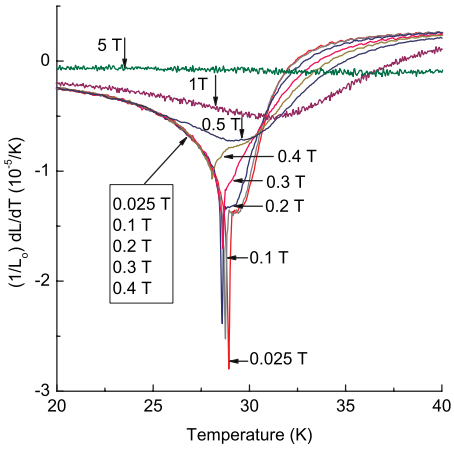

FIG. 5. (Color online) Linear thermal expansion coefficient of MnSi near the phase transition in magnetic fields ($\mathbf{H}\|[110]$). It is seen that moderate magnetic fields up to 0.4 T do not influence thermal expansion of the helical phase.

specifics of the magnetovolume effects at the Curie point in MnSi apparently result from the combination of second-order and first-order features. This would identify the phase transition as weakly first order, likely induced by fluctuations.[6–8,25] Taking into account the data of Ref. 12, where disappearance of the doublet structure in $d\rho/dT$ at pressure was observed at pressures above 0.35 GPa, one may conclude that at higher pressures the transition becomes second order and continues this way down to zero temperature.[27] Consequently, the indicated pressure 0.35 GPa should correspond to the location of a tricritical point. An alternative scenario, which could be discussed in principle, includes the interplay of weak and strong first-order transitions,[28] but it is unclear whether this would generate some sort of pseudotricritical point.

The authors are grateful to I. E. Dzyaloshinski, S. V. Maleev, S. A. Brazovsky, and J. D. Thompson for reading the manuscript and valuable remarks. The technical assistance of J. D. Thompson, V. Sidorov, and V. V. Krasnorussky is greatly appreciated. D. W. and T. A. L. wish to acknowledge the support of the U.S. Department of Energy, Basic Energy Sciences. S.M.S and A.E.P appreciate the support of the Russian Foundation for Basic Research (Grant No. 06-02-16590), the Program of the Physics Department of RAS on Strongly Correlated Systems, and the Program of the Presidium of RAS on Physics of Strongly Compressed Matter. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy, Office of Science.

*sergei@hppi.troitsk.ru

[1] I. Dzyaloshinski, J. Phys. Chem. Solids **4**, 241 (1958).
[2] T. Moria, Phys. Rev. **120**, 91 (1960).
[3] H. J. Williams, J. H. Wernick, R. C. Sherwood, and G. K. Wertheim, J. Appl. Phys. **37**, 1256 (1966).
[4] Y. Ishikawa, K. Tajima, D. Bloch, and M. Roth, Solid State Commun. **19**, 525 (1976).
[5] J. D. Thompson, Z. Fisk, and G. G. Lonzarich, Physica B **161**, 317 (1989).
[6] S. A. Brazovskii, I. E. Dzyaloshinski, and B. G. Kukharenko, Zh.

Eksp. Teor. Fiz. **70**, 2257 (1976) [Sov. Phys. JETP **43**, 1178 (1976)].
[7] I. E. Dzyaloshinski, Zh. Eksp. Teor. Fiz. **72**, 1930 (1977) [Sov. Phys. JETP **45**, 1014 (1977)].
[8] Per Bak and M. Høgh Jensen, J. Phys. C **13**, L881 (1980).
[9] C. Pfleiderer, G. J. McMullan, and G. G. Lonzarich, Physica B **206-207**, 847 (1995).
[10] C. Pfleiderer, G. J. McMullan, S. R. Julian, and G. G. Lonzarich, Phys. Rev. B, **55**, 8330 (1997).
[11] A. E. Petrova, V. Krasnorussky, John Sarrao, and S. M. Stishov, Phys. Rev. B, **73**, 052409 (2006).
[12] A. E. Petrova, E. D. Bauer, V. Krasnorussky, and S. M. Stishov, Phys. Rev. B **74**, 092401 (2006).
[13] M. Matsunaga, Y. Ishikawa, and T. Nakajima, J. Phys. Soc. Jpn. **51**, 1153 (1982).
[14] C. Pfleiderer, J. Magn. Magn. Mater. **226-230**, 23 (2001).
[15] These features have been attributed to a skyrmion texture in the paramagnetic phase of MnSi (Ref. 16).
[16] U. K. Rößler, A. N. Bogdanov, and C. Pfleiderer, Nature (London) **442**, 797 (2006).
[17] Materials Preparation Center, Ames Laboratory, U.S. DOE, Ames, IA, USA, www.mpc.ameslab.gov
[18] J. E. Jorgensen and S. Rasmussen, Powder Diffr. **6**, 194 (1991).
[19] S. Okada, T. Shishido, Y. Ishizawa, M. Ogawa, K. Kudou, T. Fukuda, and T. Lundström, J. Alloys Compd. **317-318**, 315 (2001).
[20] H. Yasuoka, V. Jaccarino, R. C. Sherwood, and J. H. Wernick, J. Phys. Soc. Jpn. **44**, 842 (2006).
[21] G. M. Schmiedeshoff, A. W. Lounsbury, D. J. Luna, S. J. Tracy, A. J. Schramm, S. W. Tozer, V. F. Correa, S. T. Hannahs, T. P. Murphy, E. C. Palm, A. H. Lacerda, S. L. Bud'ko, P. C. Canfield, J. L. Smith, J. C. Lashley, and J. C. Cooley, Rev. Sci. Instrum. **77**, 123907 (2006).
[22] Simple consideration leads to the following approximate formula for the thermodynamic temperature hysteresis: $\delta T = K(\Delta V/V),(dT/dP)$, where K is the bulk modulus, $\Delta V/V$ is the relative volume change, and dT/dP is the slope of the transition line. Then using the numerical values $K=1.37\times10^{6}$ bar (Ref. 23), $\Delta V/V=3\times10^{-6}$, and $dT/dP=1.1\times10^{-3}$ K/bar (Ref. 11), we get for the hysteresis 0.005 K, a rather low value that can hardly be observed in the current conditions.
[23] E. L. Gromnitskaya (unpublished).
[24] S. V. Grigoriev, S. V. Maleyev, A. I. Okorokov, Yu. O. Chetverikov, and H. Eckerlebe, Phys. Rev. B **73**, 224440 (2006).
[25] Striction effects also might be relevant to this case (Ref. 26).
[26] A. I. Larkin and C. A. Pikin, Sov. Phys. JETP **29**, 891 (1969).
[27] In principle two tricritical points may exist on the transition line for materials like MnSi; however, in this case a competing spin order should be observed (Ref. 7).
[28] T. Vojta and R. Sknepnek, Phys. Rev. B **64**, 052404 (2001).