On the nature of the phase transition in the itinerant helimagnet MnSi

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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. Conclusions drawn from these experiments question prevailing views on the phase diagram of MnSi and propose that the phase transition under study becomes second order at high pressure and low temperature.

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Physical properties of the cubic intermetallic compound MnSi, a weak itinerant helimagnet with Dzyaloshinski – Moria interaction [1, 2] have been studied extensively for more than for 40 years since discovery of its spin ordered phase at the 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 of MnSi was greatly enhanced by the finding that the temperature of the magnetic phase transition decreased with pressure and tended to zero at about 1.4 GPa with expectations of the quantum critical behavior [5].

Despite theoretical conclusions that phase transition in MnSi can be fluctuation-induced first-order [6, 7, 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 was observed in the temperature dependence of ac susceptibility at the phase transition under high pressure was found [9, 10] (see, also [11, 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 thermal expansion coefficient [13], heat capacity [14], temperature coefficient of resistivity [12] display a 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 systematic investigation of physical properties of MnSi with the same well-characterized sample.

To this end, heat capacity, electrical resistivity, thermal expansion in magnetic fields, dc and ac magnetic susceptibility were measured at ambient pressure on a high quality MnSi single crystal. As will be discussed, the heat capacity and 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 delta function, corresponding to a first-order phase transition. These new results suggest that the magnetic phase transition in MnSi is weakly first order at ambient and low pressure, with small volume change $\Delta V/V$ of order $10^{-6}$, and becomes second order at pressures higher than 0.35 GPa, an interpretation that reverses the prevailing view about the nature...
of the phase transition in MnSi and that suggests a new look at the physics of MnSi at temperatures close to zero and high pressure. Specifically, these conclusions suggest that the asymptotic crossing point of the phase transition line and the pressure axis at T=0 in MnSi is 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 and overall mosaicity less than 0.1°. A further indication of crystal quality is reflected in a resistivity ratio $R_{300}/R_{T \rightarrow 0}$ equal to 230. From the saturated magnetization at high field and $T=5K$, magnetic moment per atom Mn is 0.4 $\mu_B$, whereas, fitting low field (100 Oe) 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. According to results from the current experiments, the temperature of the phase transition in our sample of MnSi is confined to the limits 28.7-29 K.

Resistivity measurements were carried out by a standard four-probe technique. To avoid complications connected with possible contamination of the sample surface during cutting, polishing and etching, we use a small splinter of the MnSi crystal with dimensions of about 2 $\times$ 0.7 $\times$ 0.5 mm$^3$. Heat capacity was measured by adiabatic calorimeter with an accuracy about of 1% in the temperature interval 4-40 K. The indicated accuracy can be achieved only with temperature steps no less than 0.5 K, and to increase the resolution several subsequent runs were performed. DC magnetic susceptibility measurements were made in a Quantum Design Magnetic Properties Measurement System; whereas, ac susceptibility was measured with a two-coil set up (drive and pick up 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 [18]. In all these experiments, temperature was measured by the calibrated Cernox thermometers with potential overall resolution and accuracy not worse than 0.05 K.

As seen in Fig.1 and Fig.2 the heat capacity and the temperature coefficient of resistivity of this crystal of MnSi show well-defined shoulders on the high temperature side of the peaks that define the phase transition. This is similar to previous reports [12 [14]. A new and quite significant feature observed in the current heat capacity data, even given the accuracy and temperature resolution ($\sim 0.2$ K) of the experiments, is the sharp form of the prominent peak (Fig.1). The temperature coefficient of resistivity shows the same trend within the greater scattering of the data (Fig.2).

DC and ac magnetic susceptibility data are plotted in Fig.3(a) and the temperature derivative is given in Fig.3(b).
The unusual shape of $\chi(T)$ in the vicinity of the phase transition is seen in the inset of (a). This form can be considered as the result of a sudden jump-like increase in the magnetic susceptibility at the transition point, which well demonstrated in the Fig.3(b). Without this jump, the magnetic susceptibility curve would look like one typical of antiferromagnetic phase transition.

These indications for the first-order component of the phase transition in MnSi are reinforced the high resolution thermal expansion data (Fig.4). The existence of slightly broadened delta function developing within the continuous anomaly of the thermal expansion coefficient $\alpha = (1/L_0)dL/dT$ clearly exposes the first-order nature of the phase transition in MnSi at ambient pressure. Integration of the curve $\alpha(T)$ (inset of Fig.4) permits an estimate the relative volume change at the first-order phase transition in MnSi as $\sim 3 \times 10^{-6}$.

Now we turn to Fig.5 which illustrates the influence of magnetic field on the thermal expansion coefficient of MnSi. In case of the helical spin ordering, 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 3500 Oe [19]. As seen in Fig.6, moderate magnetic fields up to 250 Oe even sharpen the phase transition (probably a result of forming a single domain sample) and obviously do not change its nature for fields less than 4000 Oe, as anticipated. We point out that any possible effects of reorientations of the helical structure and emerging conical magnetic structure do not reveal themselves in Fig.5, but the fast degradation of the first order transition between 3000-4000 Oe clearly indicates formation of the ferromagnetic spin structure.

These results lead to the conclusion that the doublet structure of the peaks of the heat capacity, temperature coefficient of resistivity, thermal expansion coefficient and the jump in the magnetic susceptibility at the Curie point in MnSi are result from the combination of second-order and first-order features. This identifies the phase transition as weakly first order, most likely induced by fluctuations [6, 7, 8, 20]. Taking into account data [12], where disappearance of the doublet structure in $d\rho/dT$ at pressure was observed above 0.35 GPa, we conclude that at higher pressures the transition becomes second order and continues this way down to zero temperature. Consequently, the indicated pressure 0.35 GPa should correspond to location of a tricritical point. The above conclusions completely reverse the widely accepted
FIG. 6: 3D plot of linear thermal expansion coefficients of MnSi near the phase transition in magnetic fields.

view of the phase diagram of MnSi and affirm that the real, continuous quantum-critical point should be situated at the transition line at $T \to 0$ \cite{22, 25}.

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\[ \text{FIG. 6: 3D plot of linear thermal expansion coefficients of MnSi near the phase transition in magnetic fields.} \]

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