Stability of antiferromagnetism at high magnetic fields in Mn_3Si

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We report on low-temperature measurements of the specific heat, resistivity, and magnetization of the itinerant antiferromagnet Mn_3Si. The stability of the magnetic state up to 14 T inferred from the invariance of these bulk properties is incompatible with the itinerant magnetism expected for a conventional Fermi liquid.

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Weakly magnetic transition-metal compounds with small ordered moments and low transition temperatures are usually well described as a Fermi liquid with weakly exchange-split Fermi surface, where special topological features of the Fermi surface are ignored.[1] Recent experimental studies on weakly ferromagnetic metals shed doubts on the validity of this assumption.[2,3] It is also an open issue if magnetic metals with large ordered moments and small ordering temperature, that are more akin to local-moment insulators, may also be described on the basis of Fermi-liquid theory. Insight into this question may be sought in the dominant energy scales controlling the magnetic ordering temperature T_N of an itinerant antiferromagnet. In a Fermi liquid low ordering temperatures result from strong coupling of the magnetization at ordering wave vector **Q** with heavily damped spin fluctuations.[1] On the other hand, in the isotropic Heisenberg model low ordering temperatures result from weak exchange coupling of localized magnetic moments. The energy scale and nature of the magnetic ordering compared to the mode-mode or local-moment coupling, respectively, are hence fundamental to magnetism in solids.

The polarization of a magnetic state in a magnetic field allows to probe the relevant coupling strengths. In fact, a very large number of transition-metal compounds are known in which ordering temperatures of the order of 20 K are related to a high sensitivity to magnetic field of a few tesla regardless of whether they are better described in terms of Fermi-liquid theory or the Heisenberg model.[4–6] In this paper, we report on an experimental investigation in which we employ the effect of high magnetic field ($\mu_B H \approx k_B T_N$) on the bulk magnetization M, specific heat C, and electrical resistivity ρ of a cubic metallic antiferromagnet Mn_3Si, to study the strength of the coupling of the uniform mode ($\mathbf{q}=0$) with the ordering wave vector **Q**. The observed complete absence of a field dependence is surprising, because it either suggests an isotropic Fermi liquid in which the mode-mode coupling is absent or an isotropic Heisenberg magnet in which the moment coupling is exceptionally strong, despite low T_N. From either point of view the simplicity of Mn_3Si in terms of its crystallographic structure and magnetic order challenges the present day understanding of metallic antiferromagnetism.

Recent years have witnessed an increased interest in the magnetic and metallic properties of Heusler transition-metal compounds[7–10] to which Mn_3Si belongs. Ternary members of this class of materials display a wide variety of different behaviors such as disorder induced non-Fermi liquid,[9,10] half-metallic magnetic[8] and semiconducting ground states.[7] High ferromagnetic ordering temperatures of several hundred kelvin are also frequent.

Mn_3Si crystallizes as $Mn_I Mn_{II,2} Si$, DO3 ordered Fe_3Al, and with space group $Fm3m$.[11–13] The crystal structure may be described in terms of four fcc sublattices located at (0,0,0) for Mn_I, (1/4,1/4,1/4) and (3/4,3/4,3/4) for the Mn_{II} and (1/2,1/2,1/2) for Si. The Mn_I sites are hence surrounded by eight Mn_{II} nearest neighbors and have an O_h point symmetry. The Mn_{II} are on the other hand surrounded by four Mn_I nn and four Si nn, respectively. The structural symmetries encountered in Mn_3Si are extremely simple, so that studies of polycrystalline samples already supply key information.

Mn_3Si is metallic and develops incommensurate antiferromagnetic order below $T_N \approx 25$ K along $\mathbf{Q}=0.425\ \mathbf{a}^*_{111}$, where $\mathbf{a}^*_{111}$ denotes the reciprocal lattice vector along (111).[12,13] The magnetic order is best described as a sequence of ferromagnetic planes Mn_{II}-Mn_I-Mn_{II}, separated by a Si plane, all equidistant at $d=3.304$ Å. The ordered moments $\mu_I = 1.7\mu_B$ and $\mu_{II} = 0.19\mu_B$ are oriented in-plane, so that the sequence of planes form a short-wavelength double helix. The ordering wave vector **Q** is weakly T dependent without hint for a further change of magnetic structure.[13] The T dependence of the Mn_I moment follows a Brillouin function ($S=1/2$) for $T<T_N$, i.e., the transition is second order, the magnetic state essentially isotropic and a sizeable ordered moment forms already closely below T_N.[13] The key features of the magnetic structure are that (i) the order is essentially antiferromagnetic, (ii) there is no magnetic site frustration, (iii) there is no appreciable magnetic anisotropy, and (iv) the amplitude of the moments varies strongly by nearly an order of magnitude along **Q**.

Inelastic neutron scattering in Mn_3Si shows excitation spectra that are unusual in a number of ways. For $T>T_N$ large amplitude, large coherence length antiferromagnetic spin fluctuations are observed.[14,15] These fluctuations exhibit a **q** dependence that is nearly three orders of magnitude stronger between $\mathbf{q}=0$ and **Q** than the conventional Lorentzian dependence as expected for an isotropic Fermi liquid. For $T<T_N$ very slow antiferromagnetic spin waves with velocity $c_l \approx 37$ meV Å ≈ 85 km/s around **Q** below 6 meV contrast fast antiferromagnetic spin waves near the zone boundary above 6 meV, where $c_h \gg c_l$.[14] We note, however, that neither of these excitations qualify properly as propagating

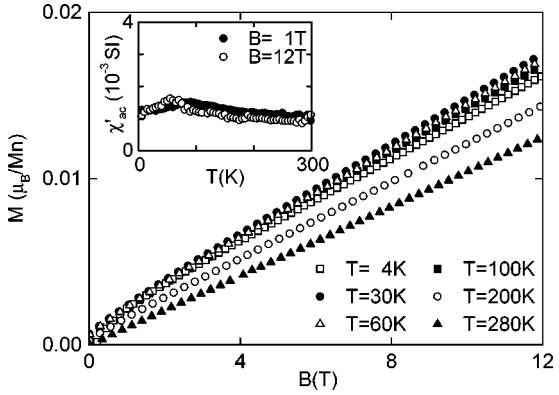

FIG. 1. Isothermal magnetization of Mn_3Si as function of magnetic field. The inset displays the T dependence of the ac susceptibility at $B=1$ T and 12 T. The average magnetic moment at 12 T is nearly two orders of magnitude smaller than the ordered magnetic moment. The linear field dependence underscores the apparent lack of a coupling between the uniform magnetic field and the ordering wave vector **Q**.

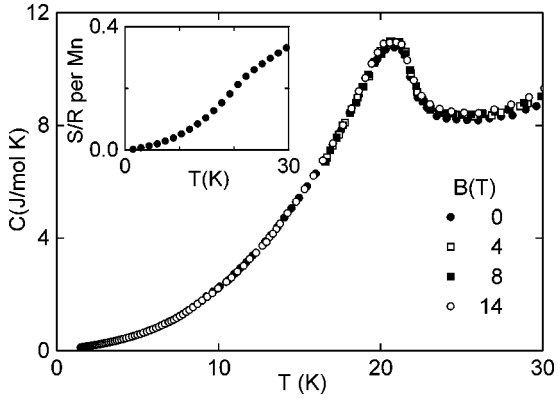

FIG. 2. Specific heat as a function of temperature at finite field up to 14 T. The inset displays the entropy as calculated from the measured specific heat. No magnetic-field dependence is observed apart from a very weak increase of the order of 3% above T_N. The entropy significantly exceeds that of typical weak itinerant magnets.

spin waves, due to their extreme broadening of $\delta\omega/\omega\approx 1$, which contrasts the spin-wave broadening conventionally observed in itinerant magnets having $\delta\omega/\omega\approx 0.001-0.1$.[16]

For our studies polycrystalline samples were synthesized from stoichiometric amounts of high-purity starting materials ($5N$ Mn, $6N$ Si) by Ar arc-melting. Samples were melted several times to promote homogeneity and subsequently annealed at 700 °C for 7 days. No measurable weight loss was observed. $\Theta-2\Theta$ powder diffraction suggested that the samples were single phased where the lattice constant $a=5.722$ Å agreed with the published value. Careful scans across polished faces of the polycrystals using microprobe analysis eventually revealed $<1\%$ of a second phase of Mn_5Si_3. This Si-rich phase may be related to a peritectic decomposition of Mn_3Si above 850 °C. Neither the polycrystalline nature of the samples nor tiny contributions from the second phase of Mn_5Si_3, for which antiferromagnetic order is very sensitive to magnetic field,[4] alter the key observations and conclusions reported here.

Shown in Fig. 1 is the magnetization M as a function of magnetic field B as measured in a conventional vibrating sample magnetometer. Up to 12 T, the highest field studied, only a tiny portion of the ordered moment of less than 3% is recovered. The magnetic response is linear in B and characteristic of a simple Pauli paramagnetic state over the entire B and T range investigated. The associated susceptibility as measured by a low-frequency technique is low even in the immediate vicinity of T_N (inset of Fig. 1). This contrasts the T dependence of the ordered Mn_I moment for $T<T_N$, which reaches $\sim 70\%$ already a few K below T_N, i.e., a large increase of M is anticipated for a field induced change of moment orientation just below T_N where the ordering energy is low as compared to the field energy.

The specific heat $C(T)$ is dominated by a pronounced anomaly just below T_N (Fig. 2). For $T\rightarrow 0$ we observe $C(T)\approx\gamma T+\beta T^3$, where $\gamma\approx 69$ mJ/mol K^2 and $\beta\approx 1.5\times 10^{-3}$ J/mol K^4 is consistent with the zero-field behavior reported before.[11] The rounding of the anomaly in $C(T)$ may be due to the polycrystalline nature of the samples studied here. Up to a field of 14 T we do not observe any variation of $C(T)$ within the resolution of the experiment, apart from a slight increase above T_N. Any anisotropy would broaden the anomaly of $C(T)$ considerably since T_N would change much less for the hard direction compared with the easy direction. Moreover, neither the specific heat nor the neutron-scattering spectra[14] show evidence of an antiferromagnetic gap over the experimental range, i.e., if there is a gap it is well below 1 K and much smaller than our field range, thus underscoring the isotropic nature of the magnetic state.

The T^3 dependence of $C(T)$ may not be accounted for by lattice contributions, which are negligibly small up to 30 K as estimated from the Debye temperature $\Theta_D=454$ K, where $\beta_D\approx 2.1\times 10^{-5}$ J/mol K^4.[17] More surprisingly, an estimated contribution of local-moment antiferromagnetic spin waves to $C(T)$ given by $\Delta C_{sw}(T)=\beta_{sw}T^3$ ($\beta_{sw}\approx 1.65\times 10^{-5}$ J/mol K^4) is two orders of magnitude smaller than experiment, where a conservative estimate of an average $J\approx 1.9$ meV, derived from the experimentally measured low-T spin-wave velocity c_l,[14,18] corresponds to a mean-field ordering temperature $T_N\approx 30$ K, in broad quantitative agreement with experiment. This highlights the presence of strong dynamics in the metallic state challenging conventional models.

The total entropy $S(T)$ (inset of Fig. 2) of the normal metallic state above T_N and the magnetic order are computed from the experimental data of $C(T)$. Near T_N the entropy reaches $R\ln 2$ per Mn_3Si formula unit, i.e., S is at most one third of the entropy expected of three localized spins of 1/2, where the lattice contribution is less than 5%. On the other hand, $S(T)$ exceeds that of typical weakly ferromagnetic transition-metal compounds by at least an order of magnitude.[1,19] This property fundamentally questions the consistency of the metallic state with conventional spin-fluctuation theory in which paramagnons essentially account for the entropy.[1]

We finally turn to the resistivity $\rho(T)$ (Fig. 3), which displays a broad shoulder near 50 K.[11] The maximum in $d\rho/dT$

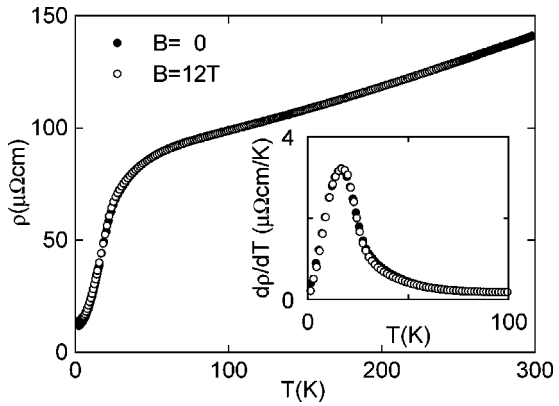

FIG. 3. Temperature dependence of the electrical resistivity $\rho(T)$ at zero magnetic field and $B=12$ T. The broad shoulder around 50 K indicates the loss of a dominant scattering mechanism associated with the antiferromagnetic ordering temperature $T_N \approx 23$ K. The inset displays the derivative of the resisitivity $d\rho/dT$, where the maximum falls just below T_N.

near T_N (inset of Fig. 3) corresponding to the shoulder in $\rho(T)$ shows that it is of electronic origin and closely related to the antiferromagnetic spin fluctuations seen in neutron scattering well above T_N. For $T<10$ K, $\rho(T)=\rho_0 + AT^2$ ($\rho_0 \approx 11\ \mu\Omega$ cm, $A \approx 0.115\ \mu\Omega$ cm/K^2) enters a quadratic dependence, where the residual resistivity ρ_0 is low, corresponding to a low level of defects. The Kadowaki-Woods ratio A/γ^2 is empirically consistent with other materials.[20] As for $C(T)$ and $\chi(T)$, the features of $\rho(T)$ are not sensitive to magnetic fields up to 12 T, even in the immediate vicinity of T_N where the magnetic field energy is very large versus the energy gain of the magnetic order.

Although numerous itinerant electron magnets display large ordered moments, e.g., $SrRuO_3$,[21] one needs to consider the possibility that Mn_3Si has in fact localized moments for the Mn_I sublattice. However, our estimate of $J \approx 1.9$ meV given above predicts a large response of the Mn_I moments in a magnetic field, contrary to what is observed. These considerations and the specific heat clearly rule out a Heisenberg model as being even remotely suitable to explain the properties observed here.

The strong interplay of the resistivity and the magnetism and the small change of entropy at T_N as well as the inelastic neutron-scattering spectra[14] unambiguously show that the magnetic order in Mn_3Si is indeed intimately connected with the metallic state. Moreover, electronic structure calculations indicate that the *d* electrons form the conduction electron bands.[8,22,23] However, the magnetization of Mn_3Si is exceptional because it is *linear* over the entire field and temperature range studied. This shows that there is no mode-mode coupling between $\mathbf{q}=0$ and $\mathbf{Q}$ despite the low ordering temperature.[24] The invariance of $C(T)$ and $\rho(T)$ with B supports the latter point. Yet, the absence of mode-mode coupling in an itinerant antiferromagnet drastically contrasts the basic assumptions of a spin-polarized Fermi liquid, namely, that the mode-mode coupling is $\mathbf{q}$ independent.[1]

Measurements of $\rho(T)$ as function of pressure show that T_N increases as $dT_N/dp \approx 0.4$ K/kbar, in agreement with the Ehrenfest relation[11,17] and many other Heusler compounds.[26] This contrasts the majority of weakly magnetic transition metal, actinide, and lanthanide compounds.[25] The *p* dependence suggests a possible link with two further unsettled condensed-matter problems: (i) the magnetic and metallic state related to the quantum phase transition on the ''left-hand side'' of the Doniach phase diagram, i.e., for low exchange coupling *J* and nearly localized moments[27] and (ii) the metallic state on the underdoped side of the superconductivity dome of the cuprates.[28] Our study suggests that these regimes are not compatible with Fermi-liquid theory.

For the remainder we consider the possible origin of deviations from Fermi-liquid behavior in Mn_3Si. To date, special features of the Fermi-surface topology have not been considered in a phenomenological, quantitative evaluation of this model.[1] But electronic structure calculations show that the Fermi surface of Mn_3Si is exceptional in two ways: (i) it is strongly nested so that the magnetic order may be understood as highly anharmonic spin-density wave (SDW)[22,23] and (ii) in the spin-polarized state the minority density of states of the Mn_I and the Mn_{II} are strongly gapped and nearly gapped, respectively, as for half-metallic magnetism.[8] Consideration of these features suggest fundamental differences of metallic magnetism in Mn_3Si with conventional theory.

For a SDW state with a nested, multisheeted Fermi surface an abundance of interband excitations is expected. This would be consistent with many features of the unusual inelastic neutron scattering spectra of Mn_3Si as noted before,[14] including a damping mechanism other than the particle-hole continuum and spin-wave interactions, e.g., a $\mathbf{q}$-dependent mechanism in the vicinity of $\mathbf{Q}$.[14,15] First-principles calculations of excitation spectra in metals support this point in general, as they are extremely sensitive to details of the band structure giving way to interband transitions.[29] Further, it is possible to show that the imaginary part of the experimentally measured dynamical susceptibility of the low-energy modes corresponds to an equation of motion that describes retarded, nonlocal diffusion.[30] This behavior is far removed from a propagating spin wave and classical spin-wave models are clearly not applicable.

It has long been pointed out that the antiferromagnetic order and the excitation spectra of Mn_3Si share many features with Cr,[14] where a SDW competes with the charge-density wave instability and lattice instability.[31,32] The amplitude variation of the ordered moment in Mn_3Si by one order of magnitude may be a strong hint at the vicinity to a charge-density wave instability. We, therefore, speculate if an abundance of charge-density fluctuations suppresses T_N. The metallic state may then be ultimately better described from the point of view of incipient spin-charge separation common to low-dimensional systems,[33] which, however, in our case would occur in a three-dimensional state. In this respect our experiments may also provide an important clue to the long-standing issue of magnetic ordering in Cr, where T_N is so large that the complete lack of field dependence does not seem a surprise for the highest field strengths of the order of 20 T studied to date.[34]

The second important topological feature of the electronic structure of Mn_3Si is that the minority bands in the spin-

polarized state are gapped at the Fermi level.[8] Thus low-energy particle-hole excitations do not involve a spin flip and are hence insensitive to magnetic field. Quasiparticle excitations involved here carry charge but no spin alongside nonquasiparticle excitations.[35] This state is referred to as half-metallic magnetism, for which the absence of a magnetic-field dependence, as observed here, is the key evidence. Besides the electronic structure calculations for Mn_3Si the class of Heusler and semi-Heusler systems such as Fe_2MnSi (Ref. 8) have long been suspected to supply prime candidates for half-metallic magnetism.[35] However, Mn_3Si represents the first experimental candidate of an antiferromagnetic half metal.[36]

The highly unusual combination of magnetic, structural, and metallic properties of Mn_3Si allows us to conclude that the microscopic underpinning of the overall spectrum of low-lying excitations is radically different from that conventionally assumed in the Fermi-liquid theory or the Heisenberg model. This calls for an alternative theoretical input possibly related to incipient spin-charge separation or half-metallic magnetism.

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[1] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985); G.G. Lonzarich and L. Taillefer, J. Phys. C **18**, 4339 (1985).
[2] C. Pfleiderer, J. Magn. Magn. Mater. **226-230**, 23 (2001).
[3] C. Pfleiderer *et al.*, Nature (London) **414**, 427 (2001).
[4] H.J. Al-Kanani and J.G. Booth, J. Magn. Magn. Mater. **140-144**, 1539 (1995).
[5] E. Stryjewski and N. Giordano, Adv. Phys. **26**, 487 (1977).
[6] *Handbook of the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, Amsterdam, 2001).
[7] J. Kübler *et al.*, Phys. Rev. B **28**, 1745 (1983); P.J. Webster, Contemp. Phys. **10**, 559 (1969).
[8] S. Fujii *et al.*, J. Phys. Soc. Jpn. **64**, 185 (1995).
[9] Y. Nishino *et al.*, Phys. Rev. Lett. **79**, 1909 (1997); Ye Feng *et al.*, Phys. Rev. B **63**, 165109 (2001).
[10] A. Slebarski *et al.*, Phys. Rev. B **62**, 3296 (2000).
[11] G.I. Kalishevich *et al.*, Sov. Phys. Solid State **16**, 1151 (1974).
[12] E.N. Babanova *et al.*, Sov. Phys. Solid State **17**, 616 (1975).
[13] S. Tomiyoshi *et al.*, J. Phys. Soc. Jpn. **39**, 295 (1975).
[14] S. Tomiyoshi *et al.*, Phys. Rev. B **36**, 2181 (1987).
[15] Y. Yamaguchi *et al.*, Physica B **213&214**, 363 (1995).
[16] M. F. Collins, *Magnetic Critical Scattering* (Oxford University Press, Oxford, 1989).
[17] S.M. Barmin, and A.A. Sevast'yanov, Sov. Phys. Solid State **26**, 917 (1984).
[18] L. J. de Jongh and A. R. Miedema, *Experiments on Simple Magnetic Model Systems* (Taylor & Francis, London, 1974).
[19] R. Viswanathan, J. Phys. F: Met. Phys. **4**, L57 (1974).
[20] K. Kadowaki and S.B. Woods, Solid State Commun. **58**, 507 (1986).
[21] D.J. Singh, J. Appl. Phys. **79**, 4818 (1996).
[22] A. Vlasov *et al.*, Sov. Phys. Lebedev. Inst. Rep. **12**, 5 (1990).
[23] P. Mohn and E. Supanetz, Philos. Mag. B **78**, 629 (1998).
[24] Nonlinearities of $M(B)$ derive from higher-order contributions to the free energy, which imply in the unconditional probability distribution of the partition function the coupling of magnetization modes $\mathbf{m}(\mathbf{q},\omega)$ (Ref. 1).
[25] See, e.g., *Conference on Non-Fermi Liquid Behavior in Metals at the Institute for Theoretical Physics, Santa Barbara, CA*, special issue of J. Phys.: Condens. Matter **8**, 9675 (1996).
[26] K. Shirakawa *et al.*, J. Magn. Magn. Mater. **70**, 421 (1987).
[27] S. Doniach, Physica B & C **91**, 213 (1977).
[28] W. Liang, J. Phys.: Condens. Matter **10**, 11 365 (1998).
[29] J.F. Cooke, J. Appl. Phys. **50**, 7439 (1979).
[30] J. Bœuf and C. Pfleiderer (unpublished); D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (W. A. Benjamin, Reading, MA, 1975).
[31] E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).
[32] C.R. Fincher, Jr. *et al.*, Phys. Rev. B **24**, 1312 (1981).
[33] A. Schofield, Contemp. Phys. **40**, 95 (1999).
[34] Z. Barak *et al.*, J. Phys. F: Met. Phys. **11**, 915 (1981).
[35] V.Y. Irkhin and M.I. Katsnel'son, Phys. Usp. **37**, 659 (1994).
[36] H. van Leuken and R.A. de Groot, Phys. Rev. Lett. **74**, 1171 (1995).