Magnetic, Thermal, and Transport-Properties of Uir2si2

Dirkmaat, A.J.; Endstra, T.; Knetsch, E.A.; Nieuwenhuys, G.J.; Mydosh, J.A.; Menovsky, A.A.; Deboer, F.R.; Tarnawski, Z.

Publication date
1990

Published in
Physical Review. B, Condensed Matter

PHYSICAL REVIEW B VOLUME 41, NUMBER 4 1 FEBRUARY 1990

Magnetic, thermal, and transport properties of UIr_2Si_2

A. J. Dirkmaat, T. Endstra, E. A. Knetsch, G. J. Nieuwenhuys, and J. A. Mydosh
Kamerlingh Onnes Laboratorium der Rijksuniversiteit Leiden, 2300 RA Leiden, The Netherlands

A. A. Menovsky, F. R. de Boer, and Z. Tarnawski*
Natuurkundig Laboratorium, Universiteit van Amsterdam, 1000 HE Amsterdam, The Netherlands
(Received 26 June 1989; revised manuscript received 5 October 1989)

Magnetization, resistivity, and specific-heat measurements have been performed on a high-quality single crystal of (tetragonal) UIr_2Si_2. In all physical quantities anomalies are found related to an antiferromagnetic transition at $T_N = 4.9$ K. No superconductivity was observed down to 40 mK. The magnetization and resistivity are strongly anisotropic. Below 4.9 K a metamagnetic transition occurs along the c axis at a field of 2.2 T. For $T > T_N$ the specific heat yields an electronic constant γ of 105 mJ/mol K^2, whereas below T_N a much higher value (290 mJ/mol K^2) is found. The magnetic entropy related to the transition is too small to be explained by an ordering of localized moments. A crystal-electric-field level scheme involving three singlets and a doublet is used in an attempt to interpret the data, but clearly effects of the heavy electrons and their hybridization must be considered.

Although magnetism is more common than superconductivity in U-based, intermetallic compounds,[1] there nevertheless remains much interesting and topical physics concerning the nature of the magnetic ordering. For example, the following questions arise: (i) How should one describe the (anti)ferromagnetic order, with (reduced) local moments or as being itinerant? (ii) How is the correlated-electron state affected by the ordering? And (iii) do crystal-electric-field (CEF) effects play a role? Here we report macroscopic experiments on a new "light" heavy-fermion system UIr_2Si_2, which exhibits a reduced-moment antiferromagnetic transition at $T_N = 4.9$ K, a metamagnetic transition below T_N around 2.2 T, and an increase in the γ value of the specific heat below T_N. The two former properties are typical for the magnetic heavy-fermion systems while the latter is not; usually γ decreases.[2] We also illustrate the usefulness of a CEF scheme for qualitatively explaining the data. The purpose of this Rapid Communication is to introduce the UIr_2Si_2 material and hopefully stimulate additional theoretical and experimental efforts on CEF effects in strongly correlated electron systems along with more microscopic measurements such as neutron scattering, muon spin resonance, and optical reflectivity.

Among the existing UT_2Si_2 compounds (where T is a transition metal), only those with T = Ir or Pt crystallize in the $CaBe_2Ge_2$ structure. All others have the $ThCr_2Si_2$ structure. This may be the reason why UIr_2Si_2 has been rather neglected in the study of new heavy-fermion materials.[3-5] In our preliminary study on polycrystalline material, an antiferromagnetic transition was observed near 5.5 K.[3] We now present the results of magnetization, resistivity, and specific-heat measurements performed on a high-quality, single-crystalline sample of UIr_2Si_2 which show that this system possesses some unusual properties and to be a good test for CEF-like effects.

The single crystal was grown employing a "tri-arc" Czochralski method.[6] The quality was demonstrated by x-ray analysis, electron probe microanalysis, and optical microscopy, i.e., no second phases were detected. The lattice parameters are $a = 4.0867$ Å and $c = 9.8291$ Å. Measurements of the magnetization were performed via a vibrating sample magnetometer up to 5 T and extended to 35 T with an induction method and a pulsed magnet. For the resistivity, use was made of a four-point dc technique for temperatures from 40 mK to room temperature. The specific heat was determined between 1.92 and 30 K by an adiabatic pulse method.

The temperature-dependent susceptibility $\chi(T) \equiv (M/B)$, measured in a field of 1 T, is shown in Fig. 1(a) for fields applied along the a and c axes. It is highly anisotropic, with the maximum in χ along the c axis greatly exceeding that along the a axis. These maxima occur at slightly different temperatures ($T_{max}^{(c)} = 4.8$ K; $T_{max}^{(a)} = 5.3$ K). As will be discussed below, this discrepancy has a physical significance within the model proposed to qualitatively describe the data. The temperature dependence of the susceptibility in both directions suggests the occurrence of a transition to an antiferromagnetic state. $\chi(T)$ along the c axis approaches a constant value at the lowest measurement temperature of 1.7 K [see inset of Fig. 1(a)], whereas along the a axis it still decreases.

Neither susceptibilities obey a Curie-Weiss law in any temperature regime, as can be seen in Fig. 1(b). The susceptibility along the c axis, however, can be reasonably well described in terms of a temperature-independent (enhanced) Pauli susceptibility χ_0 plus a Curie-Weiss contribution χ_{CW} from 300 K down to 7 K, with $p_{eff} = 1.03$, $\theta_{CW} = 1.84$ K, and $\chi_0 = 1.76 \times 10^{-3}$ emu/mol [solid line in Fig. 1(a)]. A similar description of the susceptibility [dashed line in Fig. 1(a)] along the a axis is not as successful over such a wide temperature range. A best-fit procedure above 100 K yields parameters comparable to the ones obtained above. Therefore, at the highest temperatures, the moment is only weakly anisotropic and the interactions are practically negligible. The Pauli paramagnetic contributions are quite comparable to those found for several other 1:2:2 uranium germanides.[7-10]

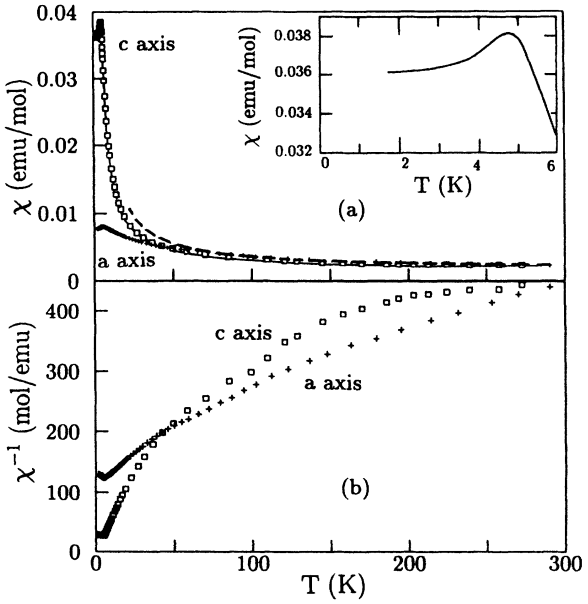

FIG. 1. (a) Magnetic susceptibility vs temperature for UIr_2Si_2. The solid (c axis) and dashed (a axis) lines represent the two-contribution fit; see text. In the inset the susceptibility along the c axis is shown in detail near its maximum. (b) The inverse susceptibility vs temperature.

The small positive Curie-Weiss temperature and the deviations observed along the a axis below 100 K might be caused by a (weak) temperature dependence of χ_0.

The most salient feature in the field dependence of the magnetization at $T=1.66$ K, shown in Fig. 2, is the sharp metamagnetic transition at $B_M=2.2$ T which is observed only along the c axis. Thus, in UIr_2Si_2 the metamagnetic transition occurs at a field value which facilitates investigation of the metamagnetic state. In comparison, for URu_2Si_2 the metamagnetic transition occurs in a field of 34 T.[11] The steps which were observed at the metamagnetic transition of URu_2Si_2 (Ref. 11) are absent here, even when the field intervals in our measurement are greatly reduced. Such a transition clearly shows that the material has an antiferromagnetically ordered low-field ground state. In contrast, along the a axis a smooth

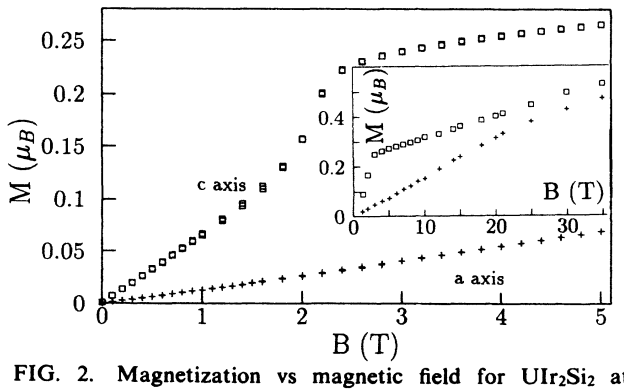

FIG. 2. Magnetization vs magnetic field for UIr_2Si_2 at $T=1.66$ K. Note the fully reversible metamagnetic transition at 2.2 T along the c axis. In the inset the measurement is shown over the entire field range.

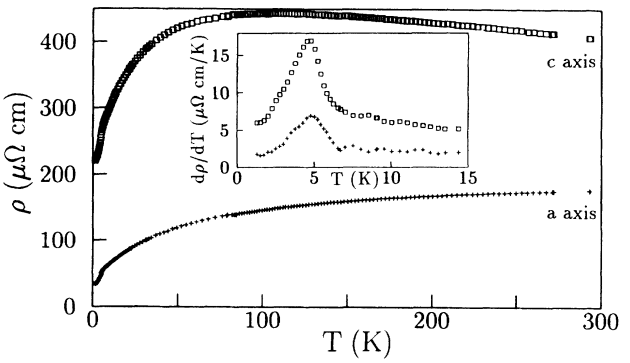

FIG. 3. Resistivity vs temperature for UIr_2Si_2. In the inset the temperature derivatives of the resistivities are shown at low T.

(nearly linear) field dependence of the magnetization is found over the entire field range of 0–35 T (see inset in Fig. 2). The magnetizations along the a and the c axes, though not saturated, approach each other at the maximum available field, reaching a rather small value of approximately $0.5\mu_B$.

The resistivities measured along the two crystallographic directions are given in Fig. 3. They differ both in magnitude and in temperature dependence. Along the c axis, the resistivity increases with decreasing temperature between 300 and 105 K. At the latter temperature, a broad maximum is found with a very high value of 450 $\mu\Omega$ cm. The decrease observed below this temperature is not monotonic, but exhibits a knee at around 6 K corresponding to a maximum in $d\rho/dT$ at 4.8 K (see inset in Fig. 3). Along the a axis there is no increase in the resistivity with decreasing temperatures downwards from 300 K. Also here, an anomaly at 6 K and a $d\rho/dT$ maximum at 4.8 K are found. As in URh_2Ge_2 (Refs. 7 and 8), the resistivity is larger along the c axis than along the a axis. This is in agreement with the expectation that the conduction is best within the Ir (or d-element) layer, but differs from the results on UFe_2Ge_2 (Refs. 7, 9, and 10) and URu_2Si_2.[12] Further considerations of the anisotropic resistivity behavior for such 1:2:2 compounds may be found in Ref. 13. When continuing the resistivity measurements down to 40 mK, no superconductivity was observed.

The specific heat, presented as c_p/T vs T^2, is shown in Fig. 4. Near the Néel temperature determined from susceptibility and resistivity, an anomaly is observed in the specific heat as a distinct maximum at 4.9 K. Above this anomaly the specific heat is not simply composed of an electronic (γT) contribution and a phonon contribution as given by the low-temperature approximation of the Debye expression (βT^3), for such behavior would result in a linear dependence in the expanded T scale of Fig. 4(b). However, when the *full* Debye expression is used, a reasonably good description of the specific heat [see Fig. 4(b)] is obtained with $\gamma=105$ mJ/mol K^2 and $\theta_D=254$ K, which results in a low-temperature coefficient $\beta=5.90\times10^{-4}$ J/mol K^4. For $T<T_N$, the specific heat may be fitted by a linear and a cubic temperature variation at least down to 1.92 K [see Fig. 4(a)]. In contradistinction to most antiferromagnetic heavy-fermion systems,[2] the γ value below the Néel temperature has remarkably in-

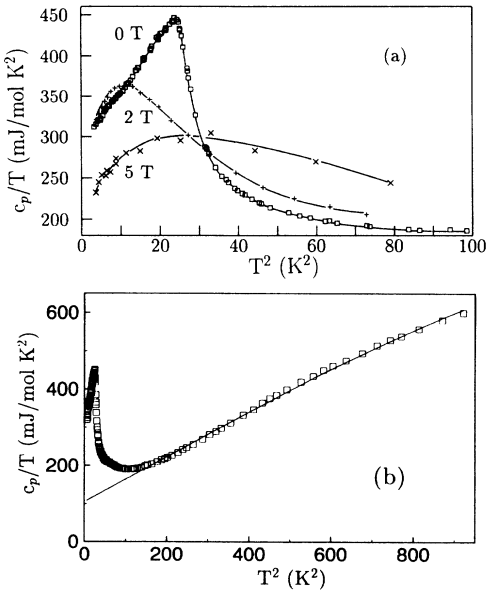

FIG. 4. (a) The specific heat divided by the temperature vs the temperature squared for UIr_2Si_2. □, $B=0$ T; +, $B=2$ T; and ×, $B=5$ T. (b) The zero-field measurement over an expanded temperature range. The solid line represents the high-temperature fit to the data mentioned in the text.

creased to 290 mJ/mol K^2. Also $\beta=6.56\times10^{-3}$ J/mol K^4 is very large compared to that deduced from the high-temperature fit (see below). We further note that both the magnitude of the anomaly and the entropy related to the transition, estimated by extrapolating the contributions mentioned above to 0 K are very small, $\Delta S=1.65$ J/mol K $=0.20$ R, further suggesting the reduced-moment behavior. The specific heat in the vicinity of the anomaly is found to be particularly sensitive to an applied magnetic field along the c axis. Between 0 and 2 T the maximum in the specific heat shifts downward and decreases in magnitude [see Fig. 4(a)], but at the lowest temperatures no marked decrease of the specific heat is observed, illustrating γ to be almost field independent in the antiferromagnetically ordered phase. Nevertheless, a very strong reduction of the anomaly is seen in 5 T $> B_M$, yielding a broad specific-heat maximum which resembles a Schottky anomaly. Also, the low-temperature value of c_p/T is seen to be greatly diminished by the field. This implies that the γ value below T_N significantly decreases when the antiferromagnetically ordered state is destroyed by the metamagnetic transition.

An attempt has been made to describe the magnetic and thermal properties of UIr_2Si_2 in terms of Nieuwenhuys' singlet-ground-state model, which has previously been applied to URu_2Si_2 and UPt_2Si_2.[14] This model is a simple application of crystal-field[15] and induced-moment[16] theory used earlier to describe Pr^{3+} and other rare-earth ions with integral J, when the CEF produces a singlet ground state. In its extension to U, the U^{4+} ($J=4$) manifold is split by the CEF with tetragonal symmetry into five singlets and two doublets. Of these states a subset consisting of three symmetry-related singlets and the lowest doublet are taken into account. If a singlet is the ground state, the magnetism is of van Vleck type, oriented along the c axis due to a magnetic-field–induced coupling between the singlets, and along the a axis via the ground state and the doublet. Since at low temperature the c axis is experimentally the magnetic easy axis, the ground state and the first excited state are inferred to be singlets. In the model, magnetic interactions between the U ions are included by a molecular-field approach. If the molecular-field parameter is large enough, below a critical temperature an internal magnetic field will arise, increasing the splitting between the lowest-lying singlets and causing an ordering of the magnetic moments.

Such a model has various merits. (i) The susceptibility at low temperatures, near the magnetic ordering, can be small, even though at high temperatures a good (CW) effective moment is observed. (ii) The susceptibility can be strongly anisotropic ($\chi_c^{\max} > \chi_a^{\max}$) while exhibiting anomalous behavior due to the transition along both a and c axes. (iii) Since the temperature dependence of the magnetic susceptibility is mainly determined by the CEF, maxima are not necessarily related to the magnetic ordering and therefore may be found at different temperatures for measurements with fields along different crystal axes. Specifically, if the doublet lies sufficiently above the first excited singlet, the susceptibility maximum along the a axis occurs at a higher temperature than that along the c axis. (iv) The transition can give rise to an anomaly in the specific heat that is much smaller than that arising from a doublet ground-state ordering.

For the evaluation of the magnetization along the c axis three parameters must be determined, viz., the splitting between the ground state and the two excited singlets (Δ and Δ') and the molecular-field parameter (λ). The temperature of the transition $T_N=4.9$ K, the field of the metamagnetic transition $B_M=2.2$ T, and the ratio between the maximum and the lowest-temperature value of the susceptibility were taken as the determining criteria. Accordingly, Δ was established to be 15 K, Δ' to be 110 K, and $\lambda=1.12$. For the calculation of the magnetization along the a axis two additional parameters have to be evaluated, viz., the splitting Δ'' and the matrix element of J_x between the ground state and the doublet. In order to obtain a proper adjustment of these two variables, the ratios between the susceptibilities along the two crystallographic directions at the maxima and at 300 K were used. These requirements yield values for Δ'' and the J_x matrix element of 70 K and 1.85. In accordance with experiment, the calculated magnetic-field dependence of the magnetization along the a axis does not show any anomalous behavior near 2.2 T.

With this set of CEF parameters the main features of the experimental magnetization and susceptibility are predicted. In addition, the field dependence of the anomaly in the specific heat can be described, i.e., the calculations show the characteristic decrease in magnitude and shift towards lower temperature for fields below 2.2 T, whereas at 5 T indeed a Schottky-like anomaly is found with a maximum at a temperature above that of the zero-field anomaly.

Despite these qualitative agreements, quantitatively large deviations from the experiments are found. The susceptibility along the c axis at the maximum is overestimated by the CEF model by a factor of 4, the magnetic-field dependence of the magnetization is much too weak along the c axis in the neighborhood of the metamagnetic transition, and the magnetization is driven too easily into saturation. Besides this, the magnetic part of the specific heat is strongly overestimated in the region around and above T_N.

Such deviations are attributable to correlations and hybridization effects that broaden the levels and reduce the moments. As the energy difference between the lowest singlets is very small (15 K) the effect of the broadening of the $5f$ states is expected to be more serious for UIr_2Si_2 than for URu_2Si_2 or UPt_2Si_2 where the splitting between the lowest states is at least twice as large.[14] In addition, the strong change in the electronic specific-heat coefficient (γ) that is observed at the transition cannot be explained in this CEF framework. It is noteworthy that the cubic term in the specific heat has also increased significantly below the transition (see above). This increase can originate from an increased lattice contribution (decreased θ_D due to magnetostrictive effects), as well as from spin waves in the antiferromagnetically ordered material. It is especially the enlarged value of the electronic specific heat for $T < T_N$ that makes this material so interesting. Until now the coefficients γ of U-based heavy-fermion systems have been found to decrease when the materials order magnetically. This usually has been attributed to an opening of an energy gap at the Fermi surface causing a lessening in the electron density of states $N(E_F)$.[17] However, another factor influencing γ is the effective mass. If the mass of the heavy quasiparticles is renormalized upwards in the magnetic transition, then, even when a gap opens, its effects on $N(E_F)$ could be overcompensated by a corresponding mass enhancement. Indeed such a coupling between the electronic and the magnetic states offers a possible explanation for the observed temperature and field dependence of the electronic specific heat.

Clearly much more is needed to describe our experiments on UIr_2Si_2 than a simple CEF-level scheme with induced moment ordering. The large γ values signal a highly correlated many-body electron system. Effects such as hybridization and CEF-level broadening must be included *a priori* along with a self-consistent band-structure calculation in any complete theoretical model. Some recent theoretical advances along both of these lines may be found in Refs. 18–22. Another theoretical approach[23] based upon CEF is that quadrupolar fluctuations, caused by the strong hybridization, lead to a Kondo-like quenching of the quadrupole degrees of freedom and thereby produce the heavy-electron behavior. Such considerations have not yet been applied to our singlet ground-state system, where indeed a small quadrupole moment exists.

Another puzzle with UIr_2Si_2 is the absence of superconductivity. A very delicate balance must exist between the magnetism and a superconducting pairing mechanism which leads to superconductivity in URu_2Si_2, but which in the present case is unfavorable.

We wish to acknowledge S.A.M. Mentink, C. E. Snel, T. J. Gortenmulder, and M. Besselink for technical assistance. This work is part of the research program of the Nederlandse Stichting voor Fundamenteel Onderzoek der Materie (FOM).

*On leave from the Academy of Mining and Metallurgy, 30059 Krakow, Poland.

[1]See, for example V. Sechovsky and L. Havela, in *Ferromagnetic Materials,* Vol. 4, edited by E. P. Wohlfarth and K. H. J. Buschow (Elsevier, Amsterdam, 1989), p. 309.

[2]Previous exceptions are the increase in the γ values below magnetic transitions that were observed in antiferromagnet $NpIr_2$ (200→400) mJ/mol K^2 [M. B. Brodsky and R. J. Trainor, J. Phys. (Paris) Colloq. **39**, C6-777 (1978)] and ferromagnetic $NpOs_2$ (92→205) mJ/mol K^2 [M. B. Brodsky and R. J. Trainor, Physica B **86–88**, 143 (1977)].

[3]T. T. M. Palstra, A. A. Menovsky, G. J. Nieuwenhuys, and J. A. Mydosh, J. Magn. Magn. Mater. **54–57**, 435 (1986).

[4]K. Hiebl and R. Rogl (unpublished).

[5]M. Solanski-Moser, B. Buffat, P. Wachter, Wang Xian Zhong, B. Czeska, B. Chevalier, and J. Etourneau, J. Magn. Magn. Mater. **63&64**, 677 (1987).

[6]A. A. Menovsky and J. J. M. Franse, J. Cryst. Growth **65**, 286 (1983).

[7]A. J. Dirkmaat, Ph.D. thesis, Leiden University, The Netherlands, 1989.

[8]A. J. Dirkmaat, T. Endstra, A. A. Menovsky, G. J. Nieuwenhuys, and J. A. Mydosh, Europhys. Lett. (to be published).

[9]A. J. Dirkmaat, T. Endstra, E. Knetsch, A. A. Menovsky, and J. A. Mydosh, J. Phys. (Paris) Colloq. **49**, C8-475 (1988).

[10]A. J. Dirkmaat, T. Endstra, E. A. Knetsch, A. A. Menovsky, G. J. Nieuwenhuys, and J. A. Mydosh, J. Magn. Magn. Mater. (to be published).

[11]F. R. de Boer, J. J. M. Franse, E. Louis, A. A. Menovsky, J. A. Mydosh, T. T. M. Palstra, U. Rauchschwalbe, W. Schlabitz, F. Steglich, and A. de Visser, Physica B **138**, 1 (1986).

[12]T. T. M. Palstra, A. A. Menovsky, and J. A. Mydosh, Phys. Rev. B **33**, 6527 (1986).

[13]R. A. Steeman, A. J. Dirkmaat, A. A. Menovsky, E. Frikkee, G. J. Nieuwenhuys, and J. A. Mydosh, in *Proceedings of the International Conference on the Physics of Highly Correlated Electron Systems, 1989* [Physica B (to be published)].

[14]G. J. Nieuwenhuys, Phys. Rev. B **35**, 5260 (1987).

[15]M. T. Hutchings, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 227.

[16]Y.-L. Wang and B. R. Cooper, Phys. Rev. B **172**, 539 (1968).

[17]T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. **55**, 2727 (1985).

[18]H. U. Desgranges and J. W. Rasul, Phys. Rev. B **36**, 328 (1987).

[19]J. M. Wills and B. R. Cooper, Phys. Rev. B **36**, 3809 (1987).

[20]P. M. Levy and S. Zhang, Phys. Rev. Lett. **62**, 78 (1989).

[21]M. R. Norman, T. Oguchi, and A. J. Freeman, Phys. Rev. B **38**, 11 193 (1988).

[22]G. Zwicknagel, J. Magn. Magn. Mater. **76&77**, 16 (1988).

[23]D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987); J. Magn. Magn. Mater. **76&77**, 53 (1988).