Gapped itinerant spin excitations account for missing entropy in the hidden-order state of URu_2Si_2

C. R. WIEBE[1,2]*, J. A. JANIK[1,2], G. J. MACDOUGALL[3], G. M. LUKE[3], J. D. GARRETT[4], H. D. ZHOU[2], Y.-J. JO[2], L. BALICAS[2], Y. QIU[5,6], J. R. D. COPLEY[5], Z. YAMANI[7] AND W. J. L. BUYERS[7]

[1]Department of Physics, Florida State University, Tallahassee, Florida 32306-3016, USA
[2]National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306-4005, USA
[3]Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada
[4]Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario L854M1, Canada
[5]NIST Center for Neutron Research, Gaithersburg, Maryland 20899-8562, USA
[6]Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA
[7]CNBC, National Research Council, Chalk River Labs, Chalk River, Ontario K0J 1J0, Canada
*e-mail: cwiebe@magnet.fsu.edu

Published online: 28 January 2007; doi:10.1038/nphys522

Many correlated electron materials, such as high-temperature superconductors[1], geometrically frustrated oxides[2] and low-dimensional magnets[3,4], are still objects of fruitful study because of the unique properties that arise owing to poorly understood many-body effects. Heavy-fermion metals[5]—materials that have high effective electron masses due to those effects—represent a class of materials with exotic properties, ranging from unusual magnetism, unconventional superconductivity and 'hidden' order parameters[6]. The heavy-fermion superconductor URu_2Si_2 has held the attention of physicists for the past two decades owing to the presence of a 'hidden-order' phase below 17.5 K. Neutron scattering measurements indicate that the ordered moment is $0.03\mu_B$, much too small to account for the large heat-capacity anomaly at 17.5 K. We present recent neutron scattering experiments that unveil a new piece of this puzzle—the spin-excitation spectrum above 17.5 K exhibits well-correlated, itinerant-like spin excitations up to at least 10 meV, emanating from incommensurate wavevectors. The large entropy change associated with the presence of an energy gap in the excitations explains the reduction in the electronic specific heat through the transition.

The central issue in URu_2Si_2 concerns the identification of the order parameter that explains the reduction in the specific heat coefficient, $\gamma = C/T$, and thus the change in entropy, through the transition at 17.5 K (ref. 6). Numerous speculations about the ground state have been advanced, from quadrupolar ordering[7], to spin-density wave formation[8], to 'orbital currents'[9] to account for the missing entropy. Here, we present cold-neutron time-of-flight spectroscopy results that shed some light on the 'hidden-order' (HO) in URu_2Si_2. We have carried out experiments above and below the ordering temperature to measure how the spin excitations evolve. It is clear from our data that above T_0 the spectrum is dominated by fast, itinerant-like spin excitations emanating from incommensurate wavevectors at positions located $0.4a^*$ from the antiferromagnetic (AF) points. From the group velocity and temperature dependence of these modes, we surmise that these are heavy-quasiparticle excitations that form below the 'coherence temperature' and play a crucial role in the formation of the heavy-fermion and HO states. The gapping of these excitations, which corresponds to a loss of accessible states, accounts for the reduction in γ through the transition at 17.5 K.

Figure 1 shows the excitation spectrum of URu_2Si_2 at 1.5 K in the H00 plane. The characteristic gaps at ∼2 meV at the AF zone centre (1, 0, 0) and ∼4 meV at the incommensurate wavevectors (0.6, 0, 0) and (1.4, 0, 0) have been known for some time[10]. The incommensurate wavevector corresponds to a displacement of $\sim 0.4a^*$ from the AF zone centres (that is, where $h+k+l =$ an odd integer, and is thus forbidden in the body-centred-cubic chemical structure). A scenario for this mode-softening at the incommensurate position was previously described with a model based on oscillatory exchange constants between near neighbours (not uncommon for Ruderman–Kittel–Kasuya–Yoshida-type interactions)[10,11].

Figure 2 shows our new neutron results at 20 K in the same H00 plane. Above the phase transition, the sharp spin waves evolve into weak quasielastic spin fluctuations at the zone centre (1, 0, 0), and strong excitations at the incommensurate positions $(1 \pm 0.4, 0, 0)$. We have considered the possibility that these incommensurate excitations may be due to magnetovibrational scattering. This can arise from a shift of the phonon excitations at (2, 0, 0) to $(1 \pm 0.4, 0, 0)$ as allowed through the neutron scattering cross-section for magnetoelastic coupling[12]. However, with the small moment size of this system, it is improbable that such a scattering process is being observed. It was also originally reported[10] that the incommensurate excitations were just quasielastic fluctuations; constant Q scans on a triple-axis spectrometer resolved a peak at a finite energy of 0.6 THz = 2.5 meV and a decrease in intensity as a function of energy typical of an overdamped response. What was previously unknown was that the quasielastic fluctuations were only the lower limit of a band of high-velocity

©2007 Nature Publishing Group

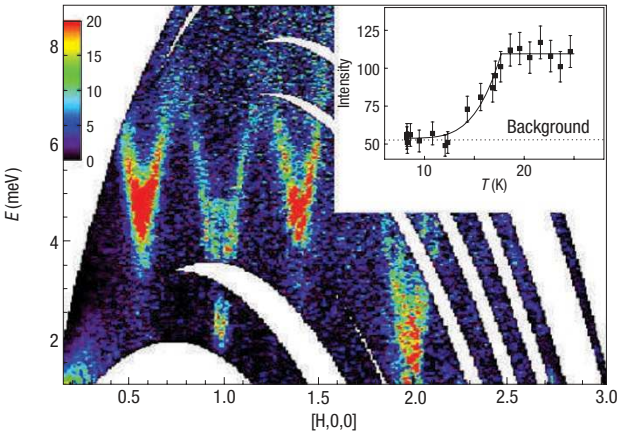

Figure 1 Inelastic neutron scattering of URu_2Si_2. Excitation spectrum of URu_2Si_2 in the H00 plane at $T = 1.5$ K (where H and L are reciprocal lattice vectors a^* and c^*, L is integrated from -0.12 to 0.12). Note the minima at the AF zone centre (100) and incommensurate positions $(1 \pm 0.4, 0, 0)$. The feature at (200) is due to phonons. The inset shows how the incommensurate excitations become gapped through the transition by counting at the point (0.6, 0, 0) at 0.25 meV transfer on a triple-axis spectrometer[16]. The error bars are determined by the square root of the intensity.

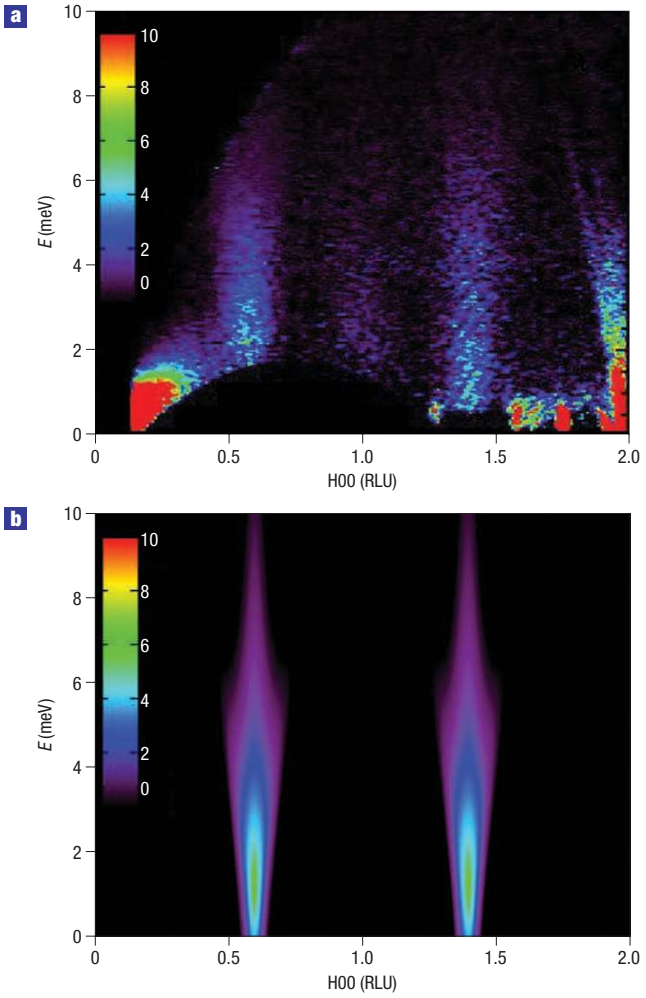

Figure 2 Itinerant spin excitations in URu_2Si_2. a, Inelastic neutron scattering of URu_2Si_2 in the H00 plane at $T = 20$ K (L is integrated from -0.12 to 0.12). Note the cone of ungapped excitations emanating from the incommensurate wavevectors $(1 \pm 0.4, 0, 0)$. **b**, Fits to the Chou model, with the parameters described in the text.

spin excitations that extend well above the upper limit of the sharp collective spin excitations of the ordered phase. As the temperature is increased, the (1, 0, 0) fluctuations decrease, and the incommensurate fluctuations remain approximately constant to at least 25 K (ref. 13).

The implications of this discovery are as follows. (1) The incommensurate excitations have a well-defined structure as a function of Q, and thus the electrons are highly correlated above 17.5 K. This is completely unexpected for a system of localized moments in a paramagnetic state, but similar dynamics above the Néel temperature, T_N, (with the formation of paramagnons[14], for example) has been observed with neutron scattering in other itinerant electron systems such as chromium and V_2O_3 (refs 14,15). (2) The dispersion is such that the maximum group velocity is at least a factor of two larger than the maximum group velocity of the excitations in the ordered state. A significant restructuring of the Fermi surface must be responsible for the HO state. (3) The gapping of these strong spin fluctuations below 17.5 K must provide a considerable portion of the entropy removal at the transition. These excitations have a structure in reciprocal space such that they occur at several symmetry-related wavevectors within the first Brillouin zone. The amount of phase space occupied by these excitations is greater than those at the (1, 0, 0) AF zone centre. Figure 3 shows constant energy cuts of the excitations in the H0L plane to emphasize this. Note the weak AF fluctuations at (1, 0, 0) and (2, 0, 1) in comparison with the excitations at the incommensurate positions (see Fig. 4). Also note how a cone of scattering develops at the incommensurate positions, whereas the AF zone centre simply decreases in intensity as energy transfer is increased. For comparison, a cut of the spin-wave spectrum at 1.5 K in the same energy window is also shown. The results at 20 K suggest a continuum of excitations within a cone of scattering (as expected for low-lying excitations at the Fermi surface), as opposed to the sharp excitations that are gapped below 17.5 K.

An estimate of the contribution to the electronic specific heat term from the removal of these low-energy spin fluctuations can be made through an analysis of the spectrum at 20 K. The specific heat of a cone of fast excitations centred on incommensurate wave vectors and extending out by an inverse correlation length $\kappa = \xi^{-1}$, is given by

$$C(T) = \frac{\partial}{\partial T}\frac{v_a}{8\pi^3}\int_0^{\xi^{-1}} dq 4\pi q^2 \int_0^{E_{max}} dE \rho_0 f(E) E$$

where v_a is the cell volume, ρ_0 is the density of states and $f(E) = \coth(E/2k_BT)$, where k_B is the Boltzmann constant. The upper limit in the energy integral has been taken to be $E_{max} = k_BT$ (above this energy, the specific heat contribution is small because df/dT approaches zero exponentially).

If we assume that the density of states is the inverse of a large damping in energy $\Gamma = c\xi^{-1}$, then the specific heat becomes

$$C_v = \frac{v_a \xi^{-2}}{3\pi^2 c} \times k_B^2 T \qquad (1)$$

where c is the characteristic spin-wave velocity. Previous work has shown that the excitations lie within the HK0 plane around (0.6, 0, 0) (ref. 16). Note that owing to the dispersion of the spin excitations, the contribution to the heat capacity is linear

©2007 Nature Publishing Group

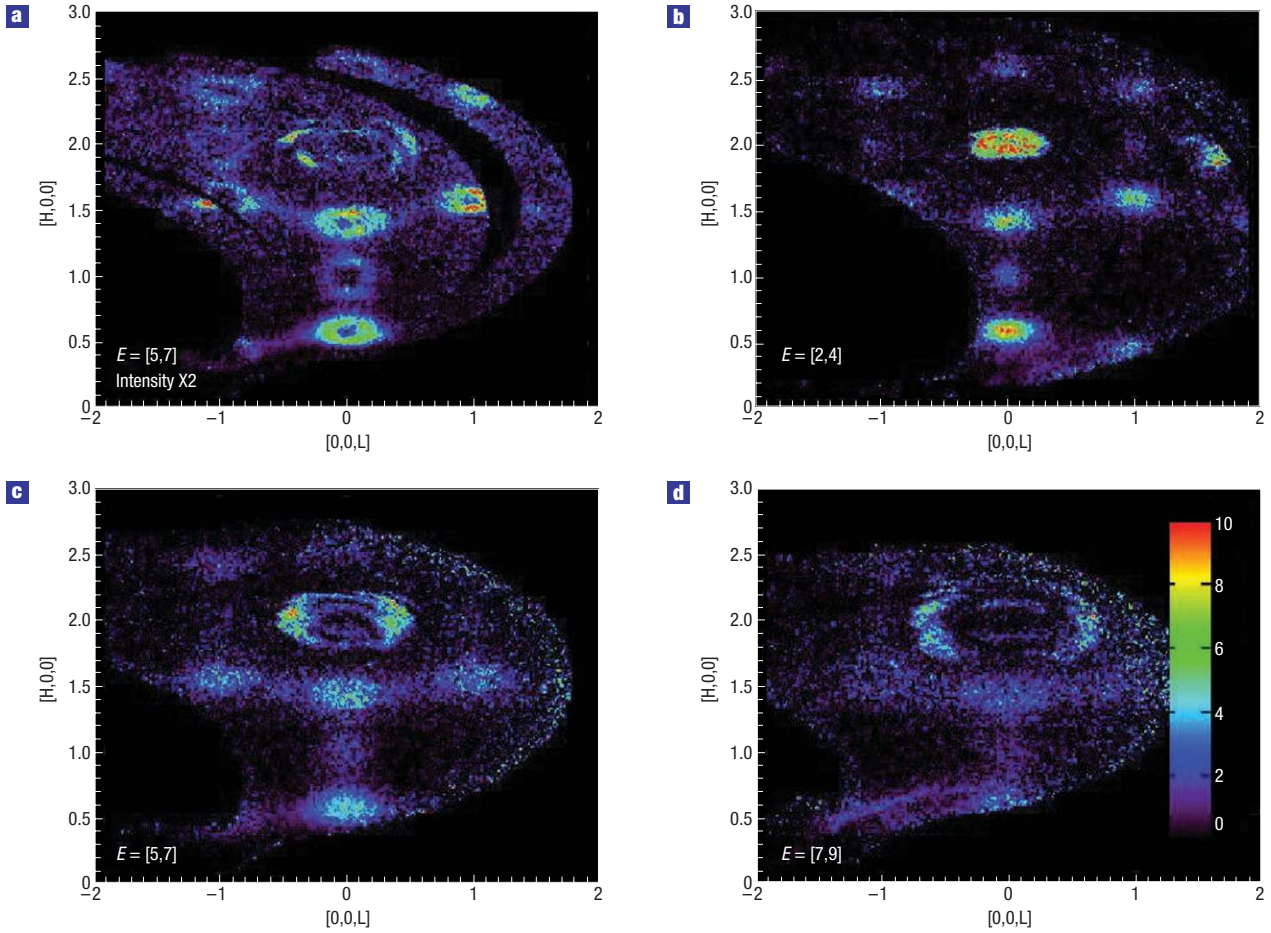

Figure 3 Evolution of inelastic scattering in URu_2Si_2. a–d, Cuts along ΔE of scattering in the H0L plane at 1.5 K (**a**) and 20 K (**b–d**). The rings at (200) correspond to phonons. Note the spin waves in **a** as rings centred on $(H+K+L)=$ odd integers (AF zone centre) and rings centred at incommensurate points separated by $0.4a^*$ from the AF zone centres. At 20 K, there are weak overdamped AF fluctuations at the zone centres, but it is clear that a cone of highly correlated excitations develops as a function of energy. The energy of integration is denoted in meV for each plot.

in temperature, which is exactly the same power-law dependence for the electronic specific heat. This term arises owing to these fast itinerant spin excitations in URu_2Si_2 and is the reason for the enhanced linear component of the specific heat above $T_0 = 17.5$ K. The calculation of a gap opening in the spin-excitation spectrum is equivalent to a calculation of the gap opening in the Fermi surface. This is demonstrated by the similarity of the matrix-element-weighted density of spin-wave states and infrared spectroscopy measurements, which measure charge excitations[11,17]. The spin and charge degrees of freedom are strongly coupled.

A characteristic correlation length and spin-wave velocity must be extracted from our data to complete this calculation. Our data have been fitted to a standard formula for paramagnetic scattering from a system of correlated spins, also known as the Chou model[18]. This has been used to extract correlation lengths and spin-wave velocities for excitations in the superconducting cuprates, for example[19–21]. With this model, $S(q,\omega)$ is represented as

$$S(q,\omega) = \frac{\hbar\omega}{1-\mathrm{e}^{-\hbar\omega/kT}} \frac{A}{\kappa^2+q^2} \left(\frac{\Gamma}{(\hbar\omega \pm \hbar\omega_q)^2+\Gamma^2} \right)$$

where $\hbar$ is the reduced Planck constant, A is an arbitrary constant, $\mathbf{q} = \mathbf{Q} - \boldsymbol{\delta}$ (where δ is the incommensurate wavevector), κ is the inverse of the correlation length ξ, and the frequencies of the damped spin waves are $\omega_q = cq$, where c is the spin-wave velocity ($\Gamma = \kappa c$). Fitting with these parameters yields a correlation length of $\xi = 14(2)$ Å and $c = 45(10)$ meV Å (see Fig. 2). This value is similar to the Fermi velocity, reported as $\sim 8.84 \times 10^3$ m s^{-1} (35 meV Å) (ref. 22), illustrating the itinerant nature of the excitations. It is interesting to note that there is a curious intersection of cuprate and heavy-fermion physics with this analysis—the fast excitations seen in the superconductor $La_{1.86}Sr_{0.14}CuO_4$ (LSCO), which have an effective mass near an electron mass, seem similar to the excitations in URu_2Si_2, albeit with a higher velocity because of their lighter effective mass[19].

The contribution of the spin excitations to the specific heat with these parameters for URu_2Si_2 is 220 ± 70 mJ mol^{-1} K^{-2} at 20 K. Comparison of this with the data in Fig. 5 shows a good agreement, with a γ of 155(5) mJ mol^{-1} K^{-2}. The gapping of these excitations leads to a dramatic reduction in γ to 38(2) mJ mol^{-1} K^{-2} (refs 23, 24). This is naturally explained through the gaps in the spin-excitation spectrum, which has minima at 2 and 4 meV. The average thermal energy below 17.5 K is less than 2 meV, and thus most of the spin excitations are inaccessible. This is the reason for the reduction of γ through the phase transition. The origin of the size of the specific heat jump at T_0 is still unresolved at this point,

©2007 Nature Publishing Group

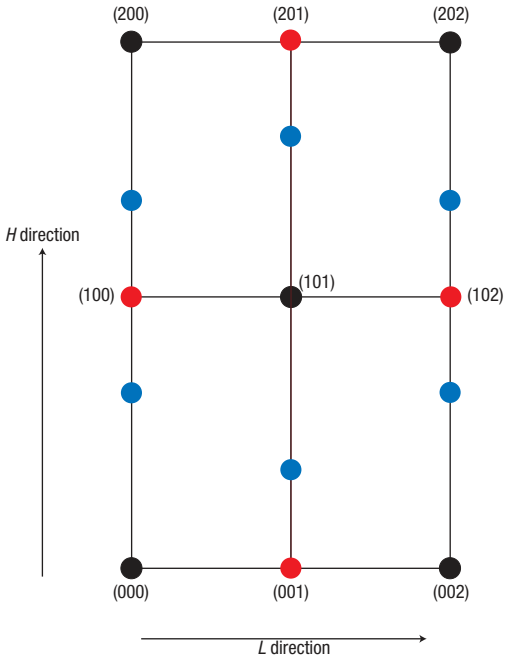

Figure 4 Reciprocal space map of the commensurate and incommensurate scattering in URu_2Si_2. Blue circles: incommensurate positions; red circles: antiferromagnetic lattice points; black circles: nuclear lattice points.

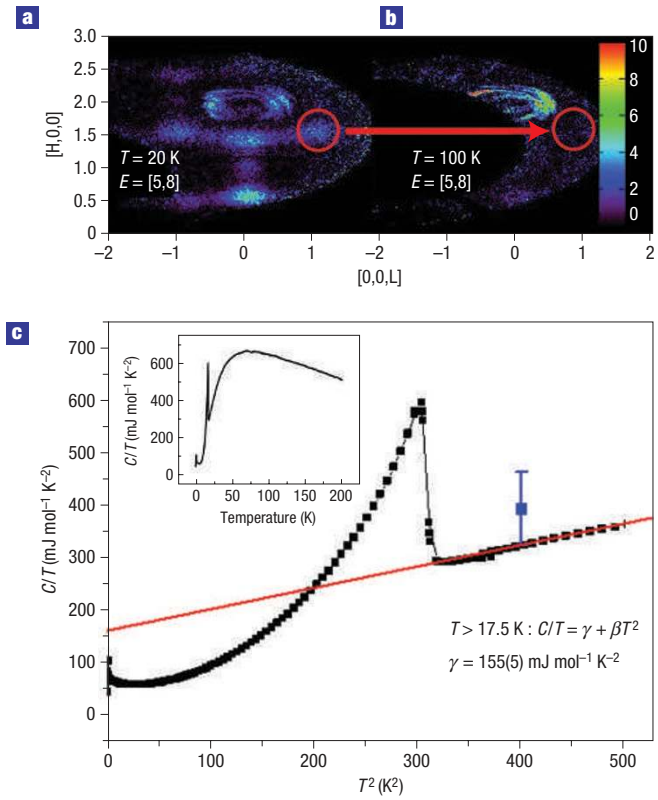

Figure 5 Correlations with features in the specific heat. a,**b**, Cuts in the H0L plane integrated from 5–8 meV at 20 K (**a**) and 100 K (**b**). Note how the incommensurate scattering at positions such as (1.6,0,1) disappears at 100 K (indicated by a circle). This is just above the 'coherence' temperature where a signature of heavy-quasiparticle formation is seen in the specific heat (inset in **c**). **c**, The specific heat C divided by temperature as a function of T^2, showing the anomaly at 17.5 K. The linear portion of the specific heat, γ, is calculated with the solid line to be 155(5) mJ mol^{-1} K^{-2}. The blue data point is the calculation of our $\gamma = 220(70)$ mJ mol^{-1} K^{-2} from the spin fluctuations observed at 20 K. The error bar was calculated from equation (1) in the text.

although its low-temperature limit arises from the removal of the spin contribution to leave a weak remanent ungapped electronic band. A gap opens in the spin-excitation spectrum with a value of ~110(10) K, but the identity of this ordered state is still unknown[16]. Through these measurements, we do know that the nature of the transition at T_0 seems to be dominated by itinerant electron physics rather than localized crystal field effects. This is why URu_2Si_2 shows a transition between itinerant and localized behaviour at T_0, as shown through thermal conductivity measurements[22]. Indeed, we have seen no evidence of crystal field excitations up to at least 10 meV ~ 110 K. The complicated crystal field schemes that have been used to explain the heat capacity anomaly at 100 K, the HO state and the anomalous thermal expansion at 60 K need to be re-examined within this framework. Our measurements show that the first excited state, if allowed by selection rules, must exist above 200 K.

The role that these excitations play with the formation of the heavy-fermion state can be examined through their temperature dependence. Figure 5 shows recent heat capacity measurements, in comparison with inelastic neutron scattering scans at 100 K. Note that the incommensurate features have disappeared at this temperature, often called the 'coherence temperature', which marks a cross-over from paramagnetic weakly correlated moments to correlated heavy-electron behaviour. They are intimately correlated with the coherence temperature and the formation of the heavy-fermion state. This energy scale also describes the temperature dependence of the heat-capacity anomaly at 17.5 K through fits to an activation law[24], and the temperature dependence of the incommensurate excitations below 17.5 K (ref. 16). This is further evidence that the gapping of these excitations is directly related to the formation of the HO state.

Our findings place constraints on all new theories of HO in URu_2Si_2. A minimum theory must account for (1) incommensurate itinerant spin excitations and (2) the lack of crystalline electric fields up to 10 meV. The HO transition seems to be a rearrangement of electrons at the Fermi surface in an itinerant rather than localized electron picture. Excitations out of this state at these incommensurate wavevectors show a mode-softening that is reminiscent of another dynamic ground state that has no translational order but a prominent specific-heat anomaly—the superfluid liquid helium transition[25]. Correlations between the heavy quasiparticles in URu_2Si_2 build up below 100 K, and at 17.5 K, there is a transition to a new condensate that remains unidentified. The true order parameter for this system has yet to be determined.

METHODS

Our measurements were made with a single crystal grown at McMaster University by the Czochralski method using elemental U, Ru and Si, followed by annealing in argon at 900 °C. The magnetic properties were confirmed through d.c. magnetometry measurements in a superconducting quantum interference device, and heat capacity and resistivity measurements in a physical property measurement system. The neutron scattering measurements were carried out at the Disk Chopper Spectrometer at the NIST Center for Neutron Research in Gaithersburg, Maryland. The 11.5 g URu_2Si_2 crystal was aligned in the H0L plane and placed in a standard Institut Laue-Langevin cryostat and

©2007 Nature Publishing Group

measurements were taken using cold neutrons of 2.5 and 5 Å. The identification of the equipment is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the equipment is necessarily the best available for the purpose.

Received 22 September 2006; accepted 2 January 2007; published 28 January 2007.

References

1. Dagotto, E. Correlated electrons in high temperature superconductors. *Rev. Mod. Phys.* **66**, 763–840 (1994).
2. Greedan, J. E. Geometrically frustrated materials. *J. Mater. Chem.* **11**, 37–53 (2000).
3. Affleck, I. Quantum spin chains and the Haldane gap. *J. Phys. Condens. Matter* **1**, 3047–3072 (1989).
4. Dagotto, E. & Rice, T. M. Surprises on the way from one- to two-dimensional quantum magnets: The ladder materials. *Science* **271**, 618–623 (1996).
5. Fisk, Z. *et al.* Heavy-electron metals—new highly correlated states of matter. *Science* **239**, 33–42 (1988).
6. Tripathi, V., Chandra, P. & Coleman, P. Itinerancy and hidden order in URu_2Si_2. *J. Phys. Condens. Matter* **17**, 5285–5311 (2005).
7. Silhanek, A. V. *et al.* Quantum critical 5f electrons avoid singularities in $U(Ru,Rh)_2Si_2$. *Phys. Rev. Lett.* **95**, 026403 (2005).
8. Mineev, V. P. & Samokhin, K. V. de Haas van Alphen effect in metals without an inversion center. *Phys. Rev. B* **72**, 014432 (2005).
9. Chandra, P., Coleman, P., Mydosh, J. A. & Tripathi, V. Hidden orbital order in the heavy fermion metal URu_2Si_2. *Nature* **417**, 831–834 (2002).
10. Broholm, C. Magnetic excitations and ordering in the heavy-electron superconductor URu_2Si_2. *Phys. Rev. Lett.* **58**, 1467–1470 (1987).
11. Broholm, C. *et al.* Magnetic excitations in the heavy-fermion superconductor URu_2Si_2. *Phys. Rev. B* **43**, 12809–12822 (1991).
12. Squires, G. L. *Introduction to the Theory of Neutron Scattering* (Dover, New York, 1997).
13. Buyers, W. J. L. *et al.* Spin wave collapse and incommensurate fluctuations in URu_2Si_2. *Physica B* **199**, 95–97 (1994).
14. Fawcett, E. Spin-density-wave antiferromagnetism in chromium. *Rev. Mod. Phys.* **60**, 209–283 (1988).
15. Bao, W., Broholm, C., Honig, J. M., Metcalf, P. & Trevino, S. F. Itinerant antiferromagnetism in the Mott compound $V_{1.973}O_3$. *Phys. Rev. B* **54**, R3726–R3729 (1996).
16. Wiebe, C. R., Luke, G. M., Yamani, Z., Menovsky, A. A. & Buyers, W. J. L. Search for hidden orbital currents and observation of an activated ring of magnetic scattering in the heavy fermion superconductor URu_2Si_2. *Phys. Rev. B* **69**, 132418 (2004).
17. Bonn, D. A., Garrett, J. D. & Timusk, T. Far-infrared properties of URu_2Si_2. *Phys. Rev. Lett.* **61**, 1305–1308 (1988).
18. Chou, H. *et al.* Neutron-scattering study of spin fluctuations in superconducting $YBa_2Cu_3O_{6+x}$ ($x = 0.40,0.45,0.50$). *Phys. Rev. B* **43**, 5554–5563 (1991).
19. Mason, T. E., Aeppli, G. & Mook, H. A. Magnetic dynamics of superconducting $La_{1.86}Sr_{0.14}CuO_4$. *Phys. Rev. Lett.* **68**, 1414–1417 (1992).
20. Rossat-Mignod, J. *et al.* Inelastic neutron scattering study of the spin dynamics in the $YBa_2Cu_3O_{6+x}$ system. *Physica B* **192**, 109–121 (1993).
21. Stock, C. *et al.* Dynamic stripes and resonance in the superconducting and normal phases of $YBa_2Ca_3O_{6.5}$ ortho-II superconductor. *Phys. Rev. B* **69**, 014502 (2004).
22. Behnia, K. *et al.* Thermal transport in the hidden-order state of URu_2Si_2. *Phys. Rev. Lett.* **94**, 156405 (2005).
23. Maple, M. B. *et al.* Partially gapped Fermi surface in the heavy-electron superconductor URu_2Si_2. *Phys. Rev. Lett.* **56**, 185–188 (1986).
24. Palstra, T. T. M. *et al.* Superconducting and magnetic transitions in the heavy-fermion system URu_2Si_2. *Phys. Rev. Lett.* **55**, 2727–2730 (1985).
25. Feynman, R. P. in *Progress in Low Temperature Physics* Vol. 1 (ed. Gorter, C.) (Interscience, New York, 1955).

Acknowledgements

The authors would like to acknowledge helpful discussions with C. Broholm, C. D. Batista, A. Leggett, C. M. Varma, J. S. Gardner, J. S. Brooks, G. S. Boebinger and B. D. Gaulin. This work was made possible by support through the NSF and the state of Florida. L.B. acknowledges support from the NHMFL in house research program and Y.J. acknowledges support from the NHMFL Schuller program. G.M.L., G.J.M. and W.J.L.B. acknowledge support through NSERC and the CIAR. The authors are grateful to the local support staff at the NIST Center for Neutron Research. Data analysis was completed with DAVE, which can be obtained at http://www.ncnr.nist.gov/dave/. The work at NIST is supported in part by the National Science Foundation under Agreement No. DMR-0454672. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-0084173, by the State of Florida, and by the DOE. Correspondence and requests for materials should be addressed to C.R.W.

Author contributions

Scattering experiments were completed by C.R.W., J.A.J., G.J.M., H.D.Z., Y.Q., J.R.D.C., Z.Y. and W.J.L.B. The crystals were grown by J.D.G. and G.M.L. Specific heat measurements were made by Y.J.J. and L.B. Data analysis and writing of the paper was completed by C.R.W., J.A.J., G.J.M., G.M.L., L.B. and W.J.L.B.

Competing financial interests

The authors declare that they have no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

©2007 Nature Publishing Group